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# Chemical Route derived Bismuth Ferrite Thin films and Nanomaterials

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## Abstract

Bismuth ferrite (BiFeO<sub>3</sub> - BFO) is a prototypical lead-free single phase multiferroic which shows strong ferroelectric and antiferromagnetic properties simultaneously, together with high ferroelectric Curie temperature ( $T_{FE}$ ~1103K) and Néel temperature ( $T_N$ ~ 643K). BFO thin films and nanomaterials (collectively termed here 'nanostructured BFO') show many fascinating functional properties are not observed in the parent bulk compound. In this review we focus on chemical route-derived nanostructured BFO: thin films, nanowires and nanoparticles. The review covers governing factors in a detailed and systematic manner so as to give readers a clear picture of the current state of the art in the development of nanostructured BFO via chemical routes. We discuss the process pathways for each of the chemical (or soft) based synthesis techniques, highlighting both the advantages and challenges faced for each method. Specific emphasis is placed on understanding the role of each processing ingredient and development of optimized precursors. Finally we identify the opportunities posed by further development of chemical routes for this fascinating materials system. The review thus sheds significant insight into successfully achieving high-quality nanostructured BFO via chemical process techniques.

#### 1. Introduction to bismuth ferrite

Bismuth ferrite (BiFeO<sub>3</sub>, BFO), is an archetypical multiferroic material that has attracted intense research interest over the past decade.<sup>1-4</sup> In particular, BFO thin films and nanomaterials (collectively termed here as nanostructured BFO) show fascinating functional properties driven by either interface-induced strain (typically in thin films)<sup>5-7</sup> or due to an intrinsic size effect.<sup>8, 9</sup> For example, epitaxially-strained BFO thin films have attractive ferroelectric and electromechanical properties that could be exploited for applications such as microelectronic memory devices or piezoelectric devices.<sup>1, 10, 11</sup> On the other hand, their magnetic properties have been explored for MERAM (Magnetoelectric Random Access Memory) devices<sup>12, 13</sup> and magnonic memories.<sup>14</sup> In addition to its multiferroic character, nanostructured BFO shows intriguing physiochemical behavior, such as enhanced photocatalytic<sup>15, 16</sup> and photovoltaic properties<sup>17, 18</sup> that may not be found in the bulk counterpart. Nanostructured BFO thus holds tremendous potential for the further advancement of next generation electronic devices. For these reasons, there is understandably a strong worldwide push toward the development of devices based on BFO thin films and nanomaterials.

When it comes to demonstration of high quality BFO (especially thin films) for purposes of device development, physical vapor deposition (PVD) routes, such as pulsed laser deposition (PLD),<sup>3, 19, 20</sup> radio-frequency (R-F) sputtering<sup>21-24</sup> and molecular beam epitaxy (MBE)<sup>7, 25</sup> have dominated the scene. However, the chemical solution deposition (CSD) technique is of particular industrial interest by virtue of its low-cost, offering accurate control of the precursor composition, and ease of processing for large-area wafers.<sup>26, 27</sup> **Table 1** summarizes the typical synthesis methods used for the fabrication of nanostructured BFO. It is evident that chemical routes are not only attractive as economic

and mass-manufacturable methods, but are the most facile (and practical) synthesis option for nanofibers and nanoparticles, when compared to physical vapor deposition techniques.

Synthesis Method	Morphologie(s) Available
PLD	Thin films, <sup>3, 19, 20</sup> Nanocrystals <sup>28</sup>
MBE	Thin films <sup>7, 25</sup>
Sputtering	Thin films <sup>21-24</sup>
CVD	Thin films <sup>29 30 31</sup> Thin film, <sup>32, 33 34</sup> Nanoparticles, <sup>8, 15</sup> Nanotubes, <sup>35, 36</sup> Nanowires, <sup>37, 38</sup>
Sol-gel	Nanofibers <sup>17, 39</sup>
Hydrothermal	Nanoparticles, <sup>40, 41</sup> Nanowires <sup>42</sup>
Microwave- Hydrothermal	Nanoparticles,43 Nanocubes44
Auto-combustion	Nanoparticles <sup>45,46</sup>

Table 1 Synthesis methods for BFO materials of various structures

Despite these advantages, the body of work on chemically-derived nanostructured BFO with excellent properties is rather limited in comparison to those prepared by the physical methods described above. We articulate the underlying reasons later, but suffice it to say that this cannot be attributed to the chemical route or lack of appropriate precursors. Indeed chemical-derived routes have been used to successfully manufacture high quality semiconductors (ZnO)<sup>47-49</sup> and even other ferroelectrics such as lead zirconate titanate (PZT)-based thin films and composite structures<sup>50</sup>. In addition, several groups have paid specific attention to metalorganic chemistry of such precursors and thereby realized excellent thin films in other complex metal oxides.<sup>51, 52</sup> This is primarily due to the chemical complex reaction pathways that must occur during the phase development step in a typical chemical-based route. Unlike physical techniques, there are rather limited options for in-situ sensing and monitoring of phase formation so as to apply corrective steps during the synthesis. Significant importance is therefore placed on the precursor composition and stoichiometry as well as the experimental conditions under which the chemical reaction is allowed to proceed. The aim of this review is to address the above factors in a detailed and systematic manner so as to give readers a clear picture of the current state of the art in the development of nanostructured BFO via chemical

routes. It touches upon problem areas that must be borne in mind during synthesis, as well as challenges posed that hinder progress. Finally we identify the opportunities available by further development of this fascinating materials system. Admittedly, a large fraction of the discussions here focus on delineating the chemical reaction pathway that is followed to achieve high quality nanostructured BFO and the factors that underpin them, as opposed to physical properties observed and their possible origins. For the latter, the reader is referred to a number of excellent reviews on the physics and applications of BFO, such as reviews by Catalan et al.<sup>1</sup>, Sando et al.<sup>53</sup>, and Yang et al.<sup>54</sup>

We begin with an introduction to the general working principles and overview of popular chemical routes used for the fabrication of complex metal oxides, with a focus on nanostructured BFO thin films and nanomaterials (Section 2). This is followed by a detailed review of the synthesis–processing-properties correlations in chemically-derived BFO thin films (Section 3). Section 4 addresses the synthesis methods and properties of 0-D nanostructures (nanoparticles) and 1-D nanostructures (nanowires/nanotubes/ nanofibers). Finally, we conclude the review in Section 5 with an outlook of the prospect of chemical routes and their role in the development of nanostructured BFO.

#### 2. Chemical route processes

As summarized in **Table 1**, the main chemical processes to fabricate BFO thin films are sol-gel processes and chemical vapor deposition (CVD), with sol-gel and hydrothermal synthesis process being the most common approaches for low-dimensional BFO nanomaterials. Other methods, such as microwave, microwave hydrothermal, combustion-method synthesis etc., have also been used to prepare BFO nanoparticles. We start with an introduction to synthesis principles and procedures for these methods.

# 2.1 Sol-gel Process

The sol-gel process is one of the most common and earliest-known chemical synthesis methods for metal oxides that can be traced back to the mid-1800s. In the 1990s the solgel process received a major boost for the preparation of multicomponent metal oxides such as perovskite materials.<sup>55, 56</sup> Today sol-gel processes are routinely used to prepare 0-D, 1-D and 2-D perovskite materials. Chemical solution deposition (CSD) is a typical chemical deposition method for thin film preparation using the sol-gel solution as the deposition precursor. It is important to consider the fundamental difference in phase formation pathways for thin film processes, such as PLD compared with CSD. In a typical PLD process, the deposition of the precursor (often of the same stoichiometry as the end material) and the high-temperature crystallization occur nearly simultaneously. In contrast, for CSD the deposition of the precursor solution onto a suitable substrate and the subsequent gelation (drying) process take place at low temperature (<100 °C) prior to a high-temperature crystallization step.<sup>27</sup> Consequently the formation of a homogenous and defect-free gel film is the first critical step, with complete bearing on the final thin-film microstructure, phase composition and ferroic properties. This key difference must also be viewed as an opportunity – it uniquely allows us to tailor the microstructure before crystallization takes place.<sup>27</sup> The intrinsic low energy of the system also results in good uniformity. Finally, we reiterate that it is also relatively an economically more viable method of mass fabrication.57

Regardless of the desired material structure, the fabrication process often starts from a chemical solution, which acts as the precursor. The typical precursor includes a metal source, a solvent and chelation agent. Under appropriate heating conditions, the precursor solution transforms into a cross-linked polymeric state,<sup>27</sup> called the "gel". Due to the liquid nature of the precursor, the end-product material can be fabricated in a range of

morphologies simply by "casting" the precursor into an appropriate template or by using different deposition approaches. For example, whilst spin-coating is suitable for thin films, pouring into template is employed for nanowires or nanotubes, and electrospinning is used for nanofibers etc. This is graphically shown in **Figure 1**. It becomes evident that the chemistry and stoichiometry of the precursor has strong influence on the ultimate quality. Again bearing in mind that phase crystallization occurs during the final annealing step, it is not commonly possible to identify and thus redress deficiencies that may stem from a poor or inappropriate precursor. It follows therefore that understanding what happens to the precursor at each processing step, and how its stoichiometry and physical features are affected, is of prime importance. In the following, we discuss the main chemical ingredients of a sol-gel precursor used for perovskite metal oxides with a particular emphasis on BFO.

# Metal compounds

In the traditional sol-gel process, aqueous precursors based on metal alkoxides in water are used as the starting materials, which follow a route of hydrolysis-condensation-gelation.<sup>27</sup> However, metal alkoxides are expensive and thus compromise the economic advantage of the CSD method. Instead, precursor derived from metal salts (metal nitrates or metal chloride) and organic solvent (2-methoxyethanol (2-MOE)<sup>58-62</sup> or ethylene glycol<sup>63</sup>) have been recently developed to prepare various perovskite materials. For BFO in particular, metal nitrates (i.e. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) have been used as universal metal sources for most BFO products, including BFO thin films<sup>32, 33</sup>, nanoparticles,<sup>15, 16, 64</sup> nanowires,<sup>37, 38</sup> nanotubes,<sup>35, 65</sup> and nanofibers<sup>17, 39</sup>. In addition to their economic advantage, metal nitrates have a low decomposition temperature which is shown to help elimination of carbon contamination in metal alkoxide.<sup>66</sup> In addition, since metal nitrates also have good water solubility, they also feature as the main metal source

for hydrothermal synthesis precursor preparation. The full reaction pathway using metal nitrate salts for BFO thin film is described in Section 3.

## (a) Solvent

For perovskite synthesis using the sol-gel process, the organic solvents 2methoxyethanol (2-MOE) and ethylene glycol (EG) are widely used as a substitute for a water-based solvent, due to the good solubility of various of starting reagents in these solvents.<sup>67, 68</sup> Both 2-MOE and EG have a linearly structured molecule, which is thought to be easier to form a dense and stable precursor molecule.<sup>68</sup> The growth of the linear or chainlike polymeric structure may also help the crystallization along a certain orientation, favoring the growth of oriented films or nanostructures.<sup>68, 69</sup> Moreover, the viscosity and surface tension of 2-MOE and EG are found to be highly suited to the spin-coating deposition process used for thin film fabrication.<sup>70</sup> One concern with using organic solvents is their toxicity, which may compromise their uptake for mass-manufacture. Compared with 2-MOE, EG has a lower toxicity; therefore, the development of EG to be used in BFO precursors and its waste treatment are important aspects to consider.

# (b) Chelating agent

Chelating agents such as acetic anhydride, acetic acid, citric acid, or tartaric acid, affect the solution viscosity and oligomeric structures during film formation.<sup>67</sup> Chelation reactions between the chelating agent and the metal source facilitate the gelation process under certain reaction conditions. The molecular structures of the different chelating agents determine the phases and morphologies of the final products; therefore the selection of a chelating agent is crucial in the successful fabrication of nanostructured BFO, especially when one desires BFO with specific morphologies.

#### **2.2 Hydrothermal synthesis**

Hydrothermal synthesis is a method to prepare high-quality crystals in hot water under high pressure and at a temperature higher than the boiling point for water.<sup>71</sup> It is popular because it is a facile route offering control by simply tuning of the solvent, temperature and pressure on the ionic reaction equilibria.<sup>72</sup> Since the mid-20<sup>th</sup> century, hydrothermal processing has seen rapid development in fabrication of micro or nanoscale materials. From the early 1990s, non-aqueous solvents have been developed for various types of hydrothermal reactions such as "ammonothermal",<sup>73-75</sup> "glycothermal",<sup>76, 77</sup> "alcohol-thermal",<sup>78, 79</sup> and a new approach, namely "solvothermal" has been used for all non-aqueous solvent based synthesis.<sup>80</sup>

In hydrothermal synthesis of BFO, the precursor of BFO is often prepared by dissolving the metal sources, bismuth and iron nitrates (Bi(NO<sub>3</sub>)<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>), in deionized (DI) water or nitric acid. Hydroxide KOH or NaOH are often used as the mineralizer to control the crystal size of nanomaterials.<sup>81, 82</sup> The iron and bismuth nitrates from the precursor first transform into Fe(OH)<sub>3</sub> and Bi(OH)<sub>3</sub> precipitates with the addition of the hydroxide. Further addition of the hydroxide mineralizer causes Fe(OH)<sub>3</sub> and Bi(OH)<sub>3</sub> to dissolve and react during the hydrothermal stage at a comparatively high temperature (~200°C) and pressure (autogenous), which takes place in a steel or Teflon pressure vessel called an autoclave. The hydrothermal process drives BFO precipitates through a supersaturated process.<sup>83</sup>

It becomes evident that in a hydrothermal process, the morphologies and properties of the desired materials are influenced by the reactive parameters between the ionic solid and fluid phases. The most critical parameters include temperature, pH values and mineralizer.<sup>72</sup>

- Typically in a hydrothermal process, temperature plays a key role in stabilization of the material phase. In the case of synthesis of transition metal oxides, it can modify the oxidation states of transition elements. It can also be tuned to optimize the size and shape of nanoparticles.<sup>80</sup>
- The pH value is important in tuning the ionization equilibrium conditions, which again control the morphology and size of the desired materials.<sup>80</sup>
- The role of the mineralizer is to act as a "catalyst" to aid formation of the seed crystals for the growth of desired nanomaterials. It is believed that the nanocrystal size and morphologies are strongly dependent on the concentration<sup>84</sup> and cationic radii<sup>82, 83</sup> of the mineralizer, which controls the dissolution, nucleation and crystallization of the metal oxide under hydrothermal conditions.<sup>82, 83</sup>
- Other factors include the formation of intermediate materials, and the solvent viscosity has also been found important to the morphology of final material, which directly affects the properties of the nanomaterials. The role of pressure is not yet clear as an autogenous pressure value is often used for synthesis.<sup>80</sup>

A distinct advantage of the hydrothermal synthesis process is that nanocrystalline or microcrystalline materials can be synthesized at much lower temperatures compared with sol-gel methods. Single-phase BFO crystallites have been prepared at as low as 200°C by using the hydrothermal synthesis process.<sup>41, 85, 86</sup> This technique thus offers significant potential to produce well-crystallized BFO powders with controlled morphology and narrow distribution of particle size. Disadvantages include the use of an expensive autoclave and the inability to perform in-situ analysis of the growing crystals due to the extremely harsh reaction environment.

