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Investigation of the new piezoelectric system $(1-x)Bi(MgTi)_{0.5}O_3–xPbTiO_3$

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Abstract

An investigation was made into the $(1-x)Bi(MgTi)_{0.5}O_3–xPbTiO_3$ (BMT-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 68 mol%BMT–32 mol%PT with a broad active region of 36 mol%PT < x < 40 mol%PT. The maximum values of the piezoelectric constants were d_{33} = 215 pm/V and d_{31} = 58 pm/V, respectively; the maximum relative dielectric constant $\varepsilon_{33}/\varepsilon_0$ was 1046. The dielectric loss is high with over 5% up to almost 9%. It was also observed that the choice for the material of the electrode influences the properties considerably. The Vicker's hardness was 5.2 GPa while the strength as measured in 3-point bending was 230 MPa.

Keywords: Dielectric properties; Mechanical properties; Piezoelectric properties; Perovskites; $Bi(Mg,Ti)O_3–PbTiO_3$

1. Introduction

Piezoelectric ceramics are nowadays commonly based on the perovskite $Pb(Zr,Ti)O_3$ (PZT) system and these materials are widely used in sensors and actuators. The traditional applications of these materials are underwater sonar, ultrasound transducers and actuators. The advances in electronics and computer controls have also led to the incorporation of these materials into common electronic devices.[1]

A large number of piezoelectric sensors and devices are nowadays present in automotive, aerospace, aircraft and related industrial applications, often as vibration sensor or cancelling systems.[2] Lately, these industries have expressed the need for actuation at higher temperatures than currently available. Currently the automotive industry considers 150 °C as the average operating temperature, with peaks as high as 300 °C. Aerospace and aircraft industry use higher standards of 500 °C up to 1000 °C. Commercially available materials are generally limited to operational temperatures of one half of the Curie temperature T_C or ≤180 °C for PZT systems. This means that current piezoelectric materials demand thermal isolation.

Moreover, industries are demanding better properties under the same minimum operational conditions. Normally, these properties can be obtained by doping, but this generally leads to a lower operational temperature. In the PZT system it is practically impossible to improve the material by doping any further without lowering the operational temperature to below 150 °C.

Finally environmental issues with lead ceramics have led to the awareness that low-lead or no-lead ceramics must be developed for the future. For these reasons, over the last few years more and more research is done into the development of new piezoelectric materials with a high T_C. Recently it was proposed by Eitel et al.[3] that in the development of high T_C piezoelectric perovskites, the Goldschmidt tolerance factor plays an important role. Taking the general formula for perovskites, $A^{XII}B^{VI}O_3{}^{VI}$ (roman numbers represent the co-

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ordination number), Goldschmidt[4] proposed that

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

in which t is the tolerance factor and r is the ionic radius of the respective ion. 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.[5] 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.

It is commonly accepted that the best piezoelectric properties can be found at the so-called morphotropic phase boundary (MPB). This is defined as the region in which the rhombohedral or monoclinic ferroelectric phase is present in equal amounts to the tetragonal ferroelectric phase.[1] Calculating the tolerance factors for the two (the rhombohedral or monoclinic and the tetragonal) end members in each system, Eitel et al.[3] have stated that a relation exists between the transition temperature at the MPB (characterized by T_C) and the tolerance factor of the rhombohedral or monoclinic end member. They propose that as the tolerance factor for the rhombohedral or monoclinic end member decreases, keeping lead titanate PT as tetragonal phase, the transition temperature at the MPB will raise. This relationship is depicted in Fig. 1. In this figure the results obtained by Eitel et al.[3] for the bismuth-based end members: $BiScCO_3$, $BiInO_3$ and $BiYbO_3$ with a tolerance factor of 0.907, 0.884 and 0.857 and a T_C of 450 °C, 550 °C and 650 °C, respectively, are included, as well as the results of this paper.

This paper investigates the presence of the morphotropic phase boundary in the system $(1-x)Bi(Mg_{1/2}Ti_{1/2})O_3$–$xPbTiO_3$ (BMT-PT) with a tolerance factor of 0.943 for BMT. Specifically the peak in dielectric and piezoelectric properties will be linked to the existence of a MPB in the system using X-ray diffraction (XRD). The T_C is determined by capacity versus temperature measurements and differential scanning calorimetry (DSC). Furthermore, the hardness and strength are studied and compared to the values for current commercially available materials.

