

Development of Large Diameter Piezo-Single Crystal PMN-PT with High Energy Conversion Efficiency[†]

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Abstract:

Large diameter (80 mm ϕ) piezoelectric single crystals of lead magnesium niobate/lead titanate (PMN-PT) grown by the one-batch melt Bridgman method display an inhomogeneous distribution of the titanium (Ti) concentration in the growth direction. This is an inevitable result of Ti segregation. Making positive use of this phenomenon, the distribution of the Ti concentration in single crystals and the dependence of dielectric/piezoelectric properties on Ti concentration were investigated. As properties of PMN-PT, it is possible to obtain a piezoelectric constant and electromechanical coupling coefficient with far higher conversion efficiency than with the conventional lead zirconium titanate (PZT: Pb(Zr,Ti)O₃) ceramics. However, strong dependence of these properties on the Ti concentration is also recognized. Moreover, even with the same Ti concentration, significant variations exist in dielectric/piezoelectric properties. It is pointed out that the establishment of a continuous feeding growth of crystal method is needed in order to achieve a homogeneous Ti composition, and optimization of poling conditions and the development of a domain control technique are needed to control dielectric/piezoelectric properties within the desirable range.

1. Introduction

Lead zirconium titanate (PZT: Pb(Zr_xTi_{1-x})O₃, x: 0.45–0.48) is now the mainstream piezoelectric material.

However, the development of a PZT-substitute material with higher electromechanical conversion efficiency was an important challenge from the viewpoints of realizing more compact piezoelectric devices, reducing drive voltage, enhancing sensitivity, and in turn, developing energy saving materials.

On the other hand, from the viewpoint of pollution prevention, a switchover from lead-based materials such as PZT to non-lead materials using bismuth and similar components is also emerging as a future social issue. Although progress has been achieved with these non-lead materials in thin film products, unfortunately, it appears that stable practical processes for bulk materials and single crystals have not yet been realized^{1,2)}.

Among PZT-substitute materials, solid solution single crystals of lead titanate (PbTiO₃) and lead compounds, which are called relaxors, have drawn attention as single crystals which possess high conversion efficiency with respect to electrical energy (voltage, charge) and mechanical energy (vibration, displacement), and thus may be considered high conversion efficiency piezo-single crystals^{3,4)}. Relaxors are a type of dielectric substance in which the frequency where the dielectric constant displays its peak value and the peak value itself depend on the specimen temperature. And, the peak is broad in comparison with that of barium titanate (BaTiO₃), etc⁵⁾.

Figure 1 shows a ternary phase diagram of a relaxer, lead zirconate (PZ), and lead titanate (PT)⁶⁾. Regions called a morphotropic phase boundaries (MPB) exist

[†] Originally published in *JFE GIHO* No. 8 (June 2005), p. 43–48



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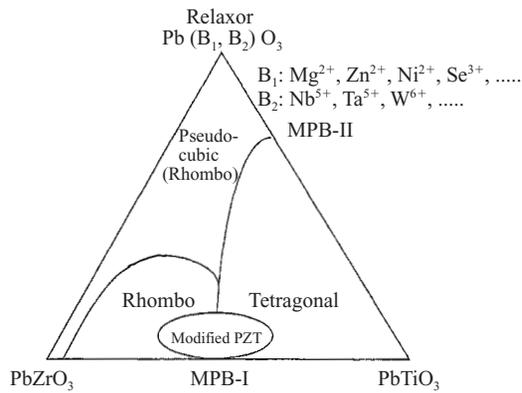


Fig.1 Ternary phase diagram of relaxor, lead zirconate (PZ), and lead titanate (PT) showing MPBs and the region of modified PZT in the diagram

in the intermediate composition between the solid solution of lead titanate (PbTiO₃) and lead zirconate (PbZrO₃) and the intermediate composition between the solid solution of lead titanate (PbTiO₃) and the relaxor (Pb(B₁,B₂)O₃), respectively, and it is known that dielectric/piezoelectric properties show large values in the vicinity of these compositions. These MPB are termed MPB I in the case of lead titanate and lead zirconate and MPB II in the case of lead titanate and the relaxor. **Figure 2** shows the arrangement of the various ions in the perovskite lattice, which is the fundamental lattice of these solid solutions. The perovskite lattice has a structure in which Pb²⁺ occupies the corners of the lattice, O²⁻ is found at the center of the faces, and the ion species referred to as B₁ and B₂ in Fig. 2 occupy the body-center of the cell. Because the average charge of the ion in the body-center position is +4, electrical neutrality is maintained.

