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# BaGeO<sub>3</sub> as sintering additive for BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composite ceramics

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BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composites (30 wt% MgFe<sub>2</sub>O<sub>4</sub>) with a small addition of BaGeO<sub>3</sub> as a sintering additive were synthesized by a one-pot Pechini-like sol–gel process. Nano-crystalline composite powders with a crystallite size of about 10 nm were obtained after reaction at 700 °C for 1 h. Magnetic investigations suggest that the nano-powder is in its superparamagnetic state at room temperature. The addition of BaGeO<sub>3</sub> leads to an improved sintering behaviour. DTA measurements reveal the formation of a liquid phase at 1164(3) °C. Dense ceramic bodies (relative density ≥ 90%) were obtained after sintering for 1 h at 1150 °C. SEM investigations prove a 0–3 connectivity and show that the addition of BaGeO<sub>3</sub> promotes the grain growth leading to particles up to 4 μm. In contrast, fine-grained composite ceramics with smaller particles up to 230 nm were obtained after a two-step sintering process. Magnetic measurements indicate a ferrimagnetic behaviour with coercivity values up to 70 Oe depending on the sintering procedure. Furthermore, addition of BaGeO<sub>3</sub> results in an increase of the relative permittivity, whereas the dissipation factor slightly decreases.

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## 1. Introduction

Multiferroic composite materials are of high interest because of their potential applications in advanced technology *e.g.* as sensors, memories and actuators.<sup>1–3</sup> Composites consisting of both ferro/ferrimagnetic and ferroelectric phases can exhibit a magneto-electrical (ME) coupling effect.<sup>4</sup> To produce BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composites (*e.g.* M = Co<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>) various synthesis routes have been reported, *e.g.* mixed-oxide-, sol–gel- and hydrothermal processes.<sup>5–8</sup> Reactions between the BaTiO<sub>3</sub> and MgFe<sub>2</sub>O<sub>4</sub> phase often lead to the formation of BaFe<sub>12</sub>O<sub>19</sub> and/or hexagonal BaTiO<sub>3</sub>.<sup>9,10</sup> Therefore, the sintering temperature for composite ceramics is limited and depends on the synthesis route and particle size. For some ferrite components, the BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composites show an insufficient sintering behaviour.<sup>11–13</sup> In particular BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> ceramic bodies exhibit low densities. Up to now this system has rarely been investigated.<sup>14–17</sup> A magneto-electrical effect in BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composites was found by Tan *et al.*<sup>14</sup> and Tadi *et al.*<sup>15</sup> As the ME coupling strongly depends on the quality of the oxide interface, dense ceramics with a close contact between the perovskite and spinel phase are advantageous for large ME coefficients. Sintering additives improve the densification, therefore the densities of the ceramic bodies increase and/or the sintering temperature can be reduced.<sup>18–20</sup> Low sintering temperatures are of special interest as they enable to obtain fine-grained ceramics.

Furthermore, fine-grained ceramics show improved mechanical properties.<sup>21</sup> The influence of sintering additives on BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> ceramics has barely been investigated to date. To our best knowledge, there are only reports on boron- and bismuth-containing fluxes as sintering additives leading to BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> glass–ceramic composites.<sup>22–24</sup> Li *et al.*<sup>25</sup> used a Li<sub>2</sub>O–Bi<sub>2</sub>O<sub>3</sub> flux for fabrication of Pb<sub>0.88</sub>La<sub>0.065</sub>Bi<sub>0.015</sub>Zr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>–CoFe<sub>2</sub>O<sub>4</sub> composites. The formation of a molten phase during sintering usually promotes grain growth and should therefore be avoided if small particle sizes are desired. Previous publications showed that the formation of a molten flux is not necessary to improve the densification of ceramic bodies when sintering additives on the basis of *e.g.* BaGeO<sub>3</sub> and SiO<sub>2</sub> are used.<sup>19–27</sup>

The aim of this paper is to investigate the influence of BaGeO<sub>3</sub> as sintering additive on BaTiO<sub>3</sub>–MgFe<sub>2</sub>O<sub>4</sub> composite ceramics with a 0–3 connectivity. The samples were synthesized using a one-pot sol–gel method leading to nano-sized powders. Phase formation during the sintering process was monitored by XRD and thermal analysis. The sintering behaviour and microstructure of resulting compacts were determined by dilatometry and SEM. Magnetic measurements were carried out both on composite powders and ceramic bodies. Furthermore, the influence of BaGeO<sub>3</sub> on the dielectric behaviour was studied.

## 2. Experimental

### 2.1. Material preparation

Composites with a weight fraction of 0.7 × (BaTi<sub>0.95</sub>Ge<sub>0.05</sub>O<sub>3</sub>)–0.3 × (MgFe<sub>2</sub>O<sub>4</sub>) (=33 mol% or 36 vol% MgFe<sub>2</sub>O<sub>4</sub>) were prepared using a modified Pechini-like sol–gel process as described

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elsewhere.<sup>17</sup> This composition is abbreviated as  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  in the following. Additionally composites with the composition  $0.7 \times (\text{BaTi}_{0.9}\text{Ge}_{0.1}\text{O}_3) - 0.3 \times (\text{MgFe}_2\text{O}_4)$  (donated as  $\text{BT}_{0.9}\text{G}_{0.1}\text{-MF-0.3}$ ) and a Ti-excess composite  $0.7 \times (\text{BaTi}_{1.0}\text{Ge}_{0.05}\text{O}_3) - 0.3 \times (\text{MgFe}_2\text{O}_4)$  (donated as  $\text{BT}_{1.0}\text{G}_{0.05}\text{-MF-0.3}$ ) were synthesized.

$\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  composites were obtained by dissolving 0.01250 mol freshly distilled  $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$  (Aldrich), 0.00066 mol  $\text{Ge}(\text{OC}_2\text{H}_5)_4$  (Alfa Aesar), 0.01316 mol  $\text{BaCO}_3$  (Merck 1713, extra pure) and 0.127 mol anhydrous citric acid in 30 g 1,2-ethanediol at 70 °C leading to a clear solution. Stoichiometric proportions of 0.00661 mol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar) and 0.01322 mol  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) were dissolved in 25 g 1,2-ethanediol and added to the above solution. The resulting mixture was continuously stirred at about 190–200 °C until it turned to a black-brown viscous gel. This gel was calcined in static air at 700 °C for 1 h (heating/cooling rate 5 K min<sup>-1</sup>).