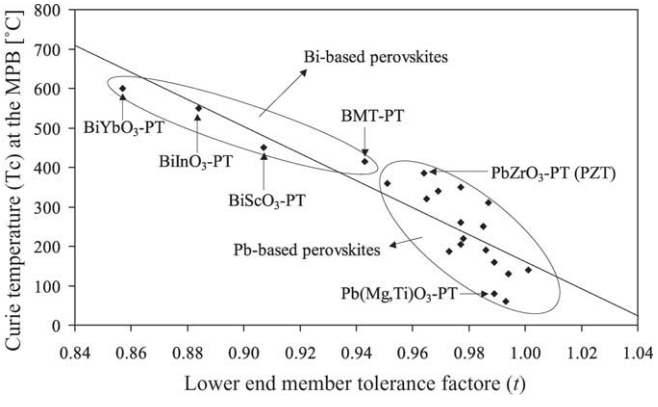

Fig. 1. Curie temperature T_C of $PbTiO_3$ (PT)-based MPBs vs. lower end member tolerance factor of the system. In all systems, PT is the tetragonal end member. The perovskite tolerance factor was calculated from tables of ionic radii given by Shannon.[5] BMT-PT is the 62BMT–38PT system investigated in this paper.

2. Experimental approach and sample preparation

Traditional mixed oxide ceramics processing has been used for the production of solid solutions of $Bi(MgTi)_{0.5}O_3$–$PbTiO_3$. 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 PbO/Bi_2O_3 of 0.5 mol% 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 alumina crucibles. Calcined powders were milled in 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.

The powders were isostatically pressed into a cylindrical shape with a diameter of 25 mm. These cylinders were sintered at 1050 °C for 4 h in closed Pt-boxes with a confirmed weight loss of less then 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 has been 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.

The samples for testing the Vicker's hardness had a thickness of 5 mm while the samples for the 3-point bend strength testing were of dimensions (length/width/height) 38 mm × 12 mm × 0.25 mm. For the strength test 10 samples were used. Phase determination for the sintered discs was done using X-ray diffraction (XRD, Rigaku Cu Kα $\lambda = 0.154$ nm). The microstructure was examined by optical microscopy after diamond polishing and chemically etching. Differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1) and temperature-dependent measurement of the capacity (home build furnace combined with a HP LCR meter) were performed on ceramics to obtain the phase transition temperature. Piezoelectric measurements were made using a Berlincourt d_{33} meter (Channel Products Model CADT) and an impedance/gain-phase analyzer (Hewlett Packard HP4194A) using IEEE resonance methods.[1] Hysteresis was measured using a Radiant high voltage test system RT6000HVS-2 and Radiant high voltage amplifier RT6000HVA-2 and accompanying calculating and acquiring computer software.

Table 1
Piezoelectric and dielectric properties of the various compositions with Ag electrode and NiCr electrode

Composition (mol%BMT–mol%PT)	ρ_{the} (g/cm^3)	ρ (g/cm^3)	Ag electrode				NiCr electrode			
			$\varepsilon_{33}/\varepsilon_0$	d_{33} (pm/V)	d_{31} (pm/V)	tan δ (‰)	$\varepsilon_{33}/\varepsilon_0$	d_{33} (pm/V)	d_{31} (pm/V)	tan δ (‰)
65–35	7.84	7.75	851	103	37	67.2	795	0	0	52.9
64–36	7.93	7.79	1036	210	56	86.4	868	0	0	68.7
63–37	7.94	7.79	1046	210	56	79.0	830	0	0	63.4
62–38	7.94	7.80	1050	215	58	70.7	867	0	0	63.3
61–39	7.94	7.78	1030	212	57	59.5	987	0	0	60.3
60–40	7.95	7.78	980	189	53	48.6	916	127	45	53.1
59–41	7.95	7.78	873	151	45	38.2	994	42	0	51.7
58–42	7.95	7.79	914	162	48	42.5	964	38	0	53.7
55–45	–	–	695	53	0	34.0	944	28	0	52.6
50–50	7.97	–	294	21	0	51.3	391	30	0	24
40–60	8.00	7.24	270	0	0	43.3	361	34	0	13

3. Results and discussion

The density of nearly all the samples after sintering at 1050 °C for 4 h is about 7.8 g/cm^3, which is approximately 98% of the theoretical density (see Table 1). Sintering at a higher temperature resulted in second phases after sintering. Sintering at a lower temperature resulted in a lower density. Optical microscopy showed a grain size, as determined by the mean linear intercept method, of 1.5 μm. A typical optical image is shown in Fig. 2.

