

New Bi(Mg_{0.75}W_{0.25})O₃–PbTiO₃ ferroelectric ceramics

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Abstract

An investigation was made into the Bi(Mg_{0.75}W_{0.25})O₃–PbTiO₃ (BMW-PT) system. The aim was to find the optimum composition with respect to piezoelectric and dielectric properties and link this to the presence of a morphotropic phase boundary (MPB). The optimum composition was found to be 62 mol% PT. The maximum values of the piezoelectric constant $d_{33} = 150$ pm/V and the maximum relative dielectric constant $\epsilon_{33}/\epsilon_0 = 1400$. The dielectric loss is high with $\tan \delta$ typically $\sim 5\%$. Results from capacity versus the temperature measurements indicate a Curie temperature of 220 °C, which is significantly lower than the predicted value.

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1. Introduction

Over the last few years an increasing amount of research has been done on the development of new piezoelectric materials with a high Curie temperature (T_C), mainly for two reasons: first, to permit the increasing application of piezoelectric ceramics at higher temperature and, second, to compensate for the doping of materials (to optimise piezoelectric properties) which generally results in a lower T_C and consequently in more limited applicability.

Turner et al.¹ have pointed out that the industrial community is expressing the need for sensors and actuation over a broader temperature range. Current piezoelectric ceramics are largely based on the Pb(Zr,Ti)O₃ (PZT) system, offering a broad range of piezoelectric constants, dielectric constants and dielectric loss. However, since a temperature $T_C/2$ is considered to be the maximum safe operating temperature, undoped PZT ceramics, with a maximum T_C of ~ 385 °C, are limited to a maximum operating temperature of ~ 190 °C.

Doping PZT to enhance the (piezoelectric) properties lowers the maximum operating temperature easily to ~ 150 °C. This temperature is equal to the norm used by the automotive industry as the average operating temperature, while peak temperatures can be as high as 300 °C. Aerospace and aircraft industries use even higher standards, demanding systems to function at from 500 to 1000 °C. In view of these demands, it is necessary to develop high T_C piezoelectric materials.

For perovskite structures like PZT with the general formula $A^{XII}B^{VI}O_3^{VI}$ (roman numerals representing the coordination number), Goldsmith defined the tolerance factor t as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

in which r is the ionic radius of the respective ion.² It has been observed that a stable perovskite may be expected to form if $0.88 < t < 1.09$, using Shannon's revised ionic radii.³ Ferroelectric perovskites with $t = 1$ may be expected to have a cubic symmetry, ferroelectric perovskites with $t < 1$ are usually rhombohedral or monoclinic while ferroelectric perovskites with $t > 1$ are commonly tetragonal.

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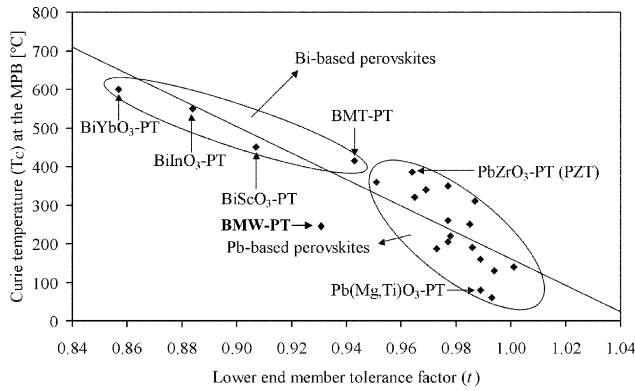


Fig. 1. Curie temperature T_C of PbTiO_3 (PT) based MPBs vs. lower end member tolerance factor of the system. In all systems PT is the tetragonal end member. The perovskite tolerance factor was calculated from tables of ionic radii given by Shannon.³ BMW-PT is the 38BMW-62PT system investigated in this paper.

