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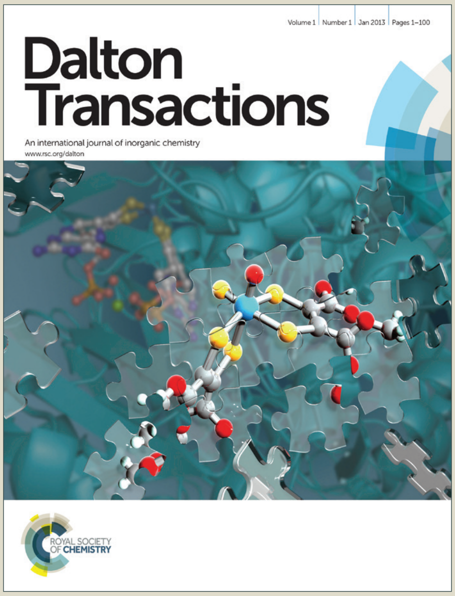

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PAPER

Rapid synthesis, structure and photocatalysis of pure bismuth A-site perovskite of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$

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$Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$, a member of a small group of pure Bi^{3+} A site perovskites, exhibiting a high ferroelectric Curie point (T_c), was rapidly synthesized by a sample method of molten salt synthesis. The purity of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ samples are directly affected by the reaction conditions such as soaking temperature, heating and cooling rates. The as-prepared $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles are well-formed, cube-shaped single-crystals ranging from 200-300 nm. The chemical states of Bi and Fe ions are Bi^{3+} and Fe^{3+} in $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$. UV-vis diffuse reflectance spectra and preliminary photocatalytic experiments indicate that the pure Bi^{3+} A site perovskite of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ has a suitable energy bandgap (1.86 eV) and shows an obvious photocatalytic activity for decolorization of methyl blue under visible-light irradiation. The present work suggest a potential future applications of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ in photocatalysis and ferroelectric photovoltaic effect.

Introduction

Due to the unique electron configuration of easily polarizable lone-pair $6s^2$, bismuth-based perovskite materials have attracted a great deal of attention due to many fascinating functional properties of multiferroic, piezoelectric, and photocatalytic.[1-4] For example, $BiFeO_3$ is well known to be one of the bismuth-based multiferroics, which exhibits high ferroelectric Curie point ($T_c \sim 827$ °C)[5] and G-type antiferromagnetic Néel point ($T_N \sim 367$ °C).[6] It also shows a potential candidate for photocatalytic materials due to its small bandgap (2.1-2.8 eV).[7] $BiMnO_3$ another highly distorted bismuth-based perovskite is ferromagnetic below -173 °C and ferroelectric temperature, and promising results for practical applications have been obtained on thin film samples showing large second and third harmonic generation.[8-11] Other bismuth-based perovskite such as $Bi(Mg_{1/2}Ti_{1/2})O_3$ and $Bi(Ni_{1/2}Ti_{1/2})O_3$ also have been used to improve the high-T_c and high performance of $PbTiO_3$ based piezoelectrics. For example, $0.51Bi(Ni_{1/2}Ti_{1/2})O_3$-$0.49PbTiO_3$ compositions possess a T_c of 400 °C and good piezoelectric properties.[12] $(1-x)Bi(Mg_{1/2}Ti_{1/2})O_3$-$xPbTiO_3$ ceramics were also been reported to have a high T_c (430 °C), good piezoelectric properties ($d_{33} \sim 255$ pC/N), and high remnant polarization ($P_r \sim 38$ μC/cm^2) for the MPB composition ($x \sim 0.37$).[13] It is well known that pure A-site Bi^{3+} perovskites can be stabilized by introduction of other perovskite like $PbTiO_3$ or $BaTiO_3$.[12-14] However, very few pure A-site Bi^{3+} perovskites are stable under ambient pressure by conventional bulk-synthesis condition, due to the small size of the Bi^{3+} ions, which can cause instability in the AO_{12} polyhedra. So far, there are only four pure A-site Bi^{3+} perovskites of $BiFeO_3$, $Bi_2(Mn_{4/3}Ni_{2/3})O_6$, $Bi(Ni_{3/8}Fe_{2/8}Ti_{3/8})O_3$ and $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ which can be obtained by conventional methods at the atmosphere pressure.[15-17]

$Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is polar in the rhombohedral *R3c* space group with a refined average structure similar to that of $BiFeO_3$,[18] which arises from A-site and B-site displacements along $[111]_p$ in relation to the $Pm\bar{3}m$ parent perovskite structure.[19] It was first synthesized via solid-state reaction at ambient pressure by Craig A. Bridges etc.[17] The synthesis of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ sample involves complex procedure which needs a high temperature and have to sinter the staring materials several times at various temperature. It is a challenge to obtain $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ by a simple method of chemical preparation. In the present work, a simple, large-scale synthesis method of molten salt synthesis (MSS) is performed to prepare $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles in $NaCl$-Na_2SO_4 salts. The phase composition, microstructure, chemical states and binding energy of Bi and Fe ions, and temperature dependence of dielectric properties of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ were investigated. We also observed that the $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles have a suitable energy bandgap (1.86 eV) and an obvious photocatalytic property under the irradiation of visible light. Both of these implies that $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ may be an candidate for photocatalysis and related areas in visible range.

Experimental Procedure

$Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ samples were prepared using MSS. Analytical reagent grade Bi_2O_3, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$, TiO_2

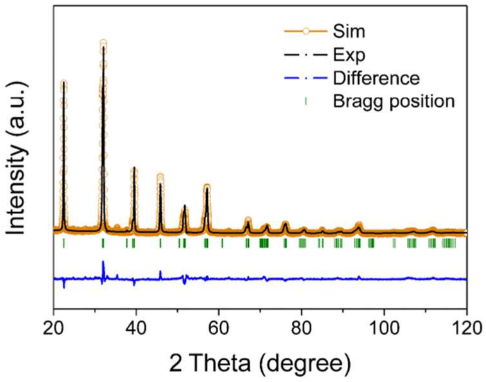

Fig. 1 Rietveld refinement for $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ from powder X-ray diffraction.

and Fe_2O_3, were mixed according to the stoichiometric ratio and ground for 20 min in an agate mortar. Then salts of NaCl and Na_2SO_4 were added in a molar ratio of NaCl : Na_2SO_4 : Bi_2O_3 = 5 : 5 : 1, and ground for 60 min. The resulting powders were placed in an alumina crucible and loaded into a furnace, where the temperature was hold at 830 °C. After chemical reaction for 1h, the sample was quenched to room temperature in air. The sample was washed one time with dilute nitric acid, then several times with distilled water to remove NaCl, Na_2SO_4 and a small amount of impurities. The remaining slurry was dried in an oven for 12 h at 100 °C. For impedance and dielectric measurements, the dried powders were mixed with a polyvinyl alcohol based binder and pressed into pellets under a pressure of 20 MPa. The pellets were pretreated at 550 °C for 1 h, and then sintered at 840 °C for 30 min before quenching to room temperature in air.

X-ray powder diffraction data (XRD) were collected using a PANalytical X′Pert PRO diffractometer with Cu Kα radiation to examine the phase composition. The XRD data were analysed by Rietveld refinement using Fullprof. The morphology microstructure and energy dispersive spectroscopy (EDS) of the powder samples were investigated with scanning electron microscope (SEM, Supra 55, Zeiss) and high-resolution transmission electron microscope (HRTEM, JEM-2010). The composition and ion oxidation states were analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5300 ESCA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to study the thermo-stability of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ sample. For dielectric and impedance measurements, both surfaces of the pellets were coated with Pt paint to make electrodes. Dielectric properties were investigated as a function of frequency and temperature using an impedance analyzer (HP4294A, Hewlett-Packard, Palo Alto, CA) in the frequency range of 10^2 ~ 10^6 Hz from room temperature to 800 °C. UV-vis diffuse reflectance spectra of the samples were obtained on an UV-vis spectrophotometer (UV2250, Shimadzu) using $BaSO_4$ as reference. Photocatalytic activities of the samples were evaluated by the photocatalytic decomposition of methyl blue (MB) under visible light at the natural pH value. A 300 W Xe lamp was used as the light source with a 420 nm cutoff filter to provide visible light irradiation. The initial concentration of MB was 10 mg L^{-1} with a catalyst loading of 2.5 g L^{-1}. Before illumination, the suspensions were stirred in the dark for 1 hour to ensure the establishment of absorption-desorption equilibrium between the photocatalyst and MB. Then the solution was exposed to visible light irradiation under magnetic stirring. At given time intervals, a small quantity of the solution was taken and centrifuged, then the concentration of MB was determined by measuring the value at approximately 664 nm using a UV-vis spectrophotometer.

