Transactions of the Materials Research Society of Japan 29[4] 1359-1364 (2004)

Crystal Growth of Relaxor Ferroelectric Solid Solution Single Crystals near a Morphotropic Phase Boundary with High Curie Temperature and Some Properties.

* N.Yasuda, Y.Itoh, H.Ohwa, Y.Yamashita[1], M.Iwata[2], Y.Ishibashi[3]
Electrical & Electronic Engineering Department, Gifu University, Gifu 501-1193 Japan,
[1]R&G Center, Toshiba Corporation, Kawasaki 212-8582, Japan,
[2]Electrical& Computer Engineering Department, Nagoya Institute of Technology,Nagoya 466-8555, Japan,
[3]Communications Department, Aichi Shukutoku University, Nagakute-cho, Aichi 480-1197, Japan

The $Pb(In_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ [PIN-PT] and $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ [PYN-PT] binary system single crystals near the morphotropic phase boundary [MPB] composition with pseudo-cubic (100) planes were grown by the conventional flux method using PbO-PbF_2-B_2O_3 flux. The PIN-PT single crystal near the MPB grown along <110> direction was obtained by the solution Bridgman method using PbO-B_2O_3 flux. The PIN single crystals undergo successively a decomposition at 1254℃, and a peritectic melting at 1399℃ upon heating. The PIN-PT(72/28) and PYN-PT(47/53) single crystals show a peritectic melting point at 1283 and 1205℃, respectively with a partial decomposition of the perovskite crystal into pyrochlore one, followed by a liquidus point at 1294 and 1253℃, respectively. The stability of the perovskite phase in PIN and PYN-PT crystals is enhanced with solid solution with PT. The Curie temperature of PIN-PT(72/28) and PYN-PT(47/53) single crystals are 276 and 404℃, respectively. The electromechanical coupling coefficient in rectangular bar mode, k_{33}'=78%, of PIN-PT(72/28) single crystal for phased array ultrasonic transducers was obtained along <001> axis in the rhombohedral phase, which is independent of temperature, and at 200℃ decreases by 5%.

Key words: PIN-PT, PYN-PT, single crystal growth, morphotropic phase boundary, high Curie temperature

1. INTRODUCTION

Recently, much attention has been given to lead-based complex perovskite relaxor ferroelectrics -normal ferroelectric $PbTiO_3$ [PT] solid solution single crystals near a morphotropic phase boundary [MPB] because of excellent electrical properties [1,2]. These materials exhibit high piezoelectric properties by utilizing engineered domain configuration for applications in ultrasonic imaging, and actuators [3,4]. $Pb(Zn_{1/3}Nb_{2/3})O_3$-PT [PZN-PT] and $Pb(Mg_{1/3}Nb_{2/3})O_3$-PT [PMN-PT] single crystals show large piezoelectric constant and electromechanical coupling constant for engineered domain[5]. One of the disadvantage of these single crystals near the MPB is a low Curie temperature Tc. The low Tc restricts the operating temperature range less than 85℃[4]. New single crystals with both a large electromechanical coupling factor and a high Tc larger than 250℃are anticipated. The $Pb(In_{1/2}Nb_{1/2})O_3$-PT[PIN-PT] and $Pb(Yb_{1/2}Nb_{1/2})O_3$-PT [PYN-PT] binary systems near the MPB belong to one of the relaxor-PT systems with higher Tc>250 ℃ . In this work, single crystal preparations of the PIN-PT and PYN-PT binary systems near the MPB have been investigated by both the conventional flux method and the solution Bridgman method. The thermodynamic data on the melting behavior and the phase stability of the PIN-PT and PYN-PT crystals are required to get large and high quality crystals. In this paper, the crystal growth, the melting behavior, the stability of phases, domain structures and electrical properties of the PIN-PT and PYN-PT single crystals are presented.