Among these relaxor + PT solid solutions, at present, single crystals with diameters of at least 50 mm ϕ , which is the size required in practical-scale materials, can be obtained with two types. These are the lead zinc niobate/lead titanate solid solution (PZN-PT), in which Zn and Nb are used as B₁ and B₂, respectively, and the lead magnesium niobate/lead titanate solid solution

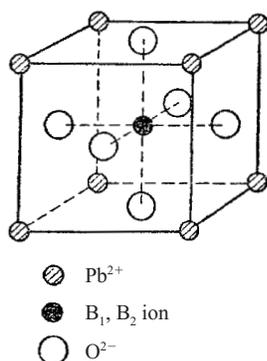


Fig.2 Unit cell of perovskite lattice structure

(PMN-PT), in which Mg is used as B₁. JFE Mineral (a subsidiary of JFE Steel) has been trying to grow large single crystals of PZN-PT and to develop a piezoelectric device substrate, and has succeeded in growing 80 mm ϕ single crystals, which is the world's largest single crystal of this material, and developing a piezoelectric device substrate using this material^{7,8}.

Growth of PMN-PT single crystals and the development of piezoelectric device substrates were also carried out in parallel with work on PZN-PT. PMN-PT has substantially the same piezoelectric properties as PZN-PT. As the single crystal growth method, growth by Bridgman method from a melt and control of the crystal orientation by the seed crystal are possible, in the same manner as with MnZn ferrite single crystals⁹.

PZN-PT is grown by the solution Bridgman method by unidirectional solidification from a melt using a flux. In contrast, PMN-PT, like MnZn ferrite, can be grown by the melt Bridgman method because dissolution of the raw materials itself is possible. One-batch growth of large diameter (80 mm ϕ) PMN-PT single crystals has been successfully achieved, and this technology has now reached a level where stable supply of single crystals weighing approximately 3.5 kg is possible, as shown in **Photo 1**. For the status of development of these piezo-single crystals at JFE Mineral, readers are invited to visit the company's homepage¹⁰.

In this paper, we will refer to other reports⁹) on PMN-PT single crystal growth. Firstly, by the distribution of the Ti concentration in the direction of single crystal growth, which is caused by segregation of Ti at the solid-liquid interface is described. The Ti concentration is obtained by measuring the Curie temperatures of wafers cut from various positions in single crystal ingots and then applying a conversion equation to the results, giving a linear approximation of the Curie temperature-Ti concentration curve in a pseudo binary diagram for PMN and PT. Secondly, the results of measurements of the Ti concentration dependence of vari-

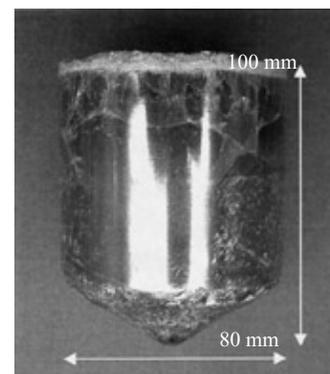


Photo 1 PMN-PT single crystal obtained by one batch Bridgman method (Diameter: 80 mm, Weight: 3 500 g)

ous dielectric/piezoelectric properties are shown. This systematic evaluation of the dielectric/piezoelectric properties of wafers with differing Ti concentrations cut from various positions in a single crystal is the first of its kind with a large diameter, 80 mm ϕ single crystal. In PMN-PT piezo-single crystals, the factors which determine dielectric/piezoelectric properties are not limited to the composition of component elements and compounds, which are represented by the Ti concentration discussed here; the domain structure also has an important effect¹¹⁾. However, in this paper, rather than making a detailed study of the domain structure and related factors, the crystal quality of the company's PMN-PT single crystals is evaluated using the reported values from systematic evaluations of dielectric/piezoelectric properties found in the literature.