The other compositions were prepared by the same procedure using corresponding stoichiometric quantities.

To obtain ceramic bodies, the calcined powders were uniaxially pressed at about 85 MPa into pellets (green density 2.0 g cm<sup>-3</sup>) without using any pressing aid or binder. These pellets were placed on a  $\text{ZrO}_2$  fibre mat. Two different sintering procedures were used; conventional sintering (heating up with 10 K min<sup>-1</sup>, soaking at this temperature, cooling down with 10 K min<sup>-1</sup>) and two-step sintering (heating up with 20 K min<sup>-1</sup> to 1150 °C ( $T_1$ ), then fast cooled with 30 K min<sup>-1</sup> to a lower temperature  $T_2$  and held at  $T_2$  for 20 h).

## 2.2. Characterization

X-ray powder diffraction patterns were collected at room temperature on a *Bruker D8-Advance* diffractometer, equipped with a one-dimensional silicon strip detector (LynxEye™) and operating with  $\text{Cu-K}_\alpha$  radiation. Crystallite sizes were determined from the XRD line broadening using the Scherrer equation and the integral peak breadth (software suite WinXPOW<sup>28</sup>). Dilatometric investigations were performed in flowing synthetic air (50 ml min<sup>-1</sup>) in a *Setaram TMA 92-16.18* dilatometer. Differential thermoanalytic (DTA) measurements in flowing synthetic air (20 ml min<sup>-1</sup>) were done using a *Netzsch STA 449* system. Scanning electron microscope images were recorded with a *Philips XL30 ESEM* in the backscattered electron mode (BSE). For magnetic measurements a *Quantum Design PPMS 9* was used. Hysteresis loops were obtained with magnetic field cycling between -90 and +90 kOe. In addition, the temperature dependent magnetic moments were measured in the temperature range of 5–300 K under field-cooled (FC) and zero-field-cooled (ZFC) conditions. An Impedance Analyzer 4192A (Hewlett Packard) was used for permittivity measurements up to 13 MHz. A eutectic Ga-In alloy was applied as electrical contact on both sides of the ceramic bodies.

## 3. Results and discussion

### 3.1. Powder characterization

In a previous paper<sup>17</sup> we reported on the preparation of  $(1-x)\text{BaTiO}_3\text{-}(x)\text{MgFe}_2\text{O}_4$  composites ( $x = \text{weight fraction}$ ) with

0–3 connectivity *via* a Pechini-like process. The  $\text{BaTiO}_3\text{-MgFe}_2\text{O}_4$  composite powders were found to have an insufficient sintering behaviour resulting in ceramic bodies with moderate densities of about 70% at 1200 °C. The maximum sintering temperature for  $\text{BaTiO}_3\text{-MgFe}_2\text{O}_4$  systems is limited because of the formation of hexagonal  $\text{BaTiO}_3$  and/or  $\text{BaFe}_{12}\text{O}_{19}$ .<sup>9,17,29</sup> As stated in ref. 30 and 31 the densification of  $\text{BaTiO}_3$  can be improved using  $\text{BaGeO}_3$  as sintering additive. Guha and Kolar<sup>32</sup> found that a maximum of 1.8 mol%  $\text{Ge}^{4+}$  (related to the occupation of the  $\text{Ti}^{4+}$  site) can be incorporated into the  $\text{BaTiO}_3$  lattice. For our investigations a much higher content of  $\geq 5$  mol%  $\text{BaGeO}_3$  was used, resulting predominantly in a mixture of (Ge-doped)  $\text{BaTiO}_3$  and  $\text{BaGeO}_3$ . For simplicity this composition is described by the formula  $\text{BaTi}_{0.95}\text{Ge}_{0.05}\text{O}_3$  in the following.

The first step of the Pechini-like sol-gel process leads to highly-viscous homogeneous gels in which the metal ions are mixed on a molecular level. To obtain composite powders, these dark-brown gels were calcined at 700 °C for 1 h. The XRD pattern of the resulting powder shows mainly reflections of  $\text{BaTiO}_3$ ,  $\text{MgFe}_2\text{O}_4$ , and only small amounts of  $\text{BaCO}_3$  (ref. 33) (Fig. 1). After this first heat treatment no peaks related to Ge-containing phases could be detected. As an example, the powder  $0.7 \times (\text{BaTi}_{0.95}\text{Ge}_{0.05}\text{O}_3) - 0.3 \times (\text{MgFe}_2\text{O}_4)$  (donated as  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$ ) was examined by the BET method and was found to possess a specific surface area of 34.5 m<sup>2</sup> g<sup>-1</sup>, corresponding to an equivalent particle size of 32 nm. The volume-weighted average crystallite sizes for both the  $\text{MgFe}_2\text{O}_4$  and the  $\text{BaTiO}_3$  phase were calculated as 10 nm from XRD line broadening. The calculated crystallite size is roughly by the factor three smaller than the size of the primary particles obtained from the BET data. This is most likely because the decomposition of the gel leads to closely joined crystallites and in turn surface areas unavailable for nitrogen adsorption.<sup>34</sup> An alternative explanation is that each primary particle may consist of several crystallite domains.

Temperature-dependent magnetic investigations ( $H = 500$  Oe) show a superparamagnetic behaviour for the  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  powder (Fig. 2A). The field-cooled (FC) curve

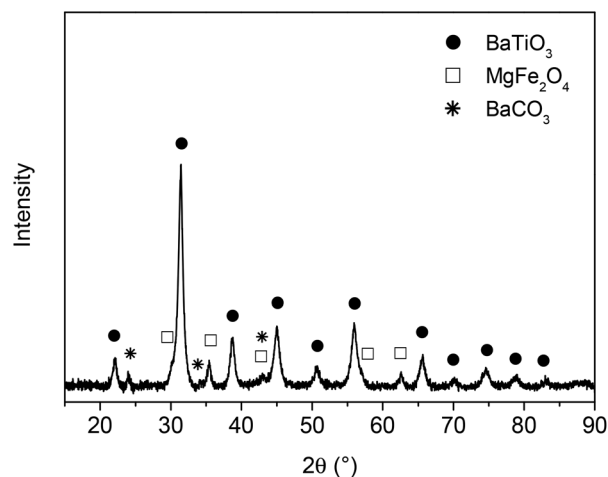


Fig. 1 Room temperature XRD pattern of the powder  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  calcined at 700 °C for 1 h.



increases continuously with decreasing temperature, while the zero-field-curve (ZFC) curve has a maximum at 20 K, the so called blocking temperature. The superparamagnetic behaviour is confirmed by field-dependent magnetic measurements. At 300 K the coercivity value is close to zero, whereas below the blocking temperature the hysteresis loop at 5 K shows a coercivity value of 146 Oe (Fig. 2B).

