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LETTER

Composition-Driven Phase Transition and Electrical Performances of 0.74BiFe$_{1-x}$Ga$_x$O$_3$-0.26BaTiO$_3$ High Temperature Lead-Free Piezoceramics

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Abstract: Morphotropic phase boundary (MPB) is very important for enhancing piezoelectric properties of piezoceramics. In general, the MPB of BiFeO$_3$-BaTiO$_3$ system ceramics locates near the composition of 0.70BiFeO$_3$-0.30BaTiO$_3$. However, higher content of BaTiO$_3$ will lead to lower Curie temperature of BiFeO$_3$-BaTiO$_3$ ceramics. Therefore, constructing an MPB for BiFeO$_3$-BaTiO$_3$ ceramics with lower BaTiO$_3$ content is a reasonable strategy to obtain both the good piezoelectric property and high Curie temperature. 0.74BiFe$_{1-x}$Ga$_x$O$_3$-0.26BaTiO$_3$ (x=0~0.05) lead-free piezoceramics were fabricated by traditional sintering methods, and effect of Ga content on the structures and electrical performances was investigated. Results show that a composition-driven phase transition from rhombohedral (R) to pseudocubic (pC) is identified as x increases from 0 to 0.05. The ceramics show symmetries of R at $x\leqslant0.01$ and pC at $0.04\leqslant x\leqslant0.05$, and the MPB with R-pC coexistence is detected in the composition range of $0.02\leqslant x\leqslant0.03$. The Curie temperature of the piezoceramics decreases slightly owing to increased tolerance factor t with the increment of Ga content. In particular, the high Curie temperature ~515 °C and improved piezoelectric property of piezoelectric coefficient d_{33} of ~127 pC/N are obtained in the ceramics near MPB.

Key words: piezoelectric materials; electrical performances; phase transition; BiFeO$_3$-BaTiO$_3$; lead-free

Environment-friendly lead-free piezoceramics with ABO$_3$ perovskite structure including (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$ (NBT), BaTiO$_3$ (BT), Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN), and BiFeO$_3$-BaTiO$_3$(BF-BT) have been extensively studied considering the toxicity of lead element in the traditional Pb(Zr, Ti)O$_3$ (PZT) system materials which are the key materials for manufacturing sensors, actuators, transducers and resonators[1-3]. Among them, BF-BT system is considered as a competitive substitute for PZT owing to its good temperature stability of piezoelectric property and high Curie temperature T_C [4, 5]. Similar to the conventional PZT materials, morphotropic phase boundary (MPB) is very important for enhancing piezoelectric properties of BF-BT system materials. In general, chemical composition design is a simple and efficient method to construct MPB for piezoelectric materials. For instance, the phase transition from rhombohedral (R) to pseudocubic (pC) was observed for BF-BT solid solution ceramics with increasing BT concentration [6-8], and an MPB was formed near the compositon of 0.70BF-0.30BT. The similar composition-driven phase transition was also broadly reported in other lead-free systems[1].

However, the T_C decreases dramatically as BT content increases for BF-BT series materials. In other words, the higher the BT content, the lower the T_C of BT-BT ceramics. To be specific, the T_C of Mn-doped 0.80BF-0.20BT with R phase is above 600 °C while the T_C of Mn-doped 0.70BF-0.30BT near MPB drops to ~434 °C[7]. Therefore, constructing an MPB for BF-BT ceramics with lower BT content is a

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reasonable strategy to obtain both the good piezoelectric property and high T_C. Herein, the structure and electrical performances of $0.74BiFe_{1-x}Ga_xO_3$-$0.26BaTiO_3$ (BFGx-26BT) piezoceramics were studied. The results revealed that the R to pC phase transition was identified with increasing x from 0 to 0.05. The improved piezoelectric property and high Curie temperature were simultaneously obtained in BFGx-26BT materials near MPB ($0.02\leqslant x\leqslant 0.03$).