2. Experimental Procedure

2.1 PMN-PT Single Crystal Growth and Preparation of Specimens for Measurement of Dielectric/ Piezoelectric Properties

First, the growth process of large diameter PMN-PT single crystals is described. To obtain seed crystals for single crystal growth, 50 mm ϕ single crystals were grown by the one-batch melt Bridgman method by spontaneous nucleation.

Growth of large-diameter 80 mm ϕ single crystals was performed by one-batch growth. However, rather than the conventional $\langle 111 \rangle$ orientation growth, $\langle 110 \rangle$ orientation growth was considered advantageous, as this makes it possible to use a smaller angle (45°) when cutting out (100) wafers (the angle is approximately 54° with the $\langle 111 \rangle$ growth), and thus can reduce the planar distribution of the Ti concentration. Therefore, seed crystals were obtained by cutting rod-shaped crystals with a $\langle 110 \rangle$ orientation from the 50 mm ϕ single crystal.

As a problem in the growth of 80 mm ϕ single crystals, cracks occur in the entire crystal. However, by analyzing and improving (1) the cooling process after growth and (2) the factors in end-portion cracks associated with composition changes in the end portion of the crystal, cracks in the straight body (cylindrical part) of the single crystal has been successfully reduced, and stable growth has now become possible.

The obtained 80 mm ϕ single crystals were sliced into two parts, following approximately the (100) direction, which is parallel to the growth direction. A rough determination of the section orientation was made by the back-reflection Laue method, and a precise determination was made using an X-ray orientation measuring

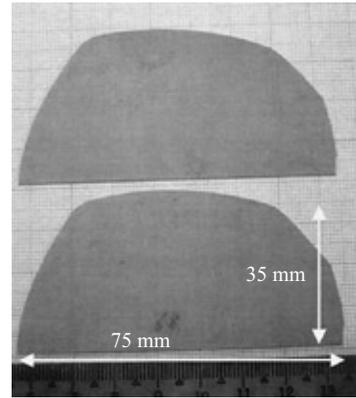
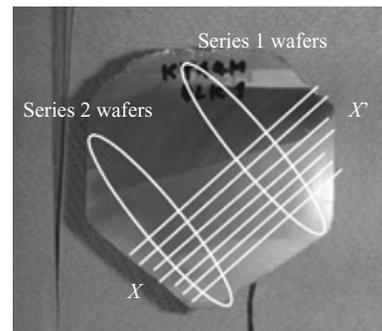


Photo 2 (100) wafers obtained from 80 mm in diameter PMN-PT single crystal ingot



Ti concentration is varying along with X - X' direction.

Photo 3 Series 1 and series 2 wafers

device. An ingot in which the orientation of the growth direction had been determined in the same manner was sliced into semicircular wafers, as shown in **Photo 2**, using an inner diamond (ID) saw or a wire saw. The semicircular wafers were cut at 45° to the crystal growth direction and have a (001) plane. As a result, the Ti concentration differs in the wafer lateral (X - X') direction. **Photo 3** shows the condition of slicing semicircular wafer from an ingot and the slicing positions of the series 1 and 2 wafers. The series 1 and 2 wafers were sliced from positions 10 mm–15 mm from the right and left edges, respectively. The size of these wafers was 13 mm \times 4 mm, which made it possible to evaluate piezoelectric properties in the lateral vibration mode (31 mode), and their thickness was approximately 0.35 mm. The wafer surface was as-sliced. The 6 surfaces of the series 1 and 2 wafers were all arranged as $\{100\}$ plane.