2. EXPERIMENTAL

2.1 Crystal preparation

2.1.1 Conventional flux method

Single crystals of the (1-x)PIN-xPT system and (1-x)PYN-xPT system near the MPB were grown by a conventional flux method using PbO-PbF_2-B_2O_3 flux[6-8]. High-purity chemicals purer than 99.9% comprising PbO, In_2O_3, Yb_2O_3, Nb_2O_3, PbF_2, B_2O_3 (Furuuchi Chemical Co.) and TiO_2 (Koujundo Chemical lab.) were used as starting materials. The charged compositions were PIN/PT (63/37 mol%) (x=0.37), PYN/PT (50/50 mol%) (x=0.5) and (40/60 mole%)(x=0.6). The by-weight ratios of PIN-PT: PbO: PbF_2 : B_2O_3 and PYN-PT : PbO : PbF_2 : B_2O_3 were 53:22:24:1 and 83:97:19:1, respectively. A total of 20g was placed into a 20 cm^3 Pt crucible with a lid. The Pt crucible was placed into a 100 cm^3 Al_2O_3 crucible to prevent lead evaporation. The temperature profile used for crystal preparation of PIN-PT system was rapid heating to 1200℃ at a rate of 300K/h, soaking at that temperature for 5 hours, cooling at a rate of 2 K/h to 850℃ and then back to room temperature. That of PYN-PT system was rapid heating 1200℃, soaking at that temperature for 5 hours, and cooling at a rate of 4K/h to 850℃, and then back to room temperature.

2.1.2 Solution Bridgman method

A single crystal of the solid solution (1-x)PIN-xPT near the MPB was obtained by a solution Bridgman method using PbO-B_2O_3 flux[4,9]. The charged composition was PIN/PT (63/37 mole%)(x=0.37) near the MPB composition. The by-weigh ratio of PIN-PT :

PbO : B_2O_3 was 53:53:1. A total charge of 50g was put into a 15mm diameter x 100mm length Pt crucible. The Pt crucible was sealed with a Pt lid to prevent lead evaporation loss during crystal growth. The crucible design a cooling rod 3.5mm in diameter was used with the aim of inducing single nucleation at the bottom of the crucible and crystal enlargement by providing a large temperature gradient. The cooling rod was cooled by air gas circularly through an alumina pipe. An electrical furnace with two heating zones, the upper one controlled at 1370℃ and the lower one at 350℃ was used to grow the single crystal. The Pt crucible was suspended and driven down through the zones at a rate of 0.4mm/h after soaking for 10 hours. Such values for setting of temperatures of heating zones and driven rate of Pt crucible were determined according to the thermodynamic data for the melting behavior in Sec.3.2. No seed materials was used to nucleate the crystal. Both heating zones were maintained for 297 hours, and then cooled to room temperature at 100K/h. The crystals were extracted from the matrix by dissolution in hot dilute nitric acid.

2.2 Experimental measurements

The Ti concentration x of the solid solution (1-x) PIN- x PT and (1-x)PYN-xPT obtained were determined using a fluorescent X-ray technique and inductive charge plasma [ICP] analysis. Thermogravimetric analysis [TG] and differential thermal analysis [DTA] were performed on a simultaneous micro-TG/DTA apparatus (RIGAKU Thermo Plus 2). Specimens of about 30mg each were put in open Pt pans heated and cooled in the temperature range of 800-1420℃ at a rate of 10K/min in a N_2 gas atmosphere. X-ray diffraction study was done at high temperatures relative to the melting and liquidus points using a RIGAKU RINT-ULTIMA powder diffractometer. The electrical capacitance was measured using an LCR meter (HP-4275A). For measurement of piezoelectric properties, bars 0.2mm x 0.5mm x 9mm were formed from the (100) crystal. Silver electrodes were formed at 650℃ for 10min on both surfaces (0.2mm x 9mm) of the specimens. A specimen was poled in a 10kV/cm electric field at 120℃ for 15min and then cooled to 25℃ in the same field in an insulating liquid. The e/m coupling factor k_{33}' was measured by the resonance and antiresonance frequency method using an impedance gain phase analyzer (HP-4194A; network mode)[4,7].