#### 2.3 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is one of the most popular routes to manufacture functional nanomaterials. It is often used to prepare high quality, high-performance thin films on large area wafers or complex patterned substrates. Since the 1970s when this method was successfully used in semiconductor manufacturing, it has experienced rapid development,<sup>87</sup> and now has become a mature process in fabrication of various coatings.<sup>29, 30, 88-93</sup> The key difference from CSD is that instead of solutions as precursors, materials are prepared by CVD via the deposition of gaseous precursor onto the substrate. Thus, it requires high vapor pressure composition as the precursor and often the substrate must be heated to a particular temperature to facilitate the deposition reaction as well as the motion of adatoms.<sup>94</sup> A typical CVD system is shown in **Figure 2**, which includes a vapor pressure feed system, a CVD reactor (for heating the substrate) and an effluent gas handling system. Vapor precursors are often metal halides but depend on the type of reaction and materials. They are flowed with a reductant (H<sub>2</sub>) or non-metal source gas (e.g. oxidant).<sup>94</sup>

Metalorganic chemical vapor deposition (MOCVD), is a popular CVD method to prepare epitaxial or polycrystalline metal oxide thin films<sup>87, 95</sup>. It has been successfully used for the fabrication of ferroelectric perovskite thin films, such as  $BaTiO_3$ ,<sup>96, 97</sup> PbTiO\_3,<sup>92</sup> Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> (PZT),<sup>93</sup> and BiFeO<sub>3</sub>.<sup>29, 30</sup> A number of metalorganic vapor sources have been developed, such as barium β-diketonate, Ba(thd)2 and Titanium isopropoxide, Ti(OC\_3H<sub>7</sub>)<sub>4</sub> for BaTiO<sub>3</sub>,<sup>96, 98</sup> tetraethyl lead, Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, zirconium t-butoxide, Zr[OC(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> (or zirconium dipivaloylmethane, Zr(DPM)<sub>4</sub>) and titanium iso-propoxide, Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> for PZT.<sup>93, 99</sup>

Popular metal sources for BFO thin films include  $Bi((CH_3)_2(2-(CH_3)_2NCH_2C_6H_4))$ , Fe(C<sub>2</sub>H<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub><sup>30, 100, 101</sup> and Tris (2,2,6,6-tetramethyl-3,5-heptanedionate) bismuth(III) [Bi(thd)<sub>3</sub>] and Tris(2,2,6,6-tetramethyl-3,5-heptanedionate) iron(III) [Fe(thd)<sub>3</sub>] in tetrahydrofuran.<sup>29</sup> The last two are liquid precursors and thus require an additional liquid delivery or injection system to feed the sources into the chamber. The liquid turns into vapor once it enters the chamber at the high temperature and low pressure for deposition.

Using a gas source precursor to prepare BFO thin films, the Bi and Fe ratio can be controlled by the input gas flow rate R.

$$R[source] = [P_i(T_v) \times l]/P_v \qquad Eqn. 1$$

where  $P_i(T_v)$ , is the vapor pressure of the source vessel temperature, *l* is the carrier gas flow rate and  $P_v$  is the pressure of the vessel. The film thickness is heavily controlled by the reaction kinetics and hence the growth time. In the CVD process, the film composition and structure are rather sensitive to the substrate temperature, the precursor delivery ratio and the vaporizer temperature.<sup>29, 102</sup>

CVD processes have the advantage of high deposition rate and low deposition temperature. Compared with the CSD process, they offer much better control over the morphology, crystal structure and orientations, and as a result are often used to prepare epitaxial thin films.<sup>87, 95</sup> In addition, CVD is the most popular method to achieve highly conformal coatings on 3-D substrates for various devices.<sup>103</sup> However, it also has disadvantages, such as possible toxic gas released from the reaction; the substrate temperature may cause phase changes or grain growth and diffusion of dopants in microelectronic components; the corrosive gas can lead to poor adhesive between film and substrate and contamination of the film, and the process has a higher cost than CSD.<sup>94</sup>

In addition to thin films, CVD has also been developed to fabricate materials with nanostructures, such as carbon nanotubes<sup>104, 105</sup> and nanotube fibers,<sup>106</sup> ZnO nanowires<sup>107</sup> and nanorods.<sup>108</sup> Although no report has been found on the fabrication such BFO nanomaterials using CVD, experience gained with other materials should provide the required guidance for BFO and this is certainly an area that needs rapid development in the future.

# 2.4 Other chemical routes

In addition to the above popular routes, other chemical routes are also available to prepare BFO nanostructures, such as microwave/microwave-hydrothermal synthesis, and combustion synthesis.

## (1) Microwave-Hydrothermal synthesis

Microwave-hydrothermal (MH) synthesis is a modified approach by involving the microwave heating techniques during the hydrothermal synthesis procedure. The microwave heating process can largely increase the reaction and crystallization rate and enhance fabrication efficiency. Recently, this method has been used to prepare BFO nanostructures such as nanoparticles and nanocubes.<sup>43, 44, 109, 110</sup> The precursor preparation is similar to the hydrothermal process, but in the MH process, the autoclave is put in the microwave oven for heating during the hydrothermal process. It often takes only 0.5-1 hour <sup>43, 44, 109, 110</sup> for the whole process instead of the 5-72 hours<sup>42, 85, 111</sup> required for traditional hydrothermal synthesis.

## (2) Auto-Combustion Synthesis

Auto-combustion method is another wet chemical route used to prepare various nanomaterials.<sup>112</sup> In a typical combustion system, it involves the reactants, often oxidizers,

and organic fuels acting as a reducing agent. Typically the reaction is triggered by an external heating source as the ignition to the exothermic redox reaction, and the following combustion reaction leads to final crystallization during the continuous heating process from the reaction. This method has been successfully adopted to prepare BFO nanoparticles using metal nitrates as the reagent (oxidizer). As the BFO nanoparticles are obtained from the direct combustion reaction of the metal nitrates and the fuels, the final product phases are largely dependent on the composition of the fuels.<sup>45, 113</sup>

Given the diverse range of available methods described above, BFO materials have been fabricated into various morphologies and sizes. The parameters and details for each process can be subtle yet critically distinct depending on the ultimate morphology and functional requirement. Next we discuss the details of each synthesis technique for the respective form of nanostructured BFO, starting with thin films and then moving on to low dimensional 0- and 1-D nanostructures.

#### 3. Bismuth ferrite thin films

In 2003, Wang et al.<sup>3</sup> reported robust multiferroic behavior in epitaxial BFO thin films which gave rise to a surge of research effort in this material. They showed high quality BFO(001) thin films can possess a high remanent polarization( $P_r$ ) up to 55  $\mu$ C/cm<sup>2</sup> and a piezoelectric coefficient d<sub>33</sub> of approximately 70 pm/V.<sup>3</sup> An even higher polarization magnitude of ~100  $\mu$ C/cm<sup>2</sup> was demonstrated in BFO (111) thin films due to the (111)-oriented spontaneous polarization direction.<sup>19, 114, 115</sup> In addition, magnetic,<sup>3, 116</sup> resistive switching<sup>11, 117, 118</sup> and photovoltaic<sup>119, 120</sup> properties have also been observed for BFO thin films. High polarizations of up to 90  $\mu$ C/cm<sup>2 121</sup> and 150  $\mu$ C/cm<sup>2 122</sup> have been reported in polycrystalline BFO/Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si thin films measured at room temperature and 90 K, respectively. Furthermore, epitaxial strain plays an important role in enhancing BFO sample having a large fraction of the strained 'super-tetragonal' phase<sup>6</sup>. PLD and R-F sputtering derived films have also shown excellent promise as templates for domain engineering,<sup>123-125</sup> domain wall nanoelectronics,<sup>126-130</sup> ferroelastic-driven magnetoelectric switching.<sup>131-133</sup>

Given these highly desirable properties and rapid advances in physically-derived films, obtaining chemically-derived BFO thin films (in particular via CSD) with properties comparable to PVD BFO remains a challenge. The typical difficulties associated with CSD in obtaining BFO thin films with robust ferroelectric properties include high leakage current,<sup>66, 134, 135</sup> the formation of secondary phases,<sup>135, 136</sup> porous microstructures<sup>27</sup> or crystallographic defects.<sup>66</sup> None of these issues is really unsolvable. MOCVD-derived BFO thin films (i.e. films prepared via an alternate chemical deposition technique) have already been reported, having good ferroelectric properties with square loops, high remnant polarization, and robust d<sub>33</sub> values.<sup>29, 30</sup> Nevertheless, demonstration of CSD-

derived epitaxial BFO thin films having high ferroelectric polarization or resistive switching at room-temperature has been rather elusive.<sup>34, 121, 137-140</sup> Until recently, the best properties of CSD-derived BFO thin films had been reported by the Nakamura et al.<sup>121, 141</sup> In a series of articles they detailed phase development of polycrystalline BFO films with good P-E loops and low leakage current. Much of their discussion in terms of the frequency behavior and electric field dependence was limited to measurements performed at 80 K.<sup>141</sup> It was only recently that the key to obtaining high quality CSD BFO thin films was understood, through a detailed investigation of what happens during gelation<sup>32</sup>. It was shown that for the BFO CSD process, the central underpinning factor is the control of the gelation process such that it yields defect-free gel films. The paper shed key insight into the chemical processes during gelation (heating). In particular, the delicate competition between solvent evaporation and precursor gelation was ultimately found to be the key that determines if a homogenous gel is achieved. Controlling this balance to yield homogenous gel films was demonstrated as mandatory in order to achieve epitaxial and phase-pure BFO thin films with robust ferroelectric properties.<sup>32</sup> In the next few subsections we give a systematic account of the understandings of CSD of BFO thin films, with particular emphasis on role of precursors, gelation step as well as crystallization heating. Following that we move on to a review of results from reports on CVD-derived BFO thin films.

# 3.1 CSD-derived BFO thin films

The crux of preparation of high quality BFO thin films by CSD is the accurate control of the Bi:Fe stoichiometry.<sup>66</sup> Often imprecision of the starting chemical composition and the subsequent volatilization of Bi during the annealing step leads to secondary phases or highly conductive films with very poor leakage resistance.<sup>135, 136</sup> To counter this problem, excess Bi is often added to the starting reagents, which brings with

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it its own complication through the formation of bismuth-rich phases. Hence, there remains the important need to develop an accurate understanding of the chemical reactions that result from the nature of the precursors that are employed as well as the subsequent heat treatment steps wherein the final perovskite phase is achieved.

# 3.1.1 BFO CSD precursor preparation

The precursor is often prepared by mixing metal nitrates with the organic solvent (2-MOE or ethylene glycol), followed by adding acetic anhydride as the chelation agent, as well as dehydrating the solution. These are carried out at room temperature before spin coating.

The bonding chemistry of the precursor before and after heating process has been investigated in detail by Zhang et al.<sup>32</sup> After adding the acetic anhydride to the metal nitrate and 2-MOE precursor solution, acetic acid is formed as shown in **Eqn. 2**. In some other reports, acetic acid is used instead of acetic anhydride.<sup>142, 143</sup> However, water formed as a result of the crystals from metal nitrate in this precursor system cannot be removed and lead to precipitates during heating due to hydrolysis.

 $(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$  Eqn.2

The reaction **in Eqn. 2** is exothermic and the heat produced triggers the esterification reaction between 2-MOE and acetic anhydride to form acetic acid and 2-methoxyethyl acetate:

 $(CH_3CO)_2O + CH_3OCH_2CH_2OH \rightarrow CH_3COOH + CH_3OCH_2CH_2OCOCH_3$ 

Eqn.3

The formation of the ester 2-methoxyethyl acetate (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>3</sub>) is a crucial step. It increases the precursor drying time during spinning and heating due to its lower vapor pressure. This serves to reduce the tendency for precipitation during gelation and consequently contributes to a more homogenous gel film. The precipitates are metal salts in the organic precursor, and they form when precursor/precursor film dries before competition of gelation due to the onset of solution saturation. The precipitates in the film can cause a bismuth and iron phase separation and lead to an inhomogeneous film with impurities. Thus, it is important to avoid precipitate formation via control over precursor recipe and following spin-coating and drying processes.<sup>32</sup> Figure 3 demonstrates how precipitates formed during gelation negatively impact the final texture of the films.

The vapor pressure of the precursor also increases with increased metal nitrate loading in the precursor. This means introducing excess Bi (in order to compensate for Bi loss during annealing) via increased metal nitrate concentration is likely to promote precipitation during gelation. On the other hand a low metal nitrate concentration in the precursor may lead to an inhomogeneous and porous surface of the thin film due to a reduced amount of metal source. Therefore there is an optimal window for metal nitrate loading: a metal nitrate concentration of 0.25 M works well in order to obtain a smooth gel film.<sup>32</sup>

# 3.1.2 Spin-coating process

Once the precursor with optimized stoichiometry and viscosity are ready, the next step is thin-film deposition, which is typically realized using a spin coating technique. This process includes four general steps. (1) Deposition: the precursor solution is dropped on the surface of substrate; (2) Spin-up: The substrate starts to spin and the solution flows fast outward of the substrate by the centrifugal force; (3) Spin-off: The substrate spins at a constant velocity and excess precursor is removed by the centrifugal force as droplets; (4) Evaporation: In the last part of the spinning process, the film becomes thinner due to evaporation.<sup>27</sup>

The film thickness in the sol-gel process is largely governed by the spinning step. Film thickness after deposition strongly depends on the precursor viscosity, precursor density, spin-coating velocity and spin coating time. The relationship between film thickness and above factors can be described as:<sup>27</sup>

$$h(t) = h_0 / (1 + 4\rho\omega^2 h_0^2 t / 3\eta)^{\frac{1}{2}}$$
 Eqn. 4

where h = film thickness;  $\eta = liquid$  viscosity;  $\rho = density$  of the liquid; t = time;  $\omega = angular$  velocity

Thus, thickness of films varies directly with precursor viscosity, whilst it varies inversely with solution density, spin-coating time and spin-coating velocity. However, thick films fabricated using a highly viscous precursor or slow spin-coating velocity are susceptible to defects like cracking or phase inhomogeneity after drying. In practical situations thicker films are often obtained by repeating the spin-coating step several times to achieve the desired thickness.

The phenomenon of evaporation actually occurs during the entire spin coating process for BFO precursors. The spin coating process can even accelerate the evaporation (drying) process due to the increasing airflow rate above the films, which again promotes the formation of precipitates. It has been shown that preheating the substrates to the gelation temperature (e.g. 70°C) before adding drops of precursor onto the substrates for spincoating deposition is an effective and elegant way to avoid precipitates. The preheating possibly triggers initial gelation of the precursor layer on the heated substrate, as well as increasing the solubility of the metal nitrates in the precursor solution, thereby inhibiting precipitation.<sup>32</sup>

#### 3.1.3 Heat treatment

After spin coating deposition, heat-treatment processes are used to transform the asdeposited gel-film into a crystallized BFO thin film. These heat-treatment processes include drying, pyrolysis and crystallization.