1 Experiment

The high-purity (>99%) raw materials including Bi_2O_3, $BaCO_3$, Fe_2O_3, Ga_2O_3 and TiO_2 were weighed according to the chemical formular of $0.74BiFe_{1-x}Ga_xO_3$-$0.26BaTiO_3$ (x=0~0.05) and ball-milled in alcohol for 12 h. The resultant mixture was dried and then calcined at 760 °C for 4 h. After re-milling and drying, the powders were mixed with 1% PVA and then pressed at 100 MPa into disks with ~1.3 mm in thickness and 14 mm in diameter. Before sintering at 980 °C for 3 h, PVA was removed at 600 °C for 3 h. Silver paste was fired at 580 °C for 20 min on both sides of the samples as electrodes. The poling was carried out at 90 °C under a DC field of 5 kV/mm for 30 min. The crystalline phase of the ceramics was characterized using X-ray diffraction (XRD, X' Pert Pro, Netherlands) with a Cu Kα radiation. The micro-structure of ceramic surfaces was observed using a scanning electron microscope (SEM, NOVA 430, Netherlands). The piezoelectric coefficient d_{33} was measured by a d_{33}-meter (ZJ-3A, CAS, China). An impedance analyzer (4294A, Agilent, American) was used to measure the dielectric permittivity ε_r and planar electromechanical coupling coefficient k_p of the samples.

2 Results and Discussion

Fig. 1a presents XRD patterns in 2θ range of 5°~80° of BFGx-26BT ceramics. All the ceramics possess pure perovskite structure without any impurity phases when $x\leqslant$ 0.04. And a trace amount of impurity phase $Bi_{22}Fe_2O_{36}$ can be detected in the ceramics with x=0.05, indicating that excess content of Ga doping can give rise to the impurity phase which is also observed in $0.70BiFeO_3$-$0.25BaTiO_3$-$0.05BiGaO_3$ ceramics[9]. The enlarged XRD patterns in 2θ of 30°~33° are presented in Fig. 1b. The peak splits near 2θ of 32° and merges gradually into single peak with increasing x from 0 to 0.05, implying the R to pC phase transition[6,10]. To analyze the phase structure of the ceramics, a full-pattern matching was carried out using a classical analysis program MAUD[11] with the Rietveld method. The fitting results, S (goodness-of-fit indicator, 1.43~1.84) and R_{wb} (reliability factor, 10.90%~14.27%), as shown in Table 1, are less than 2 and 15%, respectively. It means that the calculated and observed patterns are matched well. The ceramics with $x\leqslant$0.01 show R phase and the ceramics with $0.04\leqslant x\leqslant 0.05$ show pC phase. An MPB with R-pC coexistence is constructed in the composition range of $0.02\leqslant x\leqslant 0.03$. Besides, the lattice parameter a decreases slightly with increase of Ga content owing to smaller ionic radius of Ga^{3+} (CN=6, 0.620 nm) compared with that of Fe^{3+} (CN=6, 0.645 nm)[12].

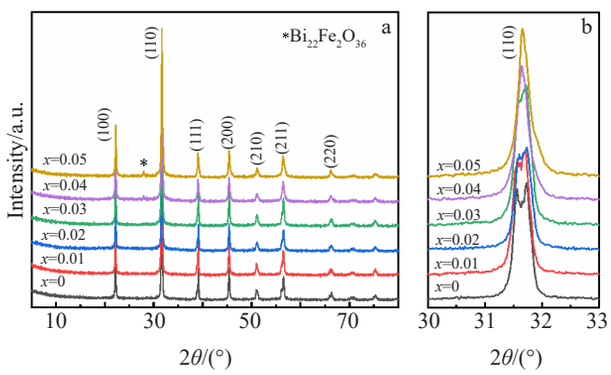

Fig.1 XRD patterns in 2θ range of 5°~80° (a) and 30°~33° (b) of BFGx-26BT specimens

SEM images of the specimens with dense microstructure are exhibited in Fig. 2. Apparently, the grain size gradually decreases from ~7 μm to ~1 μm as Ga content increases, suggesting that Ga doping inhibits the grain growth during sintering. It might be attributed to higher melting point of Ga_2O_3 (~1740 °C) compared with that of Fe_2O_3 (~1565 °C).

Fig. 3a shows temperature-dependent dielectric permittivity ε_r of BFGx-26BT specimens at 100 kHz. A dielectric anomaly peak corresponding to the Curie peak can be observed for all the samples within 550 °C. In general, the Curie temperature of the samples decreases slightly from 522 °C to 497 °C with increasing x, as shown in the inset. This may be attributable to the slightly increased tolerance factor[13] caused by Ga^{3+} (0.620 nm) substitution for Fe^{3+} (0.645 nm)[12], $t=(r_A+r_O)/[\sqrt{2}\cdot(r_O+r_B)]$ for ABO_3 perovskite, where r_A, r_O and r_B represent the radii of A, O and B ions, respectively. In addition, a broader Curie peak presenting enhanced diffuse phase transition behavior was observed for the samples with higher x due to severer cations disorder of Fe^{3+}, Ga^{3+}, Ti^{4+} at B sites in the perovskite[14].