### 3.2. Composite ceramics

DTA investigations (shown in Fig. 3) of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and  $\text{BT}_{0.9}\text{G}_{0.1}\text{-MF-0.3}$  samples show the formation of a liquid phase (Graph 3a,b). The DTA signal increases with rising  $\text{BaGeO}_3$  content. The onset temperature of the melting peak was determined as  $1164(3)^\circ\text{C}$ . In contrast, the  $\text{BT-MF-0.3}$  composite without  $\text{BaGeO}_3$  does not reveal any DTA signal up to  $1200^\circ\text{C}$  (Graph 3c).

Fig. 4 shows the non-isothermal dilatometric measurement up to  $1200^\circ\text{C}$  in flowing air of compacts from powder  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and  $\text{BT-MF-0.3}$  calcined at  $700^\circ\text{C}$  for 1 h, respectively. The shrinkage process of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  (Graph 4a) starts at about  $800^\circ\text{C}$  and the shrinkage rate achieves a maximum at  $1102^\circ\text{C}$  with a value of  $-1.68\% \text{ min}^{-1}$ . Interestingly, this shrinkage maximum occurs below the liquid phase formation at  $1164^\circ\text{C}$ . The shrinkage rate indicates that

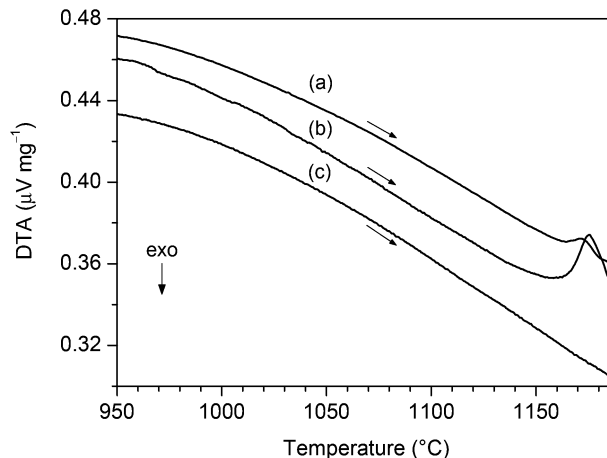


Fig. 3 DTA measurements in flowing air (heating rate  $10 \text{ K min}^{-1}$ ) of (a)  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$ , (b)  $\text{BT}_{0.9}\text{G}_{0.1}\text{-MF-0.3}$ , and (c)  $\text{BT-MF-0.3}$ .

the densification is dominated by sliding processes (viscous flow). Diffusion as the dominant process causes only shrinkage rates of about  $10^{-4}$  to  $10^{-1}\% \text{ min}^{-1}$ .<sup>35–38</sup> Investigations on the  $\text{BaTiO}_3\text{-BaGeO}_3$  system confirm that the addition of  $\text{BaGeO}_3$  promotes sliding processes.<sup>39</sup> The shrinkage has not yet been finished at the highest investigated temperature of  $1200^\circ\text{C}$ . For comparison graph 4b shows the shrinkage behaviour of  $\text{BT-MF-0.3}$  compacts without the addition of  $\text{BaGeO}_3$ . A maximum of the shrinkage rate can be observed at  $1185^\circ\text{C}$  ( $-0.80\% \text{ min}^{-1}$ ). Thus the addition of  $\text{BaGeO}_3$  leads to improved shrinkage behaviour at relatively low temperatures without involvement of a molten phase.

Fig. 5 shows the final bulk densities of ceramic bodies after isothermal conventional sintering at various temperatures in static air (heating up with  $10 \text{ K min}^{-1}$ , soaking at this temperature for 1 h, cooling down with  $10 \text{ K min}^{-1}$ ). The absolute bulk densities of the sintered bodies were determined from their

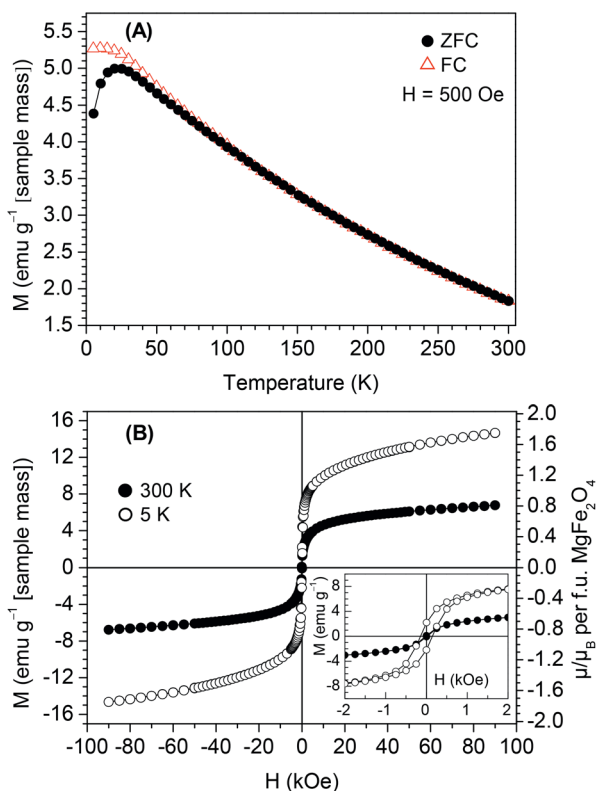


Fig. 2 (A) Temperature dependence (5–300 K) of the magnetization under zero-field cooled (ZFC) and field-cooled (FC) conditions for powder  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  calcined at  $700^\circ\text{C}$ . (B) Magnetization ( $M$ ) versus applied magnetic field ( $H$ ) at 300 and 5 K for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  powder. The inset shows  $M$  versus  $H$  in a small field range.