# (i) Drying

Drying is a step to remove the solvent by heating. As drying simply works on evaporation, its rate is sensitive to the temperature and vapor pressure.<sup>27</sup> Compared to a bulk material, thin films have a comparatively large surface area to volume ratio, so the evaporation process of a thin film is often easier and faster. As discussed above, this process can happen during spin coating and heating. For thin-film samples, gelation often happens during the drying step as well as heating. To obtain a uniform gel film after drying, it is important to ensure that the gelation step is completed before drying, so that no precipitates are formed. This can be achieved by heating the sample for gelation at a temperature higher than 70°C, followed by completely removing the remnant solvent at 270°C.<sup>32</sup>

## (ii) Pyrolysis

The drying temperature is often not sufficient to remove all the polymers in the material and a higher temperature pyrolysis process is needed before crystallization to prevent the formation of defects. Films after pyrolysis are amorphous and the nucleation-and-growth process will occur in the following sintering (crystallization) process which takes place at a higher temperature.<sup>144</sup>

## (iii) Sintering

Two different high-temperature heat-treatments are often used for ceramic thin film sintering. One is the conventional heating process, by which the materials are heated slowly to a target temperature and maintained at this temperature for a specific duration (typically minutes). The other process, called rapid thermal processing, is an increasingly popular manufacturing process which heats films to a high temperature over short timescales of several seconds.

For both heat treatments, nucleation of the amorphous thin films starts first during the heating process, followed by the grain growth. The driving force of crystallization is determined by the free energy difference between the amorphous and crystallized material, and the temperature below melting point,<sup>144</sup> as illustrated in **Figure 4**. During the sintering and densification process, the particles begin to join together and the pores become smaller until elimination due to the diffusion of materials driving by interfacial energy. Since the solid-vapor area to volume ratio in gel thin film is large, the driving force for sintering the gel is strong even at low temperature, making the final sintering temperature comparatively lower compared to bulk BFO processing.

Nucleation often takes place either in the bulk body or the substrate-film interface of the thin-films. The former is a case of *homogeneous* nucleation, leading to random oriented grains and polycrystalline thin films. The latter case is *heterogeneous* nucleation, which often contributes to oriented columnar grain nucleation and growth matched to the substrate lattice structure. Generally, the nucleation barrier for heterogeneous nucleation is lower than that for homogeneous nucleation. The free energy diagram in **Figure 4** shows that a higher heating temperature decreases the driving force, thereby preventing homogenous nucleation. Therefore, rapid heating of the dried film to a high temperature

promotes preferred heterogeneous nucleation at the interface thereby promoting textured or epitaxial grain growth.<sup>66, 144</sup>

In addition to the heating rate and the absolute temperatures, even the role of ambient has been investigated in the CSD synthesis of BFO thin films. Yun et al.<sup>145</sup> reported that using stoichiometric BFO precursor, secondary phases, such as  $Bi_2Fe_4O_9$ , form when annealing at oxygen atmosphere, while polycrystalline BFO of single phase is obtained when heating at the nitrogen atmosphere. High performance polycrystalline BFO films with pure phase and high polarization have also been achieved by using a precursor with excess Bi<sup>140, 146</sup> and annealing at nitrogen atmosphere. In addition to polycrystalline BFO, nitrogen has also been used to prepare epitaxial BFO thin films,<sup>34</sup> but the films in this particular report were leaky in nature. These results strongly suggest that phase-pure BFO can be stabilized by annealing at low oxygen pressure. Tyholdt et al. studied the effect of atmosphere on the evolution of the BFO phase during heating. When heating in oxygen atmosphere, the reduction of  $Bi^{3+}$  to Bi metal was observed at around 200°C (Ref. <sup>66</sup>). This phenomenon was attributed to the decomposition and pyrolysis of polymers when the decomposition gas creates a local oxygen deficient atmosphere and thus contributes to the reduction of Bi<sup>3+</sup>. After decomposition and pyrolysis, Bi metal was found oxidized into Bi<sub>25</sub>FeO<sub>40</sub> at ~275°C and bismuth oxide at 365°C, followed by the formation of BFO form at 460°C.<sup>66, 147</sup>.

In contrast, we recently showed when the dried gel-film is heated in an oxygen-rich atmosphere, phase-pure epitaxial BFO thin films can be obtained using stoichiometric precursors. Further to this, annealing the films in oxygen atmosphere can also reduce oxygen vacancies and thus may help improve film resistance<sup>33</sup>. Square hysteresis loops with a high remanent polarization  $2P_r=97.8 \ \mu\text{C/cm}^2$  (discussed later) were obtained at room temperature, and coercive fields (E<sub>c</sub>~100 kV/cm) were much lower when compared

to films prepared by PLD or sputtering.<sup>32, 33</sup> We found that at low oxygen pressure the loss of oxygen occurs before the loss of Bi upon the breaking of Bi-O bonds. This means although using excess Bi in the precursor can lead to a pure phase BFO at a lower oxygen pressure, the formation of metallic Bi precipitates throughout the film due to the oxygen loss at higher temperature leads to the nucleation and growth of polycrystalline BFO.

The key result of our recent report is therefore that high quality epitaxial BFO thin films via a CSD process are indeed possible. It is important to note that both atomic force microscopy (AFM) and cross-section transmission electron microscopy (TEM) did not reveal any low angle grain boundaries and diffraction spots from selective area electron diffraction were sharp and distinct.<sup>32</sup> **Figure 5** schematically portrays our recipe for high-quality BFO thin films by CSD in full detail.

#### 3.2 MOCVD derived BFO Thin films

The second chemical method covered in this review for BFO thin film preparation is MOCVD. Gas sources Bi((CH<sub>3</sub>)<sub>2</sub>(2-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)), Fe(C<sub>2</sub>H<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>, and O<sub>2</sub> are often used as the source materials.<sup>30, 100, 101, 148</sup> Dopants can also be easily introduced by adding a metalorganic gas source, such as Co(CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>.<sup>100, 101</sup> Using this precursor system, the reactor is maintained at a specific pressure (530 Pa) and the substrate heated to a temperature of 500-700°C, similar to the crystallization temperature of CSD-derived BFO thin films. The films then are deposited using pulsed introduction of the mixed gas precursor for 10 s at 5 s intervals.<sup>30, 100, 101</sup>

Alternately, liquid metalorganic precursors are prepared by dissolving Tris(2,2,6,6-tetramethyl-3,5-heptanedionate) bismuth(III) [Bi(thd)<sub>3</sub>] and Tris(2,2,6,6-tetramethyl-3,5-

heptanedionate) iron(III) [Fe(thd)<sub>3</sub>] in tetrahydrofuran, which are both based on  $\beta$ -diketonates, for BFO fabrication.<sup>29</sup> In this case the additional liquid delivery (injection) system requires a showerhead. The showerhead is heated with oil during deposition to prevent the condensation of the vaporized precursor, thereby being able to achieve the homogenous film over a large area. Thery et al.<sup>149</sup> found Bi(mmp)<sub>3</sub> (mmp = 1-methoxy-2-methyl-2-propoxide) is a more effective liquid precursor compared with Bi(thd)<sub>3</sub>, which has a close oxide growth rate with Fe(thd)<sub>3</sub>. Using a liquid precursor, the evaporation temperature is controlled below 300°C to avoid reactions between precursors before deposition. The substrate temperature is set to about 550°C which is the maximum growth rate of both Bi(mmp)<sub>3</sub> and Fe(thd)<sub>3</sub>.

For gas source precursors, the stoichiometry of Bi and Fe in the film is controlled by the input gas flow rate or gas input ratio, and is dependent on the vapor pressure of the gas source material. The Bi/Fe molar ratio of the film has been shown to be linearly dependent on the input source gas ratio for the  $Bi((CH_3)_2(2-(CH_3)_2NCH_2C_6H_4)))$ ,  $Fe(C_2H_5C_5H_4)_2$  precursor system,<sup>30</sup> making control of thin film composition easy via changing the input source material ratio. As shown in **Figure 6(a)**, a  $Bi((CH_3)_2(2-(CH_3)_2NCH_2C_6H_4))/Fe(C_2H_5C_5H_4)_2$  ratio of ~0.5 is necessary to obtain phase-pure BFO thin films.

Using liquid source precursors, a linear behavior of BFO stoichiometry as a function of input Bi/Fe ratio is observed either in the Fe(thd)<sub>3</sub> and Bi(thd)<sub>3</sub> system or Fe(thd)<sub>3</sub> and Bi(mmp)<sub>3</sub> system, as shown in **Figure 6(b)**. A higher supply ratio of Bi precursor with respect to Fe is however required using the Fe(thd)<sub>3</sub> and Bi(thd)<sub>3</sub> system. This is because the vapor pressure of Fe(thd)<sub>3</sub> is about 2.5 times higher than that of Bi(thd)<sub>3</sub> at 190°C. In addition, only about 70% Bi(thd)<sub>3</sub> is completely vaporized while the remaining 30% is not volatile. A stoichiometric composition was obtained from a Bi/Fe liquid source

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mixing ratio of 2.43.<sup>29</sup> In comparison, the Bi(mmp)<sub>3</sub> precursor is more efficient: a Bi/Fe stoichiometry of 1 is obtained in this case for a precursor ratio of only  $1.25 \pm 0.05$ .<sup>149</sup>

It is believed that a better way to control the stoichiometry of BFO films is to explore heterometallic precursors containing both Bi and Fe. Recently, a single source precursor  $[CpFe(CO)_2BiCl_2]$  was used to prepare BFO thin films on Pt/SiO<sub>2</sub>/Si substrates with low band gap of 2.0 eV and weak room temperature ferromagnetic properties (saturation magnetization  $M_s$ =8.9 emu/cm<sup>3</sup>, coercivity  $H_c$ =115-135 Oe).<sup>150</sup> However, ferroelectric properties were not reported in this work. The development of single-source precursors that can yield high quality BFO thin films would be a remarkable breakthrough for integrating BFO into manufacturing platforms.

#### 3.3 Properties of chemical route derived BFO thin films

In this section we focus on the typical structural, multiferroic, and photovoltaic properties of chemical-route derived BFO thin films. Wherever possible, we provide a comparison of these properties with their physical route counterparts.

#### 3.3.1 Structural properties

**Figure 7** compares the out-of-plane lattice parameter of CSD, CVD and PLD derived BFO thin films on STO (001) substrates with varying thicknesses. Similar to PLD derived BFO thin films, epitaxial BFO films prepared by CSD and CVD processes can also achieve a highly strained state with large out-of-plane lattice parameter in thin films below a certain critical thickness (i.e. ~50 nm).<sup>30, 148</sup> Further to this, highly strained supertetragonal (T) and T-Rhombohedral (T-R) mixed-phase epitaxial BFO thin films have also been successfully fabricated on LaAlO<sub>3</sub> (001) substrates using CSD process in our lab. The measured out-of-plane lattice constants of the BFO R- and T-phases are 0.395 nm and 0.463 nm, respectively, indicating a co-existence of a fully relaxed R-phase and fully strained T-phase.<sup>151</sup>

Thus, there is no doubt that CSD and CVD processes have the capability to realize strained crystallographic phase structures and/or tailored domain states in epitaxial BFO thin films just as is possible through PLD or sputtering processes. The next step in this process is to understand the role of textures in CSD-fabricated films. A short discussion pertaining to substrate effects is provided in the outlook and summary sections.

## 3.3.2 Ferroelectric properties

Ferroelectric performance indicators (polarization, coercive field, fatigue, etc.) are most critical for applications such as memory devices, sensors, etc. As listed in **Table 2**, both CSD and CVD have been used to successfully prepare BFO thin films with high remanent polarization at room temperature. In particular, remanent polarization ( $2P_r$ ) of approximately 100  $\mu$ C/ cm<sup>2</sup> and 120  $\mu$ C/ cm<sup>2</sup> have been achieved for 150 nm CSD derived BFO/LSMO/STO(001) thin films and 250 nm CVD derived BFO/SRO/STO(001) thin films, respectively,<sup>29, 33</sup> as shown in **Figure 8(a)-(c)**. In addition, a d<sub>33</sub> of around 50-60 pm/V has been reported on CVD-derived BFO thin films (**Figure 8(d)**), a value comparable to that shown by their PLD counterparts.<sup>3</sup>

		Thickness (nm)	$P_r$	$E_{c}$	$d_{33}$	Condition	Pof
		(1111)	<u>(μυ/cm)</u>		(piii/v)	DT	32, 33
CSD	BF0/LSM0/S10(001)	150	50	96		K.1.	24
	BFO/SRO/STO(001)	100	50	~300		80 K	34
	BFO/Pt/TiO2/SiO2/Si	250	85-90	~350-400		R.T.	121, 146
	BFO/Pt/TiO <sub>2</sub> /SiO <sub>2</sub> /Si	10-20	92	450		80 K	152
	BFO/La-STO (001)		63	~385			
	BFO/La-STO (110)	130	84	~575			
	BFO/La-STO (111)		106	~690		90 K	153
	BFO/LNO/Si	115	~6-7	~20		R.T	154
	BFO/SRO/STO(001)	250	60	~250	50-60	R.T.	29
CVD	BFO/SRO/STO(001)	480	51	~166		80 K	30
	BFO/SRO/STO(001)	400	75	~150		80 K	31
PLD	BFO/SRO/STO(001)		55	~150			
	BFO/SRO/STO(110)	200	80	~180		R.T.	19
	BFO/SRO/STO(111)		100	~240			
	BFO/SRO/STO(001)	200	50-60	~150	70	R.T	3
R.F	BFO/SRO/STO(001)		71	~150			
	BFO/SRO/STO(110)	600	86	~130		R.T.	115
Sputter	BFO/SRO/STO(111)		98	~165			

Table 2 summary of ferroelectric properties of pure BFO thin films

In addition to pure BFO thin films, doped BFO thin films, whose components can be easily manipulated precisely via chemical route, have been found with positive effect on the improvement of room temperature ferroelectric properties of BFO thin films.

Compared with other perovskite oxide, the Fe in BFO can present a mixed valence state ( $Fe^{2+}$  and  $Fe^{3+}$ ) due to the volatilization of Bi and oxygen vacancies, an unavoidable side-effect of high-temperature heat treatment, especially in an oxygen deficiency atmosphere<sup>155, 156</sup>.

This procedure can be explained using Kroger-Vink Notation:

$$2Fe_{Fe} + O_0 \rightarrow 2Fe'_{Fe} + V_{\ddot{O}} + \frac{1}{2}O_2$$
 Eqn. 5

$$2Bi_{Bi} + 3O_0 \rightarrow 2V_{Bi}^{\prime\prime\prime} + 3V_0^{\cdot\cdot} + Bi_2O_3$$
 (Volatilization) Eqn. 6

The valence of Fe changes from +3 to +2 with the formation of oxygen vacancies. Oxygen vacancies, along with the change of Fe valence, are thought to be the main

contributors to leakage in BFO, This is a particular feature of BFO, when compared with other perovskite materials.