Eitel et al.⁴ have proposed that at the morphotropic phase boundary (MPB) a relationship exists between the temperature at which the distorted, piezoelectric lattice changes into a cubic, non-piezoelectric lattice (characterized by T_C) and the tolerance factor. The MPB is defined as the region in which a rhombohedral ferroelectric phase is present in equal amounts to the tetragonal ferroelectric phase. It is commonly accepted that in this region the highest piezoelectric properties can be found. Eitel et al.⁴ plotted the tolerance factors of the pure rhombohedral or monoclinic phase, the so-called lower end member, against the transition temperature at the MPB (Fig. 1). In all cases the tetragonal phase, or upper end member, was lead titanate (PT). They state that if the lower end member has a lower tolerance factor, this will result in a higher transition temper-

ature at the MPB. For several bismuths based lower end members⁴ the relationship holds, namely BiScCO_3 , BiInO_3 and BiYbO_3 with a tolerance factor of 0.907, 0.884 and 0.857 and a T_C of 450, 550, and 650 °C, respectively. In line with these findings this investigation has explored into the $\text{Bi}(\text{Mg}_{0.75}\text{W}_{0.25})\text{O}_3$ – PbTiO_3 system, which has a lower end member tolerance factor of 0.930 and therefore an expected T_C of ~400 °C.

2. Experimental methods

Traditional mixed oxide ceramics processing has been used for the production of solid solutions of $\text{Bi}(\text{Mg}_{0.75}\text{W}_{0.25})\text{O}_3$ – PbTiO_3 . Starting materials were commercial grade Bi_2O_3 (Acros Organics), TiO_2 (Fuji Titanium Industry), PbO (Penarroya Oxide) and MgTiO_3 (Aldrich Chemical Company). Raw materials were batched stoichiometrically with an excess of 0.5 mol% $\text{PbO}/\text{Bi}_2\text{O}_3$ to compensate for evaporation losses. Aqueous suspensions were mixed on a roller bank for 4 h utilizing yttrium zirconate balls. The powder was dried at 125 °C and calcined at 800 °C for 5 h in closed Al_2O_3 crucibles. Calcined powders were milled as an aqueous suspension, with 0.5 g Dispex A40 per 100 ml water as a dispersing agent, for 24 h on the roller bank. The powders were dried at 125 °C and then crushed to pass through a 250 μm sieve. This procedure resulted in powders with a particle size distribution (PSD) of 90% of the particles smaller than 1.61 μm , 50% smaller than 0.75 μm and 10% smaller than 0.25 μm .

The powders were isostatically pressed into a cylindrical shape with a diameter of 25 mm. These cylinders were sin-

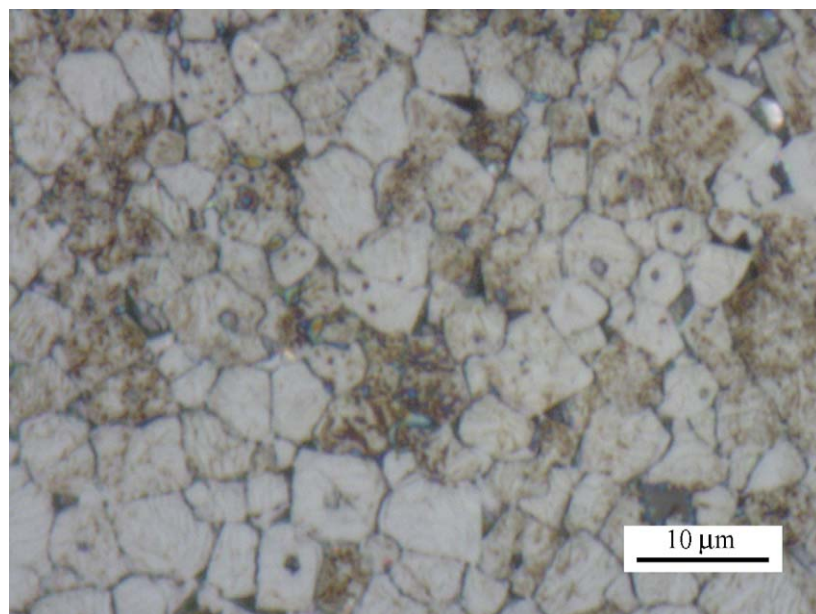


Fig. 2. Optical image of 38 mol% BMW–62 mol% PT. The average grain size is 4.1 μm .