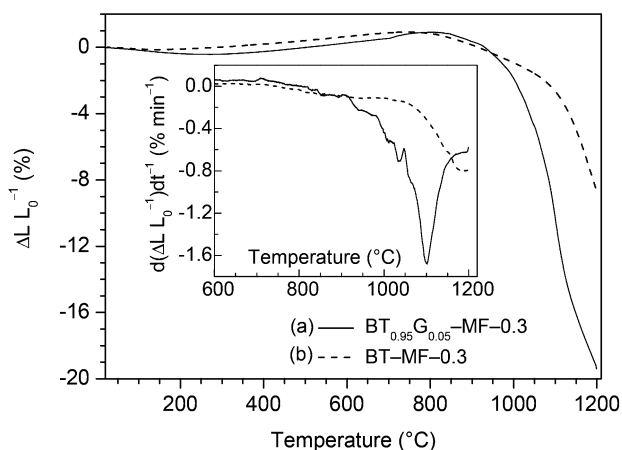


Fig. 4 Non-isothermal dilatometric measurements in flowing air for compacts of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and  $\text{BT-MF-0.3}$  (calcined at  $700^\circ\text{C}$ ) with a heating rate of  $10 \text{ K min}^{-1}$ . The inset shows the relative shrinkage rates ( $d(\Delta L/L_0)/dt^{-1}$ ).



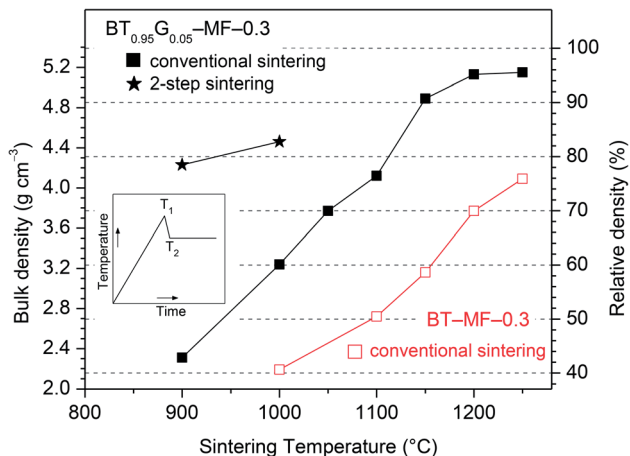


Fig. 5 Bulk densities of conventional (■ □, soaking time 1 h) and two-step sintered (★, soaking time 20 h) ceramic bodies from BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 and BT-MF-0.3 powders calcined at 700 °C. The inset schematically shows the two-step sintering process.

weight and geometric dimensions. The relative bulk densities of all ceramic bodies were calculated with respect to the theoretical density of 5.39 g cm<sup>-3</sup> for BT-MF-0.3.<sup>17,31</sup> It turned out that BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramic bodies with relative densities of 70% can be obtained even at 1050 °C. By raising the sintering temperature to 1150 °C dense ceramics with 91% relative density can be achieved. After sintering at 1200 °C the relative density further increases to 95%. According to the DTA results sintering above 1150 °C is characterized by liquid-phase sintering processes. As seen in Fig. 5 the formation of a liquid-phase is not necessary to obtain dense ceramic bodies.

Longer sintering times have little influence on the density. For example, a soaking time of 10 h at 1100 °C results only in minor increase of the relative density from 76 to 79% for BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 composites. Furthermore, an increase of the BaGeO<sub>3</sub> content to 10 mol% (BT<sub>0.9</sub>G<sub>0.1</sub>-MF-0.3) does not lead to rising densities. After sintering at 1100 °C for 1 h ceramic bodies of BT<sub>0.9</sub>G<sub>0.1</sub>-MF-0.3 with a relative density of 69% (3.71 g cm<sup>-3</sup>) were obtained. On the other hand, BaGeO<sub>3</sub>-free BT-MF-0.3 ceramics reach relative densities of only 50 and 70% after sintering at 1100 and 1200 °C for 1 h, respectively.

The SEM images of BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramic bodies depicted in Fig. 6 show a 0–3 connectivity between the spinel and the perovskite phase. In the applied BSE mode the light grains correspond to BaTiO<sub>3</sub> while the dark grains are MgFe<sub>2</sub>O<sub>4</sub>. Sintering at 1000 °C results in grain sizes between about 90 and 200 nm, which only slightly increase to 140–350 nm after sintering at 1100 °C (Fig. 6a). Up to this temperature there is no significant size difference between the BaTiO<sub>3</sub> and MgFe<sub>2</sub>O<sub>4</sub> grains. In contrast, sintering at 1150 °C for 1 h leads to a considerable grain growth with BaTiO<sub>3</sub> grains in the range between 0.25–0.9 μm and MgFe<sub>2</sub>O<sub>4</sub> grains between 0.25 and 3 μm as seen in Fig. 6b. Abnormal grain growth occurs during sintering at 1200 °C resulting in BaTiO<sub>3</sub> grain sizes between 0.5 and 1.5 μm while the size of the ferrite grains ranges between 0.5 and 4 μm. The appearance of white rods with

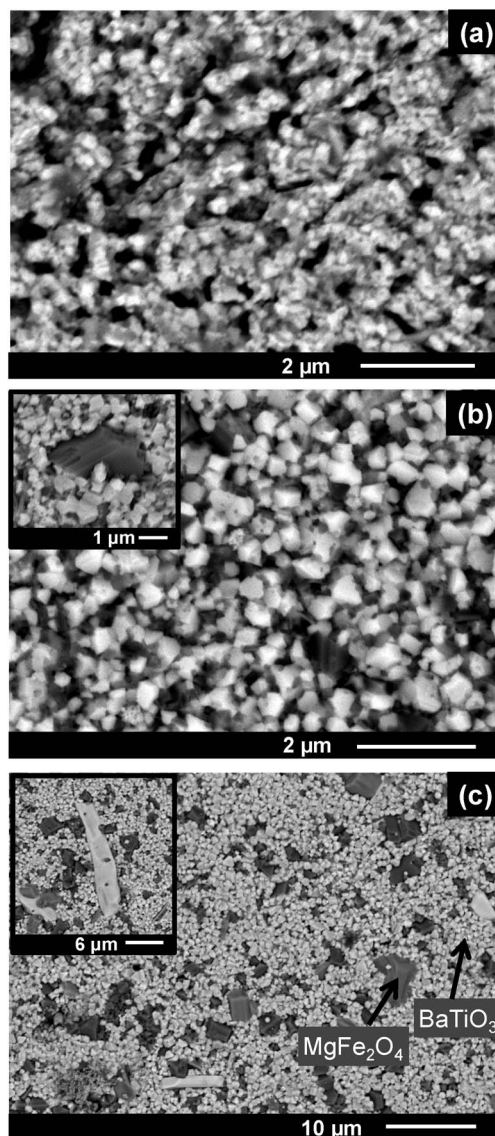


Fig. 6 SEM-BSE images of ceramic bodies sintered at (a) 1100 °C, 1 h, (b) 1150 °C, 1 h, and (c) 1200 °C, 1 h.

dimensions up to 23 × 4 μm after sintering at 1200 °C indicates the formation of hexagonal BaTiO<sub>3</sub> (ref. 40) (Fig. 6c) in accordance with the XRD results discussed below.