2.2 Measurement Method of Dielectric/Piezoelectric Property

A gold electrode approximately 100 nm in thickness was used. After forming the electrode, samples were heated from room temperature to 200°C or higher, and the dielectric constant was measured using an impedance analyzer, Yokogawa/Hewlett-Packard YHP4192A. The low temperature side of the peak position of the dielectric constant for the specimen temperature was considered to be the phase transition temperature (T_r)

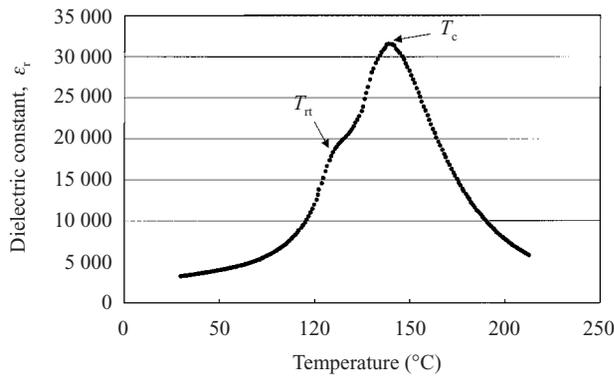


Fig.3 An example of the measurement of dielectric constant vs. sample temperature

from a pseudo cubic system to a tetragonal system, and the high temperature side was considered to be the phase transition temperature (Curie temperature: T_c) from the tetragonal system to a cubic system. The measurement frequency was 1 kHz, AC amplitude was 1 V, and no DC bias was used. An example of measurement is shown in Fig. 3. Here, the abscissa is the specimen temperature ($^{\circ}\text{C}$) and the ordinate is the dielectric constant (ϵ_r).

In measurements of the resonant frequency (f_r) and anti-resonant frequency (f_a) for calculation of the electromechanical coupling coefficient (k), which is equivalent to the square root of electrical and mechanical energy conversion efficiency, an impedance/gain-phase analyzer, Hewlett-Packard HP4194A was used. The values of f_r and f_a obtained with this device were used in calculating the electromechanical coupling coefficient (k_{31}) and piezoelectric constant (d_{31}) in the lateral vibration mode (31 mode). In order to measure the electromechanical coupling coefficient (k_{33}) in the longitudinal vibration mode (33 mode), it is necessary to use the longitudinal vibration of a rod-shaped specimen with an aspect ratio larger than 3. However, because the specimens in this work were plate-shaped (wafers), the electromechanical coupling coefficient obtained using f_r and f_a is k_t (that is, the electromechanical coupling coefficient of the longitudinal vibration mode of a plate-shaped vibrator). The piezoelectric constant (d_{33}) of the longitudinal vibration mode (33 mode) was measured directly using a d_{33} meter (Model ZJ-3D piezo d_{33} meter) manufactured by the Institute of Acoustics Academia Sinica.

3. Results and Discussion

3.1 Distribution of Ti Concentration in Growth Direction in One-Batch Single Crystals

Because it has now become possible to produce 80 mm ϕ single crystals with little cracking, as discussed

in the previous chapter, the dielectric/piezoelectric properties of the entire ingot could be evaluated. In one batch growth, distribution of the Ti concentration occurs in PMN-PT single crystals due to segregation of Ti. Because the Ti segregation coefficient in PMN-PT is smaller than 1, the Ti concentration increases toward the end portion of the crystal.

Furthermore, single crystal growth results in the deposition of a single crystal with a composition which is generally different from the composition predicted from the liquidus curve/solidus curve shown in the phase diagram. This is considered to show that solidification occurs in an unsteady condition during crystal growth. For composition-controlled growth, it is necessary to understand the relationship between the initial composition of the materials used and the composition range in the formed crystal.

The variation of the Ti concentration in the measured wafers is shown by wafer number in Fig. 4. The reason for expressing the Ti concentration in mol% is because this is equivalent to the composition of PT (lead titanate: PbTiO_3) in the solid solution, PT being a component compound in PMN-PT. The position in the ingot is shown by the wafer number. Wafers closer to the left side of the figure correspond to the part near the seed crystal (cone part). The measured values are the T_c of each wafer. These results were converted from T_c to Ti concentration using the T_c vs Ti concentration curve on the PMN-PT phase diagram shown in Fig. 5¹²⁾. The conversion equation is as follows:

$$Y = (X - 9.6267) / 4.8591 \dots \dots \dots (1)$$

where,

X : Curie temperature, T_c ($^{\circ}\text{C}$)

Y : Ti concentration (mol%)

The solid line in Fig. 4 is a polynomial fitting curve for the variation of Ti concentration. From this curve, it can be understood that the regions with large variations of Ti concentration are the cone and the end portion of the straight body. (Straight body means the part with a uniform diameter after the cone.) In particular, the variation of Ti concentration in the end portion is thought to induce large changes in the thermal expansion coefficient and other properties, and thus is a cause of cracks in the end portion of crystals. In comparison with the cone and end portion, the variation of Ti concentration in the straight body is slight. It is therefore considered possible to extend the part of the single crystal with a useful Ti concentration by extending the length of the straight body.

