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PMN-PT and PIN-PMN-PT Piezoelectric Single Crystals with Stable Properties

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Abstract:

JFE MINERAL has developed high quality $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ *(PMN-PT) and* $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ *(PIN-PMN-PT) piezoelectric single crystals for medical ultrasound transducers and sonars. This paper discusses the continuous-feeding Bridgman growth method, which was developed by JFE MINERAL and substantially improves the compositional uniformity within single crystal ingots, and the attained stable piezoelectric properties of the single crystals.*

1. Introduction

Piezoelectric materials generate an electrical charge from an applied mechanical stress or a mechanical strain in response to an applied electric field. In recent automobiles, they are used in pressure sensors which measure road conditions and back sonars which detect obstacles. $Pb(Zr,Ti)O_3$ (hereinafter, PZT) ceramics, which are one type of ferroelectric material, have been widely employed in piezoelectric applications. However, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (hereinafter, PMN-PT) and $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (hereinafter, PIN-PMN-PT) single crystals with piezoelectric performance exceeding that of PZT ceramics were developed in the past decades[1, 2)]. Because these single crystals have superior piezoelectric properties (piezoelectric constant d_{33} of up to 2 000 pC/N, electromechanical coupling factor k_{33} of up to 0.9), which can contribute to the quality of images in medical ultrasound diagnostic systems, they have been used industrially in the transducers of probes which transmit and receive ultrasound in place of the conventional PZT ceramics[3)]. These single crystals have also been studied intensively for application to sonars for submarines, UUVs (Unmanned Underwater Vehicles), etc. in order to achieve miniaturization, broadband transduction and lower energy consumption[4, 5)]. Considering performance improvement, they are also expected to replace PZT ceramics in EVs.

JFE MINERAL supplies PMN-PT and PIN-PMN-PT single crystal products to the market. The manufacturing process is as follows. First, a cylindrical single crystal ingot is crystalized from the melt of the raw materials, and large wafers are sliced from the ingot. Next, product-sized wafers are diced from the large wafers and lapped to a specific thickness, and gold electrodes are formed on both wide surfaces of these wafers by sputtering. Finally, the wafers are poled by applying a DC electric field of from 500 to 1 000 V/mm between the electrodes to function as piezoelectric materials.

Generally, the Bridgman method has been used for crystal growth. However, as this method is a unidirectional solidification process, compositional segregation is inevitable. The large composition change in the growth direction causes large changes in properties within an ingot, which results in wide property variation in the final products[6, 7)]. JFE MINERAL developed a continuous-feeding Bridgman growth method to resolve this issue[8, 9)].

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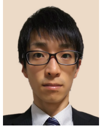

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This paper describes the continuous-feeding Bridgman growth method and the quality and properties of the single crystals grown by the method.

2. Continuous-Feeding Bridgman Growth Method

Figure 1 shows a conceptual diagram of the continuous-feeding Bridgman growth method. PMN-PT or PIN-PMN-PT ceramics are loaded in a platinum crucible as the initial raw materials. The initial materials are heated above their melting point (around 1 300°C) and a melt is formed in the crucible. As the crucible is placed under a temperature gradient in which the lower position in the furnace has the lower temperature, only the upper portion of the seed crystal is melted. When the crucible is lowered at a speed of less than 1 mm/h, the melt starts to solidify from the seed crystal, and a single crystal with the same crystal orientation as the seed crystal grows upward.

This process is similar to the conventional vertical Bridgman growth method. However, the distinctive feature of the continuous-feeding Bridgman growth method is that additional ceramics are fed continuously during crystal growth. The concentration change of a melt element ΔC_s due to segregation is described by the following equation:

$$\Delta C_s = C_o \{(1-g)^{(k-1)}-1\} \text{ , ... (1)}$$

where, C_o is the initial concentration before the start of crystal growth, g is the solidified fraction (ratio of solidified weight to melt weight) and k is the segregation coefficient. In the continuous-feeding Bridgman growth method, the concentration change ΔC_m is described by the following equation using ΔC_s :

$$\Delta C_m = \Delta C_s + \Delta C_f \text{ , ... (2)}$$

where, ΔC_f is the concentration change caused by feeding the additional ceramics. If ΔC_f can be controlled to be $-\Delta C_s$ by the feeding conditions, ΔC_m is 0. This means the concentration remains constant during crystal growth and the concentration within the ingot is uniform. The feeding conditions are the composition of the additional ceramics and the feeding rate. **Figure 2** shows examples of the TiO_2 content distributions in the growth direction simulated under the conditions of three different ratios of the feeding rate R_f to the solidification rate R_s. Under the other conditions shown in the figure, when R_f is equal to R_s, the content is constant, which means ΔC_m is 0. When R_f is less than R_s, the TiO_2 content increases in the growth direction, and conversely, when R_f is more than R_s, the TiO_2 con-