Using a two-step sintering procedure the densification at lower temperatures can be improved.<sup>30,41</sup> In this approach, the compacts were first heated rapidly (20 K min<sup>-1</sup>) to 1150 °C (*T*<sub>1</sub>), then fast cooled (30 K min<sup>-1</sup>) to a lower temperature *T*<sub>2</sub> and held at *T*<sub>2</sub> for 20 h (see inset in Fig. 5). Two-step sintering with *T*<sub>2</sub> = 900 °C leads to a relative bulk density of 78% (4.23 g cm<sup>-3</sup>), whereas upon rising *T*<sub>2</sub> to 1000 °C the ceramic bodies achieve a relative density of 83% (4.46 g cm<sup>-3</sup>). In both cases the ceramic bodies consist of grain between about 90 and 230 nm. For comparison, conventional sintering at 1000 °C for 20 h leads only to a relative density of 68%.

XRD powder patterns of selected BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramics are shown in Fig. 7. The pattern of ceramics sintered



up to 1100 °C shows only reflections of BaTiO<sub>3</sub> and MgFe<sub>2</sub>O<sub>4</sub>. At  $2\theta \approx 45^\circ$  no clear splitting of the BaTiO<sub>3</sub> (002)/(200) peak could be detected indicating a reduced tetragonality, *i.e.* a considerable lower *c/a* ratio compared to coarse-grained ceramics with more than 1 μm particles. After sintering at 1150 °C very small traces of BaFe<sub>12</sub>O<sub>19</sub> appear,<sup>33</sup> whereas after 1200 °C about 19 mol% of BaTiO<sub>3</sub> has been converted to the hexagonal modification. Sintering at 1250 °C leads to an increase of hexagonal BaTiO<sub>3</sub> to 54 mol%. The formation of the hexagonal BaTiO<sub>3</sub> modification at such comparably low temperatures is noteworthy since in pure BaTiO<sub>3</sub> samples the transition to the hexagonal structure occurs above 1460 °C.<sup>42</sup> The formation of hexagonal BaTiO<sub>3</sub> at lower temperatures in the composites is probably caused by the incorporation of small amounts of iron- and magnesium-ions into the BaTiO<sub>3</sub> lattice.<sup>43–47</sup> Peaks corresponding to BaGeO<sub>3</sub> were not found, most likely because of its small content. In contrast, BT<sub>0.9</sub>G<sub>0.1</sub>-MF-0.3 ceramic bodies with their larger BaGeO<sub>3</sub> content clearly show the formation of monoclinic α-BaGeO<sub>3</sub> (ref. 33) (Fig. 8A, Graph a).

To suppress the formation of hexagonal BaTiO<sub>3</sub> an excess of 5 mol% Ti, with respect to the Ba-content, was used in the BT<sub>1.0</sub>G<sub>0.05</sub>-MF-0.3 composite ceramics. As seen in Fig. 8A (Graph b) after sintering at 1200 °C no reflections of hexagonal BaTiO<sub>3</sub> are detectable. Whereas, after sintering at 1250 °C of BT<sub>1.0</sub>G<sub>0.05</sub>-MF-0.3 the fraction of hexagonal BaTiO<sub>3</sub> is not completely suppressed but reduced from 54 mol% to 31 mol% (Fig. 8A, Graph c). Therefore, at higher sintering temperatures an excess of more than 5 mol% Ti is needed to completely avoid the formation of hexagonal BaTiO<sub>3</sub>. On the other hand, the titanium excess leads to an increase of BaFe<sub>12</sub>O<sub>19</sub> as seen in Fig. 8B. This finding is in accordance with investigations by van den Boomgaard and Born<sup>10</sup> on BaTiO<sub>3</sub>-Ni(Co,Mn)Fe<sub>2</sub>O<sub>4</sub> composites that showed a continuous increase of BaFe<sub>12</sub>O<sub>19</sub> with rising titanium excess, most likely cause by the partial replacement of Fe<sup>3+</sup> ions in BaFe<sub>12</sub>O<sub>19</sub> by Ti<sup>4+</sup>.<sup>48,49</sup>

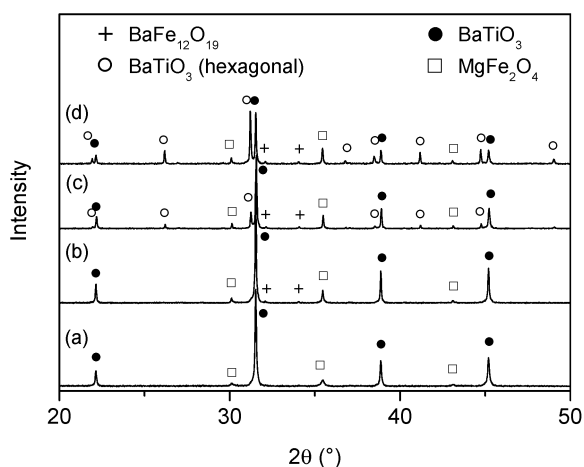


Fig. 7 Room temperature XRD patterns of BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramic bodies after sintering for 1 h (rate: 10 K min<sup>-1</sup>). (a) 1100 °C (b) 1150 °C, (c) 1200 °C, (d) 1250 °C. For clarity only a section of the measured range is shown.