Piezoelectric properties of d_{33} and k_p of BFGx-26BT samples are shown in Fig.3b. As Ga content increases, the d_{33} increases to 127 pC/N at x=0.03 and then drops to 30 pC/N at x=0.05. The variation trend of k_p is similar to that of d_{33}. These

Table 1 Fitting results R_{wb} and S of XRD patterns of BFGx-26BT ceramics

Ga content,	Lattice parameters		Msss	R-factors	
x/mol	$a=b=c/\times10^{-1}$ nm	$\alpha=\beta=\gamma$/(°)	fraction/%	R_{wb}/%	S
0	3.9924(7)	89.69	-	11.07	1.43
0.01	3.9917(3)	89.73	-	12.68	1.64
0.02	3.9926(7)	89.74	79.6^{R}	12.59	1.63
	3.9830(2)	-	20.4^{pC}		
0.03	3.9925(4)	89.75	77.8^{R}	10.90	1.45
	3.9829(9)	-	22.2^{pC}		
0.04	3.9896(6)	-	-	14.09	1.81
0.05	3.9892(9)	-	-	14.27	1.84

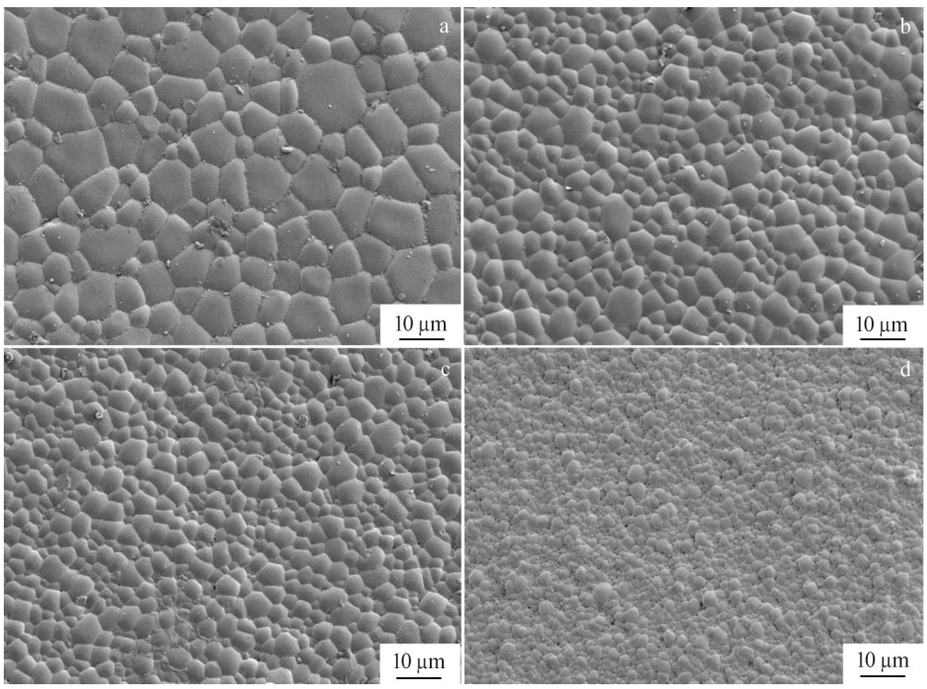

Fig.2 SEM images of BFG*x*-26BT ceramic surface: (a) *x*=0, (b) *x*=0.01, (c) *x*=0.02, and (d) *x*=0.04

