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Peculiar properties of a high Curie temperature $Pb(In_{1/2}Nb_{1/2})O_3-PbTiO_3$ single crystal grown by the modified Bridgman technique

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Abstract

$(1-x)Pb(In_{1/2}Nb_{1/2})O_3-xPbTiO_3$ single crystal near the morphotropic phase boundary has been grown directly from the melt by the modified Bridgman technique, in which an allomeric PMNT 69/31 seed crystal was used. It was found the use of seed crystal has some advantages for the control of spontaneous nucleation, parasitic growth and for restraining the formation pyrochlore phase. The electric properties of the single crystals oriented along [001] axis have been characterized. It exhibited an abnormal high permittivity ($\varepsilon_{33}/\varepsilon_0$) of more than 4000 at room temperature, Curie temperature (T_c) higher than 200 °C, piezoelectric constant (d_{33}) > 2000 pC/N, and electromechanical coupling factor $k_{33} \approx 92\%$, $k_t = 59.2\%$. Our results show that the peculiar properties e.g. the larger dielectric constant at room temperature and lower T_c than that of previous reports should attribute to the diffuseness of magnesium ion into the PINT single crystal during crystal growth. X-ray fluorescence analysis revealed the composition of the crystals was in the range of $0.23Pb(Mg_{1/3}Nb_{2/3})O_3-0.46Pb(In_{1/2}Nb_{1/2})O_3-0.31PbTiO_3$ to $0.19Pb(Mg_{1/3}Nb_{2/3})O_3-0.46Pb(In_{1/2}Nb_{1/2})O_3-0.35PbTiO_3$. It implied that the ternary system of $xPb(Mg_{1/3}Nb_{2/3})O_3-yPb(In_{1/2}Nb_{1/2})O_3-(1-x-y)PbTiO_3$ (PMINT) should have good perovskite phase thermal stability, larger dielectric constant at room temperature, and ultrahigh piezoelectric properties. © 2002 Published by Elsevier Science Ltd.

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Keywords: A. PIN-PT single crystal; B. Crystal growth; D. Dielectric properties; D. Piezoelectric properties; D. Curie temperature

1. Introduction

Recently, there is considerable interest in single crystals of solid solutions of lead-based complex perovskite $Pb(B_1,B_2)O_3$ (B_1 = Mg, Zn, Sc, In; B_2 = Nb) relaxor ferroelectrics and the normal ferroelectric $PbTiO_3$ (PT) system near the morphotropic phase boundary (MPB), for their potential application in ultrasonic transducers, non-destructive testing (NDT), and high strain actuators. Much of this interest has been centered on $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PMNT) and $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PZNT) single crystals, which exhibit superior piezoelectric properties by utilizing domain engineering [1–5]. For example, $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ (PMNT 67/33) single crystals show an ultrahigh piezoelectric constant ($d_{33} \sim 2500$ pC/N), extremely large piezoelectric strain (>1.7%), and very high electromechanical coupling factor ($k_{33} \sim 94\%$) [6]. These values are much larger than that of $d_{33} \sim 700$ pC/N, $k_{33} < 80\%$ and $k'_{33} < 70\%$ of conventional $Pb(Zr,Ti)O_3$ (PZT) ceramics [7,8]. One of the disadvantages of PMNT and PZNT single crystals near the MPB is their relatively low T_C of 150 and 170 °C, respectively, which comes with the expense of more temperature dependent properties, and less polarization stability. It restricts the operating temperature range to less than 85 °C [9,10]. A relatively high T_C ($T_C \approx 300$ °C) of the MPB composition $0.63Pb(In_{1/2}Nb_{1/2})O_3-0.37PbTiO_3$ (PINT 63/37) ceramics have been reported [11], as shown in Fig. 1.