Piezoelectric constants d_{31}, d_{33} and dielectric constant ε_{33} versus compositional changes in the $(1-x)Bi(MgTi)_{0.5}O_3$–$xPbTiO_3$ (BMT-PT) system were measured for a range of 35 mol%PT to 60 mol%PT to determine the composition with the highest properties. The best properties were found in the region of 36 mol%PT to 39 mol%PT (Table 1) using silver (Ag) electrodes. The value for d_{31} was found to be 55 pm/V (±3) throughout this region. The samples with nickel-chromium (NiCr) electrodes showed no piezoelectric activity and lower dielectric properties compared to the samples with an Ag electrode in the region up to 39 mol%PT (Table 1). However, in the region higher than 40 mol%PT the dielectric properties of the samples with NiCr electrodes are higher than the samples with Ag electrodes. Only for the 40 mol%PT sample a value for d_{31} has been found of 45 pm/V. Furthermore in the upper mol%PT region, the piezoelectric property d_{33} vanishes when using a silver electrode, but using a NiCr electrode it levels off at 30 pm/V. It might be that annealing (like for Ag electrodes) is required for proper measurement with NiCr electrodes. However, for very comparable materials measurements with NiCr electrodes yielded very similar results as with Ag electrodes. Therefore the influence of the electrode on the properties remains unclear.

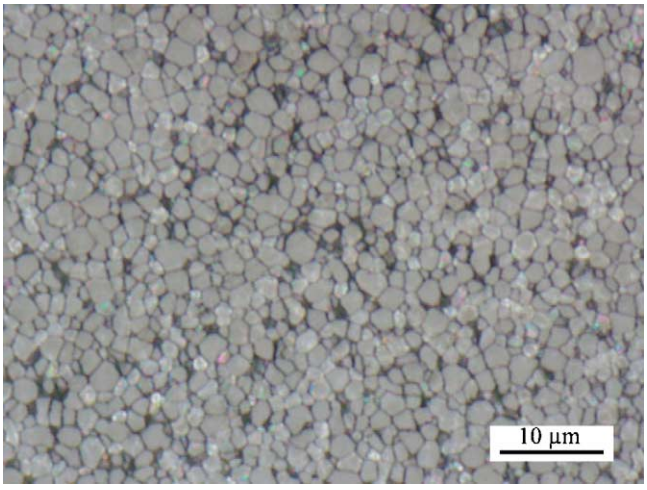

Fig. 2. Optical image of the surface of 62 mol%BMT–38 mol%PT. The average grain size is 1.5 μm.

Considering that the material is a hard piezoelectric material and comparing it to a normal hard material, its performance with respect to dielectric loss is extremely poor. The dielectric loss of BMT-PT varies in the most active region from 6% up to almost 9%, whereas commercially available hard material (Morgan Electro Ceramics PXE-42 grade) has a typical dielectric loss of 0.25%. It was concluded from these results that the best composition is 62 mol%BMT–38 mol%PT and best electrode material is silver.

Hysteresis measurements were done on 62 mol%BMT–38 mol%PT samples and are presented in Fig. 3. The maximum polarization was found to be 14 μC/cm^2 and the remnant polarization was 9.6 μC/cm^2. Full saturation was not reached and most notable, the maximum polarization did not occur at the highest field, but on the return to zero field. Slower experiments, higher electric fields or higher temperature could not be performed due to limitations of the testing equipment. It is expected that slower measurements or higher fields will result in higher polarizations. The coercive field of the material is 4.1 kV/mm.

