



# Article High-Temperature Piezoelectric Response and Thermal Stability of BiGaO<sub>3</sub> Modified BiFeO<sub>3</sub>–BaTiO<sub>3</sub> Lead-Free Piezoelectric Ceramics

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Abstract: BiGaO<sub>3</sub> doped BiFeO<sub>3</sub>–BaTiO<sub>3</sub> ceramics were prepared by the traditional solid-phase synthesis process. The phase analysis, microstructure, piezoelectric, ferroelectric, dielectric properties, and thermal stability of 0.7BiFeO<sub>3</sub>-(0.3 – *x*)BaTiO<sub>3</sub>-*x*BiGaO<sub>3</sub> (Abbreviated as BF–BT-*x*BG) were investigated. The results show that the ceramics have rhombohedral (*R*) and tetragonal (*T*) structures. Particle dimensions gradually get bigger with the increase of BiGaO<sub>3</sub> concentration, and dense ceramic grains were observed through SEM. Electrical properties of BF–BT-*x*BG are improved after adding a small amount of BiGaO<sub>3</sub>: piezoelectric constants *d*<sub>33</sub> = 141 pC/N, electromechanical coupling coefficient *k*<sub>p</sub> = 0.314, mechanical Quality Factor *Q*<sub>m</sub> = 56.813, dielectric loss tan $\delta$  = 0.048, residual polarization intensity *P*<sub>r</sub> = 18.3 µC/cm<sup>2</sup>, Curie temperature *T*<sub>c</sub> = 485.2 °C, depolarization temperature *T*<sub>d</sub> = 465 °C for *x* = 0.003. The "temperature-piezoelectric performance" curve under in situ *d*<sub>33</sub> indicates that piezoelectric properties *d*<sub>33</sub> increase rapidly with increasing temperature. Remarkably, the piezoelectric response *d*<sub>33</sub> reaches a maximum of 466 pC/N at a temperature *T* = 340 °C, and afterward, reduces gradually to zero with increasing temperature until 450 °C.

Keywords: BiFeO<sub>3</sub>–BaTiO<sub>3</sub>; BiGaO<sub>3</sub>; in situ *d*<sub>33</sub>; piezoelectric response; thermal stability

## 1. Introduction

High-temperature piezoelectric ceramics are used in aircraft, aviation, military, oil prospecting, and other fields [1–3]. PbNb<sub>2</sub>O<sub>6</sub> and BiScO<sub>3</sub>–PbTiO<sub>3</sub> are the most commonly used materials in the area of high-temperature piezoelectric ceramics. The performances of PbNb<sub>2</sub>O<sub>6</sub> system piezoelectric ceramics are  $d_{33} = 70$ –190 pC/N and  $T_c = 370$ –610 °C [4,5]. BiScO<sub>3</sub>-bTiO<sub>3</sub> piezoelectric ceramics have a high properties  $d_{33} = 400$  pC/N and  $T_c = 450$  °C [1,6]. Following increased awareness of environmental protection during the 20th century, the use of lead became more and more regulated by law. Therefore, the research on low-cost, non-toxic, and high-quality lead-free piezoelectric ceramics is of major significance. So far, potential materials like (K, Na) NbO<sub>3</sub> (KNN), Bi<sub>1/2</sub>Na<sub>1/2</sub>TiO<sub>3</sub> (BNT), and BaTiO<sub>3</sub>(BT), each with their own strengths and weaknesses [7–9]. KNN has a high  $d_{33}$ , but the piezoelectric properties gradually decrease as the temperature rises [10,11]. BNT has a large strain but a low depolarization temperature [12,13]. BiFeO<sub>3</sub>–BaTiO<sub>3</sub> ceramics are attracting more attention due to their excellent properties.