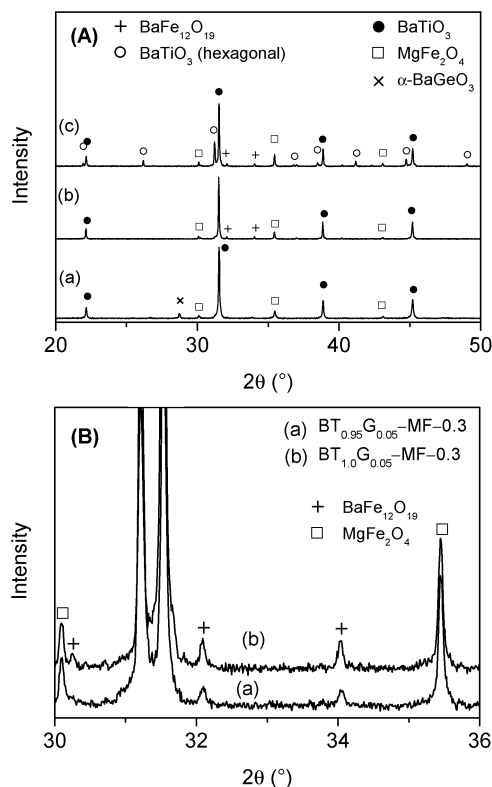


Fig. 8 (A) Room temperature XRD patterns of ceramics after sintering of 1 h of (a) BT<sub>0.9</sub>G<sub>0.1</sub>-MF-0.3 sintered at 1100 °C, (b) BT<sub>1.0</sub>G<sub>0.05</sub>-MF-0.3 sintered at 1200 °C, and (c) BT<sub>1.0</sub>G<sub>0.05</sub>-MF-0.3 sintered at 1250 °C. For clarity only a section of the measured range is shown. (B) Detail of the XRD patterns in the range of  $2\theta = 30\text{--}36^\circ$  of BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 and BT<sub>1.0</sub>G<sub>0.05</sub>-MF-0.3 sintered at 1250 °C.

### 3.3. Magnetic and dielectric measurements of ceramic bodies

Fig. 9A shows the *M*-*H* loops at 300 K of BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramic bodies conventionally sintered between 1000 and 1200 °C for 1 h. Small coercivity values (*H<sub>c</sub>*) up to 64 Oe and saturation magnetizations (*M<sub>s</sub>*) of 7.9–9.1 emu g<sup>-1</sup> were observed. *M<sub>s</sub>* values were calculated by a linear extrapolation of the magnetization at highest field to *H* = 0, assuming the increase in magnetization at high-field is dominated by a paramagnetic contribution (see below). The values of *H<sub>c</sub>* and *M<sub>s</sub>* depend on the sintering temperature as seen in Fig. 9B. The coercivity values show a maximum at 1100 °C, whereas the *M<sub>s</sub>* only slightly decreases for samples sintered between 1000 °C and 1100 °C. Sintering at higher temperatures leads to a stronger decrease of *M<sub>s</sub>*. The reduction of *M<sub>s</sub>* is probably due to the reaction between BaTiO<sub>3</sub> and MgFe<sub>2</sub>O<sub>4</sub>. On the other hand cation redistribution between Mg<sup>2+</sup> and Fe<sup>3+</sup> and thus a change of the inversion parameter is also possible because a similar behaviour was observed in pure MgFe<sub>2</sub>O<sub>4</sub> samples, too.<sup>50</sup>

Two-step sintering with *T*<sub>2</sub> = 1000 °C and 900 °C leads to similar hysteresis loops at 300 K, which are characterized by *M<sub>s</sub>* = 9.1 emu g<sup>-1</sup> and *H<sub>c</sub>* = 68 and 70 Oe, respectively (not shown).

Temperature-dependent magnetic measurements with an applied field of *H* = 60 kOe of a BT<sub>0.95</sub>G<sub>0.05</sub>-MF-0.3 ceramic



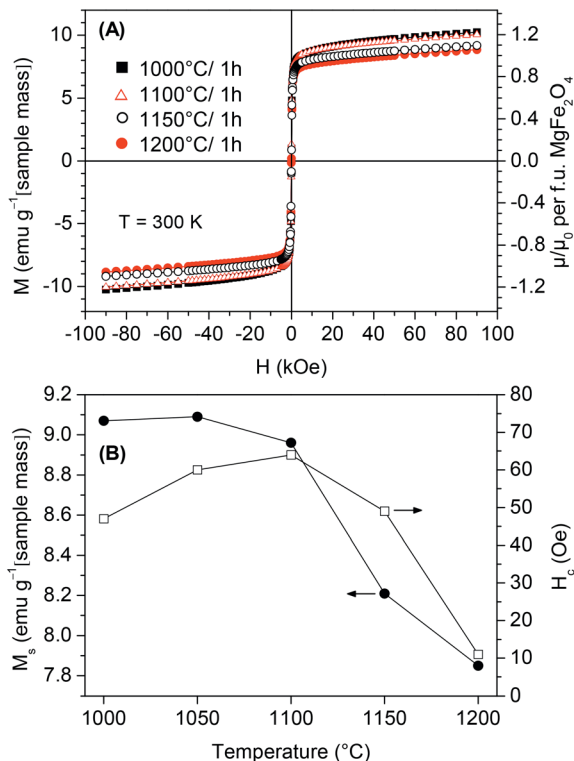


Fig. 9 (A) Magnetization ( $M$ ) versus applied magnetic field ( $H$ ) at 300 K for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramic bodies conventionally sintered at the indicated temperatures for 1 h. (B) Dependence of the saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) on the sintering temperature (soaking time 1 h).

sintered at 1000 °C show identical values under FC and ZFC conditions, therefore in Fig. 10 only the FC curve is presented. A slight increase at lowest temperatures was found in contrast to a pure  $\text{MgFe}_2\text{O}_4$  ceramic sample indicating a minor paramagnetic contribution in the composites. This small paramagnetic moment is probably caused by diffusion of Fe-ions at the grain boundaries from the  $\text{MgFe}_2\text{O}_4$  to the  $\text{BaTiO}_3$  phase.<sup>51–53</sup>

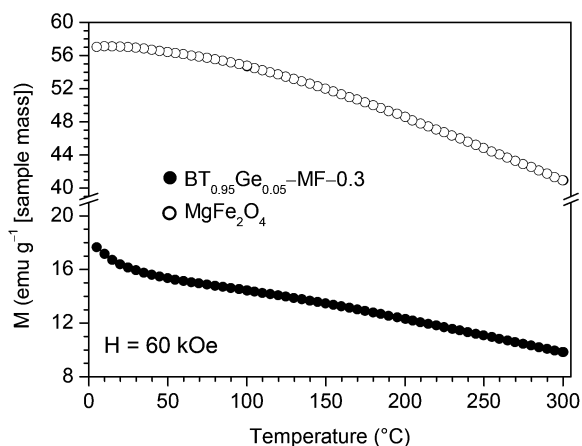


Fig. 10 Temperature dependence (5–300 K) of the magnetization at  $H = 60$  kOe under field-cooled (FC) conditions for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and pure  $\text{MgFe}_2\text{O}_4$  ceramics both sintered at 1000 °C/1 h.