Dopants at either the A- or Bi-site by alio-valent cations has been widely used to effectively suppress generation of oxygen vacancies and thus tackle the leakage current problem. Possible A-site (Bi<sup>3+</sup>) dopants include La<sup>2+,157</sup> Ce<sup>4+,158</sup> Ba<sup>2+,159</sup> Ca<sup>2+,160</sup> and in the B-site (Fe<sup>3+</sup>), dopants of Mn<sup>4+,155,161</sup> Cr<sup>3+,162</sup> Ti<sup>4+,163</sup> Zn<sup>2+,164</sup> have been used. A-site substitutions can suppress generation of oxygen vacancies and B-site substitution by high valence ions, such as Ti<sup>4+</sup>, Mn<sup>4+</sup> can also decrease oxygen vacancies by consuming them<sup>161</sup>. For example, CSD derived Mn, Ca-codoped BFO(Bi<sub>0.90</sub>Ca<sub>0.10</sub>Fe<sub>0.90</sub>Mn<sub>0.10</sub>O<sub>3</sub>) thin films present a high polarization of 89  $\mu$ C/cm<sup>2</sup> and d<sub>33</sub> of 51 pm/V,<sup>160</sup> Cr-doped BFO (BiFe<sub>0.97</sub>Cr<sub>0.03</sub>O<sub>3</sub>) thin films achieved a high polarization 61  $\mu$ C/cm<sup>2</sup>-100  $\mu$ C/cm<sup>2,34,162</sup> In particular, many studies have shown that Mn doping BFO can effectively decrease the leakage current by controlling the amount of Fe<sup>2+</sup> in BFO. Wu et al.<sup>165</sup> compared doping of Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> and found that Fe<sup>2+</sup> concentration increases with the valence of Mn, leading to decreased oxygen vacancy concentration and lower leakage in BFO.

It is important to keep in mind that substitution of ions with higher or lower valence for Bi<sup>3+</sup> or Fe<sup>3+</sup> ions can create additional cation or anion vacancies. <sup>58, 134</sup> For example, when Ce<sup>4+</sup> ion substitutes Bi<sup>3+</sup>, <sup>158</sup> it acts as a donor in the oxygen octahedron:

$$2\text{CeO}_2 + \text{V}_{\ddot{\text{O}}} \rightarrow 2\text{Ce}_{Bi} + \text{V}_{\ddot{\text{O}}} + 4\text{O}_0$$
 Eqn. 7

Thus, it consumes the oxygen vacancy concentration and restrains the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  according to Eqn. 7. However, if one inadvertently introduces more  $CeO_2$  than oxygen vacancies, remnant  $CeO_2$  can cause much worse leakage problems:

$$2\text{CeO}_2 \rightarrow 2\text{Ce}_{Bi} + 4\text{O}_0 + 2\text{e}'$$
 Eqn. 8

Since the mobility  $\mu_0$  of electrons is much higher than that of oxygen vacancies, the conductivity caused by electrons will be higher than that by oxygen vacancies.

## 3.3.3 Other: magnetism and photovoltaic properties

In addition to desirable ferroelectric properties, BFO thin films show great potential for applications that exploit their ferromagnetic and photovoltaic properties. For example, a 30 nm BiFeO<sub>3</sub> film prepared by CVD shows a saturation magnetization of ~70 emu/cm<sup>3</sup> and a coercive field of ~130 Oe, (**Figure 8(e)**)<sup>149</sup>, comparable to PLD-grown BFO thin films.<sup>3</sup> Also, a low bandgap of 2.0-2.2 eV has been achieved in the CVD derived BFO thin films<sup>150</sup> using the single-source heterobimetallic precursor [CpFe(CO)<sub>2</sub>BiCl<sub>2</sub>]. These films show a better photocatalytic performance for water oxidation than commercial standard TiO<sub>2</sub> films under UVA and simulated solar irradiation, as shown in **Figure 8(f)**. Clearly this is an area that is currently attracting immense interest and presents as an opportunity for further development in the BFO community.

#### **4 Bismuth ferrite nanostructures**

In addition to thin films, popular forms of nanostructured BFO include 0-D structures (i.e. nanoparticles) and 1-D structures (i.e. nanotubes, nanowires, nanofibers). Figure 9 summarizes the progress of the past decade on BFO thin films and nanomaterials taken from Web of Science using keywords "bismuth ferrite nanoparticles", "bismuth ferrite nanotubes/nanotube", "bismuth ferrite nanowires/nanowire" and "bismuth ferrite nanofibers/nanofiber". Although studies focused on BFO thin films dominate those carried out for low-d BFO nanomaterials, there is a clear increasing trend for both in the past 5 years. This is in large part due to recent revelations that found nanostructured BFO (particularly low-d BFO nanomaterials) possess significantly modified or enhanced physio-chemical properties, as compared to bulk BFO. The change in the form of the BFO nanostructure and its effect on the properties is captured in **Figure 10** with the table listing corresponding properties. When it comes to low-dimensional BFO materials, chemical techniques "rule the roost". Chemical solution deposition (or sol-gel), hydrothermal synthesis, microwave-hydrothermal synthesis and combustion synthesis approaches have yielded nanoscale BFO with exciting new functionalities. We start therefore with 0-D nanoparticles followed by 1-D nanostructures (nanowires, nanotubes and nanofibers), in order to systematically elucidate the understanding of size effects on the functional properties.

#### 4.1 Nanoparticles

Nanoparticles are defined as the particles with dimensions between 1 and 100 nm whose properties are not found in the bulk material of the same composition.<sup>166</sup> The microstructures of typical BFO nanoparticles are shown in **Figure 11**.

#### 4.1.1 Synthesis methods

## (1) Sol-gel process

The sol-gel process is a simple and popular method for preparing nanoparticles. It also has the advantage of being easily able to incorporate dopants, which can effectively manipulate the particle size, band gap and magnetic properties, as discussed later. The whole process includes precursor preparation, drying, pyrolysis and annealing.

As for the thin film precursor, metal nitrates act as the metal source materials in nanoparticle sol-gel precursor and it is also flexible for doping. The dopants can be simply introduced by adding the corresponding metal salts, such as  $Eu(NO_3)_3 \cdot 5H_2O_1^{156}$ ,  $^{167, 168}$  Co(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O<sub>2</sub>,  $^{156}$  Gd(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O<sub>2</sub>,  $^{16, 169}$  Ba(NO<sub>3</sub>)<sub>2</sub>,  $^{170, 171}$  Sr(NO<sub>3</sub>)<sub>2</sub>,  $^{170}$  CaCl<sub>2</sub>·2H<sub>2</sub>O<sub>2</sub>,  $^{170}$  and Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O<sup>172</sup> in the bismuth and iron nitrate precursor with the desired molar ratio. When compared to thin film preparation, the fabrication process for nanoparticles is therefore more flexible, as there is no requirement on the roughness and coherency with substrate. There are three general sol-gel preparation methods for BFO nanoparticle precursor system, as described in the following.

## (a) Traditional route

The simplest method begins with the mixing of the metal nitrates with an organic solvent (2-MOE or EG) and stirring at 70-80°C for a few hours to obtain a homogenous, transparent blackish red solution. The precursor is then heated at a higher temperature (i.e. 120-160°C) to obtain the xerogel powder.<sup>15, 156, 173, 174</sup>

## (b) Acid assisted sol-gel method

Using this method, acid is introduced into the solution system. One typical acid used for BFO nanoparticle preparation is tartaric acid ( $C_4H_6O_6$ ).<sup>16, 64, 168, 169, 175</sup> In the tartaric

acid assist sol-gel route, the precursor is prepared by mixing the metal nitrates with organic solvent (2-MOE or EG), followed by adding tartaric acid (1:1 molar ratio with respect to the metal nitrates) to the precursor under a continuous stirring at 60-80°C when the clear sol turning into brownish gel.

Alternatively, acetic acid<sup>156, 167</sup> can also be used to prepare BFO nanoparticles. Precursor preparation is similar to the tartaric acid sol-gel route in that the initial precursor is prepared by mixing metal nitrates with the organic solvent, but  $NH_3 \cdot H_2O$  is added to adjust the pH of the solution to ~5 before adding acetic acid to the precursor. The solution is then constantly stirred at ~70°C to form the sol. The xerogel powder is then obtained by drying the brownish gel at approximately 120°C. In this precursor system, acetic acid acts as an unidentate complexing agent and the organic solvent (i.e. ethylene glycol) acts as a polar-coordinating solvent. After the addition of acetic acid and ethylene glycol, the Fe ions are octahedrally coordinated with nondentate acetic ions during heating. Then esterification occurs between acetate ligands and ethylene glycol during heating at 70°C. The resultant esters initiate the subsequent formation of Fe-O-Bi bonds at 120°C. <sup>167</sup>

## (c) Aqueous based sol-gel method

The last method is an aqueous based technique in which no organic solvent is involved in precursor preparation. The precursor system is formed by dissolving the metal nitrates in dilute nitric acid, followed by the addition of tartaric or citric acid.<sup>9, 40, 176, 177</sup> Using this method, the metal complex is formed with the addition of acid in the aqueous metal nitrate precursor, and the BFO nanoparticles begin to form at the calcination after the decomposition of the precursor.

Following any of the above methods, the dried gel powder is then ground and preheated to above 400°C for pyrolysis to remove organic impurities, and followed by further annealing at approximately 500-600°C to obtain the final nanoparticles.<sup>170, 172, 173, 178, 179</sup> In some studies, after the final sintering, the samples are washed in distilled water several times, followed by centrifuging and drying at 80°C.<sup>180</sup> The annealing temperature is found to be an effective method to control BFO nanoparticle size. The sizes of nanoparticles can vary from less than 15 nm to more than 100 nm by annealing at as low as 350 °C to approximately 650°C.<sup>8, 9, 177</sup>

In methods (b) and (c), it is believed that the chelating agent acids (i.e. tartaric acid, citric acid) play an important role in the synthesis process and nanoparticle phase and morphology. Using an aqueous based precursor, it has been shown that the synthesis temperature of the citric acid precursor is about 100°C lower than that of the tartaric acid precursor, bringing the temperature to form BFO nanoparticles using citric acid as low as 350°C.<sup>177</sup> On the other hand, it has also been found that impurities such as Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> form with the BFO nanoparticles when citric acid is used as the chelating agent and annealing temperature is at 600°C. In the aqueous precursor, ethylenediamine-tetraacetic acid (EDTA) on the other hand, as the chelating agent in the aqueous precursor, contributes to phase-pure BFO nanoparticles due to the formation of heterometallic polynuclear complexes in the solution.<sup>181,182</sup> The addition of acrylaminde and bisacrylamide monomers have also been found to be useful for controlling BFO particlar size by providing a framework for the growth of nanoparticles and tuning the pore size of the gel, respectively. That said, the overdose of bisacrylamide can lead to inhomogeneities and/or irregular shape of the particles, as well as impurities.<sup>182</sup>

Impurity phases have also been found in BFO nanoparticles derived from organic solvents (i.e. method (a) above) using citric acid as the chelating agent. This is due to the

dimeric nature of the citrate complex and the excess carbonaceous materials, that the impurities are often formed at a higher temperature during auto ignition process.<sup>178, 180</sup> In contrast, when tartaric acid is adopted, it forms bonds with metal ions via two carboxyl and two hydroxyl groups, leading to a stable polynuclear complex. The esterification then occurs between the metal complex and ethylene glycol to form the gel.<sup>180</sup>

The addition of an acid chelating agent also affects the size of the nanoparticles. As illustrated in **Figure 12**, the particle sizes of BFO nanoparticles derived from citric acid at 350°C and tartaric acid at 450°C are as small as 4 nm and 12 nm, respectively. <sup>177</sup>

# (2) Hydrothermal synthesis

Hydrothermal synthesis is a popular chemical route to synthesize metal oxide nanostructures, and nanoparticles in particular. Similar to the sol-gel process, it starts from the preparation of a precursor, but the crystallization phase takes place during a hydrothermal process rather than a high temperature annealing treatment. The final nanoparticles are obtained after washing, filtering, and final drying processes.

# (a) Precursor preparation

The most common hydrothermal synthesis method used to prepare BFO nanoparticles are via mineralizer-assisted route, in which mineralizers such as KOH  $(NaOH)^{81, 83, 84, 183}$  or  $KNO_3^{41, 86}$  are used to prepare the precursors. Via this method, the precursor can be simply prepared by resolving the metal nitrates in a distilled water and KOH solution before hydrothermal synthesis.<sup>184</sup> More often, the aqueous precursor is first formed by dissolving the metal nitrates in dilute nitric acid. The KOH solution is then added to the system to form Fe<sup>3+</sup> and Bi<sup>3+</sup> precipitates. The precipitates are filtered and washed by

distilled water to remove NO<sub>3</sub><sup>-</sup> and K<sup>+</sup> ions. After that, the cleaned precipitates are mixed with KOH or NaOH solutions, followed by adding additional KNO<sub>3</sub> under constant stirring.<sup>41, 85, 86</sup> As well as the above methods, other additives such as triethanolamine (TEA)<sup>183</sup> or sodium lauryl sulfate (SDS)<sup>111</sup> can be incorporated into the precursor system to modify nanoparticle properties. In particular, it is found that the addition of TEA forms a Fe-TEA complex and prevents the precipitation of Fe hydroxide, and it can decrease the synthesis temperature to as low as 130°C.<sup>183</sup>

Hydrothermal methods can also be modified without involving the mineralizer.<sup>40</sup> The  $Bi(NO_3)_3 \cdot 5H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$  are mixed in equal parts of citric acid ((metal: citric acid molar ratio) =1:1) to obtain the starting precursor. Then the precursor is dissolved in DI water by stirring the mixture for a few hours to get a homogenous precursor with complete mixture of metal ions with citrate ions. After that, the ammonia solution is added to the solution to neutralize the unreacted citric acid and adjust the pH to ~9.<sup>40</sup> Using this modified mineralizer-free method, the dried powder is finally calcined at 350°C for 6 h to obtain the final nanoparticles, which is highly phase-pure BFO with an average particle size of 55 nm.

## (b) Hydrothermal reaction

After obtaining the precursor, the solution is put in a Teflon linear autoclave for hydrothermal processing at 150°C-220°C for 5-20 hours.<sup>85, 86, 111</sup> Then the autoclave is cooled naturally to room temperature, the obtained precipitate is filtered and washed using deionized water (or/and 10% acetic acid) and absolute ethanol to remove all the soluble salts. Finally, the nanoparticles are obtained by drying the wet samples at 70-160°C for a few hours.<sup>41, 85</sup>

The synthesis of the BFO phase by the hydrothermal method is thought to be a dissolution-crystallization mechanism. Bi<sup>3+</sup> and Fe<sup>3+</sup> ions are first transformed into hydroxide Fe(OH)<sub>3</sub> and Bi(OH)<sub>3</sub> in the precursor, and then dissolved in the precursor with the presence of alkaline mineralizer (e.g. KOH, NaOH, LiOH) in hydrothermal conditions. When the ion concentration in the alkaline solution surpasses the saturation point, the BFO phase begins to nucleate and precipitate from the supersaturated hydrothermal fluid, followed by crystal growth.<sup>83, 185 82</sup> The size and morphology of BFO particles are dependent on the nucleation and crystal growth rate, which in turn are affected by the degree of supersaturation. A highly supersaturated precursor with high KOH concentration and high pH value will result in a high nucleation rate but low growth rate, and thus smaller particle size.<sup>84, 185</sup>

It is suggested that the phase and morphologies of the final product are very sensitive to the addition of mineralizer and reaction conditions during the hydrothermal process. Han et al.<sup>185</sup> and Chen et al.<sup>83</sup> studied the hydrothermal synthesis process for BFO phases with respect to the mineralizer KOH concentration, reaction temperature and reaction time. They successfully fabricated phase-pure BFO powders using 8M and 4M KOH, respectively, by maintaining the precursor at 175-225°C and 200-220°C, respectively, for 6 hours. The observed deviation from nominally-optimal conditions (i.e. KOH concentration) may arise from differences in the raw materials, and the different hydrothermal equipment and conditions.