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BiFeO<sub>3</sub> is a material with high  $T_c = 870$  °C and high residual polarization strength [14,15]. At room temperature,  $BaTiO_3$  is a perovskite material with a tetragonal structure, which has a high dielectric constant ( $\epsilon_r$ ) and low tan $\delta$ . BiFeO<sub>3</sub> and BaTiO<sub>3</sub> can form a perovskite solid solution with excellent piezoelectric properties and thermal stability [16,17]. BF–BT is a kind of piezoelectric ceramic with high  $T_c$  and high  $T_d$  [18,19]. Kumar et al. Found that BF–BT has a rhombohedral structure and tetragonal structure, respectively, when the content of BiFeO<sub>3</sub> is higher than 70% and lower than 4%. It changes to a cubic structure when the content of BiFeO<sub>3</sub> is higher than 4% and lower than 70% [19]. In the process of synthesizing pure BF, some second phases will be produced, such as Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, Bi<sub>25</sub>FeO<sub>39</sub>, Bi<sub>25</sub>FeO<sub>40</sub>, or Bi<sub>46</sub>Fe<sub>2</sub>O<sub>72</sub> [20,21]. On the other hand, doping other elements will enhance the electrical performance of BF-BT. It has been reported that many ions doped to enhance the electric performances of BF-BT, such as Cr<sup>3+</sup>, Sc<sup>3+</sup>, Nd<sup>3+</sup>, Ga<sup>3+</sup>, and so on [22-25]. BiGaO<sub>3</sub> has huge tetragonal distortion and a P4mm space group [26]. Liu et al. have shown that the resistivity of  $0.7Bi(Ga_xFe_{1-x})O_3-0.3BaTiO_3$  ceramics increases with the Ga content increasing [27]. Zhou et al. synthesized 0.71Bi(Fe<sub>1-x</sub>Ga<sub>x</sub>)O<sub>3</sub>-0.29BaTiO<sub>3</sub> ceramics with good Curie temperature, and they obtained good electrical performances:  $d_{33} = 157 \text{ pC/N}$ ,  $k_p = 0.326$ ,  $T_c = 467 \text{ }^\circ\text{C}$  [28]. Myang Hwan Lee et al. studied  $0.67Bi_{1.05}$ -(Fe<sub>1-x</sub>Ga<sub>x</sub>)O<sub>3</sub>-0.33BaTiO<sub>3</sub> ceramic and obtained  $d_{33}$  = 402 pC/N,  $T_c$  = 454 °C by quenching process [29]. Akram et al. prepared  $(1 - x)(0.65Bi_{1.05}FeO_3 - 0.35BaTiO_3) - xBiGaO_3$ ceramics and obtained  $d_{33} = 165 \text{ pC/N}$ ,  $k_p = 0.25$  for this system of ceramics at x = 0.01 [30]. Guan et al. has been reported that  $0.67BiFeO_3-0.33BaTiO_3-xBiGaO_3$  ceramics have good piezoelectric performances:  $d_{33} = 170 \text{ pC/N}$  and  $T_c = 434 \text{ }^{\circ}\text{C}$  [25]. Recently, Myang Hwan Lee et al. increased the  $d_{33}$  of 1 mol% BiGaO3-doped BF33BT (BG) ceramics from 402 to 454 pC/N [31]. As an additive,  $MnO_2$  was added to BF–BT ceramics to enhance the DC resistance and electrical properties of the ceramics [32,33]. Recently, in situ  $d_{33}$  has been used to characterize the  $d_{33}$  in the actual operating state of piezoelectric ceramics [34,35].

In this work,  $0.7BiFeO_3$ - $(0.3 - x)BaTiO_3$ - $xBiGaO_3 + 0.01MnO_2$  (BF–BT-xBG) piezoelectric ceramics were produced by the traditional solid reactive method. BiGaO\_3 influences on the crystalline structure, piezoelectric, ferroelectric, dielectric properties, and thermal stability have been systematically investigated. By designing this experiment, it is expected to obtain high performances at high temperatures, and at room temperature, polarization still has good piezoelectric properties of ceramics. The results showed that BF–BT-0.003BG ceramics have good piezoelectric performances with  $d_{33} = 466$  pC/N at 340 °C. When MnO<sub>2</sub> is added to the pre-fired ceramics, it also has good piezoelectric properties after polarization at room temperature. It represents the piezoelectric performance of ceramics in the actual working state. These findings show that BF–BT ceramics have a great possibility of replacing PZT ceramics.

#### 2. Experimental Methods

0.7BiFeO<sub>3</sub>-(0.3 - x)BaTiO<sub>3</sub>-xBiGaO<sub>3</sub> + 0.01MnO<sub>2</sub> ceramics are synthesized by traditional solid-state sintering. Bi<sub>2</sub>O<sub>3</sub> (99.99%), Fe<sub>2</sub>O<sub>3</sub> (99.99%), BaCO<sub>3</sub> (99.99%), TiO<sub>2</sub> (99.99%), MnO<sub>2</sub> (99.99%) (Xilong Chemical Plant, Shantou, China) and Ga<sub>2</sub>O<sub>3</sub> (99.99% Macklin) were used as raw materials for synthesis. Due to the volatilization of Bi during the sintering process, an excess of 2 mol% Bi was added. The powder was weighed following a certain stoichiometric ratio into a bottle, mixed with alcohol, and ball mill for 12 h with 1000 r/min. The mixed particles were calcined at 800 °C for 6 h with a heating speed of 5 °C/min. MnO<sub>2</sub> was added to the calcined powder and poured into the bottle for the second grinding. Then, sintered at 1020 °C for 9 h with a heating rate of 5 °C/min. Both sides of the fired ceramic sheets were coated with silver electrodes and fired at 600 °C for a holding time of 30 min for electrical properties testing. The thickness of the measured sample is about 0.8 mm.

