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Multiferroic Materials

Super High Threshold Percolative Ferroelectric/Ferrimagnetic Composite Ceramics with Outstanding Permittivity and Initial Permeability**

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Ferroelectric/ferromagnetic composites (FFC) have attracted increasing attention because of their ferroelectric and magnetic properties.[1–5] They can be used to produce inductance–capacitance integrated filters,[6,7] which will reduce the space occupied on circuit boards and promote integration and miniaturization.[8] However, the capacitance (inductance) reduces with reducing the ferroelectric (ferromagnetic) phase fraction according to the compound law. Therefore, it is hard to obtain both high capacitance and high inductance from general FFCs. It is well known that the dielectric properties may be distinctly increased through the percolation effect near the percolation threshold.[8–14] However, the universal percolation threshold is very low (<0.2). Even though we have prepared a percolative FFC with comparatively high percolation threshold (about 0.5) and high dielectric properties (about 10 times higher than that of the original perovskite phase) by the conventional ceramic method (CCM),[4] the percolation threshold (the content of ferrite phase) was not high enough and the permeability was only 20% of pure magnetic ferrite. Therefore, the content of the ferrite phase should be significantly increased while the ferrite particles are prevented from connecting with each other. These requirements seems very hard to achieve by CCM.[4,8–16]

Therefore, it is of great importance to find a new method to produce the ferrite well surrounded by only a thin perovskite layer, which can avoid connection among the ferrite particles. If this can be achieved, on the one hand, the percolation threshold and thus the permeability of the FFCs can be increased, and, on the other hand, the permittivity can be increased significantly owing to the thinner perovskite layer. It is well known that molecular scale homogeneity can be ideally realized by sol–gel processes, and consequently homogeneous dispersions of components in composites can be obtained. In addition, the sol–gel method can be used for in situ formation of two phases, either alternately arranged or homogeneously dispersed as a two-phase system. A high threshold system with a high content and low connection of the conductive phase would likely be formed in this way.

Herein, we propose two typical biphasic systems and a sol–gel preparation method, as well as an in situ multiphase formation process. The first system is $PbTiO_3$ (PTO)/$NiFe_2O_4$ (NFO). The second is $BaTiO_3$ (BTO)/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ (NZFO). It is worth noting that PTO and BTO are typical ferroelectric phases with low conductivity ($\sigma \approx 10^{-10}\,S\,cm^{-1}$), and NFO and NZFO are typical ferrimagnetic phases with comparatively high conductivity ($\sigma \approx 10^{-3}\,S\,cm^{-1}$) and are suitable for percolating conditions.

In this work, homogenously dispersed multiphase composites with extremely high content of ferrimagnetic phases were formed in situ by sol–gel processes. Typical XRD patterns of the PTO/NFO and BTO/NZFO ceramic composites (Figure 1) exhibit peaks for the tetragonal perovskite phase PTO (BTO) and the spinel phase NFO (NZFO),

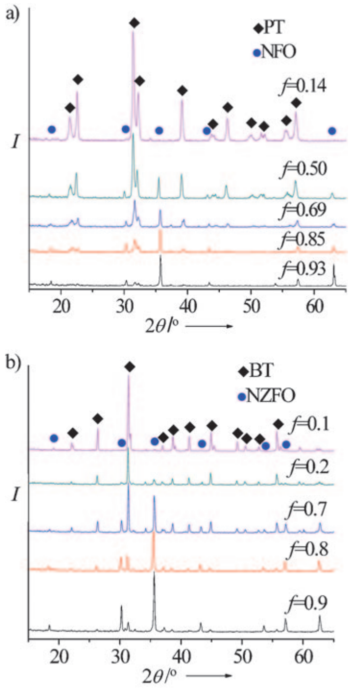

Figure 1. XRD patterns of a) PTO/NFO ceramic composites with volume fractions of NFO from 0.93 to 0.14 presintered at 550 °C for 1.5 h and sintered at 1150 °C for 2 h and b) BTO/NZFO ceramic composites with volume fractions of NZFO from 0.9 to 0.1 presintered at 750 °C for 1.5 h and sintered at 1300 °C for 12 h.

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respectively, without any additional phases. SEM images of the morphologies of the composites are shown in Figure 2. They show that the spinel phase, observed as black areas, is typically well wrapped homogeneously by the perovskite phase, observed as white areas (up to $f_{NFO} = 0.85$ for the PTO/NFO composite).