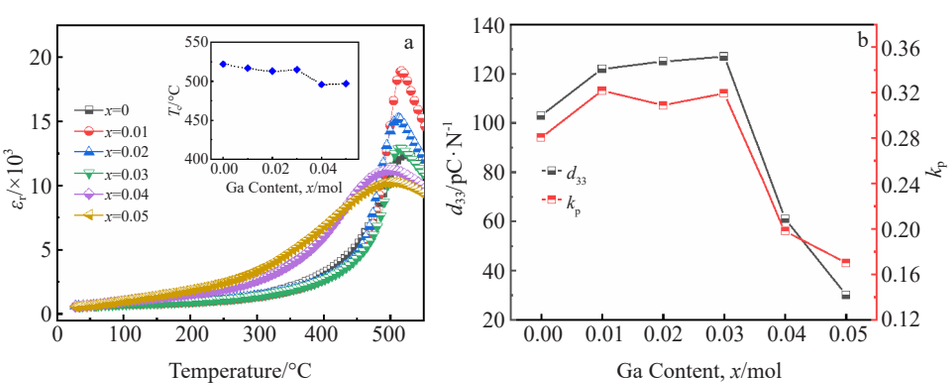

Fig.3 Temperature-dependent dielectric permittivity ε_r (a), planar electromechanical coupling coefficient k_p and piezoelectric coefficient d_{33} (b) of BFG*x*-26BT specimens

results imply that an appropriate content of Ga doping favors piezoelectric property improvement of the materials, which should be mainly attributed to the construction of MPB as mentioned above.

It is well accepted that MPB construction is very important for improving piezoelectric activities of piezoceramics[1]. For BF-BT system materials[6-8], by adjusting BT content, composition-driven phase transition from R to pC is widely reported and the phase boundary locates near the composition of 0.70BF-0.30BT. In this work, by optimizing Ga content, the composition-driven phase transition is also observed in BFG*x*-26BT ceramics, which may be ascribed to the octahedra distortion caused by Ga^{3+} substitution for Fe^{3+} [15]. Meanwhile, the piezoelectric property is improved for the BFG*x*-26BT ceramics near the MPB. In addition, owing to the lower T_C (about 120 °C) of BT, the higher content of BT may lead to lower T_C of BF-BT ceramics. Significantly, the high T_C (about 515 °C) is obtained in BFGa0.03-26BT, which is higher than that of conventional PZT (T_C=190~370 °C)[1] based ceramics and Mn-doped 0.70BF-0.30BT ceramics (~434 °C)[7] because of lower content of BT in BFG*x*-26BT than that in 0.70BF-0.30BT. Consequently, this work provides a new path to construct MPB for BF-BT based materials with high Curie temperature.

3 Conclusions

1) The R to pC phase transition is identified as Ga content increases in the $0.74BiFe_{1-x}Ga_xO_3$-$0.26BaTiO_3$ piezoceramics and the MPB can be constructed in the range of $0.02 \leqslant x \leqslant 0.03$, in which the piezoelectric properties are improved.

2) The finer grains are observed for the ceramics with Ga doping. The T_C decreases slightly with the increase of Ga

content and enhanced diffuse transition behavior is observed for the ceramics with higher Ga content. The enhanced piezoelectric properties with d_{33} of ~127 pC/N and high Curie temperature of ~515 °C can be simultaneously achieved in the piezoceramics.

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$0.74BiFe_{1-x}Ga_xO_3$-$0.26BaTiO_3$高温无铅压电陶瓷的相变行为及电性能

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摘　要：准同型相界（MPB）对提升压电陶瓷的压电性能具有重要的作用。$BiFeO_3$-$BaTiO_3$体系的准同型相界通常位于0.70$BiFeO_3$-0.30$BaTiO_3$组分附近。然而，对于$BiFeO_3$-$BaTiO_3$体系，$BaTiO_3$含量越高其居里温度越低。因此，在较低的$BaTiO_3$含量组分附近构建准同型相界是使其同时获得良好的压电活性和高居里温度的有效策略。采用固相法制备了$0.74BiFe_{1-x}Ga_xO_3$-$0.26BaTiO_3$（x=0~0.05）系列无铅压电陶瓷，研究了Ga含量对其物相结构与电性能的影响。结果表明：随着Ga含量的增加，陶瓷样品从三方相逐渐向赝立方相转变。当x≤0.01，陶瓷样品为三方相结构；而当0.04≤x≤0.05，陶瓷样品为赝立方结构，在0.02≤x≤0.03形成了准同型相界（三方-赝立方）。另外，由于容忍因子的升高，该系列陶瓷的居里温度随着Ga含量的增加而略有降低。位于准同型附近的陶瓷样品表现出良好的压电活性和较高的居里温度。

关键词：压电材料；电性能；相变；$BiFeO_3$-$BaTiO_3$；无铅

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