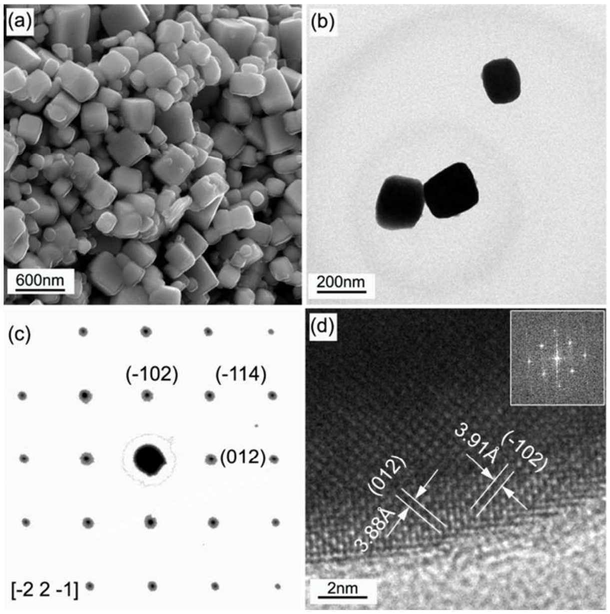

Fig. 2 (a) SEM image, (b) TEM image, (c) Selected area electron diffraction pattern of a typical individual crystal, and (d) HRTEM image of a single $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particle.

Results and discussion

The synthesis of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is limited in a very narrow range of reaction conditions in molten NaCl-Na_2SO_4 salts. $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ can be formed only by rapid reaction at a temperature range of 830 ± 15 °C and quenching to room temperature. The high heating and cooling rates which can avoid the formation of impurities, such as $Bi_{12}TiO_{20}$ and $Bi_{25}FeO_{40}$, are important factors of the present synthesis method. Another important factor of the synthesis of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is temperature. If the sample was reacted at a lower temperature such as 810 °C or a higher temperature such as 850 °C, the content of impurities, such as $Bi_{12}TiO_{20}$, $Bi_{25}FeO_{40}$ and Fe_3O_4, will increase rapidly (Fig. S1 in the supporting information). The present method of MSS for preparation of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is similar to the preparation of another pure A-site Bi perovskite of $BiFeO_3$.[20]

The Rietveld refinement of powder X-ray diffraction data of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ at room temperature was performed on the basis of the rhombohedral *R3c* structure (Fig. 1). It is revealed that the sample is highly crystallized, exhibits a perovskite structure and only a small amount of impurities can be detected. $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ crystallizes in the *R3c* space group, but cations displacement away from the rhombohedral axis ([111] in the parent cubic perovskite unit cell). The refined unit-cell parameters of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ are $a = b = 5.5771$ Å and $c = 13.7988$ Å. The Bi-O and Fe-O bond lengths are 2.412-2.546 Å and 1.798-2.270 Å, respectively. Compare to $BiFeO_3$ (JCPDS 86-1518, space group *R3c*, *a* = *b* = 5.5775 Å, *c* = 13.8618 Å, Bi-O bond lengths 2.314-2.523 Å, Fe-O bond lengths 1.940-2.115 Å), the *c* axis of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is smaller, the Bi-O bond lengths are longer, and the Fe-O bond lengths are very similar. It is interest to observe that $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ behaves a large spontaneous polarization (P_s) 73.9 μC/cm^2 lower than that of $BiFeO_3$ (90-100 μC/cm^2).[21-22] The displacements of Bi^{3+} lead to the decrease in lattice distortion, *c* axis and *c/a*,19 finally impact the P_s value and T_c of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$.