tered at 1050 °C for 4 h in closed Pt-boxes with a confirmed weight loss of less than 0.5%. Finally, they were ground down to a diameter of 16 mm and sawn into discs with a thickness of 1 mm for dielectric and piezoelectric testing with both fired on silver electrodes, firing temperature 750 °C, and evaporated nickel–chromium (NiCr) electrodes. Poling was done at 30 °C in three steps to prevent cracking of the material: 3 min at 4.5 kV/mm, 3 min at 6 kV/mm and 2 min at 6.5 kV/mm. Practical limitations prevented the application of higher fields.

The final ceramic samples typically had a density of $\sim 8.10 \text{ g/cm}^3$, which is over 99% of theoretical density. Occasionally a higher than theoretical density was obtained which is likely due to second phases. Optical microscopy investigation was used to examine microstructure and a typical micrograph is shown in Fig. 2. The average grain size as determined by the mean linear intercept was 4.1 μm .

Dielectric and piezoelectric properties were measured to obtain the composition with maximum properties, at which the MPB is to be expected. The piezoelectric constant d_{33} was measured using a Berlincourt d_{33} meter (Channel Products Model CADT) and the dielectric constant using an impedance/gain-phase analyzer (Hewlett Packard HP4194A) using IEEE resonance methods.⁵

3. Results and discussion

The results of the dielectric and piezoelectric experiments are shown in Fig. 3 and Table 1. It was found that the best properties exist at 38 mol% BMW–62 mol% PT with values for d_{33} of $\sim 150 \text{ pm/V}$ and for the relative dielectric constant ϵ_{33}/ϵ_0 a value of ~ 1400 . The dielectric loss found was $\sim 5\%$, which is relatively high for a hard material. For comparison, commercially available hard material (Morgan Electro Ceramics PXE-42 grade) has a typical dielectric loss of 0.25%. To confirm piezoelectric activity, the hysteresis curve was measured on samples with a thickness of 0.20 mm using a Radiant high voltage test system RT6000HVS-2 and Radiant high voltage amplifier RT6000HVA-2 and accompanying calculating and acquiring computer software. The

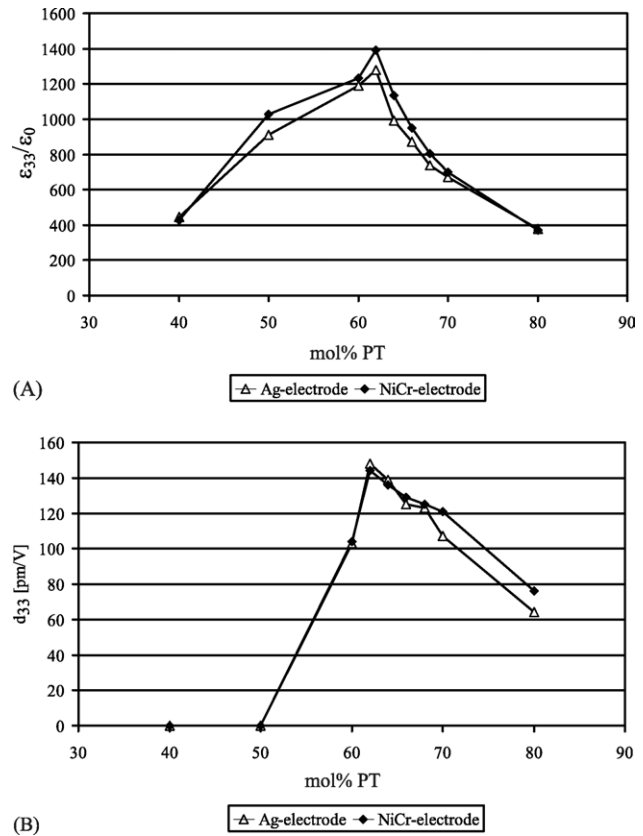


Fig. 3. Dielectric and piezoelectric properties of the $(1-x)\text{BMW}-x\text{PT}$ system vs. the mol% PT. (A) The relative dielectric constant ϵ_{33}/ϵ_0 and (B) the piezoelectric constant d_{33} .