The crystal structure of the ceramic was tested by using an X-ray diffractometer with Cu K $\alpha$  (Smart Lab 9 kw, Rigaku, Tokyo, Japan). The morphology of the ceramic surface was photographed using a scanning electron microscope (JSM-7610FPlus). Density was calculated by Archimedes's drainage method. Piezoelectric properties were tested

by the quasi-static  $d_{33}$  tester (Institute of Acoustics, Chinese Academy of Sciences). *P-E* curves were measured by a ferroelectric test system (aixACCT TF Analyzer 1000, Aachen, Germany) at room temperature. Thermal stability was measured by the LCR analyzer (keysight, 4980A) from 25 °C to 550 °C. The depolarization temperature was measured ex situ. The in situ  $d_{33}$  was obtained by using a high-temperature in situ  $d_{33}$  test instrument (Wide-temperature-range  $d_{33}$  m: TZFD-900, Harbin Julang Technology Co., Ltd., Harbin, China, Figure S1). In the in situ  $d_{33}$  test method: the ceramic plate is placed in the apparatus, and the  $d_{33}$  operating state of the ceramic piece is tested in the furnace as the temperature rises. In ex situ  $d_{33}$ , the ceramic piece is placed in a furnace, heated to a certain temperature, removed and cooled to room temperature, and then tested for its  $d_{33}$ .

#### 3. Results and Discussion

Figure 1a shows the XRD of BF–BT-*x*BG ceramics and the standard diffraction peaks for BF (R3c, PDF#71-2494) with the *R* phase and BT (P4 mm, PDF#75-1169) with the *T* phase. The ceramics display a perovskite structure with a few  $Bi_{25}FeO_{40}$  impurity phases in Figure 1a, which has been reported in other studies [36–38]. The structure of BF–BT-*x*BG ceramics is a coexistence of the *R* phase and *T* phase. Figure 1b shows the BF–BT-*x*BG XRD pattern of 39°. The peak of 39° has no obvious change as the BG concentration increases.



**Figure 1.** The XRD patterns of BF–BT-*x*BG ceramics from (**a**) 20–80°, (**b**) 38–40°, \* is impurity phases  $Bi_{25}FeO_{40}$ .

As shown in Figure 2, the Rietveld refinement method was used to analyze the phase structure of the BF–BT-*x*BG ceramics. The *R* phase is R3c (PDF#71-2494), and the *T* phase is P4mm (PDF#75-1169) through fitting analysis. The *R* phase weight fraction increases from 29.478% to 41.662% as BG concentration increases from 0 to 0.006. Then, the *R* phase content decreases as BG concentration increases from 0.006 to 0.012. Table 1 shows the Rietveld refinement structure parameters. The XRD refinement data are consistent with the results in Figure 1b.

Figure 3 shows the microstructure of the BF–BT-*x*BG ceramic after sintering at 1020 °C for 9 h. The results show that all ceramic surfaces are dense without obvious pores, that the grains are regular polygons, and that the grain boundaries are clear. Figure 3 shows the particle dimension distribution of the BF–BT-*x*BG ceramics after sintering at 1020 °C for 9 h. The particle dimensions of the BF–BT-*x*BG ceramics were measured using Nano Measurer software. It was shown that the particle dimensions of ceramics increase gradually as the BG concentration increases, and the average particle dimensions increase from 7.02 µm at

x = 0 to 13.37 µm at x = 0.012. It can be concluded that the addition of BiGaO<sub>3</sub> promotes an increase in particle dimensions. There are two reasons for this: one is that the incorporation of Ga<sup>3+</sup> ions boosts the formation of the liquid phase and the sintering of the ceramic, which increases the size of the grain [28]. The other one is that more Bi<sub>2</sub>O<sub>3</sub> is added with the addition of BiGaO<sub>3</sub>, resulting in the generated impurity phase Bi<sub>25</sub>FeO<sub>40</sub> leading to the generation of a more liquid phase and promoting the growth of ceramic grains [36,37]. On the other hand, in pure dense ceramics, the parabolic law indicates that the grain boundary mobility controls grain growth [39], and the doping of BiGaO<sub>3</sub> may promote grain boundary migration. The relative density of BF–BT-*x*BG ceramics is shown in Figure 3. It was shown that the relative density of ceramics first grew and then reduced as the BG concentration increased, reaching the highest value of 95.79% at x = 0.003.



**Figure 2.** Rietveld refinement results for BF–BT-*x*BG ceramics by GSAS (**a**) x = 0, (**b**) x = 0.003, (**c**) x = 0.006, (**d**) x = 0.009, (**e**) x = 0.012.