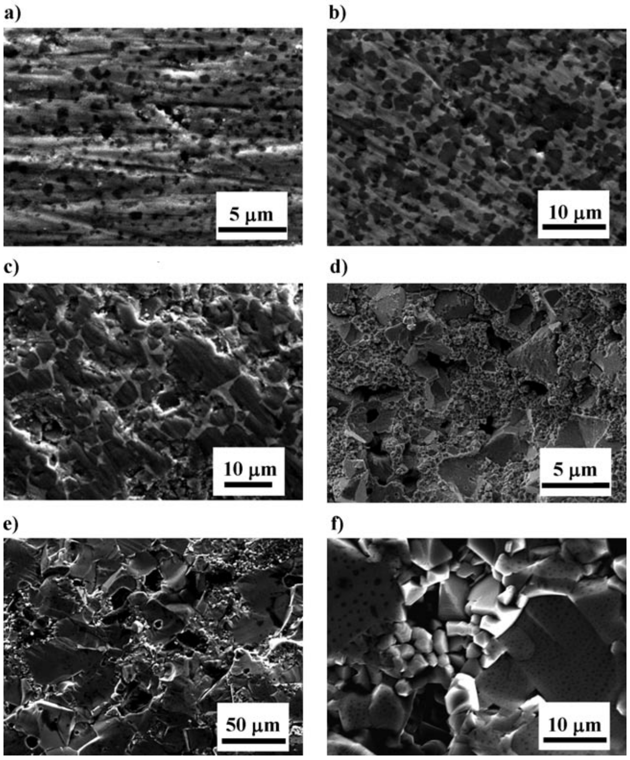

Figure 2. SEM photographs of the polished surfaces of the PTO/NFO composites with ferrite volume fractions of a) 0.27, b) 0.6, and c) 0.85, presintered at 550°C for 1.5 h and sintered at 1150°C for 2 h; and cross-sectional SEM photographs of d) PTO/NFO composite presintered at 550°C for 1.5 h and sintered at 1150°C for 2 h with ferrite volume fraction of 0.69 and e,f) BTO/NZFO composites with ferrite volume fraction of 0.9.

Figure 3 shows the variation of the dielectric constant (ε) of the PTO/NFO and BTO/NZFO composites with ferrite volume fraction. The dielectric constant increases slightly initially and then rapidly with increasing spinel phase, which indicates the occurrence of percolation behavior. The value of the dielectric constant of the composites can reach as high as 9432 for the PTO/NFO composite and 75000 for the BTO/NZFO composite, both of which are about 40–45 times higher than that of the perovskite matrix and about two times higher than that of the conventionally synthesized percolative composite.[4] In our work, the percolation threshold of the BTO/NZFO composites (0.95) was much higher than the theoretical value(less than 0.2). The ultrahigh percolation threshold is attributed to two factors: 1) Ferrite is a semiconductor with lower conductivity than normal percolating fillers, such as metals. 2) More significantly, the composites were prepared in situ by a sol–gel process. During calcination of the composite prepared by the in situ sol–gel process, the ferrite phase nucleates and initially grows homogeneously in a noncrystalline uniform phase because of its higher relative ease of formation relative to the perovskite phase.[17–20] As the ferrite phase continuously and uniformly grows larger, the surplus components in the noncrystalline phase are still dispersed homogeneously regardless of the content of the composite. Thus, the perovskite phase formed finally from the surplus components enwraps the ferrite phase tightly, which results in the ferrite crystalline phase being separated completely in the composite even though it has less than 0.05 volume fraction in BTO/NZFO. Therefore, not only a super high dielectric constant, but also comparatively high permeability of the composite can be obtained by the in situ sol–gel preparation. Such high values can are hard to reach in the composites prepared by CCM. The dielectric losses of the composites increase with increasing value of $f_{ferrite}$ (insets in Figure 3). Although they are much higher than for the perovskite matrix, the losses are lower than 0.7 for the PTO/NFO composite at $f_{NFO} \leq 0.85$ and lower than 0.6 for the BTO/NZFO composite at $f_{NZFO} \leq 0.95$. These values are still acceptable for applications such as the traditionally synthesized composite.[4]

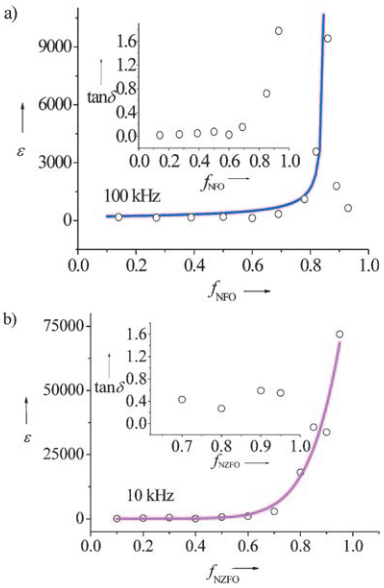

Figure 3. Variations of the dielectric constant (ε) of a) PTO/NFO and b) BTO/NZFO ceramic composites with ferrite volume fraction, measured at 100 kHz and 10 kHz, respectively. The insets show the dependence of dielectric loss on ferrite volume fraction. The continuous lines represent a fit of Equation (1) (see the Supporting Information) to the experimental points.