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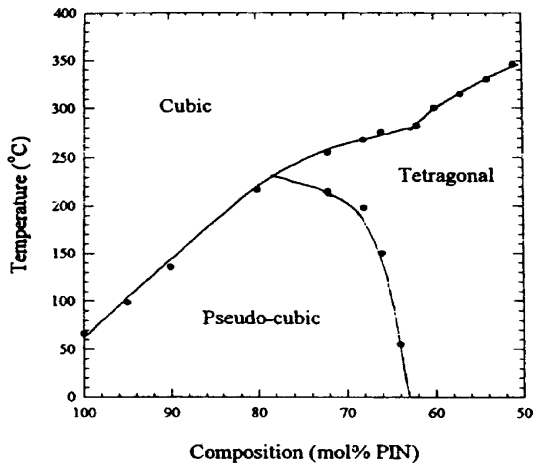


Fig. 1. PINT phase diagram based on transition temperatures of poled ceramics [11].

But it was very difficult to be synthesized in pure-phase perovskite bodies as PZNT, for the tolerance and the electronegativity difference of PIN are very low compared with other perovskite compounds such as PMN [12]. The PINT single crystals have been grown by a flux method, but the PINT crystals grown by that method was not ideal in the compositional uniformity, crystal size, and electric properties ($d_{33} \sim 700$ pC/N, $\varepsilon_{33}/\varepsilon_0 \sim 790$) yet [9,10]. It was our intention in this study to seek a new method to grow PINT single crystals and to discuss the new discoveries and problems in practical growth.

2. Experimental

Single crystals of PINT 66/34 (the starting composition) were grown directly from melt by the modified Bridgman technique. The structure of the Bridgman furnace has been previously reported [13]. The control of nucleation and growth become effective in this method since the allomeric seed crystals (PMNT 69/31) can be used and come into operation in the control of the spontaneous nucleation and parasitic growth. Chemicals of high purity better than 99.99%, comprising PbO, In_2O_3, TiO_2, and Nb_2O_5 were used as the starting materials. To prevent the sublime of In_2O_3 and the formation pyrochlore phase during crystal growth, Wolframite phase oxide $InNbO_4$ was formed by reacting In_2O_3 with Nb_2O_5 for 24 h at 1000 °C. Then PbO, $InNbO_4$, and TiO_2 were mixed and a total of 130 g were put into an 80 cm^3 platinum crucible, the Pt crucible was sealed to prevent the evaporation of lead. The temperature profile used for crystal preparation was rapid heating to 1380 °C, soaking at that temperature for 5 h, the crucible was dropped at a rate of 0.1–1.0 mm/h. At the end of growth process, the furnace temperature was cooled at rate of 25 °C/h to room temperature.

Fig. 2. As grown PMINT single crystal boule by the modified Bridgman technique.

In order to get the melting behavior and the thermal stability of the grown crystals, a differential thermal analysis (DTA) and thermal gravity analysis (TG) were performed on a simultaneous micro-DTA/TGA apparatus (NETZSCH-STA429). The compositions of the crystals were determined using an X-ray fluorescence analyzer (XRFA). The crystal structure was studied by X-ray diffraction (XRD) after pulverizing the single crystals. Single crystals were orientated along [001] crystallographic axis using the X-ray diffractometer.

For electric characterization, the crystals (001) plane with thickness 0.6 mm were polished with Al_2O_3 powders, and silver paste was painted on the crystal surfaces and fired at 550 °C for 30 min. The specimens were immersed in silicon oil and poled in a 10 kV/cm field. The electric field was applied at a temperature of 150 °C for 15 min, and the specimens were cooled to room temperature in the field. Dielectric properties were measured as a function of temperature by using a computer controlled HP4192A impedance analyzer at frequencies 100 Hz, 1 kHz and 10 kHz, and piezoelectric constant d_{33} was measured by a quasi-static meter of Berlincourt type at about 55 Hz. The electromechanical coupling factors of the thickness mode (k_t) and longitudinal bar mode (k_{33}) were calculated from resonance and anti-resonance frequencies.

3. Results and discussions

3.1. The feature of the PMINT system

Single crystals PINT 66/34 (the starting composition) were obtained with the size about 20 mm in diameter and 40 mm in length. They were light yellow in color (Fig. 2). Fig. 3 shows the XRD patterns of the crystal and indicates the formation of the complete solid solution in a single rhombohedral phase. There are no evidences of the existence of pyrochlore phase. Lattice constant $a_r = 4.055$ Å for the rhombohedral single crystals was calculated from the position of the perovskite (200) peak (Fig. 3).