Composition	Phase	Lattice	Volume	Fitting
	fraction	parameters	$(V_R/V_T)$ (Å <sup>3</sup> )	parameter
		a c (Å)		Rwp/Rp
x = 0	R3c 29.478	5.64780 (3)	386.48 (6)	Rwp = 0.0402
		13.99083 (6)		Rp = 0.0296
	P4 mm 70.522	3.99613 (1)	63.98 (2)	
		4.00659 (1)		
x = 0.003	R3c 38.808	5.65280 (2)	388.76 (2)	Rwp = 0.0425
		14.04836 (9)		Rp = 0.03
	P4 mm 61.192	3.99815 (5)	64.11 (8)	-
		4.01106 (1)		
x = 0.006	R3c 41.662	5.68791 (5)	388.58 (9)	Rwp = 0.0422
		13.86928 (7)		Rp = 0.0299
	P4 mm 58.338	3.99785 (9)	64.25 (1)	*
		4.02001 (1)		
x = 0.009	R3c 37.181	5.69049 (9)	388.10 (4)	Rwp = 0.0439
		13.83939 (5)		Rp = 0.0317
	P4 mm 62.819	3.99542 (0)	63.89 (6)	*
		4.00266 (2)		
x = 0.012	R3c 35.102	5.65378 (9)	389.47 (8)	Rwp = 0.0358
		14.06932 (2)		Rp = 0.0253
	P4 mm 64.898	3.99647 (3)	63.95 (2)	-
		4.00407 (4)		

Table 1. Rietveld refinement structure parameters for unpoled BF-BT-xBG ceramics.



**Figure 3.** The microstructure of BF–BT-*x*BG ceramics after sintering at 1020 °C for 9 h (**a**)  $x = 0 \mod\%$ , (**b**)  $x = 0.3 \mod\%$ , (**c**)  $x = 0.6 \mod\%$ , (**d**)  $x = 0.9 \mod\%$ , (**e**)  $x = 1.2 \mod\%$ , (**f**) the relative density (five-pointed star) of BF–BT-*x*BG ceramics.

Figure 4a shows the  $d_{33}$  of BF–BT-*x*BG ceramics polarization at room temperature (rp) and polarization at 100 °C (100p), of which the  $d_{33}$  has little difference. It can be seen that the  $d_{33}$  of ceramics grew at first and then reduced as the BG concentration grew, which reaches the highest  $d_{33} = 141$  pC/N (rp) when x = 0.003. There are two reasons for this: one is that the ion radius Bi<sup>3+</sup> = 1.38 Å (CN = 12), Ga<sup>3+</sup> = 0.62 Å (CN = 6), Ba<sup>2+</sup> = 1.61 Å (CN = 12), Ti<sup>4+</sup> = 0.605 Å (CN = 6). A small amount of BiGaO<sub>3</sub> doped into BaTiO<sub>3</sub> will lead to lattice distortion, which promotes the movement of ferroelectric domains and enhances the piezoelectric performances. Another reason is that the addition of a small amount of

BiGaO<sub>3</sub> may produce polar nano micro-regions (PNRs). It destroys the long-range ordered ferroelectric state, strengthens the electromechanical coupling effect, and improves the intrinsic piezoelectric activity [40]. Meanwhile, BiGaO<sub>3</sub> doping promotes the formation of liquid phase and grain growth, and the relative density is maximum at x = 0.003, when the piezoelectric performance is the best. Ga<sup>3+</sup> replaces Ti<sup>4+</sup> to produce oxygen vacancy when the BiGaO<sub>3</sub> content is high [41]. The movement of the oxygen vacancy pinning domain causes the decrease of d<sub>33</sub>. MnO<sub>2</sub> decomposes to Mn<sub>2</sub>O<sub>3</sub> above 900 °C. In our experiment,  $MnO_2$  is added after the pre-combustion, so that more  $MnO_2$  becomes  $Mn_2O_3$  [33,42]. According to this reaction:

$$\begin{pmatrix} a \\ 145 \\ 140 \\ 135 \\ 130 \\ 125 \\ 125 \\ 120 \\ 155 \\ 120 \\ 105 \\ 0.000 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.012 \\ 0.29 \\ 0.28 \\ 0.27 \\ 0.26 \\ 0.20 \\ 0.29 \\ 0.28 \\ 0.27 \\ 0.26 \\ 0.20 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.012 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.012 \\ 0.000 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.012 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.051 \\ 0.050 \\ 0.000 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.003 \\ 0.006 \\ 0.009 \\ 0.012 \\ 0.011 \\ 0.000 \\ 0.0$$

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2 \uparrow (\geq 900 \ ^\circ C)$$

$$Mn^{3+} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$$

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Figure 4. (a) The  $d_{33}$  of BF–BT-xBG ceramics polarization at room temperature (rp) and polarization at 100 °C (100p), (b) the changes of  $k_p$  and  $Q_m$  of ceramics with BG concentration, (c) the change of dielectric constant  $\varepsilon_r$  with BG concentration, (d) the change of dielectric loss tand with BG concentration

Mn<sub>2</sub>O<sub>3</sub> can better inhibit the conversion from Fe<sup>3+</sup> to Fe<sup>2+</sup>, and improve the thermal stability of ceramics. Therefore, ceramics still have excellent piezoelectric properties under rp conditions.