Room-temperature dielectric measurements between 1 kHz and 13 MHz for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramics sintered under various conditions are shown in Fig. 11. All composite ceramics show slightly decreasing trends in the relative permittivity ( $\epsilon_r$ ) with increasing frequency (Fig. 11A) indicating dielectric dispersion due to the Maxwell–Wagner interface polarisation.<sup>54,55</sup> The permittivities of conventionally sintered samples increase with rising sintering temperature because of increasing densities and grain-sizes of the ceramics. It is known that the permittivity depends on the porosity and thus on the density of ceramic bodies because of pore-charging effects.<sup>56,57</sup> The dissipation factor ( $\tan \delta$ ) decreases for samples sintered at  $\leq 1100$  °C, whereas sintering at 1150 °C and 1200 °C leads to an increase of  $\tan \delta$  (Fig. 11B). The two-step sintered ceramic bodies show the lowest dissipation factors and the relative permittivities vary between 238–224 ( $T_2 = 1000$  °C) and 201–184 ( $T_2 = 900$  °C), respectively. The decrease of the dissipation

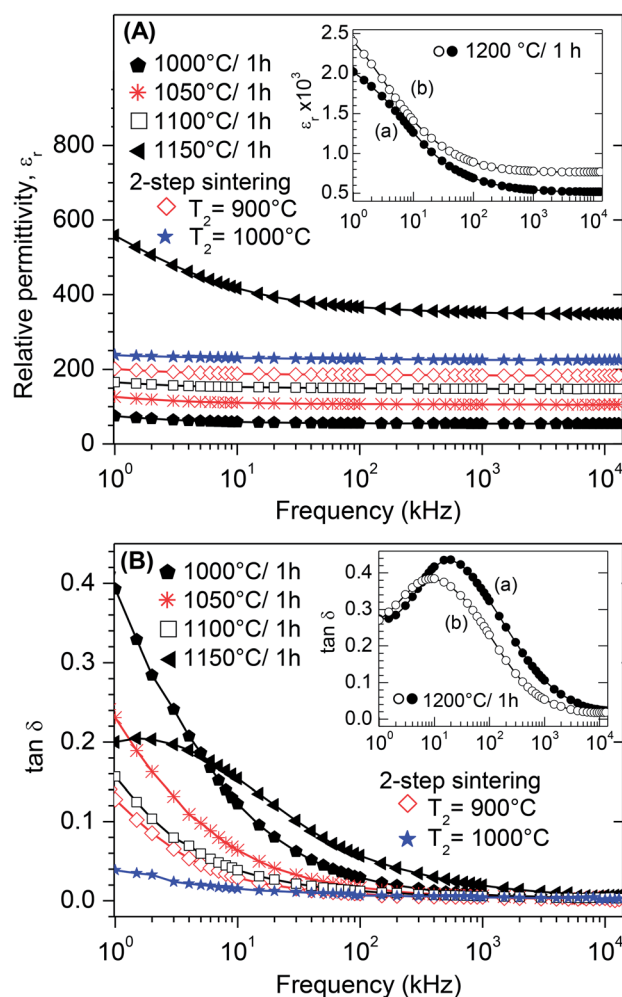


Fig. 11 Frequency dependence of the room-temperature dielectric properties of composite ceramic bodies sintered at the indicated regimes. (A) Real part of the relative permittivity ( $\epsilon_r$ ) of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramics. The inset shows the permittivity of (a)  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and (b)  $\text{BT}_{1.0}\text{G}_{0.05}\text{-MF-0.3}$  ceramics. (B) Dissipation factor ( $\tan \delta$ ) of composite ceramics. The inset shows  $\tan \delta$  of (a)  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and (b)  $\text{BT}_{1.0}\text{G}_{0.05}\text{-MF-0.3}$  ceramics.



factor and increase of  $\epsilon_r$  of the two-step sintered ceramics, compared to the conventional sintered ones, is most likely due to the improved density and a decrease of lattice defects because of the long soaking time at low temperatures.<sup>58,59</sup> Dielectric measurements on ceramic bodies of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and  $\text{BT}_{1.0}\text{G}_{0.05}\text{-MF-0.3}$  sintered at  $1200^\circ\text{C}$  (see insets in Fig. 11A and B) show that the titanium excess, needed for the suppression of hexagonal  $\text{BaTiO}_3$ , only slightly influences the dielectric properties resulting in slightly higher  $\epsilon_r$  and lower  $\tan \delta$  values.

Fig. 12 demonstrates dielectric measurements of both  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  and  $\text{BT-MF-0.3}$  (*i.e.* otherwise identical samples with and without  $\text{BaGeO}_3$  as sintering additive) composite ceramics after conventional sintering. Considerably higher permittivity values are obtained for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramics primarily due to their higher densities caused by the addition of  $\text{BaGeO}_3$ .<sup>60</sup> Up to a sintering temperature of  $1150^\circ\text{C}$  the  $\tan \delta$  values of  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  are significantly lower than for the  $\text{BT-MF-0.3}$  ceramics (inset in Fig. 12). The decrease of  $\tan \delta$ , resulting from the  $\text{BaGeO}_3$  addition, is probably related to the increase in grain boundary resistivity.<sup>61,62</sup>

The development of the relative permittivity and the dissipation factor between  $-5^\circ\text{C}$  and  $180^\circ\text{C}$  at a frequency of 1 kHz for selected  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramics was additionally studied. Fig. 13A shows ceramics sintered up to  $1100^\circ\text{C}$ , whereas samples sintered at  $1150$  and  $1200^\circ\text{C}$  are represented in Fig. 13B. The relative permittivities of all samples considerably increase roughly above  $50\text{--}70^\circ\text{C}$  and reach a maximum at about  $170^\circ\text{C}$ . Similar temperature dependencies were found in various  $\text{BaTiO}_3$ -ferrite ceramics.<sup>63-69</sup> A clear ferroelectric/paraelectric phase transition of the  $\text{BaTiO}_3$  phase was not observed. The ceramic bodies consist of  $\text{BaTiO}_3$  grains less than  $1.5\ \mu\text{m}$ , which are known to lead to a reduction of the permittivity and to a flattening of the phase transition peak.<sup>70,71</sup> Furthermore, reactions between  $\text{BaTiO}_3$  and  $\text{MgFe}_2\text{O}_4$  at the grain boundaries lead to impurities and defects resulting in a lower tetragonality. Furthermore, it was shown elsewhere<sup>72</sup> that