3. RESULTS AND DISCUSSIONS

3.1 Single-crystal preparation

For PIN-PT crystals obtained using a conventional flux method, crystals shaped irregularly and rectangularly in Fig.1(a) were clustered near the top surface around the edge of the crucible and found at the bottom and in the center of the crucible, respectively. The rectangular-shaped crystal with a pseudocubic (001) plane in a habit was colored light yellow. Some wafers with (001) plane were shown in Fig.1(b). For PYN-PT crystals as shown in Fig.2,

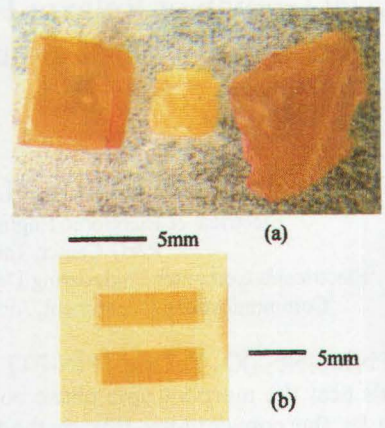

Fig.1 (a) As-grown crystals and (b) wafers with (001) plane for the PIN-PT(72/28).

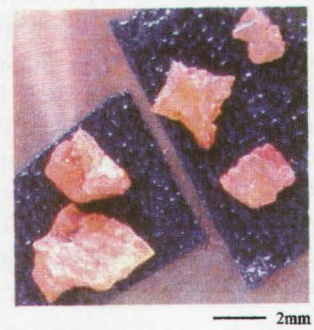

Fig.2 As-grown crystals of the PYN-PT near the MPB.

crystals shaped rectangular with a pseudocubic (100) plane in habit were yellowish in color, and some of the crystals were agglomerated. The others were irregularly shaped. Some inclusions such as PbO flux and pyrochlore regions were observed in the crystals. The coagulated solid solution resulting from the growth, using the solution Bridgman method, from the PIN-PT-PbO-B_2O_3 system is shown in Fig.3(a). A yellowish wafer cut at 2mm from the bottom of the as-grown PIN-PT single crystal is shown in Fig.3 (b). Unfortunately, some of the crystal wafers were cracked by the slicing saw. There are

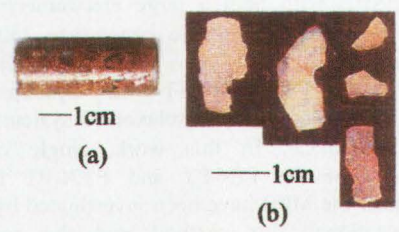

Fig.3 (a) Coagulated solid solution of the PIN-PT(63/37)-PbO-B_2O_3 system and (b) wafers cut at 2mm from the bottom of as-grown PIN-PT(63/37) single crystal.

some inclusions such as PbO flux and pyrochlore regions in the wafer. Transparency of the wafer

was not very good and opaque areas were seen in the wafer.

3.2 Melting behavior

The high-temperature thermodynamic properties of PIN-PT and PYN-PT system were investigated by means of micro-TG/DTA analysis combined with an X-ray diffraction study.

3.2.1 PIN-PT solid solution system

Figure 4 shows the TG/DTA results for the PMN, PIN,and PIN-PT(72/28) crystals. PMN crystals is known to have the pseudo congruent melting point[6]. For the TG/DTA result of PMN crystals, a first sharp endothermic DTA peak of the λ -shape indicating the melting point was detected at 1317℃, followed a braod peak detected at 1330℃ indicating the liquidus point.

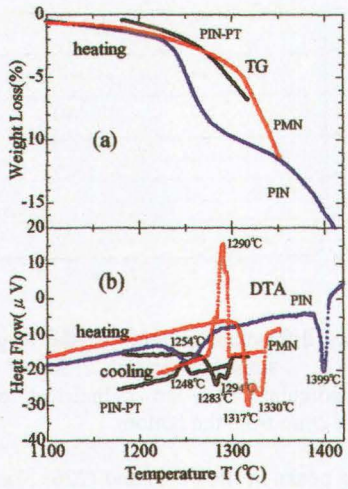

Fig.4 (a) TG and (b) DTA curves for PMN, PIN, and PIN-PT(72/28) single crystals.