Figure 4b shows the  $k_p$  and  $Q_m$  of BF–BT-*x*BG ceramics. The  $k_p$  rises first and then drops as the BG concentration increases, and reaches the highest 0.314 when x = 0.003.  $Q_{\rm m}$ changes little as the BG concentration increases. The change of  $k_p$  is consistent with  $d_{33}$ , and the reason is the same as that of  $d_{33}$  described above. Figure 4c shows the change of dielectric constant  $\varepsilon_r$  with BG concentration. The  $\varepsilon_r$  increases first from 751.843 at x = 0to 853.149 at x = 0.003, and then decreases to 670.483 at x = 0.012. The addition of a small amount of Ga<sup>3+</sup> causes lattice distortion and contributes to the enhancement of  $\varepsilon_r$ . Figure 4d shows the change of dielectric loss  $tan\delta$  with BG concentration. It can be concluded that tan  $\delta$  decreases first to 0.048 at x = 0.003 and then increases as the BG concentration grows, indicating that a small amount of  $BiGaO_3$  incorporation is conducive to enhancing the dielectric properties of ceramics.

Figure 5a–f show the variation in impedance and phase angle  $\theta$  with frequency at 25 °C. It has been shown that the polarization phase angle  $\theta$  reaches the maximum value  $\theta$  = 58.917 when *x* = 0.003, which corresponds to the component point when *d*<sub>33</sub> is at the maximum value, indicating that the ceramic has sufficient polarization and the highest performance when *x* = 0.003.



Figure 5. (a-f) The variation of impedance and phase angle with frequency at room temperature.

Figure 6a–e shows the *P*-*E* hysteresis loop diagram of the BF–BT-*x*BG ceramic at room temperature. It can be seen that the morphology of the hysteresis loop tends to saturate with increasing electric field at the same component point, and gradually changes from flat to well-saturated. It shows that the ferroelectric performances of ceramic increase gradually with the enhancement of the electric field. Figure 6f shows the *P*-*E* hysteresis loops of different component points under the same electric field of 50 kv/cm. All hysteresis loops are saturated. The asymmetric shape of the *P*-*E* hysteresis line is due to the internal bias field of the ceramic during the test [2]. Figure S2 shows the internal bias field at different composition points of 50 kV/cm. The *E*<sub>i</sub> at all component points is between 2 and 3 kV/cm. The main doped ferroelectric produces oxygen vacancies to maintain its own electrical neutrality, which in turn leads to the formation of defective dipoles, which are oriented in the polarization direction after sufficient polarization aging, so that the directionally arranged defective dipoles form the internal bias field *E*<sub>i</sub>.



Ec (kV/cm)

**Figure 6.** (**a**–**e**) The *P*-*E* hysteresis loop diagram of BF–BT-*x*BG ceramic at room temperature, (**f**) the *P*-*E* hysteresis loops of different component points under the same electric field 50 kV/cm.

Ec (kV/cm)

Figure 7a shows the changes in residual polarization intensity  $P_r$  and coercive field  $E_c$  at different composition points at room temperature. The results show that  $P_r$  rises first and then drops as the BG concentration grows, reaching the highest value,  $P_r = 18.3 \,\mu\text{C/cm}^2$ , when x = 0.003.  $E_c$  does not change much as the BG concentration increases. The reason why  $P_r$  reaches the maximum at x = 0.003 is that a few doping of BiGaO<sub>3</sub> improves the lattice aberration of the ceramic, which increases the ferroelectric activity. Another reason may be that a few doping of BiGaO<sub>3</sub> improves the order of ceramic domains and then improves  $P_r$ . Figure 7b shows the *P*-*E* hysteresis loop of BF–BT-0.003BG ceramics at 40 kV/cm with different temperatures.  $P_r$  rises, and  $E_c$  drops gradually with the increase in temperature. The reason for this is that the high-temperature environment diminishes the pegging effect of the defective dipole and contributes to the flipping of the ferroelectric domains. Because of the internal bias field in this ceramic, there is an asymmetry in the *P*-*E* hysteresis loop [2].



**Figure 7.** (a) The changes of residual polarization intensity  $P_r$  and coercive field  $E_c$  at different composition points at room temperature, (b) *P*-*E* hysteresis loop of BF–BT-0.003BG ceramic variable with temperature.