In one-batch growth, a concentration distribution

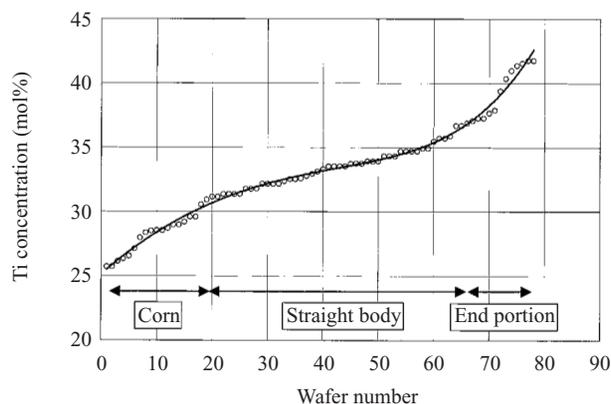


Fig. 4 Variation of Ti concentration along with the growth direction straight line is a polynomial fitting curve

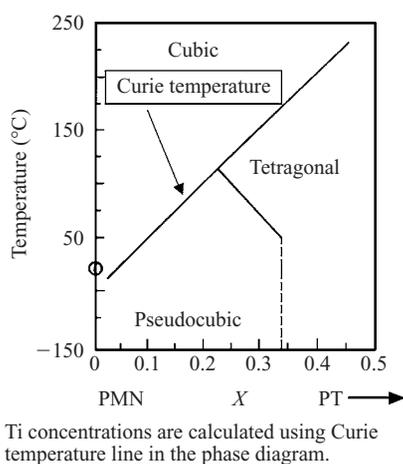


Fig. 5 Pseudo binary phase diagram of PMN-PT as a compound of PMN and PT

inevitably occurs due to segregation of Ti. Therefore, in order to control the entire single crystal ingot within a range of Ti concentrations which show excellent dielectric/piezoelectric properties, as discussed in the following sections, it is essential to develop a technology similar to the continuous feeding technology for MnZn ferrite single crystals, which has been commercialized at JFE Mineral. In this growth method, the compositions of Fe_2O_3 , MnO, and ZnO, which are the main components of MnZn ferrite, are controlled to within $\pm 0.5\text{mol}\%$ ¹³⁾. The company is currently developing a continuous feeding technology for PMN-PT.

3.2 Dependence of Curie Temperature (T_c) and Phase-Transition Temperature (T_{rt}) on Ti Concentration

Figure 6 shows the dependence of T_c and T_{rt} on Ti concentration in the series 1 and 2 wafers, respectively. The straight line (T_c line) in the highest temperature part of the figure corresponds to the results of the conversion equation, as discussed previously, and coincides with the T_c line in the phase diagram in Fig. 5. The values of

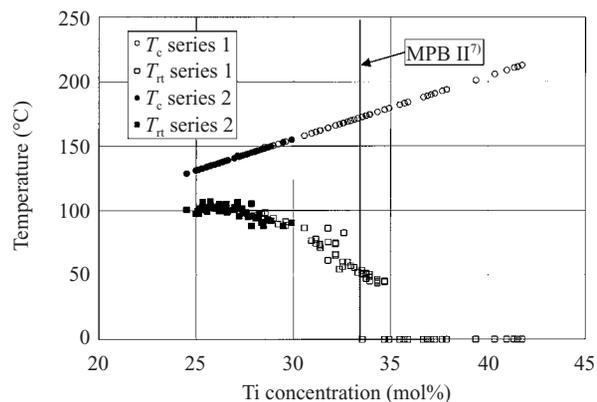


Fig. 6 Curie temperature (T_c)(circles), which are plotted according to the phase diagram of Fig. 5, and phase transition temperature (T_{rt}) from pseudocubic to tetragonal phase (T_{rt}) measured in this experiment vs. Ti concentrations