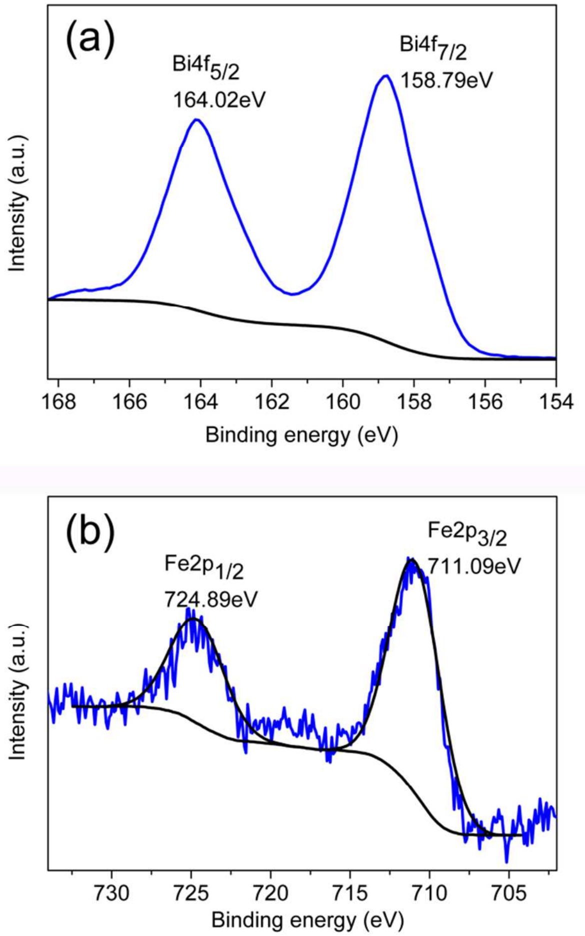

Fig. 3 XPS patterns of (a) Bi 4f and (b) Fe 2p for as-prepared sample of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$.

The SEM and TEM images of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ powders are shown in Fig. 2a and 2b. It can be seen that the sample is made up of well-formed, cube-shaped particles, typically 200-300 nm in dimension. Selected area electron diffraction (SAED) data taken from individual particle show the presence of sharp diffraction spots, which are indicative of the formation of well-formed, single-crystalline $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ (Fig. 2c). In Fig. 2d, the HRTEM image obtained from individual $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particle is displayed in order to further confirm the a single-crystalline nature of as-prepared $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ samples. In addition, EDS attached to SEM was used to measure the Bi : Fe : Mg : Ti ratio in the sample. The quantitative analysis reveals the ratio of Bi : Fe : Mg : Ti is 8 : 2.08 : 2.90 : 3.11, which coincides with the normal chemical formula of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$.

In order to clarify the crystal structure of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$, the chemical states and binding energy of Bi and Fe ions were investigated by XPS (Fig. 3). For the evaluation of XPS, the backgrounds have been subtracted from the spectra by the Shirley method. For the $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$, the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks are observed at 158.79 eV and 164.02 eV, respectively, both of which match the data well for the Bi^{3+} ions (Fig. 3a). Compared to the $BiFeO_3$ sample (Bi4$f_{5/2}$ 164.97 eV and Bi4$f_{7/2}$ 159.73 eV), [23] the binding energy of Bi is smaller in $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ (Fig. 3a), which indicates that the Bi-O bond length is longer in $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$. The increase in length of Bi-O bond indicates the decrease in Bi-O hybridization and lattice distortion, indicating a decrease in the P_s for the $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$. This conclusion is consistent with the result of Rietveld refinement of XRD. For Fe 2p lines of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$, the peaks at 724.89 eV and 711.09 eV corresponds to the $2p_{1/2}$ and $2p_{3/2}$ orbit peaks of Fe^{3+} (Fig. 3b), with a spin-orbit splitting energy of 13.8 eV for Fe 2p. It can be confirm that the oxidation state of Fe ion is Fe^{3+}, but not Fe^{2+}.[24] The binging energy of Fe in $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is similar to that in $BiFeO_3$ (Fe2$p_{1/2}$ 172.90 eV and Fe2$p_{3/2}$ 711.14 eV),[23] which indicates that the Fe-O bond lengths are similar. The result is also in good consistence with the XRD Rietveld refinement.