In Han's study, minor  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> is obtained when 4 M KOH is used. They suggest that the metal nitrates react with KOH and form  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and iron hydroxide phase in the precursor:

$$2\mathrm{Bi}(\mathrm{NO}_3)_3 + 6\mathrm{KOH} \rightarrow \mathrm{Bi}_2\mathrm{O}_3 + 6\mathrm{K}^+ + 6\mathrm{NO}_3^- + 3\mathrm{H}_2\mathrm{O} \qquad \text{Eqn. 9}$$
$$Fe(NO_3)_3 + 3KOH \rightarrow Fe(OH)_3 + 3K^+ + 3NO_3^-$$
Eqn. 10

At a lower KOH concentration, the  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase will remain in the precursor, but it can be dissolved into Bi<sup>3+</sup> at a higher KOH concentration:

$$Bi_2O_3 + 2Fe(OH)_3 \rightarrow 2BiFeO_3 + 3H_2O$$
 Eqn. 11

The reaction temperature also plays an important role in the synthesis process. At lower temperatures (e.g. 150°C),  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase are formed as the main product. Increasing the temperature from 150°C to 175°C enhances the dissolution rate of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and phase-pure BFO is attained. Once one is able to obtain the pure BFO phase, further increasing of the temperature from 175°C to 225°C will only increase the particle size, but not change the phases.<sup>185</sup> A similar trend has also been observed by Chen et al.<sup>83</sup>

Further, with the presence of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase, increasing the pH, reaction time and temperature can effectively increase the solubility of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>, contributing to pure BFO phases. However, secondary phases may form from the precursor for an excessively long reaction time or with excess KOH when the ion concentration and pH changes with the precipitation of BFO phases. A higher KOH concentration will also bring in excess OH<sup>-</sup> ions, which may lead to particle agglomeration.<sup>83, 185</sup>

On the other hand, Yang et al found that the secondary phase of  $Bi_2Fe_4O_9$  forms at a low concentration of KOH. Because  $Bi^{3+}$  has a stronger affinity with OH- compared with  $Fe^{3+}$ , a low OH- concentration in the hydrothermal reaction solution leads to a more  $Fe^{3+}$ ions dehydrated into bismuth ferrite species in the hydrothermal condition, which contributes to the formation of  $Bi_2Fe_4O_9$ . With the increase of KOH concentration, the dehydration rate of  $Bi^{3+}$  and  $Fe^{3+}$  becomes balanced and thus the BFO phase is formed. <sup>186</sup>

When NaOH is used instead of KOH for hydrothermal synthesis, the strongly alkaline precursor solution and a high reaction temperature yield stoichiometric products. That is, for more alkaline conditions (pH=14) the addition of a small amount of H<sub>2</sub>O<sub>2</sub> can contribute to phase-pure BFO,<sup>84</sup> while a moderately alkaline precursor solution with pH of 8-12 and a low reaction temperature yield a nonstoichiometric product Bi12Fe0.63O18.945.84 Thus, in addition to the reaction conditions, the chemistry of the synthesized phase also strongly depends on the alkali metal ions. It has been found that pure BFO nanoparticles can be obtained at 200°C by using 7 mol/L KOH and 12 mol/L KOH, but NaOH and LiNO<sub>3</sub> solutions will stabilize  $Bi_2Fe_4O_9$  and  $Bi_{12}(Bi_0 5Fe_{0.5})O_{19.5}$ phases, respectively, in the final products regardless of concentration.<sup>85</sup> By adding KNO<sub>3</sub>, phase-pure nanoparticles of a much smaller size (~5 nm) are obtained<sup>86</sup>. This result suggests that alkali metal ions (K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup>) from the mineralizer play an important role in the formation of rhombohedral BiFeO<sub>3</sub>, orthorhombic Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, and cubic  $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$  by means of changing the solubility of  $Bi^{3+}$  and  $Fe^{3+}$  hydroxides.<sup>187</sup> while the  $NO_3$  may effectively decrease the growth speed of BFO nuclei in the supersaturated hydrothermal solution and accelerate the nucleation of BFO, thereby significantly reducing particle size.<sup>86</sup>

In addition, the cationic radii of mineralizers also play an important role in the size and morphology of nanoparticles. Hojamberdiev et al. found that final particle size decreases with decreasing cationic radii of the added mineralizers: average particle sizes of  $200\pm 10$  nm,  $120\pm 5$  nm,  $64\pm 3$  nm are obtained by using KOH, NaOH and LiOH, respectively.<sup>82</sup>

The synthesis temperature of hydrothermal processes is often controlled below 250°C and can be as low as 130°C,<sup>85 86, 183 184 111</sup> i.e., much lower than the sol-gel process. Nevertheless, the particle size of the obtained nanoparticles is often larger than 100 nm,<sup>85,</sup>

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<sup>183</sup> <sup>111</sup> which compromises the desired size effects and physical properties of the system. In addition, compared with sol-gel process, the path to phase-pure BFO is more complex for the hydrothermal route.

## (3) Microwave-Hydrothermal Synthesis

Microwave-hydrothermal (MH) synthesis is a modified synthesis approach based on the hydrothermal process. The precursor is quite similar to the hydrothermal synthesis precursor, but Na<sub>2</sub>CO<sub>3</sub> is often used with KOH as the mineralizer<sup>43, 44</sup> to obtain perovskite BFO crystals. After transferring the precursor into a Teflon autoclave, it is put into the microwave oven for the hydrothermal reaction by heating at 160-230°C for 30-60 minutes<sup>43, 44, 109, 110</sup>. The particle size prepared by MH methods can be as small as 10-50 nm<sup>43</sup> which is below the average particle size prepared by hydrothermal synthesis. In addition, MH has also been used to fabricate BFO nanocubes with an average size of 50-200 nm and low band gap of 2.1 eV.<sup>44</sup>

## (4) Auto-combustion synthesis

In this system, bismuth and iron nitrates are often used as the oxidizer, whereas glycine ( $C_2H_5NO_2$ ), sucrose ( $C_{12}H_{22}O_{11}$ ), ethylene glycol ( $C_2H_6O_2$ ), ethanolamine ( $C_2H_7NO$ ), citric acid ( $C_6H_8O_7 \cdot 6H_2O$ ), urea ( $CON_2H_4$ ), stearic acid ( $C_{18}H_{36}O_2$ ), etc. can be used as fuels. The metal nitrates are first mixed with dilute nitric acid <sup>45</sup> or distilled water<sup>46</sup> to form an aqueous solution, followed by addition of the fuels to the solution under constant stirring. The resulting precursor is then transferred into a container which can be heated at 80-200°C <sup>45, 46</sup> to form a thick gel-like product. The gels are then heated to above 300°C in a furnace to trigger the auto combustion reaction where the final BFO nanomaterials are obtained.<sup>45</sup>

		Chelating agent/		Synthesis		Band	Hc	Mr	Ms	Ref.
Method	dopants	mineralizer /Fuel	Solvent	Temp.(°C)	particle size (nm)	gap(eV)	(kOe)	(emu/g)	(emu/g)	
					14		0.058		1.55	8
	N/A				95		1.55		0.36	
					77 (BFO)	1.8	0.22	0.09	0.41	170
					34 (BBFO)	2.3	0.14	0.46	2.38	
	Ba, Sr,				29 (BSFO)	2.3	0.09	0.073	0.64	
	Ca	N/A	EG	550	28 (BCFO)	2.3	1.78	0.33	0.91	171
	_	/ .					3.92-	0.215-		1/1
	Ba	N/A	EG	650	20 - 63		4.77	2.681		188
	Dy, La	N/A	EG	600						100
					65 (BFO)				0.66	173
					28				1.01	
					$(\mathrm{Bi}_{0.9}\mathrm{Dy}_{0.1}\mathrm{FeO}_3)$				1.27	
	D	27/4	D.C.	(00	24 (D: D E O)					
	Dy	N/A	EG	600	$(B1_{0.8}Dy_{0.2}FeO_3)$		0.22	0.00	0.41	172
					70 (BFO) 27		0.22	0.09	0.41	
0 1 1					$(\mathbf{Pi}, \mathbf{C}_2, \mathbf{F}_2\mathbf{O})$		0.102	0.22	2.02	
Sol-gel					$(B1_{0.90}Cc_{0.01}CC_{3})$		0.110	0.49	5.05 1.17	
					(Bio or Ceo or FeOr)		0.101	0.10	1.17	
					17					
	Ce	N/A	EG	550	$(Bi_{0.95}Ce_{0.05}FeO_3)$					
	N/A	N/A	EG	500	35	2.06				178
	N/A	N/A	EG	500	90	2.55				179
	1011	1.011	20	200	40 (BLFO)	2.13				64
	Zn, La	Tartaric acid	EG	500	70 (BLZFO)	2.17				
	,				25 (BFO)				3.21	169
					15				10.11	
	Gd	Tartaric acid	EG	400	$(Bi_{0.9}Gd_{0.1}FeO_3)$					
			2-MOE +			2.56			~0.420	156
	Eu, Co	Acetic acid	EG	550	13 (BFO)					167
	Gd	Tartaric acid	2-MOE	820	100 (BFO)					10
								0.13		168
	Eu	Tartaric acid	2-MOE	820	100 (BFO)			(BEFO)		

## Table 3 Summary of characterization of BFO nanoparticles

	27/4	<b>T</b>	EG, nitric	500	60.00	2.6			180
	N/A	l artaric acid	acid 2-MOE, nitric acid	500	60-90			1.5	174
	N/A	Citric acid	PEG distilled water; nitric	500	60-120				176
	N/A	Tartaric acid Citric acid /	acid DI water.	425-575 350	18-248 4 (Citric acid)				177
	N/A	tartaric acid	nitric acid 2-MOE, nitric acid,	450	12 (Tartaric acid)	2.18	0.1	0.99	15
	N/A	Citric acid Tartaric acid /Malic acid/	PEG distilled water;	400-700	80-120				9
	N/A	Maleic acid	nitric acid Water, nitric acid, glucose,	400-650	11-86				181
		Ethylenediamine- tetraacetic acid	ammonia, acrylamide						
	N/A	(EDTA)	monomers, Distilled	600	110				184
	N/A	KOH KOH, KNO3 ( or	water Diluted	220	65-90				85
	N/A	LiNO <sub>3</sub> )	nitric acid Diluted	200	250 250 (without KNO <sub>2</sub> )				86
	N/A	KNO <sub>3</sub> , KOH	nitric acid Diluted	200	5 (with KNO <sub>3</sub> ) 5 (24 h)	2.19			41
Hydrothermal	N/A	KNO <sub>3</sub> , KOH	nitric acid Distilled water, nitric	200	50 (48 h)	2.10 2.12			183
	N/A	КОН	acid; TEA, Distilled water, nitric acid, ammonia	130	100				111
	N/A	КОН	solution,	200	170				

40

				sodium lauryl sulfate Citric acid, DI water, ammonia				0.225	7.2 (50kOe)	40
		N/A	N/A	solution	750	55				
			$Na_2CO_3$	Distilled			2.1			<sup>44</sup> *
1	Microwaya	N/A	KOH	water	180	50-200				
1	with the wave-			Distilled						43
1	iyurotnermar		$Na_2CO_3$	water,						
		N/A	KOH	nitric acid	180	10-50				
				Distilled				0.147		46
1	Auto-	N/A	glycine	water	unknown	25**				
(	combustion			Diluted						45
		N/A	$\alpha$ -alanine	nitric acid	300	32**				
		* M.	l ** No	amantallin a aina						

\* Nanocubes; \*\* Nanocrystalline size

The combustion reactions by using glycine and sucrose as fuels are shown below, where BFO is the only solid metal oxide product, while by-products  $CO_2$ ,  $H_2O$  and  $N_2$ can be easily removed during or after the reaction.

$$Bi(NO_3)_3 + Fe(NO_3)_3 + 3.33C_2H_5NO_2$$

$$\rightarrow$$
 BiFeO<sub>3</sub> + 6.66CO<sub>2</sub> + 8.33H<sub>2</sub>O + 4.66N<sub>2</sub> Eqn.12

However, the process may be more complex as impurity phases are often formed with BFO. Although Farhadi et al.<sup>113</sup> used sucrose  $(C_{12}H_{22}O_{11})$  to obtain phase-pure nanoscale BFO powders, later studies by Yang et al.<sup>45</sup> on the effect of the fuel composition on the resultant BFO phases found that glycine  $(C_2H_5NO_2)$  or ethanolamine  $(C_2H_7NO)$  show better performance. Generally the perovskite BFO phase is obtained with a few impurity phases and control over the combustion process for phase-pure BFO thus remains a challenge.

**Table 3** captures the key characteristics of the various chemical-route-derived BFO or doped BFO nanoparticles discussed in this section. This list by no means is comprehensive but has sufficient data to make the following observations with confidence: (i) smaller particles (<100 nm) are best obtained using sol-gel method by heating at 400-600°C; (ii) heating temperatures can also easily tune the size of particles from less than 20 nm to more than 200 nm without the introduction of impurities;<sup>176</sup> (iii) in comparison, the particle size prepared using hydrothermal synthesis is often larger, although the synthesis temperature is as low as 200°C, and finally (iv) scant is the information available on characterization and physical properties of BFO nanoparticles fabricated by microwave-hydrothermal and combustion synthesis processes.

### 4.1.2. Characterization and properties of BFO nanoparticles

The size-dependent functional properties and potential applications of BFO nanoparticles are discussed in this section.