Figure 4 shows the variation of the initial permeability (μ_i) of the PTO/NFO and BTO/NZFO composites with the ferrite volume fraction. As expected, the experimental values of μ_i increase with increasing ferrite volume fraction, thus obeying compound behavior. The calculated results of μ_i from the well-known Maxwell–Garnett (MG) and Bruggeman–Hanai (BH) equations exhibit similar dependence on the ferrite volume fraction.[4] The experimental data are more agreeable with the MG than the BH expression over a wide range of $f_{ferrite}$ values up to 0.85 for PTO/NFO and 0.6 for BTO/NZFO

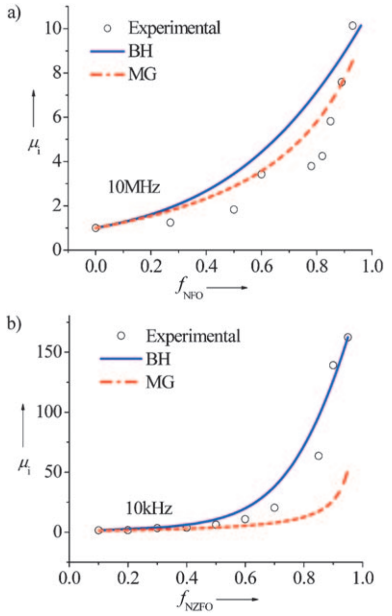

Figure 4. Variation of the initial permeability (μ_i) of a) PTO/NFO and b) BTO/NZFO ceramic composites with ferrite volume fraction at applied frequency of 10 MHz and 10 kHz, respectively. Also shown are the calculated lines from the Maxwell–Garnett (MG) and Bruggeman–Hanai (BH) equations (see the Supporting Information).

(Figure 4), although the MG equation is applicable only when the filler content is small in the universal case. The good agreement of the results with the MG equation results from the lower connection probability of the particles for high ferrite contents. However, for high ferrite volume fractions (above 0.85 and 0.6 for PTO/NFO and BTO/NZFO, respectively), the interactions between the ferrite particles cannot be neglected. The experimental results are thus more agreeable with the results from the BH equations than those from the MG equation, although there is some deviation from the equation as a result of interaction between the perovskite and ferrite phases in the in situ sol–gel system. Howsoever, for the composites (especially the lead-free system BTO/NZFO) with super high ferrite fraction of $f_{\mathrm{NZFO}} = 0.95$, the μ_i value is as high as 162, which is about 74 % of that contributed by pure NZFO and 8 times higher than that of the composite synthesized by CCM.[4]

Figure 5 shows the dependence of their initial permeability on applied frequency. The cutoff frequency decreases and μ_i increases with increasing ferrite content in both composites. This phenomenon still satisfies Snoek's law,[21] so the required cutoff frequency and permeability can be obtained by adjusting the ferrite content to suit the application.

In summary, FFC ceramics with super high percolation thresholds have been synthesized in situ by a sol–gel process. The spinel particles are homogeneously dispersed, completely wrapped, and well separated by thin perovskite phase layers. Percolation thresholds of 0.85–0.95 for the composites are thus obtained. As a result, the composites simultaneously exhibit super high dielectric constants and reasonably high initial permeability as a result of the percolation effect and the super high percolation threshold. Moreover, the permeability is frequency-independent, and the dielectric loss remains acceptable. Therefore, these ceramics have a great potential to become a new type of excellent multifunctional FFC materials.

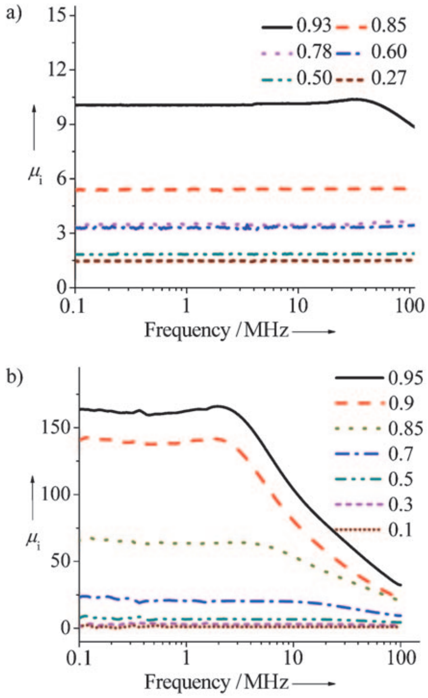

Figure 5. Frequency dependence of the initial permeability (μ_i) of a) PTO/NFO and b) BTO/NZFO ceramic composites for various ferrite volume fractions.