The capacity and dielectric loss versus temperature measurements on the composition 62 mol%BMT–38 mol%PT are presented in Fig. 4. It reveals a maximum capacity at 410 °C. Above this temperature the capacity does not appear to follow the Curie–Weiss law as required for the determination of the T_C. However, the high dielectric loss in this region makes it hard to make reliable measurements on

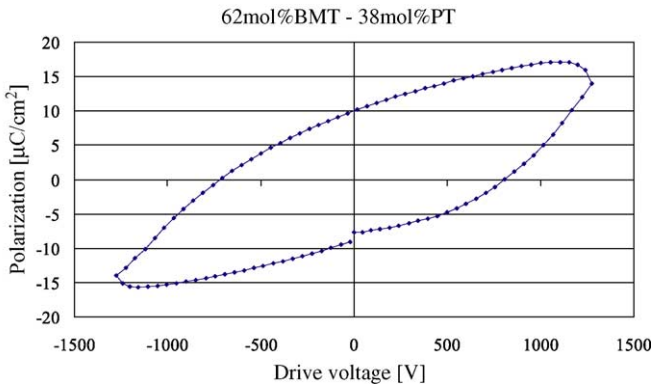

Fig. 3. Hysteresis curve of 62 mol%BMT–38 mol%PT. Full saturation could not be reached. The measurement was too fast for the material to respond to the applied field, which resulted in the maximum properties not to occur at the maximum applied field.

the capacity. DSC measurements on unpoled, unelectroded samples with composition 62 mol%BMT–38 mol%PT gave a transition temperature of 420 °C. Therefore it is concluded that T_C is in the region of 410 °C to 420 °C. Using the relationship proposed by Eitel et al.,[3] a T_C of 355 °C is predicted, which is lower than the experimental values. However, similar deviations from this relation have also been observed for other compounds, e.g. the T_C of $Pb(Zr,Ti)O_3$ is 385 °C,[3] where the relationship of Eitel et al.[3] predicts 285 °C.

The existence of a region with higher piezoelectric and dielectric properties indicates the possibility of a morphotropic phase boundary (MPB). To ascertain the existence of the MPB, X-ray diffraction (XRD) studies have been made of the samples $x = 36\%$, 38% and 42%. The results of these measurements are presented in Fig. 5. Typical rhombohedral symmetry was observed in the sample 36 mol%PT and typical tetragonal at 42 mol%PT. The rhombohedral symmetry at 36 mol%PT, which can be identified by the splitting of the pseudocubic peak {1 1 1}, shifts to the typical tetragonal symmetry at 42 mol%PT, identified by the {1 1 0} and {1 0 0} splitting. At 38 mol%PT the transition is half-way. These

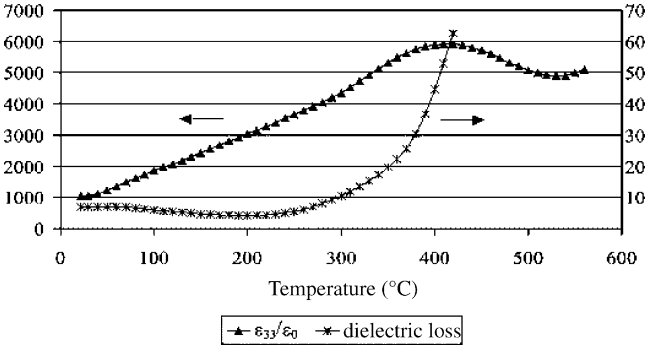

Fig. 4. Capacity and dielectric loss (%) vs. temperature measurement on the sample 62 mol%BMT–38 mol%PT.