The TG/DTA results of PIN crystals are characterized with the thermal event of a partial decomposition detected at 1254℃ before the melting point detected at 1399℃in Fig.4. For the PIN-PT(72/28) crystals, a λ -shape endothermic DTA peak detected at 1283℃ indicates the melting point, followed a broad peak at 1294℃. The broad peak at 1294℃ indicates the liquidus point. Such phenomena on the melting behavior with heating are similar to those for PMN. A DTA exothermic peak with cooling for the PMN crystal is sharper rather than for the PIN-PT crystal. The weight loss in the PIN-PT crystal increases rapidly, reaching about 4% at 1283℃ with heating. With cooling, a strong exothermic DTA peak was detected at 1248℃. The thermal hysteresis in the thermal events is about 40℃. Thus, the remarkable effect on the melting behavior in PIN crystals of the solid solution with PT is seen in Fig.4. On the other hand, the perovskite phase for the PIN-PT(72/28) single crystal is known from the high temperature X-ray diffraction (XRD) pattern of the ground crystal in Fig.5 to persist even at 1320℃. The pyrochlore phase developed at higher temperatures with enhanced intensity. Therefore, the PIN-PT(72/28) crystal melted incongruently at 1283℃ with peritectic character, leading to the decomposition of the perovskite phase into the pyrochlore phase, followed by a liquidus point of 1294℃.

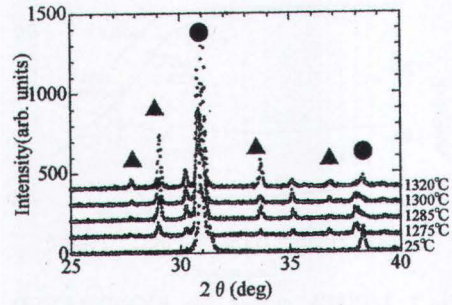

Fig.5 X-ray powder diffraction patterns of the PIN-PT(72/28) single crystal at 25, 1275, 1285, 1300 and 1320℃, respectively: Perovskite phase (●), Pyrochlore phase (▲).

Such a melting behavior is similar to that for the PMN-PT(68/32) crystal with the pseudo congruent melting point rather than for the PZN-PT(91/9) crystal with the thermal event of a partial decomposition before the melting point[10]. The liquidus point 1294℃ is lower than both the melting point, 1399℃, of PIN crystals and that, 1295℃, of PT[11]. This suggests a possible eutectic behavior in the pseudo-binary PIN and PT system[10,12]. The PIN-PT system shows a stable perovskite structure. The close-tube TG/DTA result for the composition 53wt% PIN-PT(72/28) -53wt%PbO -1wt%B_2O_3 in Fig.6 shows the two endothermic peaks at 835 and 1175℃ corresponding to eutectic melting point and liquidus point of the PIN-PT(72/28) -PbO -B_2O_3 system, respectively with heating. Two exothermic

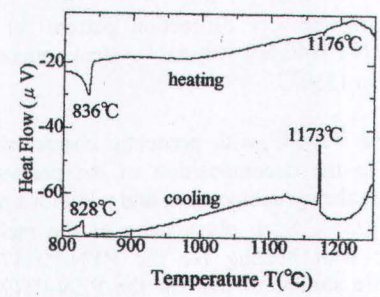

Fig.6 DTA curves of 53wt% PIN-PT(72/28) – 53wt% PbO – 1wt% B_2O_3 system in closed tube analysis.

peaks at 1172 and 828℃ with cooling indicate the solidus and the eutectic solidification, respectively, confirming the reversible solid-liquid phase transitions with a thermal hysteresis at heating/cooling rate of 10℃/min. The PIN-PT(72/28) -PbO -B_2O_3 system exhibits a typical eutectic behavior.[6,10]

3.2.2 PYN-PT system

From the TG/DTA results for the PYN-PT(47/53) single crystal in Fig.7, a strong endothermic DTA peak detected at 1205 ℃ indicates the melting point. A minor heat flow at

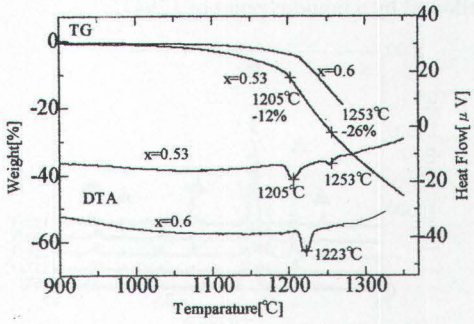

Fig.7 TG/DTA curves for PYN-PT(47/53) and (40/60) single crystals.