#### 4.1.2.1 Ferroelectricity in BFO nanoparticles

It is commonly expected that ferroelectricity would be vanish at small sizes due to decreased long-rang ordering of dipoles.<sup>163, 189</sup> Direct measurement of ferroelectricity in 0-D nanostructures and the identification of a true ferroelectric size-effect is a highly challenging task. Firstly making electrical contact to an individual nanoparticle is only possible using scanning probe approaches, and to the best of our knowledge no report yet has ever published quantitative ferroelectric hysteresis properties of a single nanoparticle. The situation is compounded by not only the extremely small size, but also the leaky nature of BFO nanoparticles on account of their reduced band gap and switching voltages that may be very close to dielectric breakdown.<sup>190</sup>

Vasudevan et al.<sup>190</sup> used band excitation piezoresponse spectroscopy (BEPS) and piezoresponse force microscopy (PFM) to study the ferroelectric character of BFO nanoparticle clusters prepared by autocombustion methods (larger than 50 nm). They confirmed the existence of ferroelectric nature of the nanoparticles by obtaining a typical symmetric piezoresponse loop for a single cluster distributed on the LSMO/STO substrate with a coercive voltage of ~8 V (**Figure 13(a)**). In addition, they found ferroelectric domain structures (**Figure 13(b**)) within the particle clusters similar to those observed in BFO thin films.<sup>190</sup> On the other hand there is often a direct link between the ferroelectricity and the lattice strain (via the well-known strain-polarization coupling). This means detailed structural investigations on the lattice parameter or individual displacement of the cations can shed significant insight. This is best exemplified in the systematic investigation of the relationship between nanoparticle size and BFO lattice parameter as conducted by Selbach et al.<sup>9</sup> As shown in **Figure 14**, these authors found that nanoparticles of sizes larger than 30 nm exhibit lattice parameters comparable to bulk BFO. In contrast, the lattice parameter of BFO nanoparticles below 30 nm starts to deviate from bulk and approaches a cubic (i.e. paraelectric) perovskite structure. That is, there is a decrease in the rhombohedral distortion of the unit cell (i.e. reduction in c/a). It becomes equal to unity when the rhombohedral angle becomes 60°, which is the ideal cubic perovskite.<sup>9</sup>

Using an empirical model to fit the size-dependent tetragonality of BFO, a critical size  $d_c$  of 9±1 nm for ferroelectricity was obtained.<sup>9</sup> For 13 nm nanoparticles, the spontaneous polarization as determined by the displacement of the Bi<sup>+3</sup> and Fe<sup>+3</sup> cations was determined to be a 75% of the bulk value. This makes the BFO nanoparticles an exciting class of multiferroic materials — they are able to possess both strong magnetic moment (discussed below) and sufficient ferroelectric polarization for novel applications.<sup>9</sup>

#### 4.1.2.2 Magnetic properties

In contrast to their typically reduced ferroelectric properties, BFO nanoparticles have typically been found to show enhanced magnetic properties. In the bulk, BFO is a G-type antiferromagnetic material, with absence of coercivity at either room temperature or down to  $4K^{191, 192}$ . With the reduction of BFO material size down to the nanoscale, M-H coercivity starts to appear, suggesting the enhancement of magnetic properties.<sup>8,40</sup>

As listed in **Table 3**, the magnetic properties of sol-gel BFO nanoparticles show a coercive field (H<sub>c</sub>) of 0.05-1.55 kOe<sup>8</sup> <sup>170</sup> <sup>172</sup> and remanent magnetization (M<sub>r</sub>) of 0.09 emu/g.<sup>170, 172</sup> The M<sub>r</sub> can further enhanced to higher than 0.4 emu/g by the adding dopants to the system.<sup>170-172</sup> However, reports discussing the magnetic properties of hydrothermal derived BFO nanoparticles are relatively scarce possibly due to the larger average nanoparticle size.<sup>40</sup>

Park et al.<sup>8</sup> studied the relationship between BFO particle size and their magnetic properties. They found that when the particle size is larger than 245 nm, the properties are similar to those in bulk BFO (**Figure 15(a)**). Nevertheless, the magnetic response of BFO particles starts to increase when the particle size decreases to 95 nm and below, with a rapid increase of 270%-460% as the size drops to 62 nm. For nanoparticles with size between 41 nm to 95 nm, their magnetization shows a linear dependence as a function of inverse diameter (**Figure 15(b)**). However, the magnetization of the decreased particle size (i.e. 14 nm) is observed to deviate from the linear relationship, indicating that the magnetic response for this particle size can no longer be explained by the model of superposition of an antiferromagnetic core and a ferromagnetic surface.<sup>8</sup>

According to Selbach et al.<sup>9</sup>, the lattice distortion observed with reduction of the BFO nanoparticle size induces additional strains and distortions and disorder of the lattice at the particle surface.<sup>40</sup> This could promote suppression of the material's intrinsic spiral spin structure.<sup>8, 193</sup> Indeed it has been shown that strain and associated lattice distortion is an effective method for suppressing the cycloidal spin order in BFO thin films.<sup>14</sup> As the particle size is reduced to extremely small scale, instead of surface pinning, the surface strain introduces coordination distortion and lattice disorder that affects the entire particle due to the high surface-to-volume ratio.<sup>8</sup> It is believed that this surface anisotropic strain frustrates the spin structure and dominates the magnetic behavior of the nanoparticles.<sup>8</sup>

The large magnetic moment has been proposed to arise from uncompensated spins at the surface of the particles.<sup>8 173, 194 195</sup>

#### 4.1.2.3 Photocatalytic property

Compared with BFO thin films which have a typical band gap of ~2.7 eV,<sup>15, 196, 197</sup> BFO nanoparticles prepared by chemical routes exhibit a band gap as low as 1.8- 2.3 eV.<sup>15, 16, 41, 64, 170, 198</sup> thus making them attractive for application in photocatalysis. Enhanced photocatalytic performance has been observed for nanosized BFO particles, which can be used for the application of degradation of organic pollutant, such as dye compounds of Methyl Orange (MO), Methylene Blue (MB), Congo Red (CR) or Rhodamine B (RhB). For example, Gao et al.,<sup>15</sup> confirmed that BFO nanoparticles, in addition to their response to UV light, show excellent MO degradation ability under visible light irradiation [**Figure 16(a)**]. Guo et al. found that the Gd-doped BFO nanoparticles can further develop its photocatalytic properties by increasing RhB degradation rates from 79% for BFO to 94% for Bi<sub>0.9</sub>Gd<sub>0.1</sub>FeO<sub>3</sub>,<sup>16</sup> as shown in **Figure 16(b**).

One concern with using BFO as a photocatalyst is its photostability, which affects photocatalytic efficiency under visible light. Dunn et al.<sup>199</sup> studied the nonphotostability of BFO nanoparticles by studying the RhB dye decolorization at pH 2, 4 and 6.7, as shown in **Figure 16(c)**. They found that photocorrosion occurs through the dissolution of Fe from the Fe-O bond in the RhB dye solution, resulting in nonphotostability. This photocorrosion can be explained as an offshoot of the band offset of BFO with respect to the RhB dye, where holes can be injected from RhB dye into the BFO valence band. By replacing the BFO nanoparticles in the RhB solution at regular intervals, one can achieve a much higher decolorization rate, which can even exceed TiO<sub>2</sub> as shown in **Figure 16(d)**.

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This makes BFO nanoparticles highly promising for visible-light driven photochemistry.<sup>199</sup>

In addition, BFO nanoparticles have also been used to modify the photocatalytic properties of the exceedingly popular titania ( $TiO_2$ ) by mixing them in a  $TiO_2$ nanofiber/nanotube precursor to prepare BiFeO<sub>3</sub>/TiO<sub>2</sub> nanocomposite nanofibers<sup>198</sup> or nanotubes.<sup>200</sup> Prior to BFO, TiO<sub>2</sub> had been studied for years as a photocatalyst due to its excellent photochemical stability, low cost and non-toxicity.<sup>201-204</sup> However, the currently available TiO<sub>2</sub> photocatalysts often have a large band gap energy (Eg=3.2 eV for anatase) and exhibit rapid recombination of photo-induced carriers. In addition, the photoefficiency of TiO<sub>2</sub> is also limited to the visible light region.<sup>205</sup> Thus, there is a significant push to develop alternatives. The presence of BFO nanoparticles has a significant effect in enhancing the photodegradation efficiency under visible light, as well as hindering the recombination of photogenerated electrons and holes, due to the p-n junction formed at the interface of p-type BFO and n-type TiO<sub>2</sub>.<sup>198</sup> As shown in Figure 17(a), the photodegradation efficiency of TiO<sub>2</sub> nanofibers on MB only reaches 3% within 150 mins, while this efficiency can be enhanced to nearly 100% when 5 mol% and 10 mol% BiFeO<sub>3</sub> nanoparticles are embedded in the TiO<sub>2</sub> nanofibers.<sup>198</sup> However, the increased density of BFO nanoparticles also leads to a detrimental effect in photocatalytic activity as they can cover the active TiO<sub>2</sub> sites and hinder electron transfer at the BFO/TiO interface.<sup>198</sup> Similarly, the photoconversion efficiency of BFO/TiO<sub>2</sub> nanotubes in а 0.01 M Na<sub>2</sub>SO<sub>4</sub> solution can be enhanced from 0.7% for pure TiO<sub>2</sub> nanotubes to 3.2% for composite BFO/TiO<sub>2</sub> nanotubes under visible light,<sup>200</sup> as shown in Figure 17(b). Other modifications, such as a BFO-graphene nanohybrid has also been found to exhibit enhanced photocatalytic performance.<sup>206</sup>

The above-described enhanced magnetic and visible-light photocatalytic performance of BFO nanoparticles render them excellent candidates for further development and applications. Next we review the synthesis of BFO nanostructures with higher dimensions, such as nanotubes, nanowires and nanofibers, following with a discussion of their properties.

#### 4.2 BFO nanotubes, nanowires, and nanofibers

In general, 1-D nanomaterials are defined as materials being nanoscale (<100 nm) in two-dimensions (i.e. diameter) and having a large length to width ratio. Typical 1-D BFO nanostructures as shown in **Figure 18** include nanowires (solid wire-like- **Figure** 18(a)(b)), nanotubes (hollow center - **Figure 18(c)(d)**) and nanofibers (flexible wires-**Figure 18(e)**). The diameters of the as-prepared 1-D nanostructures are restricted to sizes below 50 nm for nanowires and below 150 nm for nanofibers. Nanotubes often have a larger diameter to accommodate the core, but the wall thickness is restricted to the nanoscale, approximately 20 nm on average. The most dominant fabrication method used for these 1-D structures is typically a sol-gel process with various modifications to suit the need, although hydrothermal synthesis has also been adopted to prepare simple 1-D nanostructures such as nanowires.

#### 4.2.1 Template-based BFO nanotube/nanowire synthesis

#### **4.2.1.1 Precursor preparation**

Anodic aluminum oxide (AAO) membranes are often used as templates to prepare nanotubes or nanowires. The structure of an AAO template prepared by anodization<sup>207</sup> with a nanoscale pore size is shown in **Figure 19(a)**. It is suggested that the walls of the pores are positively charged after anodization, but the charge can be reversed by changing

the AAO synthesis conditions.<sup>207</sup> 1-D nanostructures are fabricated by filling the pores with the precursor due to the driving force created by a capillary action [see **Figure 19(b)**].<sup>195</sup> The diameter *d* and the length of the 1-D nanostructures are controlled via the pore size and thickness of the AAO template respectively. It should be noted that the annealing temperature of BFO in an AAO template should be controlled below 800°C (ideally below 600°C), as BFO can easily react with Al<sub>2</sub>O<sub>3</sub> at temperatures above 800°C and form Bi<sub>2</sub>Fe<sub>4-x</sub>Al<sub>x</sub>O<sub>9</sub>.<sup>189</sup>

The precursor to be filled into the pores is often similar to those used by sol-gel process. Both aqueous and non-aqueous precursors have been reported, as discussed in the following.

## (i) Aqueous sol-gel process

An aqueous based sol-gel process has been reported by Wei et al. <sup>195</sup> Instead of using 2-MOE or EG as the solvent, dilute nitric acid and deionized water are used to dissolve starting metal nitrates (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and citric acid is added as the chelating agent. Ammonia is then added to adjust the solution pH to near neutral followed by adding urea (molar ratio of cations and urea is 1:20) to the solution. Then the template is put into the vessels with the above solution and kept at 80°C for 20 h. <sup>195</sup>

In this system, the chelating agent citric acid interacts with the metal nitrate sources and forms a metal-citrate complex to stabilize the aqueous solution. When heating at 80°C, urea undergoes hydrolysis as follows:

$$(NH_2)_2CO + 3H_2O \rightarrow 2NH^{4+} + 2OH^{-} + CO_2$$
 Eqn.14

The OH<sup>-</sup> then then can negatively charge the sol particles by combining with the metal-citrated complex, whilst the templated pore walls are positively charged. Thus the

sol particles are easily filled into the pores from the wall area and gradually extend to the center of the pores. The filled templates are then heated to 650°C for 5 h to obtain the final perovskite BFO nanotube.<sup>195</sup>

## (j) (ii) Non-aqueous sol-gel process

In this method a non-aqueous precursor solution (sol) is prepared by mixing the metal nitrate sources (i.e.  $Bi(NO_3)_3 \cdot 5H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$ ) with an organic solvent such as 2-MOE (Ref. <sup>208</sup>) or EG (Ref. <sup>35</sup>). An acid such as acetic acid<sup>34</sup> is added as the chelating agent. This solution is heated to 60-80°C under constant stirring to obtain a homogenous transparent precursor sol, followed by cooling to room temperature. Then the organic solvent is added again to adjust the metal concentration and form the final precursor.

For both aqueous and non-aqueous route, the pH plays an important role in the sol-gel synthesis of BFO nanowires/nanotubes. In a high pH reaction environment,  $Bi^{3+}$  and  $Fe^{3+}$  may react with OH<sup>-</sup> and form unwanted precipitates. A neutralization reaction may also occur between the chelating agent (i.e. citric or acetic acid) and OH<sup>-</sup>, and hinder the formation of the desired metal-complex due to reactions between the acid and  $Bi^{3+}$  and  $Fe^{3+}$ .<sup>38</sup> For this reason, the pH is often controlled between 3-6. <sup>37 38 209 208</sup>

#### 4.2.1.2 Deposition and fabrication of nanowires/nanotubes

For the sol-gel route, after obtaining the precursor, the AAO template is placed into the precursor and immersed for 1 h to enable the filling of precursor into the AAO pores. The BFO precursor can easily fill the pores of the AAO template through the capillary effect. If poor wettability of the template poses a challenge, a syringe is used to inject the sols onto the porous AAO template surface under pressure.<sup>35</sup>

Nanowires are obtained when the AAO templates holes are fully filled. On the other hand, if the sol particles are deposited only onto the AAO pore walls due to electrostatic attraction, then nanotubes are formed following drying and high temperature heat treatment.<sup>208</sup> The final morphology and form of the 1-D nanostructures, such as the size and wall thickness of nanotube are governed by; (1) metal concentration and precursor viscosity; (2) duration of immersion time; and (3) size of the AAO template pores and thickness. In particular, switching between nanowires and nanotubes has been realized by changing template immersion temperature and time.<sup>210</sup> A tube structure was first formed for immersions in the precursor for short times or at a low temperature. With increasing time or temperature the nanotube wall thickness increases until the tubes close in on the hollow core, thus forming nanowires.<sup>210</sup>

#### 4.2.1.3 Final drying and heat treatment

Once immersion is complete, the AAO template along with the inside precursor are dried at 100-150°C for 1-2 h, followed by heating at 400-450°C for pyrolysis and 650°C to obtain the final BFO phase in AAO templates. To remove BFO from the AAO template, the AAO is immersed in 4-6 M NaOH solution at room temperature for 10-24 hours and followed by centrifugation.<sup>35, 37, 208, 210</sup>

Of note is that as the nucleation of the BFO precursor starts from the AAO template walls during heat treatment, it is more likely to form polycrystalline BFO nanotubes with a random orientation due to the polycrystalline nature of the AAO template.<sup>35</sup> Also, the size of the nanotube is slightly smaller than the AAO pore size due to its shrinkage under heat treatment.<sup>195</sup>

#### 4.2.2 Template-free synthesis of BFO nanowires by hydrothermal techniques

Template-free methods have recently been developed using hydrothermal synthesis to prepare nanowires of various materials.<sup>42, 211, 212</sup> Liu et al.<sup>42</sup> successfully fabricated BFO nanowires using Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O as starting materials. These were mixed in a stoichiometric ratio in acetone with stirring and ultrasound until completely dissolved. Distilled water and concentrated ammonia were then added until the pH of the mixed solution reached 10–11. Then, the obtained sediment was centrifuged out and washed with distilled water several times until the pH value was neutral. After adding another 5 M NaOH to the system, the solution was transferred to a sealed, Teflon-lined steel autoclave and heated at 180°C for 72 h for the hydrothermal process. The black powder obtained after filtration was washed with distilled water and ethanol and dried at 60 °C. The individual BiFeO<sub>3</sub> nanowires had a diameter of 45–200 nm and a length from hundreds of nanometers to several microns. It is believed that the initial morphology of precursors and the concentration of NaOH play important roles in forming the nanowires without a template.<sup>42</sup> Just as is observed for nanoparticles, hydrothermal techniques typically yield nanowires with large diameter, due to the low synthesis temperature.