the series 1 and 2 wafers change continuously on the T_c and T_{rt} curves. These values also overlap in some parts, showing that the Ti concentration has become homogeneous in the plane perpendicular to the growth direction. The results of this experiment suggest that the existence of a phase transition from a pseudo cubic system to a tetragonal system, which is shown by T_{rt} , beyond the Ti composition of the morphotropic phase boundary (MPB II) given in the literature¹²⁾. Here, MPB II is indicated by the solid line at around Ti concentration $\approx 33\text{ mol}\%$. Although the present results differ from the past literature, a recent report¹⁴⁾ has discussed that a complex crystal phase exists in the vicinity of the phase boundary, and it is therefore necessary to examine the compatibility between these studies.

At Ti concentrations of 31 mol% and less, $T_{rt} > 90^\circ\text{C}$ is obtained. In applications which attach importance to the service temperature of PMN-PT. Although a composition with a Ti concentration of 31 mol% or less is considered suitable, it is necessary to consider the balance with other properties. Moreover, this work also revealed that a tetragonal system exists from room temperature when (Ti concentration) $> 35\text{ mol}\%$. This result is somewhat different from the literature¹²⁾.

3.3 Dependence of Dielectric/Piezoelectric Properties on Ti Concentration

3.3.1 Relative dielectric constant (ϵ_r)

Figure 7 shows the dependence of the dielectric constant, ϵ_r on Ti concentration. In the (001) wafers, the dielectric constant at $> 33\text{ mol}\%$, which is the composition for a tetragonal system structure, is < 2000 , and thus it is not suitable of practical application. On the other hand, at $< 33\text{ mol}\%$, which is a pseudo cubic system, $\epsilon_r > 3000$. Although this is a practical level, in the

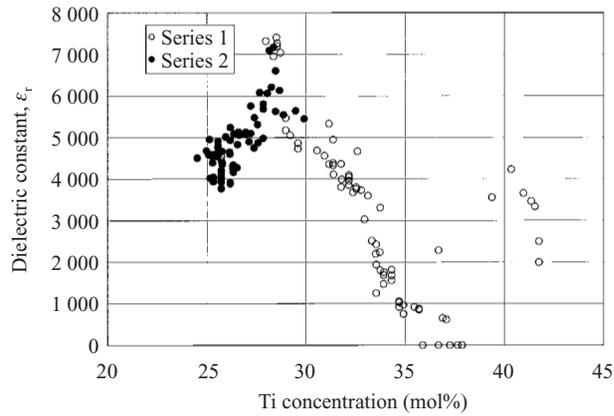


Fig.7 Dependence of dielectric constant (ϵ_r) on Ti concentration

individual measured wafers, there is significant variation in the values of the dielectric constant at maximum in the order of 2 000 irrespective of the fact that the wafers had identical Ti concentrations. Because a fine domain structure (domain structure with the aligned spontaneous poling direction in fine regions) in the as-grown crystal is thought to be one cause of this variation, it is considered possible to control these deviations to a smaller region by optimizing the poling conditions.

As shown in Fig. 7, a large peak which gives a dielectric constant $> 6\,000$ exists in the region where the Ti concentration is 28–29 mol%. The reason why this sharp peak is observed in this small concentration region is still unclear. According to a previously-cited reference¹⁴⁾, a monoclinic region exists in the pseudo cubic structure in the vicinity of the morphotropic phase boundary (MPB II). In this case, a dielectric constant different from that of the pseudo cubic system might be measured. However, the literature indicates that the Ti concentration at which these crystal systems exist is 30–36 mol%, which is higher than the concentration where the peak was measured in this study. In the present measurements, as discussed in section 3.2, the results showed deviation of MPB II to the high Ti concentration side. Thus, there is a possibility that the Ti concentration was overestimated in these calculations, but in that case, the concentration which gives the peak dielectric constant

would be even lower, and the difference from the value given in the literature¹²⁾ would be greater. Accordingly, further study of the cause of the large dielectric constant obtained here is required.