results are presented in Fig. 4. It is seen that the coercive field of the material is 4.2 kV/mm. Complete saturation was not reached at 10 kV/mm, but the equipment is limited to maximum applied field of 2000 V and, with a practical lower limit of the sample thickness of 0.20 mm, this makes a maximum applicable field of 10 kV/mm. This also means that the samples for dielectric and piezoelectric measurements were not poled ideally and it is expected to produce better results when poled at $>10 \text{ kV/mm}$. The maximum polarization was found to be $34 \mu\text{C/cm}^2$ with a remnant polarization of $23 \mu\text{C/cm}^2$.

Table 1

Piezoelectric and dielectric properties of the various compositions for the NiCr electrode and the Ag electrode

Composition (mol% BMW–mol% PT)	ρ_{the} (g/cm^3)	ρ (g/cm^3)	NiCr electrode			Ag electrode		
			ϵ_{33}/ϵ_0 (–)	d_{33} (pm/V)	$\tan \delta$ (‰)	ϵ_{33}/ϵ_0 (–)	d_{33} (pm/V)	$\tan \delta$ (‰)
60–40	8.20	7.89	428	0	67.1	444	0	67.3
50–50	8.18	8.10	1028	0	97.0	912	0	90.0
40–60	8.13	8.10	1232	104	62.7	1189	103	62.5
38–62	8.12	8.16	1393	144	50.7	1278	148	46.0
36–64	8.11	8.18	1135	136	36.2	994	139	33.1
34–66	8.10	8.10	950	129	33.4	872	125	33.1
32–68	8.09	8.11	804	125	27.6	739	123	25.4
30–70	8.08	8.08	700	121	21.2	670	107	22.4
20–80	8.03	7.93	370	76	32.5	379	64	20.5

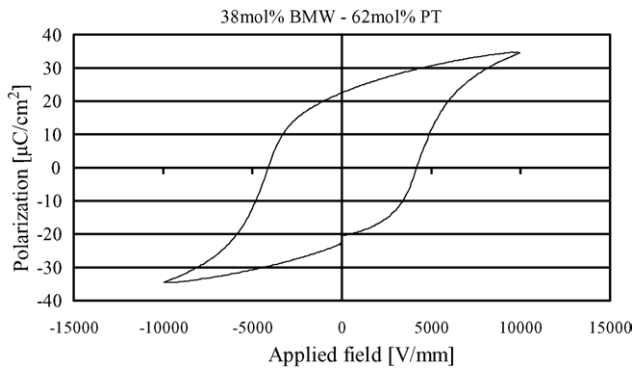


Fig. 4. The hysteresis curve of 38 mol% BMW–62 mol% PT.

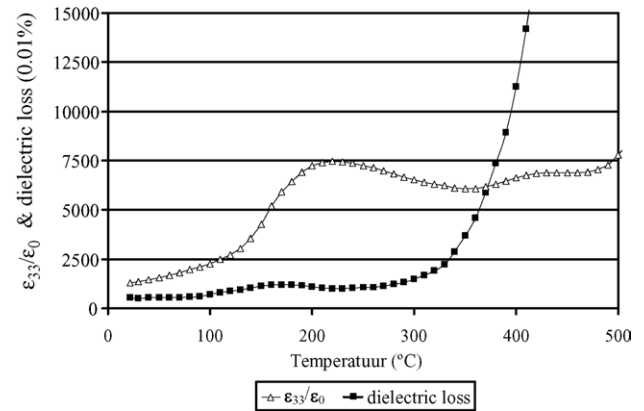


Fig. 6. Dielectric constant and dielectric loss vs. temperature measurement on the sample 38 mol% BMW–62 mol% PT.