## 4.2.3 Preparation process for BFO nanofibers

BFO nanofibers are often fabricated by electrospinning process using precursors obtained via a sol-gel process. The current state of the art is described below.

#### 4.2.3.1 Precursor preparation of nanofibers

Similar to all other BFO sol-gel processes, metal nitrates  $(Bi(NO_3)_3 \cdot 5H_2O)$  and  $Fe(NO_3)_3 \cdot 9H_2O$  are used as the starting materials, dissolved in an organic solvent such as

2-MOE, to form the precursor. Doped BFO nanofibers are also possible by adding the corresponding dopant metal salts to the Bi/Fe metal nitrates organic precursor, such as tin chloride  $(SnCl_4 \cdot 5H_2O)^{213}$ , nickel acetate  $(Ni(CH_3COO)_2)$ ,<sup>39</sup> silver chloride (AgCl),<sup>39</sup> copper chloride  $(CuCl_2)$ ,<sup>39</sup> or lead chloride  $(PbCl_2)^{214}$  Then, acetone mixed with N,N-dimethyl formamide (DMF) in a ratio of  $1:2^{39, 213, 214}$  is added with the polymer poly (vinyl pyrrolidone) (PVP with molecular weight of 1,300,000) to the precursor to adjust the viscosity of the precursor and form a homogenous precursor under constant stirring. The concentration of PVP is approximately 0.04 g/ml-0.06 g/ml. <sup>39, 213, 214</sup>

The PVP concentration has been found to have a significant influence on nanofiber morphology. The weight ratio X=0.6, 0.75 and 0.9 of PVP over iron nitrate in the solution has been studied. As shown in **Figure 20**, the discontinued nanofibers and droplets are obtained using X=0.6 wt% PVP precursor because of its low viscosity. On the other hand, the nanofibers suffer extreme shrinking after annealing due to the large amount of PVP, when the PVP ratio increases to 0.9 wt%. The optimized PVP ratio is 0.75 wt% <sup>17</sup>

Alternatively, instead of using the 2-MOE organic solvent, the precursor can be prepared by dissolving the metal nitrates in distilled water and acetone (in a volume ratio of 1:2), followed by adding nitric acid and PVP in ethanol to the precursor under constant stirring. Finally 2,4-pentanedione (acetylacetone, or acac,  $C_5H_8O_2$ ) is added to the solution to form the final precursor solution.<sup>17</sup> The role of 2,4-pentanedione is to act as a chelating agent, helping to stabilize the sol system. In addition, it is able to bridge metal ions and help form a metal-complex with a relatively low decomposition temperature.<sup>17</sup>

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## 4.2.3.2 Deposition and fabrication of nanofibers via electrospinning processes

After preparing the precursor solution, the next step is to fabricate nanofibers via electrospinning. The typical electrospinning process is shown in **Figure 21(a)**. The solution is loaded into a syringe with a stainless steel needle. The distance between the tip of the syringe needle and an aluminum (Al) plate which acts as a collector, is fixed at approximately 10-13 cm.<sup>17, 39, 214</sup> The needle is connected to a high voltage supply (up to 40 kV) and the Al collector is grounded. During electrospinning, the feed rate is set to 0.5-0.9 ml/h<sup>17, 39, 214</sup> via the syringe pump. The droplet from the needle, which is charged and stretched because of the electrostatic repulsion and surface tension, forms a stable liquid jet in shape of a fiber towards the collector. The nanofibers are typically collected on substrates placed on the Al plate collector. The substrates can be Au/SiO<sub>2</sub>/Si,<sup>17</sup> Pt/Ti/SiO<sub>2</sub>/Si<sup>215</sup> wafers or clean glasses.<sup>39, 213, 214</sup>

Electrospinning can also be used to prepare multi-phase composite with complex structures<sup>159, 216</sup>, such as core-shell, Januz, or random structures.<sup>215, 216</sup> The setting for BFO-CFO bi-phase core-shell nanofibers is shown in **Figure 21(b)**. This system consists of two syringe pumps with different diameters and lengths of commercial needle. During the electrospinning process, the syringe loaded with core materials is positioned vertically to the needle with a smaller diameter size, and the syringe filled with the shell materials is horizontally connected to a needle with larger diameter size.<sup>215</sup> In this manner nanofibers with core-shell structure are fabricated during electrospinning.

During electrospinning, the accelerating voltage during spinning plays an important role in forming the uniform and nanoscale fibers, and it influences the morphology of the BFO nanofibers. As shown in **Figure 22**, thinner nanofibers are obtained with a higher voltage. However, the distribution of the nanofibers' diameter become less uniform when the voltage is too high (i.e.  $\sim 18$  kV).<sup>17</sup>

After collecting the nanofibers, the fibers along with the substrate are dried at 60-120°C for 2-4 h, followed by calcination at 550°C for 2 h in air in an oven at a heating rate of 5 °C min<sup>-1</sup>.  $^{39, 213, 214}$ 

The above synthesis details are summarized in Table 4 which provides is an exhaustive list of 1-D BFO nanostructures prepared by chemical route processes.

		(a)	Nanov	vires and n	anotudes			
	Chemical		pН	Deposition	Final	Diameter	Length	
Nanostructure	route	Solvent	value	method	Temp (℃)	(nm)	(um)	Ref.
		2-MOE, nitric acid	4-5	AAO	750	50	5	37
		Nitric acid, citric	5-6					
	Sol-gel	acid, NH <sub>3</sub> ·H <sub>2</sub> O		no AAO	400	8-10	0.1-0.2	38
Nanowire		2-MOE, nitric acid	3-4	AAO	600	20		209
		Acetone,	10-11					
	Hydrothermal	NH <sub>3</sub> ·H <sub>2</sub> O, distilled						(2)
		water,		no AAO	180	45-200	>1	42
						240-300		
						(wall: 20-		25
		EG		AAO	600	50)	50	35
			1-2			250		26
		2-MOE, nitric acid		AAO	700	(wall: 20)	6	30
		2-MOE,		AAO	700	150-200		201
		2-MOE, acetic	4					
		acid		AAO	650	190		208
		2-MOE, acetic				200		
Nanotube	Sol-gel	acid		AAO	600	(wall 20)	60	217
						230-310		
		2-MOE,		AAO	600	(wall 20)	5-20	218
		Nitric acid, oxalic				65		
		acid		AAO	600	(wall:16)	3.5	219
		Citric acid, DI						
		water, ammonia,				150-190		
		urea,		AAO	650	(wall 20)		195
			1-2			250		
		2-MOE		AAO	500	(wall 50)	4-5	65

# Table 4 Summary of characterization of BFO 1-D nanostructures

# (b) Nanofibers

Nanostructures	Solvent	Deposition method	Voltage used (V)	Final Temp (℃)	Diameter (nm)	Ref
	Acetone, distilled water, nitric acid, PVP in ethanol,					
	2,4-pentanedione	Electrospinning	12-14	400-600	165	17
Nanofibers (by Sol-gel)	2-MOE, acetone, DMF, PVP	Electrospinning		550	57-68	213
	2-MOE, acetone, DMF, PVP	Electrospinning		550	20-130	39
	2-MOE, acetone, DMF, PVP	Electrospinning	20	550	30-120	214

#### 4.2.4 Functional properties of 1-D BFO nanostructures

Similar to the case for nanoparticles, the most studied functional characteristics of 1-D BFO nanostructures are ferroelectricity, magnetism, and photonic properties. The effect of the reduced size is most beneficial for the magnetic and photocatalytic properties. We start with magnetism, followed by the photocatalytic properties and finally touch upon the ferroelectric and electromechanical behavior.

## 4.2.4.1 Magnetic properties

Nanowires with a diameter, or nanotubes with a wall thickness, smaller than a critical size (i.e. 62 nm; the length of the spin cycloid), will have incomplete spin compensation, giving rise to, in principle, an enhanced magnetic moment at room temperature.<sup>8, 195</sup> Compared to the typically linear M-H relationship found in bulk BFO, BFO 1-D nanostructures were found with a remnant magnetization and coercivity due to the aforementioned size effect.<sup>8, 42, 195</sup> As shown in **Figure 23(a)**, high M<sub>r</sub>, M<sub>s</sub> and H<sub>c</sub> of 0.94 emu/g, 4.22 emu/g and 177 Oe have been obtained in the sol-gel derived nanowires of 10 nm diameter size at room temperature<sup>38</sup>. Nanofibers have also been reported with comparable enhanced magnetic properties. **Figure 23(b)** shows the in-plane and out-of-plane magnetic properties of sol-gel based BFO nanofibers. The saturated magnetization is measured as large as 4 emu/g and coercive field is about 200 Oe.<sup>220</sup> This saturation magnetization is comparable with prior reports for BFO nanoparticles<sup>8</sup> where again the enhancement is believed to originate from finite-size effects.

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization behavior of 1-D BFO nanostructures as a function of temperature have also piqued interest. In particular, for the 1-D nanostructures, the length-to-diameter ratio is rather large such that the magnetic field along the structure's length is much larger than that along the diameter axis. Thus, under FC conditions, the magnetization will be enhanced due to the directionally ordered magnetic domains. <sup>37</sup> Gao et al.<sup>37</sup> found that the for both FC and ZFC ferromagnetic states of nanowires remain weak from RT to 42 K and slightly decreases from 42 K to 30 K, however, M starts to increase rapidly from 30 K to 5 K, as shown in **Figure 24(a)**. Later, the same tendency was observed for the FC curves of BFO nanowires and nanotubes down to mK temperatures.<sup>42, 221</sup> However, a critical maximum point (called the blocking temperature (T<sub>B</sub>) or freezing temperature (T<sub>f</sub>)) has been found in the ZFC curve at around 45-55 K, as shown in **Figure 24(b)**. This suggests a superparamagnetic nature of these BFO 1-D nanostructures, a commonly-observed phenomenon in nanoparticles.<sup>221-223</sup> The reason that no blocking point was observed in **Figure 24(a)** may be that this temperature could be below 5 K.<sup>224</sup> Clearly, this is an area that would benefit further from the recent developments in proximal probe techniques such as magnetic force microscopy (MFM),<sup>225, 226</sup> spin-polarized scanning tunneling microscopy (STM)<sup>227, 228</sup> and photoemission electron microscopy (PEEM).<sup>229</sup>

**Figure 24(c)** compares the M-H curve of hydrothermal-derived [221]-oriented single crystal BFO nanowires at 300 K and 5 K. It is evident that the enhanced magnetization is obtained at low temperature due to a spin glass transition, consistent with the temperature dependence of nanowire magnetization as discussed above.

#### 4.2.4.2 Photocatalytic and photovoltaic properties

1-D BFO nanomaterials have also shown tremendous promise for solar-based applications on account of their photocatalytic and photovoltaic properties, however in comparison to BFO nanoparticles, 1-D nanostructures possess a higher band gap (2.5  $eV^{37, 195, 218}$ ). It has nevertheless been argued that for semiconductor nanowires, their radial dimension and large surface-to-volume ratio helps promote the diffusion of

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electrons and holes generated at illumination, thereby hindering their recombination and increasing separation efficiency of charge carriers.<sup>230</sup>

BFO nanowires with photo-induced oxidization ability were found to produce oxygen in the AgNO<sub>3</sub>/H<sub>2</sub>O system with a considerable initial efficiency of 1876.28 mol·h<sup>-1</sup>g<sup>-1</sup>.<sup>37</sup> Further enhancement of this photoactivity was realized by Li et al.<sup>231</sup> by using modified hybrid BFO nanowires which contained Au nanoparticles adsorbed on their surface, as shown in **Figure 25(a)**. In this structure, the Au nanoparticles play the role of an electron-trap center when the photogenerated electrons are injected into the BFO nanowire. Additionally they also act as catalytic sites for gas generation from water oxidation under visible light illumination.<sup>231</sup> It was found [**Figure 25(b)**] the Au/BFO hybrid nanowires show significantly better photocatalytic performance over pure BFO nanowires, where the amount of oxygen generated from Au/BFO nanowire is about 3 times of that produced using pure BFO nanowires during the first 10 hours. This difference is even higher for the first 4 hours. This indicates that visible-light photocatalytic properties of BFO nanowires can be significantly improved by using this modified Au-embedded nanostructure.<sup>231</sup>

In addition to photocatalytic properties, one more important property of 1-D BFO nanostructures is their photovoltaic behavior. Compared with nanoparticles, the increased dimensionality makes it possible to fabricate devices and measure photovoltaic characteristics, as shown in **Figure 26(a)**. **Figure 26(b)** and **(c)** show the I-V curve of BFO nanofibers and nanowires under dark and illumination conditions, respectively. For both samples, it is clear that a much higher current is generated under the illumination condition compared to the dark condition, illustrating the excellent photovoltaic behavior of BFO 1-D nanostructures.<sup>17 18</sup>

It has been found that the current density of BFO nanofibers (~200 nm) in response to the applied voltage is about 1 mA/cm<sup>2</sup>, which is 2-10 times that of BFO thin films<sup>17</sup>. One reason proposed for the enhanced photovoltaic properties in nanofibers is that due to its freestanding feature the ferroelectric domains are easier to switch. It is also believed that nanofibers can trap more photons due to their geometric confinement.<sup>17</sup> Additionally the depolarization field may help to drive electrons and holes in opposite directions, hindering their recombination and thereby enhancing photovoltaic and photocatalytic performance.<sup>18</sup>

## 4.2.4.3 Ferroelectric and electromechanical properties

Similar to nanoparticles, weak ferroelectric and piezoelectric properties of nanofibers (200 nm diameter) have been observed using SPM.<sup>220</sup> <sup>17</sup> Domain sizes were measured to be ~100 nm but these could also be an artifact of the difficulty of landing a tip with robust contact onto a nanofiber, in addition to the complex electromechanical coupling between the tip and the fiber. It was found that to switch the domains of the nanofiber, a high voltage is required. The coercive field of BFO nanofibers is about 150 MV/m which is considerably higher than for epitaxial BFO thin films.<sup>3</sup>, <sup>29</sup>, <sup>33</sup> These intuitively seems contradictory to the hypothesis presented in the previous section and these issues thus require further detailed investigation. The maximum displacement induced by the external field is about 700 pm and the linear piezoelectric coefficient d<sub>33</sub> is about 22 pm/V on average. This value is smaller when compared to that found for epitaxial BFO thin films,<sup>3</sup> an observation that may due to the polycrystalline nature of the nanofibers.<sup>220</sup>

## 5. Future directions and outlook

Having discussed the synthesis and characterization details for chemical route-derived nanostructured BFO, we now focus our attention to the future of these techniques applied to this exciting class of functional materials. From a thin film perspective the next (obvious) step is to understand epitaxial strain-induced modulation of the functional properties, as well as understanding the role of textures. <sup>6 232 5, 7, 233, 234</sup> A considerable body of work now exists on how epitaxial strain, particularly using oxide substrates, can be exploited to engineer new properties in PVD derived films.<sup>235, 236 5, 234 237</sup> For example, using substrates which induce large in-plane compressive strains super-tetragonal (T), monoclininc (R) or mixed-phase (R-T) BFO thin-films have been demonstrated. These films have remarkably high electromechanical responses<sup>232</sup> and also intriguing magnetic properties.<sup>238</sup> It has already been shown that using BFO films fabricated by PLD and sputtering pathways, it is possible to induce a morphotropic phase boundary purely based on epitaxial strain.<sup>7</sup> However corresponding studies in chemical route derived BFO thin films are lacking. We previously have shown that phase pure epitaxial films with robust properties are indeed possible using chemical routes. Therefore the next step is to prepare these films on a variety of substrates. The lattice parameters of some common perovskite materials of thin films or substrates, as shown in Figure 27, adapted from Ref.<sup>239</sup>. The most common substrate used for BFO thin-film is SrTiO<sub>3</sub>,<sup>3, 24</sup> which has a pseudocubic aaxis lattice parameter of 3.905 Å and small lattice mismatch of 1.4 % with BFO, leading to a weak compressive strain. Other substrates, such as  $LaAlO_3^{235, 236}$ ,  $LaSrAlO_4^{5, 234}$  or  $NdScO_3^{237}$  are now being explored in our lab to make highly strained sol-gel derived epitaxial thin BFO thin films<sup>232, 237</sup>. Furthermore the possibilities via texture and domain engineering have not even been touched upon using sol-gel BFO thin films. We also do not yet understand how domain wall conductivity<sup>126, 240</sup> and resistive switching.<sup>118</sup>,

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exciting new avenues for polarization mediated transport devices, are affected in films fabricated by chemical routes. For example, whilst oxygen vacancies are always prevalent in PVD techniques due to the high temperatures and relatively low oxygen partial pressures during synthesis, BFO films made via CSD method are always annealed in richer oxygen environments. Whether this subsequently would impact domain wall conductivity or band offsets, both of which are shown to be heavily oxygen vacancydependent,<sup>241, 242</sup> is an open question. These are avenues we are ardently pursing in our lab and we hope to report exciting results in the near future.