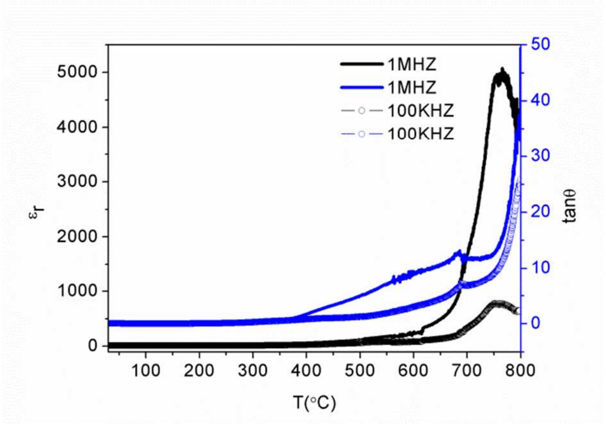

Fig. 4 Temperature dependence of dielectric constant (black lines) and loss (blue lines) measured at 1 MHz and 100KHz for $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$.

As the thermal decomposition temperature of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is about 850 °C (Fig. S2 in the supporting information shows the DSC data of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$), we investigated the temperature dependence of dielectric constant (ε_r) and loss (tanδ) of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ range from 50 °C to 800 °C at 1 MHz and 100 KHz (Fig. 4). The peak in permittivity at 760 °C is characteristic of high T_c of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ (left axis of Fig. 4) similar to the sample prepared by the conventional solid-reaction method by Craig A. Bridges etc (730 °C).17 It needs to note that the T_c of the present pure Bi A-site composition of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is lower than that of $BiFeO_3$ (T_c = 830 °C). The P_s of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is slightly lower than that of $BiFeO_3$. The relative lower T_c of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ can be well understood according to the Landau theory,[25] $T_c \sim \alpha P_s^2$, where T_c is highly correlated to the square of polarization. Dielectric loss remains low up to 400 °C that may be a reflection of the low conductivity of the Mg^{2+} containing material. The intensity of the peak for the dielectric constant is increasing with the increasing of frequency. The locations of the peak for the dielectric constant at different frequencies are similar indicates the high T_c was frequency independent.

The UV-vis diffuse reflectance spectra of the as-synthesized $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ sample shows that the absorption cut-off wavelength of the sample is about 600 nm, which implies the possibility of photocatalytic activity under visible light irradiation (Fig. 5). The energy bandgap of the sample can be estimated from the tangent line in the plot of the square root of Kubelka-Munk functions F(R) against photo energy,[26] as shown in the inset of Fig. 5. The tangent line, which is extrapolated to $(F(R))^{1/2}=0$, indicates the energy bandgap of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ is 1.86 eV. Such an energy bandgap is smaller than the bandgap of TiO_2 (3.2 eV), Bi_2O_3 (2.84 eV), [27] and any other reported Bi-based perovskite such as bulk (2.8 eV) and nanoparticle (2.18 eV) of $BiFeO_3$. [28 - 29] The suitable bandgap of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ indicates a possibility of utilizing more visible light for photocatalysis and ferroelectric photovoltaic effect.

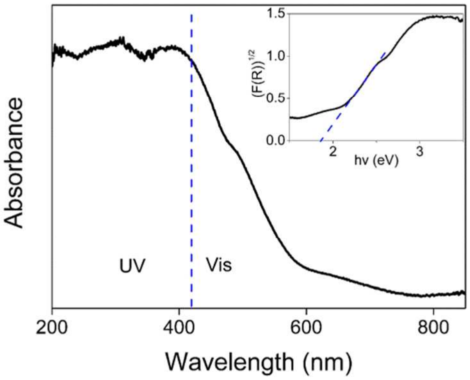

Fig. 5 UV-vis diffuse reflectance spectra of the as-synthesized $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$. The inset shows the calculation of bandgap by Kubelka-Munk function.