Experimental Section

Lead acetate ($Pb(CH_3COO)_2{\cdot}3H_2O$), barium acetate ($Ba(CH_3COO)_2$), tetrabutyltitanate ($Ti(OC_4H_9)_4$), nickel acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$), zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$), and ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) as raw materials and acetic acid (CH_3COOH) and ethylene glycol monomethyl ether ($CH_3OCH_2CH_2OH$) as solutions were initially used to prepare sol precursors with different stoichiometric proportions of PTO/NFO and BTO/NZFO. The sol precursor was dried and heat-treated at 550 °C and 750 °C for 90 min for the PTO/NFO and BTO/NZFO powders, respectively. Composite ceramics of PTO/NFO and BTO/NZFO were obtained after the powders were pressed to toroids and then sintered at 1150 °C for 2 h and 1300 °C for 12 h, respectively. More details can be found in the Supporting Information.

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Keywords: ceramics · magnetic properties · percolation · sol–gel processes · solid-state structures

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[1] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science* **2004**, *303*, 661 – 663.

[2] T. Kanai, S. Ohkoshi, A. Nakajima, T. Watanabe, K. Hashimoto, *Adv. Mater.* **2001**, *13*, 487 – 490.

[3] G. Srinivasan, C. P. DeVreugd, C. S. Flattery, V. M. Laletsin, N. Paddubnaya, *Appl. Phys. Lett.* **2004**, *85*, 2550 – 2552.

[4] J. Q. Huang, P. Y. Du, L. X. Hong, Y. L. Dong, M. C. Hong, *Adv. Mater.* **2007**, *19*, 437 – 440.

[5] Y. L. Dong, X. Wang, X. Y. Chai, W. J. Weng, G. R. Han, P. Y. Du, *Surf. Rev. Lett.* **2008**, *15*, 7 – 11.

[6] C. L. Miao, J. Zhou, X. M. Cui, X. H. Wang, Z. X. Yue, L. T. Li, *Mater. Sci. Eng. B* **2006**, *127*, 1 – 5.

[7] S. D. Kim, K. H. Shin, J. W. Kim, Y. Hak, S. H. Lim, S. G. Geon, *J. Magn. Magn. Mater.* **2006**, *304*, e391 – e393.

[8] X. W. Qi, J. Zhou, Z. X. Yue, Z. L. Gui, L. T. Li, S. Buddhudu, *Adv. Funct. Mater.* **2004**, *14*, 920 – 926.

[9] C. Pecharromán, F. Esteban-Betegón, J. F. Bartolomé, S. López-Esteban, J. S. Moya, *Adv. Mater.* **2001**, *13*, 1541 – 1544.

[10] Z. R. Wang, T. Hu, L. W. Tang, N. Ma, C. L. Song, G. R. Han, W. J. Weng, P. Y. Du, *Appl. Phys. Lett.* **2008**, *93*, 222901.

[11] J. Q. Huang, P. Y. Du, W. J. Weng, G. R. Han, *J. Electroceram.* **2008**, *21*, 394 – 397.

[12] Y. Shen, Z. X. Yue, M. Li, C. W. Nan, *Adv. Funct. Mater.* **2005**, *15*, 1100 – 1103.

[13] C. Pecharromán, J. S. Moya, *Adv. Mater.* **2000**, *12*, 294 – 297.

[14] J. S. Moya, S. Lopez-Esteban, C. Pecharromán, *Prog. Mater. Sci.* **2007**, *52*, 1017 – 1090.

[15] J. Q. Huang, H. Zheng, Z. H. Chen, Q. Gao, N. Ma, P. Y. Du, *J. Mater. Chem.* **2009**, *19*, 3909 – 3913.

[16] J. Q. Huang, L. X. Hong, G. R. Han, W. J. Weng, P. Y. Du, *Acta Phys. Sin.* **2006**, *55*, 3664 – 3669.

[17] D. H. Chen, X. R. He, *Mater. Res. Bull.* **2001**, *36*, 1369 – 1377.

[18] S. Kim, M. C. Jun, S. C. Hwang, *J. Am. Ceram. Soc.* **1999**, *82*, 289 – 296.

[19] A. Verma, D. C. Dube, *J. Am. Ceram. Soc.* **2005**, *88*, 519 – 523.

[20] G. Pfaff, *J. Mater. Chem.* **1992**, *2*, 591 – 594.

[21] G. G. Bush, *J. Appl. Phys.* **1988**, *63*, 3765 – 3767.