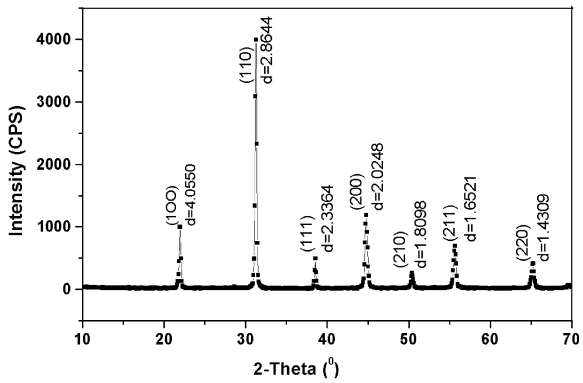


Fig. 3. X-ray diffraction (XRD) pattern of the PMINT single crystal.

To reveal the uniformity in composition of the single crystals, the X-ray fluorescence analysis was carried out. It shows that the $PbTiO_3$ content increases during the growth of solid solution PINT single crystals due to segregation, which is similar to the growth of PMNT single crystals [14]. In addition, it was observed that MgO was also present in the crystals. The Mg^{2+}, a B-site cation has a lower valency and a smaller radius than In^{3+} ($r^{2+}_{Mg} = 0.072$ nm, $r^{3+}_{In} = 0.080$ nm), so it should attribute to the diffuseness of magnesium ion into the PINT single crystal during crystal growth. The results of XRFA show that the composition of the crystals cutting from the seed end and the boule end of a boule are PMINT 23/46/31 (mol%) and PMINT 19/46/35, respectively.

Fig. 4 shows the thermal properties of one of the PMINT single crystals investigated by TG and DTA. Upon heating, a sharper endothermic DTA peak appears at 1290 °C, which corresponds to the melting of the PMINT crystal. The TG curve shows that the PMINT crystal decomposes gradually about 1000 °C, but it hardly changes below this temperature. It indicates that PMINT crystal has a good thermal stability. Perovskite compounds with both low electronegativity difference and tolerance factor tend to form pyrochlore phase and the perovskite phase can be stabilized by solid solutions in which electronegativity difference or tolerance factor is increased. The electronegativity difference and tolerance factor of PIN are much smaller than those of PMN. Thus it was evident that the diffuseness of magnesium ion into PINT promoted the formation of perovskite phase by increasing both electronegativity difference and tolerance factor as the addition of the simple perovskite PT (or $BaTiO_3$) suppresses the generation of pyrochlore phase and increases the phase stability in other complex perovskite systems. It should be the reason for PZNT, which can also been grown directly from the melt by the modified Bridgman technique with the allomeric PMNT seed crystals [14].

3.2. Electric properties

For the poled (001) plates, the temperature dependence of the relative permittivity ($\varepsilon_{33}/\varepsilon_0$), and the dielectric loss tangent (tan δ), for different samples are shown in Fig. 5. It is seen that the curves have peaks at the Curie point T_C (= 200 °C for sample No. 1 and 218 °C for sample No. 2) and then a shoulder at the phase transition temperature $T_{R\text{-}T}$ (= 113 °C for sample No. 1 and 82 °C for sample No. 2). Such temperature dependence of the permittivity indicates the sequence of transition of cubic–tetragonal–rhombohedral phases in the system. On the other hand, it exhibited an abnormal high permittivity ($\varepsilon_{33}/\varepsilon_0$) of more than 4000 at room temperature; while the permittivity is lower than 2000 for the binary PINT system after poling [8,9,11]. Piezoelectric performances were also measured, the results show that the piezoelectric coefficient d_{33} is higher than 2000 pC/N, and electromechanical coupling factor $k_{33} \approx 92\%$ for the longitudinal bar mode, $k_t \approx 59.2\%$ for the thickness mode which are comparable to that of PMNT 67/33 and PZNT 91/9 single crystals. It shows that the diffuseness of magnesium ion into the PINT single crystal is favorable for dielectric and piezoelectric properties.