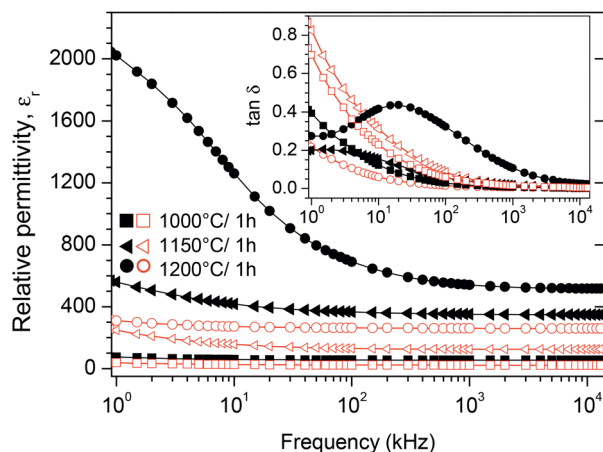


Fig. 12 Frequency dependence of  $\epsilon_r$  and  $\tan \delta$  at room temperature for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  (solid symbols) and  $\text{BT-MF-0.3}$  (open symbols) ceramic bodies conventionally sintered at the indicated temperatures.

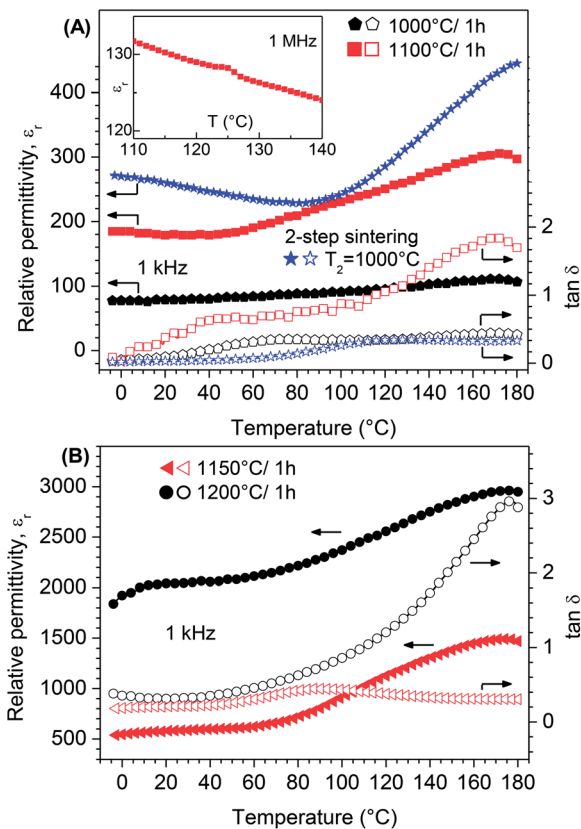


Fig. 13 Temperature dependence of  $\epsilon_r$  and  $\tan \delta$  at 1 kHz for  $\text{BT}_{0.95}\text{G}_{0.05}\text{-MF-0.3}$  ceramic bodies. (A) Conventional sintering at  $1000$  and  $1100^\circ\text{C}$  for 1 h and two-step-sintering at  $T_2 = 1000^\circ\text{C}/20\text{ h}$ . The inset shows  $\epsilon_r$  at 1 MHz after sintering at  $1100^\circ\text{C}$ . (B) Conventional sintering at  $1150$  and  $1200^\circ\text{C}$  for 1 h.

the ferroelectric/paraelectric phase transition peak continuously decreases and disappears with increasing ferrite content. Investigations by Sakanas *et al.*<sup>55</sup> and Gupta and Chatterjee<sup>73</sup> revealed that the phase transition peaks of  $\text{BaTiO}_3$  are more visible at high frequencies because of the space charge polarisation in the composites. In fact our temperature depended dielectric measurements at a higher frequency of 1 MHz showed for a sample sintered at  $1100^\circ\text{C}$  an anomaly between roughly  $120$  and  $130^\circ\text{C}$  (inset in Fig. 13A) which can be assigned to a ferroelectric/paraelectric phase transition.<sup>73</sup>

## 4. Conclusions

The effect of the sintering additive  $\text{BaGeO}_3$  on  $\text{MgFe}_2\text{O}_4\text{-BaTiO}_3$  composites was investigated. Composite samples with a composition of  $0.7 \times (\text{BaTi}_{0.95}\text{Ge}_{0.5}\text{O}_3) - 0.3 \times (\text{MgFe}_2\text{O}_4)$  were prepared by a one-pot Pechini-like synthesis. Calcination at  $700^\circ\text{C}$  leads to a nano-sized powder showing a superparamagnetic behaviour. DTA investigations reveal the formation of a liquid phase with an onset temperature of  $1164(3)^\circ\text{C}$ . The addition of  $\text{BaGeO}_3$  clearly improved the densification process of compacted powders. Conventional sintering between  $1000$  and  $1200^\circ\text{C}$  results in ceramic bodies with relative densities of  $60\text{--}96\%$ . A two-step sintering process at  $1000$  and



900 °C with a prolonged soaking time of 20 h results in relative bulk densities of 83 and 78% with grains between about 90 and 230 nm. Small traces of BaFe<sub>12</sub>O<sub>19</sub> appear after sintering at 1150 °C and the partial formation of hexagonal BaTiO<sub>3</sub> is observed at 1200 °C. Magnetic measurements reveal typical ferrimagnetic behaviour with coercivity values up to 70 Oe depending on the sintering procedure. Dielectric measurements show that the addition of BaGeO<sub>3</sub> leads to an increase of the relative permittivity, whereas the dissipation factor slightly decreases. Additionally, it is shown that the sintering regime also influences the dielectric behaviour. Sintering at 1150 °C leads to dense and coarse-grained ceramic bodies possessing high  $\epsilon_r$  and moderate  $\tan \delta$  values over a wide temperature range. On the other hand, fine-grained ceramic bodies with high densities can be obtained after a two-step sintering process showing relative permittivities up to 238 at room-temperature and the lowest  $\tan \delta$  values. The resulting composite ceramics are potential candidates for ME applications.

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