In order to test the property of visible light photocatalysis for the present composition of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$, the preliminary experiments were performed to evaluate the time-dependent degradation of the typical organic contaminant MB under visible light illumination (Fig. 6). Blank test (MB without photocatalyst of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles) under visible light exhibits little photolysis, which shows that the self-degradation of MB is slow. Only 18% of MB was photolyzed after 5.5 h. However, with $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles as photocatalyst, more than 85% of MB was decolorized after 5.5 h under visible light irradiation, showing efficient photocatalytic activity of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles under visible light illumination. Compared with the normal photocatalyst TiO_2,[29] which only has response to UV irradiation, $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles show their obvious advantage making use of the visible light. It is worth pointing out that the stability of a given photocatalyst during photoreaction is a curial factor for any practical applications. To study the stability of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles, the crystal structure of the $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles were investigated by XRD spectra after the reaction with MB (Fig. S3 in the supporting information). The position and the ratio of peaks are the same as those of fresh photocatalyst, clearly indicating the high stability against chemical reaction of photocatalysis. The present pure bismuth A-site perovskite of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ may be an attractive candidate for photocatalysis and ferroelectric photovoltaic effect .

Conclusions

A pure bismuth A-site perovskite $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles ranging from 200-300 nm were prepared by a sample molten salt synthesis. The purity of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ samples are directly affected by the reaction temperature, heating and cooling rates of the synthesis method. The as-prepared single-crystalline $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles exhibit a perovskite structure and have a high P_s value which is in well agreement with the observed high T_c (760 °C). The chemical states of Bi and Fe ions are Bi^{3+} and Fe^{3+} in $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$. UV-vis diffuse reflectance spectra and photocatalytic experiments of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ indicate that $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles have a suitable energy bandgap (1.86 eV) and show obvious photocatalytic ability for decompose of methyl blue under visible-light irradiation, suggesting potential future applications of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles in photocatalytic and related areas in visible range.

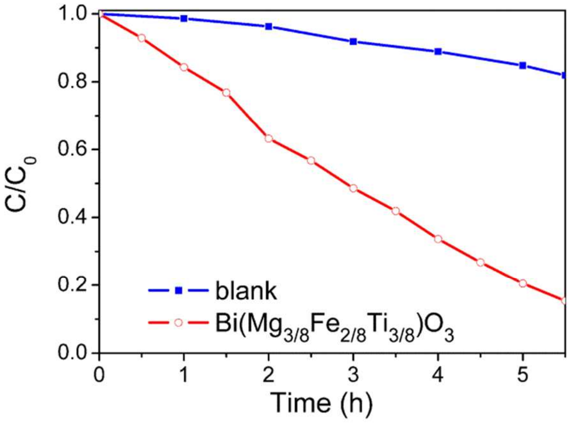

Fig. 6 Photocatalysis of $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ particles on degradation of methyl blue under visible light irradiation.

Acknowledgments

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Notes and references

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†Electronic Supplementary Information (ESI) available:

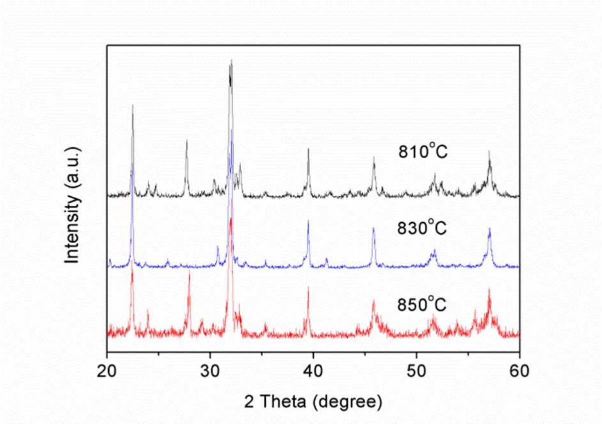


Fig. S1 The XRD patterns of Bi($Mg_{3/8}Fe_{2/8}Ti_{3/8}$)O_3 obtained at synthesizing temperature of 810 °C, 830 °C, and 850 °C.