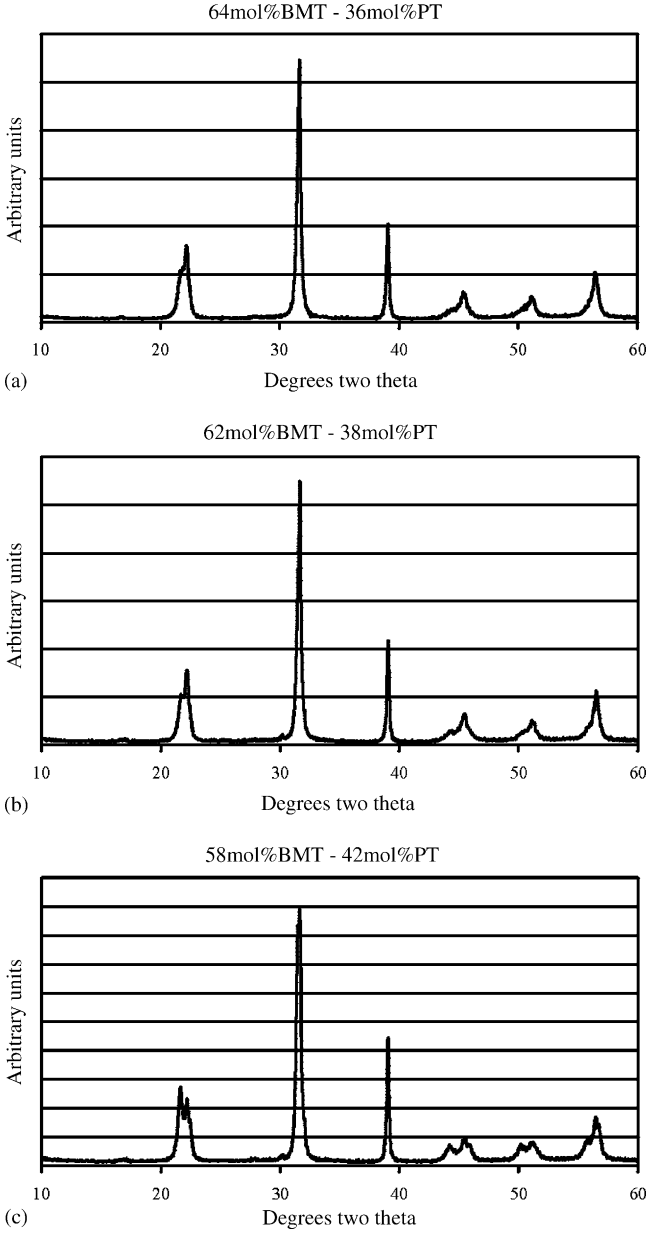

Fig. 5. X-ray diffraction patterns for ceramic samples for $(1-x)$BMT–xPT, (a) $x = 0.36$ with rhombohedral symmetry on lower mol%PT side of the MPB, (b) $x = 0.38$ at the MPB, and (c) $x = 42$ with the tetragonal symmetry at the upper mol%PT side of the MPB.

shifts from rhombohedral to tetragonal symmetry supports the presence of the MPB at 36 mol%PT $< x <$ 40 mol%PT.

Finally, for the 38 mol%PT sample, the Vicker's hardness and 3-point bend strength were determined. Using different loads (25 indentations in total) it was determined that the Vicker's hardness (H_V) is 5.2 GPa while the average 3-point bending strength was 230 MPa. This is to be compared with the corresponding data for commercially available PZT material (Morgan Electro Ceramics) with an H_V of 3.6 GPa and average strength of 110 MPa. The average deflection at failure was 1.0 mm and 1.5 mm, respectively, indicating that the

simple 'strength-of-materials' formulae used are but limitedly valid.

4. Conclusions

$(1-x)Bi(MgTi)_{0.5}O_3$–$xPbTiO_3$ (BMT-PT) solid solution ceramics were prepared using pressureless sintering at 1050 °C. This resulted in ceramics with densities of over 98% of theoretical density and an average grain size of 1.5 μm.

Piezoelectric and dielectric measurements indicate that the optimum properties are at 62 mol%BMT–38 mol%PT. Using a silver electrode, the piezoelectric constants were d_{33} = 215 pm/V and d_{31} = 58 pm/V, while the relative dielectric constant $\varepsilon_{33}/\varepsilon_0$ was 1046. The dielectric loss was found to be extremely high for a hard material, being over 5%. Using nickel-chromium electrodes gave inferior results in comparison to samples with silver electrodes.

Similar to the PZT system, it was proposed that the maximum properties would be found at the morphotropic phase boundary (MPB). X-ray diffraction confirms the presence of a MPB at 62 mol%BMT–38 mol%PT. The Curie temperature obtained from the temperature dependency of the capacitance was 410 °C while the Curie temperature resulting from DSC was 420 °C.

The maximum polarization was found to be 14 μC/cm^2 and the remnant polarization was 9.6 μC/cm^2. Due to limitations in equipment the measurements were poor and it is to be expected that higher polarization levels can be reached using better equipment. The coercive field was 4.1 kV/mm.

Finally, mechanical properties were examined. The Vicker's hardness was determined as 5.2 GPa while the average 3-point bending strength was 230 MPa.

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