1253℃ characterized with a broad peak indicates the liquidus point. The weight loss in the PYN-PT(47/53) crystal was about 12% at 1205℃, increased steadily on further heating, and reached about 26% at 1253℃. Some amount of perovskite phase was left after melting and decomposition at 1350 ℃, since the quenched molten sample indicated some pyrochlore phase as shown in Fig.8. The PYN-PT(47/53) crystal shows an incongruent

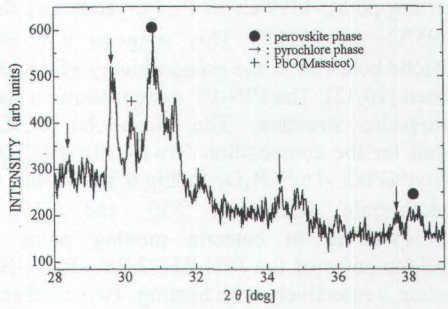

Fig.8 X-ray powder diffraction pattern for the PYN-PT(40/60) crystal system quenched from 1350℃.

melting at 1205℃ with peritectic characteristic, leading to the decomposition of the perovskite phase into the pyrochlore one, and a liquidus point around 1253℃.Such phenomena of the melting behavior with heating for the PYN-PT(47/53) crystal are similar to that for the PZN-PT(91/9) crystals with the thermal event of a partial decomposition before the melting point rather than for the PMN-PT(68/32) crystal with the pseudo congruent melting point[10]. On the other hand, it is noted from the change in the melting behavior with PT contents in Fig.7 that the TG/DTA curves for the PYN-PT(40/60) crystal are similar to that for the PMN-PT system rather than the PZN-PT one in contrast to the PYN-PT(47/53) crystal[10]. The weight loss corresponding to the thermal events for PYN-PT(40/60) crystal was reduced in comparison with the PYN-PT(47/53) crystal. The stability of perovskite phase was enhanced with the solid solution with increasing PT contents in the tetragonal region.

3.3 Crystallographic properties

The crystal structure of PIN-PT(72/28) single crystal at room temperature was confirmed by an X-ray diffraction study[13] to be a single perovskite phase. The structure of the PIN-PT(72/28) single crystal was identified to the rhombohedral one with $a=4.064\pm0.001$ Å and $\alpha=89°\ 55'\pm1'$ at room temperature. Figure 9 shows the typical X-ray single crystal diffraction pattern at room temperature for the as-grown PIN-PT single crystal ingot cut perpendicularly to the cylindrical single crystal length (see Fig.3).

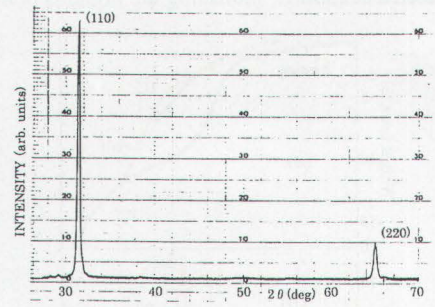

Fig.9 X-ray diffraction pattern for the as-grown PIN-PT single crystal ingot cut perpendicularly to the cylindrical crystal length 2mm from the bottom.