Figure 8a–e shows the temperature-dependent  $\varepsilon_r$  and tand of the ceramic with different BG concentrations as a function of temperature. The test frequencies are 1, 10, and 100 kHz, respectively. There is a high-temperature dielectric anomaly peak and no obvious frequency dependence at low temperatures. As the temperature increases, the frequency dependence becomes more pronounced. This behavior is associated with the chemical heterogeneity of the material and the decomposition of the macro-nano domain into a nanodomain structure near the ferroelectric paraelectric phase transition. Ferroelectrics can be classified as normal ferroelectrics, dispersion ferroelectrics, and relaxor ferroelectrics [43]. Normal ferroelectrics are distinguished by a sharp phase change peak, dispersed ferroelectrics by a broad phase change peak, and relaxor ferroelectrics by a broad phase change peak, which gradually shifts to higher temperatures as the frequency increases. Figure 8 shows that the ceramics in this system exhibit all the characteristics of a relaxor ferroelectric. There are many defects in the ceramic sintering process. These defects have little influence on the dielectric performances of ceramics at low temperatures and have no obvious frequency dependence. The influence of the defects on the ceramic becomes stronger, and the ceramic shows an evident dependence on frequency as the temperature continues to increase. The  $\varepsilon_r$  initially remains unchanged and then increases rapidly with increasing temperature, and then drops gradually after arriving at the peak. Oxygen vacancies require less energy to be excited and can be excited at low temperatures. Cation excitation requires more energy and is not easy to excite at a lower temperature; therefore, the  $\varepsilon_r$  is low. The energy of the excited cation is satisfied at high temperatures, so it may be excited, leading to a high dielectric constant [44]. On the other hand, it may be due to the directional arrangement of ferroelectric domains in the polarization process of ceramics, and the lattice energy in the stable state is locked. At this time, the energy is difficult to make the long-range ordered macro domain move, and the domain wall cannot move as the electric field is applied. The relaxing time is long, resulting in a very low dielectric constant. Then, the energy required for the thermal motion is achieved as the temperature continues to increase, which makes the electric domain of the ceramics change from the long-range ordered state to the short-range disorder state, resulting in a large dielectric response and a rapid increase in  $\varepsilon_r$  [23]. The temperature of this peak is the  $T_c$  (phase change temperature from the ferroelectric phase to the paraelectric phase). Ceramics exhibit a ferroelectric phase below  $T_{c}$ , and the ferroelectric domains remain in an ordered state with piezoelectric properties. Ceramic is a paraelectric phase above  $T_{c_r}$  and the electrical domain is disordered without piezoelectric properties. Tand rises slightly at low temperatures, and it rises quickly at high temperatures. The reason is that there are a lot of oxygen vacancies in the ceramic during the sintering process, and the energy needed to excite the cations of these oxygen vacancies is more, which has no effect on the tan $\delta$  at low temperatures. Cations gain more energy

and are excited at higher temperatures, leading to a rapid increase in tan $\delta$ . Tan $\delta$  increases slowly with the BG concentration increasing at low temperatures, and the loss is mainly relaxation loss. Then, the tan $\delta$  increases rapidly when a definite temperature is achieved, which is mainly the leakage loss. Figure 8f shows the change in the ceramic dielectric constant at different BG concentrations under 1 kHz. As the BG concentration grows, the curve shifts first to high temperatures and then to low temperatures. Figure S3 shows the local enlargement of the dielectric temperature spectrum of BF–BT-*x*BG ceramics and the variation of  $T_f$  at different composition points. The temperature at which the normal ferroelectric transforms into a non-ergodic relaxor ferroelectric is the freezing temperature ( $T_f$ ).  $T_f$  reduces and then rises with the increase of BG concentration. The temperature at which the transition from the paraelectric state to the ergodic relaxor state is called Burns Temperature ( $T_B$ ). In this system of ceramics,  $T_c$  corresponds to the  $T_B$ .



**Figure 8.** (**a**–**e**) Temperature dependences of  $\varepsilon_r$  and  $tan\delta$  for BF–BT-*x*BG ceramics at 1, 10, and 100 kHz; (f) temperature dependences of dielectric constant  $\varepsilon_r$  for BF–BT-*x*BG ceramics at 1 kHz.

Figure 9a–f shows the curve of  $\ln(1/\varepsilon_r - 1/\varepsilon_m)$  as a function of  $\ln(T - T_m)$  for the BF–BT-*x*BG ceramics under 1 kHz. These points are almost in a straight line. Perovskite

ferroelectrics are generally divided into normal ferroelectrics, dispersed ferroelectrics, and relaxor ferroelectrics [43]. According to Curie Weiss's law:

$$1/\varepsilon_{\rm r} - 1/\varepsilon_{\rm m} = (T - T_{\rm m})^{\gamma}/C$$

where  $\gamma$ ,  $T_{m}$ ,  $\varepsilon_{m}$ , and C represent the diffusion coefficient, phase transition temperature, maximum  $\varepsilon_{r}$ , and Curie constant, respectively [45,46].



**Figure 9.** (**a**–**e**) The curve of  $\ln(1/\varepsilon_r - 1/\varepsilon_m)$  as a function of  $\ln(T - T_m)$  for the BF–BT-*x*BG ceramics under 1 kHz. The blue squares are the corresponding points.

It can judge what kind of ferroelectric the ceramics is. All  $\gamma$  values are higher than 1, showing that the ceramics are relaxor ferroelectrics. The  $\gamma$  value decreases first and then increases with the BG concentration increasing, and reaches the minimum value  $\gamma = 1.538$  when x = 0.006. A few doping of BiGaO<sub>3</sub> reduces the relaxation characteristics of the ceramics.