3.3.2 Electromechanical coupling coefficient (k_t , k_{31})

Figure 8 shows the dependence of k_t and k_{31} on Ti concentration. k_t , which is the coefficient for the thickness direction, is 55–60%. The sharp peak at 28–29 mol% which was seen in the dielectric constant, as mentioned above, is not observed with k_t . Although the factors are unclear, because vibration in the thickness direction displays a mixed mode rather than a simple mode, some effect of this difference is conceivable. This is also a topic for future investigation.

For k_{33} , which is the longitudinal vibration mode, measurement using a rod-shaped sample with an aspect ratio larger than 3 is necessary. As noted previously, this was not possible with the present wafer-shaped specimens. However, the results of measurements using rod-shaped samples with different Ti concentrations taken from other ingots are shown in Table 1. In the range of 28–32 mol%, k_{33} showed values of more than 90% in all cases. The maximum value for the lateral vibration mode, k_{31} , at approximately 60%, is about 3/4 that of PZN-PT, which shows a maximum value of approxi-

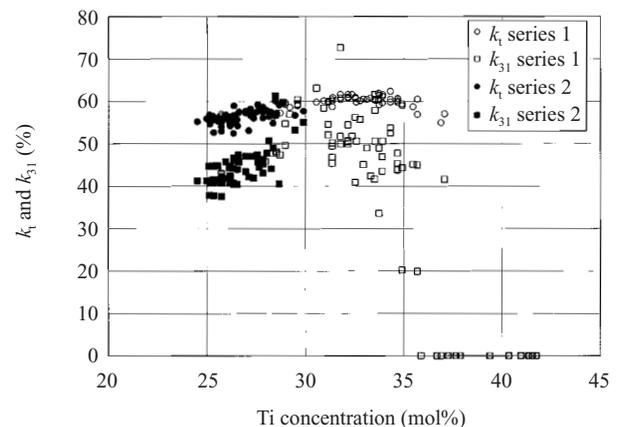


Fig.8 Dependence of electro-mechanical coupling constant (k_t , k_{31}) on Ti concentration

Table 1 Dielectric and piezoelectric properties of rod sample

Item	Before poling			After poling								
	Density (g/cm ³)	C (nF)	ϵ_r	C (nF)	ϵ_r	f_r (kHz)	f_a (kHz)	k_{33} (%)	d_{33} (pC/N)	T_c (°C)	T_{rt} (°C)	T_1 (mol%)
Sample A	8.10	0.020	2 484	0.043 5	5 429	84.0	194.0	91.7	1 594	148	94	28.1
Sample B	8.10	0.018	2 436	0.041 5	5 493	78.5	194.5	92.9	1 741	152	83	29.4
Sample C	8.10	0.019	2 322	0.044 1	5 446	67.5	196.5	94.9	2 060	164	57	31.8

Sample dimension: 9.2 mm \times 2.9 mm \times 2.9 mm

Direction of poling and vibration is [001].

mately 80%¹⁵). In this respect, as with the dielectric constant, the samples show a peak in the range of Ti concentrations of 28–31 mol%. However, the values are 1.5 times greater than the 30% value of k_{31} shown by PZT ceramics. Because conversion efficiency is proportional to the square of the coupling coefficient, this means that the conversion efficiency of PMN-PT is 2.25 higher than that of PZT.

3.3.3 Piezoelectric constant (d_{33} , d_{31})

Figures 9 and 10 show the dependence of the piezoelectric constant d_{33} for the thickness direction and d_{31} for the lateral vibration mode on Ti concentration. Both of these constants show concentration dependence similar to that of the dielectric constant. In particular, the constants show large peaks in the vicinity of Ti concentration at 28–30 mol%. The maximum value of d_{33} is approximately 2 700 pC/N, while the maximum value of d_{31} reaches approximately $-1\ 100$ pC/N. However, the variation of values between wafers with the same Ti concentration is large as mentioned in the section on the dielectric constant. As in the case of the dielectric