The strong peaks of the (110) and (220) planes of the perovskite phase in Fig.9 was found to have grown along the direction normal to the bottom surface of the crucible and near the [110] direction. Figure 10 shows the X-ray powder diffraction patterns on the ground samples of the wafer cut 2mm, 4mm and 20 mm from the bottom of the PIN-PT single crystal at room temperature, respectively. The crystal structure was confirmed from Fig.10 to be perovskite phase in the change from rhombohedral to tetragonal phase with growth away from the bottom surface of the

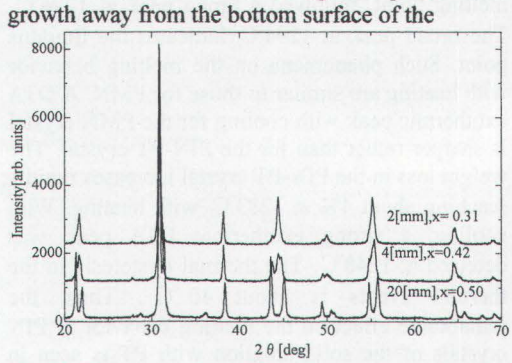

Fig.10 X-ray powder diffraction patterns for the as-grown PIN-PT single crystals cut perpendicularly to the cylindrical crystal length 2, 4 and 20 mm from the bottom, respectively.

crucible. The Ti contents of these wafers cut at 2mm, 4mm, and 20mm were determined from the ICP chemical analysis to be 0.31,0.42 and 0.50, respectively. The Ti content of as-grown PIN-PT (63/37: charged composition) single crystal increases with growth away from the nucleation point. Such a distribution of Ti content with distance from the nucleation point was in contrast to the distribution of Ti to decrease with growth away from the nucleation point reported previously for PZN-PT(91/9) single crystal produced by the Bridgman method[3,4]. The lattice parameters of PIN-PT single crystals calculated from XRD patterns are shown with PT contents x in Fig.11. X-ray powder diffraction patterns of the PYN-PT (47/53) and (40/60) single crystals at room temperature are shown in Fig.12.

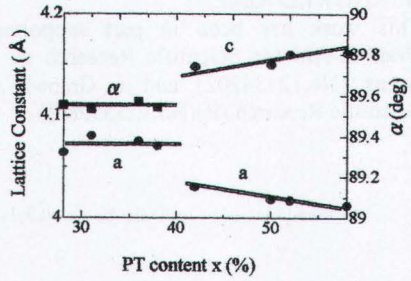

Fig.11 Composition dependence of the lattice parameters calculated from XRD patterns of PIN-PT single crystals.

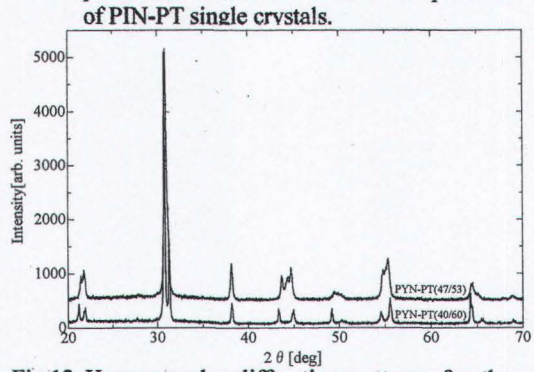

Fig.12 X-ray powder diffraction patterns for the PYN-PT(47/53) and (40/60) single crystals at room temperature.

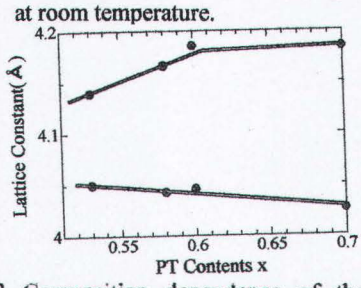

Fig.13 Composition dependence of the lattice parameters calculated from XRD patterns of PYN-PT single crystals.

The structure of the PYN-PT(47/53) (x=0.53) single crystal was identified to be tetragonal with a=4.05 ± 0.01 Å and c=4.14 ± 0.01 Å at room temperature. The lattice parameters calculated from XRD patterns are shown with PT contents x in Fig.13.

When the PIN-PT(72/28) and PYN-PT(47/53) crystal (001) plates were placed between crossed polarizers, the domain patterns were observed in Fig.14 (a) and (b), respectively.