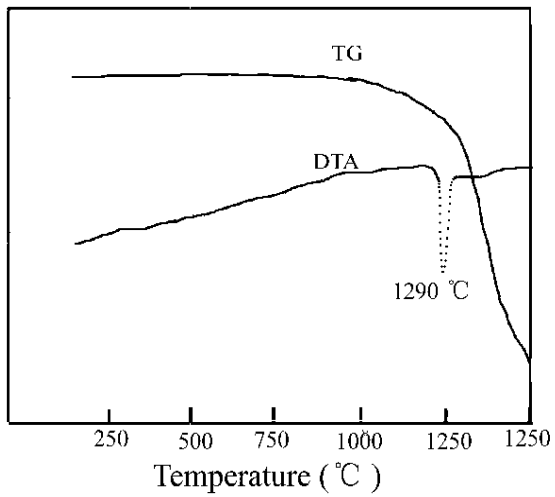
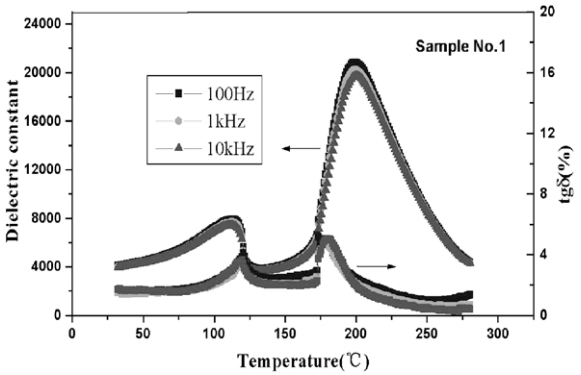


Fig. 4. A simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves for one of the PMINT single crystals.

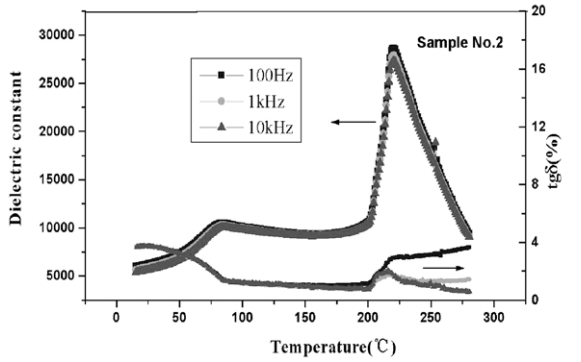
So we can conclude that the ternary system of $x\,Pb(Mg_{1/3}Nb_{2/3})O_3 - y\,Pb(In_{1/2}Nb_{1/2})O_3 - (1 - x - y)PbTiO_3$ should have good perovskite phase thermal stability, larger dielectric constant at room temperature and ultrahigh piezoelectric properties which are promising for a wide range of electromechanical transducer applications. Further studies are in progress with a view to determining the MPB line and to characterizing the performances of the ternary PMINT system.

4. Conclusions

Single crystals PINT 66/34 (the starting composition) with perovskite phase were grown by the modified



(a)



(b)

Fig. 5. Temperature frequency dependence of the dielectric constant and dielectric loss of poled plates cut from the seed end and boule end of a boule along [100] direction, (a) seed end (b) boule end.

Bridgman technique with the allomeric PMNT 69/31 seed crystals without any flux. But it shows some peculiar properties, e.g. a relative higher perovskite phase stability and lower T_C ($= 200-218\,^{\circ}C$) than that of PINT 66/34; abnormal high dielectric constant (>4000) at room temperature, ultrahigh piezoelectric constant (d_{33}) $>$ 2000 pC/N and electromechanical coupling factor $k_{33} \approx 92\%$, $k_t = 59.2\%$ along [001] direction in the rhombohedral phase. XRFA results reveal that it should attribute to the diffuseness of magnesium ion into the PINT single crystal during crystal growth. The composition of the crystals was in the range of PMINT 23/46/31 to PMINT 19/46/35. It portends that the ternary system of $x\,Pb(Mg_{1/3}Nb_{2/3})O_3-y\,Pb(In_{1/2}Nb_{1/2})O_3-(1-x-y)PbTiO_3$ should have good perovskite phase thermal stability, larger dielectric constant at room temperature and ultrahigh piezoelectric properties for a wide range of electromechanical transducer application.

Acknowledgments

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