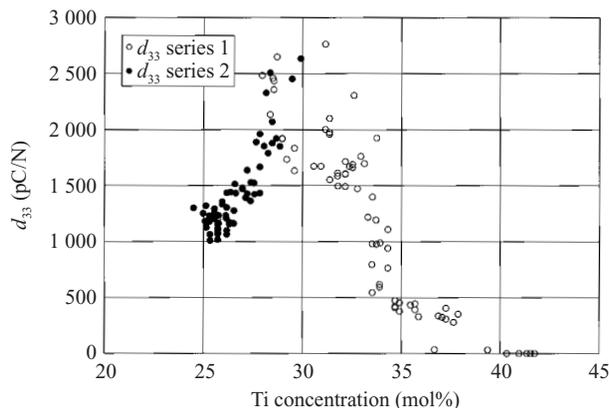


Fig.9 Dependence of piezoelectric constant (d_{33}) on Ti concentration

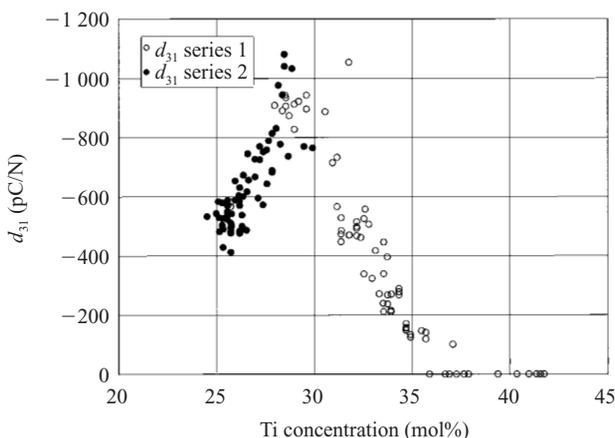


Fig.10 Dependence of piezoelectric constant (d_{31}) on Ti concentration

constant, control of this variation is necessary. When d_{33} was measured using rod-shaped samples, values of 1 600–2 060 pC/N were obtained, as shown in Table 1. These values are large in comparison with the d_{33} of 500 pC/N and d_{31} of -200 pC/N shown by PZT ceramics, which are currently the mainstream material.

4. Conclusion

Stable growth of large diameter piezo-single crystals of lead magnesium niobate/lead titanate (PMN-PT) with high conversion efficiency was successfully achieved using one-batch Bridgman growth. These single crystals weigh 3.5 kg and have a diameter of 80 mm ϕ , which belongs to the world's largest class. (001) wafers with an angle of 45° relative to the $\langle 110 \rangle$ crystal growth orientation were cut from the entire single crystal obtained by this process. Because the position in the ingot growth direction is different, small-size rectangular wafers were sliced with (001) direction as series 1 and series 2 in order to investigate the variation of Ti concentration along the growth direction of a single crystal ingot. It was found that concentration variations are large in the crystal tip (cone) and end portion, but are comparatively slight in the straight body section, where stable growth occurs, and the Ti concentration is constant at the same position in the ingot. Using the same rectangular wafers, the dependence of the relative dielectric constant (ϵ_r), the electromechanical coupling coefficient (k_t , k_{31}), and the piezoelectric constant (d_{33} , d_{13}) on Ti concentration were measured. As a result, it was found that the values of these physical properties shown large dependence on the Ti concentration. In particular, conspicuous peak values were observed at Ti concentrations of 28–30 mol%. As the cause of these peaks, the authors noted that it is necessary to consider the relationship with the monoclinic system which appears around these Ti concentrations. It was also shown that a continuous feeding growth technology of crystal growth is essential for controlling the entire single crystal to a Ti concentration range which gives excellent values for dielectric/piezoelectric properties by citing a reference literature discussing the practical application of a similar technology to MnZn ferrite single crystal. Furthermore, these property values also showed significant variation at an identical Ti concentration. As a countermeasure, it was pointed out that domain control by optimizing poling conditions is a key technology for reducing these variations.

The authors believe that the evaluation of piezoelectric/dielectric properties presented in this paper will be useful in deciding the raw material composition for PMN-PT growth, determining the delivery specifications for users, and comparing properties with other materials, and will become basic data for deciding the

optimum composition for individual applications.

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