We have already found that the morphology of mixed phase (R-T) BFO thin films made via sol-gel is qualitatively different from those made via PLD. In sol-gel one can assume that the flux of atoms is dramatically different to PLD (in the sense that the material that needs to be crystallized is already present). Therefore we expect that the strain relief mechanisms that were found for PLD or sputtering may not hold true here. In addition to the substrates with different lattice parameters, the strains within thin films can also be controlled via the film thickness<sup>7, 234, 243</sup>. Although we did show some thickness dependence in Ref<sup>33</sup>, it was not as comprehensive as has been done for the PVD counterparts.<sup>154, 244-246</sup>

From a technical perspective, the community needs to think about in-situ methods of diagnosis for chemical route derived films. For example, could the film be heat-treated in a PLD chamber with reflective high energy electron diffraction (RHEED) capabilities such that the phase development occurring during the BFO crystallization process can be traced? We have shown that when used in transmission mode, the electron diffraction pattern can reveal significant insight in the synthesis of epitaxial magnetic oxide nanocrystals.<sup>247</sup> Therefore clearly the next steps in this area should be control and characterization of interface driven phenomena that underpin the synthesis stage.

From a synthesis perspective a significant challenge in chemical techniques is the sensitivity of the prepared precursors towards the reaction conditions, such as temperature, pH value, pressure, humidity, concentrations, and the various unclear intermediate products during the synthesis process. Again new in-situ modes in analysis methods such as nuclear magnetic resonance (NMR), Raman spectroscopy, etc. will help us design new more stable precursors. Of course nowadays one cannot overlook the implications of damage to the environment and operator health. A number of the chemicals used are not only toxic but also pose numerous waste removal challenges. Therefore more efforts need to go into a comprehensive understanding of the chemical routes such that green alternatives can be realized.

In terms of materials development, the role of dopants, and in particular how they affect ferroelectric and electromechanical performance, in chemical route-derived BFO needs to be understood. It is already known that rare-earth modification in PLD-fabricated epitaxial BFO or ceramics made by solid-state sintering techniques leads to enhanced electromechanical response. Should the same be expected when using sol-gel or CVD methods? How one may incorporate compositional multilayers remains an area of great interest and promise.

For low dimensional nanostructures the most challenging task ahead is ferroelectric characterization. For this proximal scanning probes are unavoidable but perhaps we can look beyond the now almost routine PFM methods of characterization. For example researchers at Oak Ridge have recently shown how to use the acoustic response to map ferroelectricity for films.<sup>248</sup> Can this technique be extended to image and measure ferroelectricity for these BFO nanomaterials? There is also a tremendous opportunity to develop spin-based proximal characterization probes.

There is no doubt that BFO thin films and nanostructures are of significant fundamental scientific and applications interest. They show clear and promising potential in the applications of ferroelectric or magnonic memory devices, photocatalytic and photovoltaic devices. By understanding the role of chemical-routes in the development of BFO materials, the multiferroic community can unlock the full potential of this amazing materials system which has already shown to be a treasure-trove of functional properties. Indeed while fundamental physical questions and exciting device concepts can be explored using BFO fabricated via sophisticated PVD methods, a great hurdle for such methods is their unsuitability to mass manufacture. The focus for the next decade should be the enhancement of the function properties of BFO derived from chemical routes, and the realization of the practical and efficient nanoscale devices. This will bring mass manufacture within our grasp and in doing so, the possibility that BFO can indeed truly shape our daily lives. Figures



Figure 1. Preparation of various structures via the sol-gel approach.



Figure 2. Schematic diagram of a chemical vapor deposition (CVD) system.









Figure 4. Diagram of the free energies of a sol-gel derived amorphous film<sup>144</sup> Reproduced with permission from Ref 144, copyright 1997 American Chemical Society.



Figure 5. Chemical solution deposition process for BFO thin film preparation.



Figure 6. Bi/Fe molar ratio in films as a function of the input Bi to Fe ratio from the source material, (a) R[Bi((CH<sub>3</sub>)<sub>2</sub>(2-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>))] and R[Fe(C<sub>2</sub>H<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] source material system <sup>30</sup>, reproduced with permission from Ref 30, copyright 2005 The Japan Society of Applied Physics. (b) Fe(thd)<sub>3</sub> and Bi(thd)<sub>3</sub> system and Fe(thd)<sub>3</sub> and Bi(mmp)<sub>3</sub> system<sup>149</sup>, reproduced with permission from Ref 149, copyright 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



Figure 7. Out-of-plane lattice parameter of BFO thin films derived from various processes as a function of the film thickness<sup>30</sup> (♦ CSD films by Zhang et al.<sup>33</sup>; □ CVD films by Ueno et al.<sup>30</sup>; ▲ PLD films by Wang et al.<sup>3</sup>; ● PLD films by Eerenstein et al.<sup>249</sup>). Adapted from Ref 30.



**Figure 8.** (a) Room temperature P-E hysteresis loops of 150 nm CSD drived BFO thin films measured at 2 kHz-100 kHz,<sup>32</sup> reproduced with permission from Ref 32, copyright 2015 Royal Society of Chemistry (b)Room temperature pulsed polarization of 70 nm and 150 nm CSD derived BFO thin films as a function of electric field,<sup>33</sup> reproduced with permission from Ref 33, copyright 2014 American Institute of Physics; (c) Room temperature P-E hysteresis loops and (d) Piezoelectric coefficient loops,  $d_{33}$  of a 250 nm-thick BiFeO<sub>3</sub> film prepared by CVD,<sup>29</sup> reproduced with permission from Ref 29, copyright 2005 American Institute of Physics; (e) Magnetization of a 30 nm MOCVD derived BiFeO<sub>3</sub> film as a function of applied magnetic field,<sup>149</sup> reproduced with permission from Ref 149, copyright 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (f) continuous oxygen evolution of both BiFeO<sub>3</sub> and TiO<sub>2</sub> (Activ) films as a function of solar irradiation period,<sup>150</sup> reproduced with permission from Ref 150, copyright 2014 Royal Society of Chemistry.



**Figure 9.** Publication trends of BFO thin films and nanomaterials over the last decade. Data are obtained from web of science (Year 2005 to Dec 2015) using keywords BiFeO<sub>3</sub> thin film, BiFeO<sub>3</sub> nanoparticles, BiFeO<sub>3</sub> nanowire/nanowires, BiFeO<sub>3</sub> nanotube/nanotubes, and BiFeO<sub>3</sub> nanofiber/nanofibers, respectively.

	3-D	2-D	1-0	0-D
	Bulk	Thin-film	Nanowires Nanotubes Nanofibers	Nanoparticles
$P_r(\mu C/cm^2)$	$100^{250}$ (single crystal) $\sim 40^{251}$ (bulk ceramic)	50-100 <sup>19, 32 29</sup>	N/A	N/A
M <sub>s</sub> (emu/g) H <sub>c</sub> (kOe)	N/A	~70 emu/cm <sup>3149</sup> 0.13 <sup>149</sup>	$\sim 4^{38, 220}$ $\sim 0.2^{38, 220}$	0.36-7.2 <sup>8,40</sup> 0.058-1.55 <sup>8</sup>
Band gap (eV)	2.7 <sup>252</sup>	2.0-2.5 <sup>150</sup>	2.5 <sup>37, 195,</sup> 218	1.8-2.3 <sup>170</sup>

Figure 10. BFO with various dimensional structures and related properties



Figure 11. (a) TEM images of typical BFO nanoparticles; (b) a single BFO nanoparticle with a diameter of ~12 nm, <sup>43</sup> reproduced with permission from Ref 43, copyright 2011 American Ceramic Society.



Figure 12. Nanoparticle size and morphologies using (a) tartaric acid and (b) citric acid,<sup>177</sup> reproduced with permission from Ref 177, copyright 2011 Hindawi Publishing Corporation


Figure 13. (a) Piezoresponse and phase hysteresis loops of a single BFO nanoparticle. Out-of-plane PFM amplitude (b) and phase (c) images of a nanoparticle cluster, before and after applying +10 V, 5 s pulse to the center of the cluster. Insets in (b) and (c) show the PFM amplitude and phase before applying the bias, respectively, the above measurement were done on the LSMO surface,<sup>190</sup> reproduced with permission from Ref 190, copyright 2011 American Institute of Physics.



Figure 14. Normalized lattice parameters of nanocrystalline  $BiFeO_3$  as a function of crystallite size *d*. (*a lattice parameter* (open circle), *c lattice parameter* (open square), and pseudo-tetragonality c/a (red filled triangle)). Inset shows the unit-cell volume as a function of crystallite size,<sup>9</sup> reproduced with permission from Ref 9, copyright 2007 American Chemical Society.

(a)

M (emu/g) 0

1

-2



nanoparticles with various particle sizes. (b) Expanded plots of the magnetization of as synthesized BiFeO<sub>3</sub> nanoparticles in (a), the return branches are removed for clarity. The inset of (a) and (b) show the magnetization value at 50 kOe as a function of BFO nanoparticle size (diameter, d) and as a function of 1/d, respectively,8 reproduced with permission from Ref 8, copyright 2007 American Chemical Society.







Figure 17. (a) The visible-induced photocatalytical activity of a-TiO<sub>2</sub>, b-BiFeO<sub>3</sub>, c-80%TiO<sub>2</sub>/20%BiFeO<sub>2</sub>, d-85%TiO<sub>2</sub>/15%BiFeO<sub>2</sub>, e-92%TiO<sub>2</sub>/8%BiFeO<sub>2</sub>, f-95%TiO<sub>2</sub>/5%BiFeO<sub>2</sub>, g-90%TiO<sub>2</sub>/10%BiFeO<sub>2</sub>. (percentage in molar ratio), <sup>198</sup> reproduced with permission from Ref 198, copyright 2014 Royal Society of Chemistry; (b) photoconversion efficiency for the BiFeO<sub>3</sub>/TiO<sub>2</sub>- nanotubes and TiO<sub>2</sub>-nanotubes electrodes under visible-light irradiation as a function of applied electric potential in a 0.01 M Na<sub>2</sub>SO<sub>4</sub> solution,<sup>200</sup> reproduced with permission from Ref 200, copyright 2014 American Chemical Society



**Figure 18.** (a) TEM image of BiFeO<sub>3</sub> nanowires and (b) individual BFO nanowires, <sup>42</sup> reproduced with permission from Ref 42, copyright 2011 Royal Society of Chemistry; (c) SEM image of BFO nanotubes; inset shows a vertical BFO nanotube arrays at a higher magnification (scale bar = 100 nm),<sup>195</sup> reproduced with permission from Ref 195, copyright 2007 Published by Elsevier Ltd. on behalf of Acta Materialia Inc.; (d) BFO nanotubes prepared in AAO template with 200 nm diameter pores (inset shows the SAED patterns of a individual nanotube),<sup>35</sup> reproduced with permission from Ref 35, copyright 2004 Royal Society of Chemistry (e) BFO Nanofibers prepared by electrospinning,<sup>17</sup> reproduced with permission from Ref 17, copyright 2015 American Chemical Society.



**Figure 19.** (a) AAO template<sup>253</sup> and (b) template filling with BFO sol-gel solution,<sup>36</sup> reproduced with permission from Ref 253, copyright 2008 American Chemical Society and from Ref 36, copyright 2005 American Institute of Physics.



Figure 20. Morphology of BFO nanofibers as a function of PVP weight ratio,<sup>17</sup> reproduced with permission from Ref 17, copyright 2015 American Chemical Society.



**Figure 21.** Schematic setup of (a) a general electrospinning system<sup>212</sup> and (b) coaxial electrospinning system, <sup>215</sup> reproduced with permission from Ref 212, copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim and from Ref 215, copyright 2014 Materials Research Society.



**Figure 22.** Morphology of BFO nanofibers as a function of applied voltage for electrospinning,<sup>17</sup> reproduced with permission from Ref 17, copyright 2015 American Chemical Society.



Figure 23. (a) Magnetic hysteresis of as-prepared and 400°C annealed BFO nanowires (via sol-gel combustion method) measured at room temperature, and the M-H loop of the bulk BiFeO<sub>3</sub> under identical condition for comparison,<sup>38</sup> reproduced with permission from Ref 38, copyright 2012 SpringerLink (b) Room temperature inplane and out-of-plane M-H loops for sol-gel derived BFO nanofibers,<sup>220</sup> reproduced with permission from Ref 220, copyright 2008 American Institute of Physics



Figure 24. (a) and (b) M-T curves for the BFO nanowires measured under ZFC and FC (H=0.1 T) conditions. The inset in (a) presents the ZFC data below 75 K.<sup>37 42</sup> (c) M–H hysteresis loops for BiFeO<sub>3</sub> nanowires measured at 5 and 300 K, <sup>42</sup> reproduced with permission from Ref 37, copyright 2006 American Institute of Physics and from Ref 42, copyright 2011 Royal Chemical Society.



**Figure 25.** (a) TEM images of the BFO/AU nanowires; (b) Oxygen evolution over time for the BFO and BFO/Au nanowires upon visible light ( $\lambda > 380$  nm) illumination of the FeCl<sub>3</sub> suspension (4 mmol/L, 50 mL), <sup>231</sup> reproduced with permission from Ref 231, copyright 2013 Royal Chemical Society



Figure 26. (a) Schematic illustration for the measurement setup of BFO nanofiber based photovoltaic devices<sup>17</sup> (b) I-V curve for nanofibers<sup>17</sup> and (c) nanowires,<sup>18</sup> reproduced with permission from Ref 17, copyright 2015 American Chemical Society and from Ref 18, copyright 2015 Elsevier Ltd.



Figure 27. Pseduocubic a-axis lattice parameters of BFO and some popular substrates of current interest.

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