Figure 10a displays the variation of  $d_{33}$  with temperature for BF–BT-*x*BG ceramic. The  $d_{33}$  at the same component point x remains stable with rising temperature, and drops abruptly when it reaches a definite temperature. This temperature is determined as the depolarization temperature  $T_{\rm d}$  [34]. The domains are arranged orderly when the temperature is low, and the ceramics have high  $d_{33}$ . The domain progressively returns to a disorderly state when the temperature rises to a certain value, which  $d_{33}$  decreases progressively. Figure 10b shows the  $T_c$  and the  $T_d$  at different BG concentrations of BF–BT-xBG ceramics. The  $T_c$  reaches the maximum of 485.9 °C when x = 0.006. The  $T_d$  increases first when the BG concentration grows, achieving the highest of 465 °C at x = 0.003 and x = 0.006, and then drops when the BG concentration grows. The higher the amount of *R* phase, the higher the  $T_{\rm c}$  and  $T_{\rm d}$ , which is in agreement with the XRD refinement results (Table 1). It has been shown that a few doping of BiGaO<sub>3</sub> increases the  $T_c$  and  $T_d$  of ceramics. Because a few doping of BiGaO<sub>3</sub> enhances the lattice distortion and anisotropy of the ceramic, it increases the  $T_c$  and  $T_d$ . At the same time, lattice distortion means a higher phase transition barrier, resulting in a higher  $T_c$  [47]. Part of Bi<sup>3+</sup> and Ga<sup>3+</sup> accumulate on the grain boundary surface when too much Bi<sup>3+</sup> and Ga<sup>3+</sup> are doped, which reduces the lattice distortion and reduces the  $T_c$  and  $T_d$ . On the other hand, too much Bi<sup>3+</sup> and Ga<sup>3+</sup> doping may introduce defects and disrupt the long-range ordered structure of the ceramic, reducing  $T_c$  and  $T_{\rm d}$  [48].



**Figure 10.** (a) Variation of  $d_{33}$  with the temperature at different composition points *x* of BF–BT-*x*BG ceramic, (b) the  $T_c$  and the  $T_d$  at different composition points *x* of BF–BT-*x*BG ceramics.

Figure 11a shows the variation of  $\varepsilon_r$  and tan $\delta$  with temperature for x = 0, x = 0.003, and x = 0.012; the  $\varepsilon_r$  grows slowly at low temperatures and grows rapidly when it reaches a certain temperature. The tan $\delta$  increases gradually with increasing temperature, decreases after achieving a definite temperature, and then rises rapidly. The specific mechanism is explained in Figure 8. Figure 11b shows the ex situ depolarization plots for x = 0, x = 0.003, and x = 0.012. The  $d_{33}$  of different components remained stable with the rise of temperature, and when reaching a certain temperature  $(T_d)$  [34],  $d_{33}$  decreases quickly. Figure 11c shows the in situ  $d_{33}$  of BF–BT-*x*BG ceramic with high temperature. This in situ  $d_{33}$  represents the variation of  $d_{33}$  with temperature in the actual working condition of the ceramic. It shows that the  $d_{33}$  of the ceramic gradually rises with rising temperature, and decreases quickly after achieving the maximum at high temperature. Interestingly, ceramics have a large piezoelectric response  $d_{33}$  = 466 pC/N at 340 °C when x = 0.003. According to the formula  $d_{33} = 2Q\varepsilon P_s$  [49], where Q is the electrostrictive coefficient,  $\varepsilon$  is the dielectric constant, and  $P_s$ is the spontaneous polarization. The enhancement of the piezoelectric properties is related to the ferroelectric and dielectric properties. The increase from  $d_{33}$  at low temperature corresponds to the change in residual polarization intensity  $P_r$  in Figure 7b. The  $d_{33}$  rises when the temperature rises because the rise of temperature will increase  $\varepsilon$  and  $P_s$ . As the ceramic is cooled in the furnace, oxygen vacancies will be generated, resulting in lattice defects. Oxygen vacancies will gather at grain boundaries and domain walls, preventing the

movement of ferroelectric domains. The movement of ferroelectric domains and domain walls becomes active when temperature increases, improving piezoelectric response and piezoelectric properties. The flattening of the Gibbs free energy curve caused by the temperature variation leads to an increase in the dielectric sensitivity and piezoelectric response of the material under test [50,51]. The in situ  $d_{33}$  increase is influenced by both  $P_s$ and  $\varepsilon$  factors. It is mainly affected by  $P_s$  at low temperatures and  $\varepsilon_r$  at high temperatures, so it increases nonlinearly [52]. The depolarization process starts with a further increase in temperature. The microdomain returns to its initial state with a further increase in temperature. At this time, the ferroelectric domain changes from normal ferroelectric to non-ergodic relaxor ferroelectric, and the local microdomain is decomposed into randomly oriented nanodomains. It promotes the transition of the ferroelectric relaxor phase, so  $d_{33}$ decreases sharply [35]. It shows that a small amount of  $BiGaO_3$  can improve the thermal stability of ceramics. By comparing Figure 11a-c, it can be found that the ceramics of this system have an extremely high piezoelectric response in practical work. GuO and Wang reported PZT ceramics with  $d_{33} = 910 \text{ pC/N}$ ,  $T_c = 184 \degree \text{C}$  and  $d_{33} = 680 \text{ pC/N}$ ,  $T_c = 330 \degree \text{C}$ , respectively [53,54]. Compared with PZT ceramics, the present work has a high Curie temperature and good  $d_{33}$  at high temperatures. It provides great research value for the use of lead-free piezoelectric ceramics. Table 2 shows the piezoelectric properties of the BF-BT system synthesized using the conventional solid-state reaction and quenching process. A high  $d_{33}$  of 466 pC/N was achieved in this work.