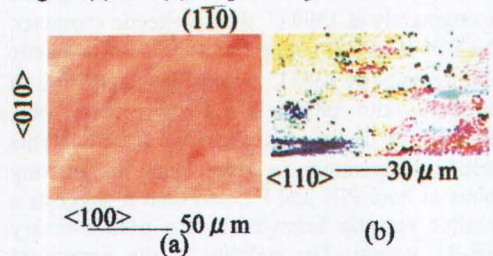

Fig.14 Domain patterns observed on (a) PIN-PT(72/28) and (b) PYN-PT(47/53) (001) crystal plate.

3.4 Electrical properties.

From the measurement of the temperature dependence of the relative permittivity ε of the PIN-PT and PYN-PT single crystals with various PT contents[7,15], the values of ε were confirmed to have a peak at the Curie temperature Tc; peak value of 35000 at 1kHz at 260℃ for PIN-PT(72/28) single crystal and that of 15000 at 1kHz at 404℃ for PYN-PT(47/53) one. The phase diagram of the PIN-PT single crystal with PT contents determined dielectrically[7,10] is shown in Fig.15. The electromechanical coupling coefficient in the rectangular bar mode, k_{33}'=78%, was determined from the resonance and antiresonance frequency characteristics of impedance and phase for the PIN-PT(72/28) single crystal oriented along the <001> axis in the

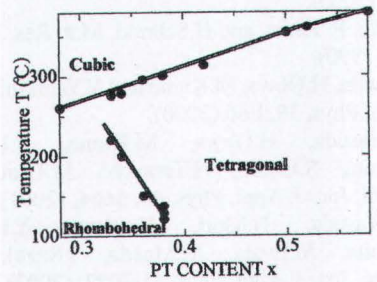

Fig.15 Phase diagram of the PIN-PT single crystal with PT contents.

rhombohedral phase at 25℃[7]. The temperature dependence of k_{33}' was determined from the change in the resonance and antiresonance frequency characteristics of impedance and phase for the PIN-PT(72/28) single crystal oriented along the <001> axis with temperature[14]. The value of k_{33}' is almost independent of temperature, and even at 200℃ decreases by only 5%.

4.CONCLUSION

The PIN-PT and the PYN-PT solid solution single crystals near the MPB with pseudo-cubic (001) planes were grown by the conventional flux method using PbO-PbF_2-B_2O_3 flux. The single

crystal of about 15 mm diameter of the PIN-PT solid solution system near the MPB was obtained by the solution Bridgman method using PbO-B_2O_3 flux. The PIN single crystal underwent a partial decomposition at 1254 ℃, and then melted incongruently at 1399℃ with peritectic character. The PIN-PT(72/28) single crystal has a peritectic melting point of 1283℃ with a decomposition of the perovskite phase into a pyrochlore one, followed by a liquidus point of 1294℃. This melting temperature is lower than the melting points of both PIN and PT, and then it suggests a possible eutectic behavior in the pseudo-binary PIN-PT system. The stability of the perovskite phase in PIN crystals was enhanced with solid solution with PT. The PYN-PT(47/53) single crystal has incongruent melting point at 1205℃ with peritectic character, leading to the decomposition of the perovskite phase into pyrochlore one, followed by a liquidus point of 1253℃. The stability of the perovskite phase in the PYN-PT crystals was enhanced with solid solution with increasing PT contents in the tetragonal region. The crystal growth using the solution Bridgman method was almost along the [110] direction. The Curie temperature Tc increases gradually with growth away from the nucleation point, due to the gradual increase in the Ti content with the distance from the nucleation point. The PIN-PT(72/28) single crystal has the electromechanical coupling coefficient in rectangular bar mode, k_{33}'=78%, along the <001> direction which is almost independent of temperature and decreases only by 5% even at 200℃. Large PIN-PT single crystals near the MPB of good quality can be grown using the solution Bridgman method, and they may have potential as piezoelectric materials for application.

ACKNOWLEDGMENT

This work has been in part supported by a Grant-in-Aid for Scientific Research on Priority Areas (No.12134202) and a Grant-in-Aid for Scientific Research (B)(No.12555086).

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(Received October 13, 2003; Accepted July 1, 2004)