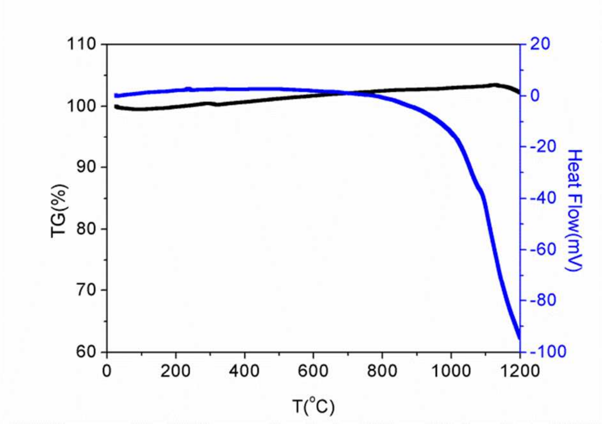


Fig. S2 The DSC-TG patterns of as-synthesized Bi($Mg_{3/8}Fe_{2/8}Ti_{3/8}$)O_3. The falling branch of the heat flow curve indicates that the Bi($Mg_{3/8}Fe_{2/8}Ti_{3/8}$)O_3 sample begins to decompose at 850 °C

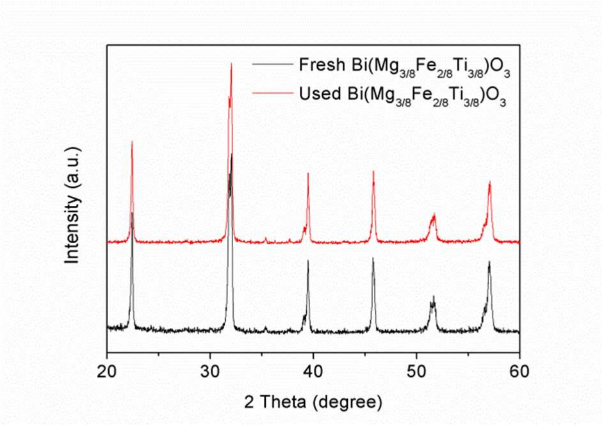


Fig. S3 The XRD patterns of the used and fresh powders of Bi($Mg_{3/8}Fe_{2/8}Ti_{3/8}$)O_3 for the photocatalytic experiment.

1 N. A.Hill, *J. Phys. Chem. B*, **2000**, 104, 6694.

2 J.Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wutting and R. Ramesh, *Science*, **2003**, 299, 1719.

3 X. M. Chen, G. D. Hu, W. B. Wu, C. H. Yang and X. Wang, *J. Am. Ceram. Soc.*, **2010**, 93, 948.

4 R. Q. Guo, L. Fang, W. Dong, F. G. Zheng and M. R. Shen, *J. Phys. Chem. C*, **2010**, 114, 21390.

5 J. Dho, X. Qi, H. Kim, J. L. MacManus-Driscoll and M. G. Blamire, *Adv. Mater.*, **2006**, 18, 1445.

6 P. Fischer, M. Polomska, I. Sosnowska and M. Szymanksi, *J. Phys. C*, **1980**, 13, 1931.

7 G. Catalan and J. F. Scott, *Adv. Mater.*, **2009**, 21, 2463.

8 E. Montanari, G. Calestani, A. Migliori, M. Dapiaggi, F. Bolzoni, R. Cabassi and E. Gilioli, *Chem. Mater.*, **2005**, 17, 6457.

9 A. M. Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham and C. N. R. Rao, *Solid State Commun.*, **2002**, 122, 49-52.

10 A. Sharan, J. Lettieri, Y. Jia, W. Tian, X. Pan, D. G. Schlom and V. Gopalan, *Phys. Rev. B*, **2004**, 69, 214109.

11 A. Sharan, I. An, C. Chen, R.W. Collins, J. Lettieri, Y. Jia, D. G. Schlom and V. Gopalan, *Appl. Phys. Lett.*, **2003**, 83, 5169.

12 S. M. Choi, C. J. Stringer, T. R. Shrout and C. A. Randall, *J. App. Phys.*, **2005**, 98, 034108.

13 C. A. Randall, R. Eitel, B. Jones and T.R. Shrout, *J. App. Phys.*, **2004**, 95, 3633–3639.

14 Q. Zhang, Z. R. Li, F. Li, and Z. Xu, *J. Am. Ceram. Soc.*, **2011**, 94, 4335.

15 V. S. Filip'ev, N. P. Smolyaninov, E. G. Fesenko and I. N. Belyaev, *Kristallografiya*, **1960**, 5, 958.

16 H. Hughes, M. Allix, C. A. Bridges, J. B. Claridge, X. Kuang, H. Niu, S. Taylor, W. Song and M. J. Rosseinsky, *J. Am. Chem. Soc.*, **2005**, 127, 13790.