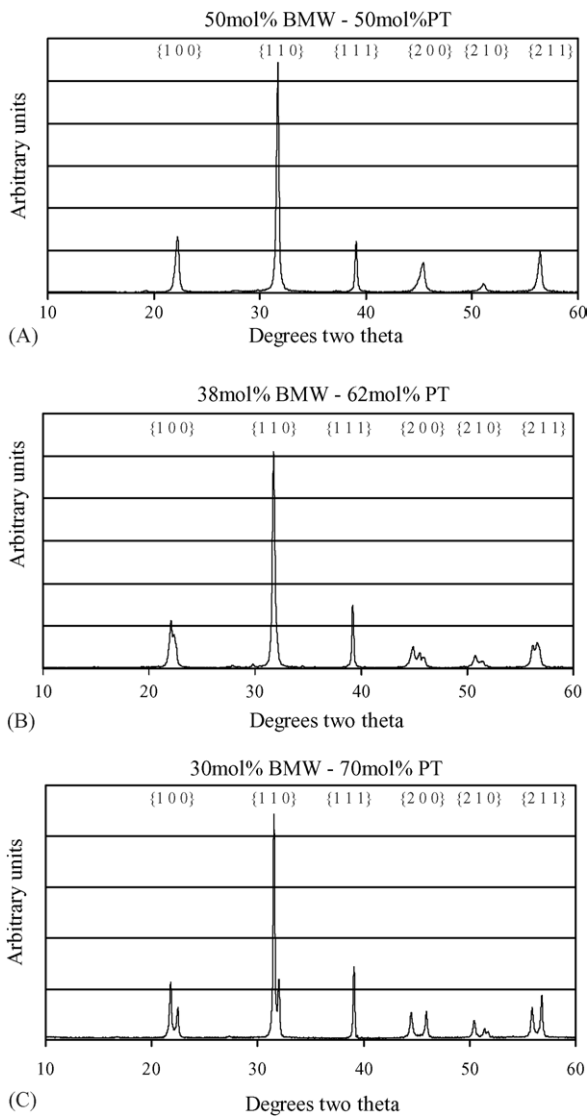


Fig. 5. X-ray diffraction diagrams of (A) the rhombohedral region with $x = 50$ mol% PT, (B) the morphotropic phase boundary at $x = 62$ mol% PT and (C) the tetragonal region with $x = 70$ mol% PT.

To confirm the presence of a MPB X-ray diffraction (XRD, Rigaku Cu $K\alpha$ $\lambda = 0.154$ nm) studies were conducted on samples $x = 50$, 62 and 70 mol% PT. The results are shown in Fig. 5. Typical rhombohedral symmetry was observed in the sample 50 mol% PT and typical tetragonal at 70 mol% PT. The rhombohedral symmetry at 50 mol% PT, which can be identified by the splitting of the pseudocubic peak $\{111\}$, shifts to the typical tetragonal symmetry at 70 mol% PT, identified by the $\{110\}$ and $\{100\}$ splitting. At 62 mol% PT the transition is halfway. This shift from rhombohedral to tetragonal symmetry supports the presence of the MPB at 62 mol% PT (Fig. 5).

The temperature dependences of the capacity and dielectric loss (home build furnace combined with HP LCR meter) of samples with composition 38 mol% BMW–62 mol% PT are presented in Fig. 6. The capacity shows a peak at 220 °C. This indicates a Curie temperature near 220 °C. This is much lower than the expected value using the relationship proposed by Eitel et al.,⁴ which predicts a value of 400 °C. It is also lower than current PZT materials. The reason is unclear, however, it should be remarked that several other compounds also deviate significantly from the Eitel predictions (see Fig. 1).

4. Conclusions

The morphotropic phase boundary in the $\text{Bi}(\text{Mg}_{0.75}\text{W}_{0.25})\text{O}_3\text{--PbTiO}_3$ system can be found at 62 mol% PT. The maximum properties obtained were a d_{33} of 150 pm/V and a relative dielectric constant ϵ_{33}/ϵ_0 a value of 1400 after poling. Hysteresis measurements indicate that the coercive field of the material is 4.2 kV/mm and that saturation is not reached up to 10 kV/mm. This indicates that better poling likely will yield higher properties for this system. Results from capacity versus the temperature measurements indicate a Curie temperature of 220 °C, which is significantly lower than the predicted value.

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