**Figure 11.** (a) The variation of  $\varepsilon_r$  and tan $\delta$  with temperature for x = 0, x = 0.003, and x = 0.012, (b) the ex situ depolarization plots for x = 0, x = 0.003 and x = 0.012, (c) the in situ  $d_{33}$  of BF–BT-*x*BG ceramics for x = 0, x = 0.003 and x = 0.012 at high temperature.

Systems	<i>d</i> <sub>33</sub> (pC/N)	k <sub>p</sub>	$E_{\rm c}$ (kV/cm)	$P_{\rm r}$ (µc/cm <sup>2</sup> )	$T_{c}$ (°C)	$T_{\rm d}$ (°C)	Ref.
$0.725 BiFe_{0.98}Sc_{0.02}O_3 - 0.275 BaTiO_3 + 0.01 MnO_2$	127	0.366	48	19.1	636	450	[55]
$0.67BiFeO_3 - 0.33BaTiO_3 + 0.02BiGaO_3 + 0.0035MnO_2$	170	0.306	22.059	25	434	422	[25]
$0.75 \text{ BiFeO}_3 - 0.25 \text{BaTiO}_3 + \text{MnO}_2$	116	-	39.3	22.9	619	469	[32]
0.75 BiFeO <sub>3</sub> - 0.25BaTiO <sub>3</sub> + 0.01NdCoO <sub>3</sub> + 0.01MnO <sub>2</sub>	110	-	-	8.2	605	525	[56]
0.7BF - 0.3BT(SBT)	210	0.34	30	31.2	514	400	[57]
0.67Bi <sub>1.05</sub> (Fe <sub>0.97</sub> Ga <sub>0.03</sub> ) - 0.33BaTiO <sub>3</sub> (water-quenching)	402	-	-	-	454		[29]
$0.67BiFeO_3 - 0.33BaTiO_3 + 0.01BiGaO_3$ (water-quenching)	454				451		[31]
$0.7BiFeO_3 - 0.297BaTiO_3 - 0.003BiGaO_3 + 0.01MnO_2$	466 (340 °C) 141 (RT)	0.314	30.84	18.3	485.2	465	This work

**Table 2.** Electrical properties of reported BiFeO<sub>3</sub>–BaTiO<sub>3</sub> Lead-free piezoelectric ceramics. Room Temperature: RT.

#### 4. Conclusions

Lead-free high-temperature piezoelectric 0.7BiFeO<sub>3</sub>-(0.3 – *x*)BaTiO<sub>3</sub>-*x*BiGaO<sub>3</sub> (BF–BT-*x*BG) after pre-sintering with MnO2 system ceramics were fabricated by solid-state sintering technique and their phase analysis, microstructure, piezoelectric, ferroelectric, dielectric properties and thermal stability, were studied. XRD results show that BF–BT-*x*BG ceramics have co-existed *R* and *T* phases structure. SEM shows that the particle dimensions of ceramics gradually grow with the increase of Bi<sup>3+</sup> and Ga<sup>3+</sup> incorporation. The electrical property reaches the maximum value when *x* = 0.003: *d*<sub>33</sub> = 141 pC/N, *k*<sub>p</sub> = 0.314,  $Q_{\rm m} = 56.813$ ,  $P_{\rm r} = 18.3 \,\mu\text{C/cm}^2 T_{\rm c} = 485.2 \,^{\circ}\text{C}$ ,  $T_{\rm d} = 465 \,^{\circ}\text{C}$ . Lattice distortion leads to improved room-temperature piezoelectric and dielectric properties. The excitation of cations at high temperatures leads to the improvement of dielectric properties at high temperatures leads to the improvement of piezoelectric properties at high temperatures. This study shows that doping BiGaO<sub>3</sub> into BF–BT has excellent electrical properties, making it a potential application for high-temperature piezoelectric devices.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst13071026/s1, Figure S1: Wide-temperature-range d33 meter (TZFD-900, Harbin Julang Technology Co., Ltd., Harbin, China). Figure S2: Internal bias field Ei for different component points at 50 kV/cm. Figure S3: Local enlargement of the dielectric temperature spectrum of BF-BT-xBG ceramic and the variation of Tf at different composition points. (a) x = 0, (b) x = 0.003, (c) x = 0.006, (d) x = 0.009, (e) x = 0.012, (f) the variation of Tf at different composition points.

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**Data Availability Statement:** The data used to support the findings of this study are available from the corresponding author upon request.

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