17 C. A. Bridges, M. Allix, M. R. Suchomel, X. Kuang, I. Sterianou, D. C. Sinclair and M. J. Rosseinsky, *Angew Chem. Int. Ed.*, **2007**, 46, 8785.

18 F. Kubel and H. Schmid, *Acta Cryst.*, **1990**, B46, 698.

19 S. Y. Chong, R. J. Szczecinski, C. A. Bridges, M. G. Tucker, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, **2012**, 134, 5836.

20 J. Chen, X.R. Xing, A. Watson, W. Wang, R. B. Yu, J. X. Deng, L. Yan, C. Sun and X. B. Chen, *Chem. Mater.*, **2007**, 19, 3598.

21 J. B. Neaton, C. Ederer, Waghmare U. V., Spaldin N. A., Rabe1 K. M., *Physical Review B*, **2005**, 71, 014113.

22 J. Chen, K. Nittala, J. L. Jones, P. H. Hu and X. R. Xing, *Appl. Phys. Lett.*, **2010**, 96, 252908.

23 D. Rout, K. S. Moon and S. J. L. Kan, *J. Raman Spectrosc.*, **2009**, 40, 618.

24 Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu and Z. G. Liu, *Appl. Phys. Lett.*, **2004**, 84, 1731.

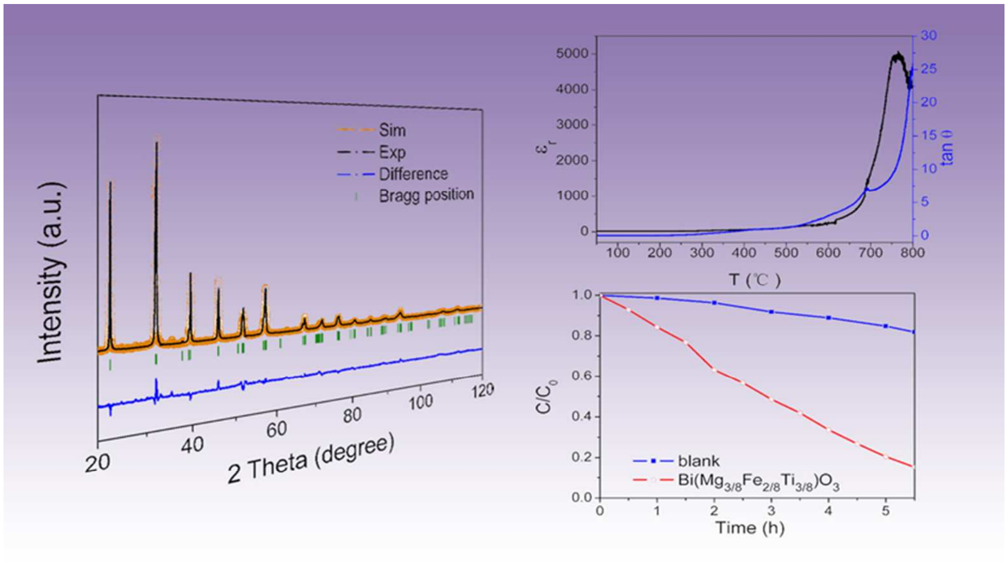
25 S. C. Abrahams, S. K. Kurtz and P. B. Jamieson, *Phys. Rev.*, **1968**, 172, 551.

26 Y. I. Kim, S. J. Atherton, E. S. Brigham and T. E. Mallouk, *J. Phys. Chem.*, **1993**, 97, 11802.

27 S. X. Wu, J. Z. Fang, W. C. Xua and C. P. Cen, *J. Chem. Technol. Biotechnol.*, **2013**.

28 S. J. Clark and J. Robertson, *Appl. Phys. Lett.*, **2007**, 90, 132903.

29 F. Gao, X. Y. Chen, K. B. Yin, S. Dong, Z. F. Ren, F. Yuan, T. Yu and Z. G. Zou, *Adv. Mater.*, **2007**, 19, 2889.



A pure bismuth A-site perovskite Bi(Mg3/8Fe2/8Ti3/8)O3 particles were prepared by a sample molten salt synthesis.
71x40mm (299 x 299 DPI)