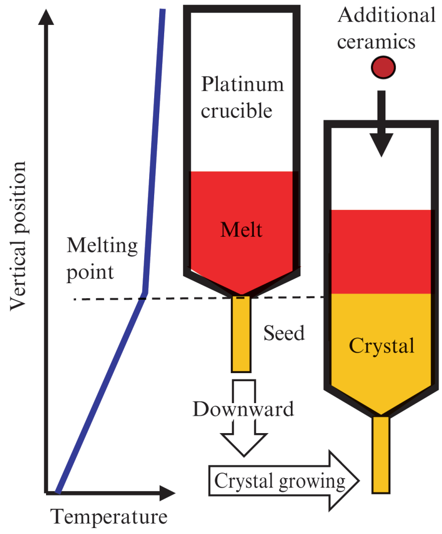


Fig. 1 Conceptual diagram of continuous-feeding Bridgman growth method

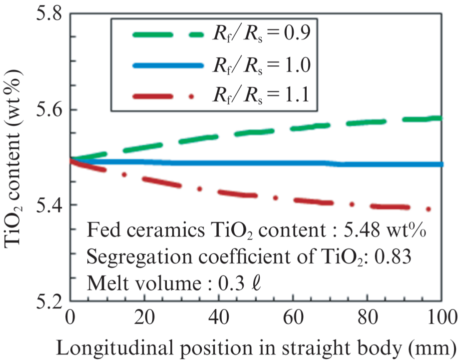
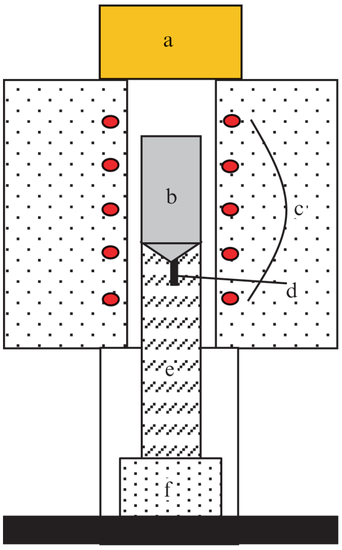


Fig. 2 Calculated TiO_2 content distributions under various ratios of feeding rate R_f to solidification rate R_s



a. Feeding mechanism; b. Crucible;
c. Heater; d. Seed; e. Support tube;
f. Levitation mechanism

Fig. 3 Schematic diagram of growth system for continuous-feeding Bridgman growth tent decreases in the growth direction. It should be noted that a content variation occurs except at the appropriate R_f. Therefore, the feeding conditions must be optimized to realize the uniform composition within an ingot.

Figure 3 shows a schematic diagram of the system for continuous-feeding Bridgman growth. Although the basic components such as heaters, a crucible levitation mechanism and a crucible support tube are common to conventional vertical Bridgman furnaces, the continuous-feeding system also includes a feeding mechanism which can continuously weigh and drop additional ceramics with the designated weight into the crucible. As shown in Fig. 2, the feeding rate is one quite important parameter for determining composition uniformity. Therefore, the feeding mechanism must have sufficient feeding rate accuracy.

3. Quality of Single Crystal Ingot

Photo 1 shows the appearance of a PMN-PT single crystal ingot grown by the continuous-feeding Bridgman growth method. The ingot diameter is 80 mm and the length is 320 mm, which is the longest in the world to the best of the authors' knowledge. The left tip and the right edge correspond to the crystal growth start position and end position, respectively. The crystal orientation of the growth direction is <011>. The white marks on the surface are very shallow scratches that were formed when the platinum crucible was stripped from the ingot. The continuous-feeding Bridgman growth method is advantageous for the growth of long ingots, and because additional ceramics are fed, the melt volume held in a crucible is much smaller than in the conventional Bridgman growth method, which can reduce the chemical and thermal damage to the crucible. A large volume melt can easily cause melt leakage from the crucible or crucible deformation, which makes the crystal growth difficult.

Photo 2 shows the appearance of a {001} oval wafer sliced from the ingot at 45° to the growth direction. There are no defects and no damage from the shallow scratches observed on the ingot surface. The straight edges on the left and bottom sides are the orientation flats formed by grinding to identify the <100> direction.

Figure 4 shows the longitudinal TiO_2 content distributions of the PMN-PT single crystal ingots grown by the continuous-feeding Bridgman growth method and the conventional Bridgman growth method. The content is normalized by the content at a position near the tip of each ingot. The longitudinal position is shown by the ratio of the length from each ingot tip to the total ingot length. In the conventional Bridgman growth method, the TiO_2 content increases monotonically in the growth direction, and the change within the ingot reaches 20%. In contrast, the content distribution of the continuous-feeding Bridgman growth method is almost uniform over a region of 90% of the ingot. Thus, it is obvious that the continuous-feeding Bridg-

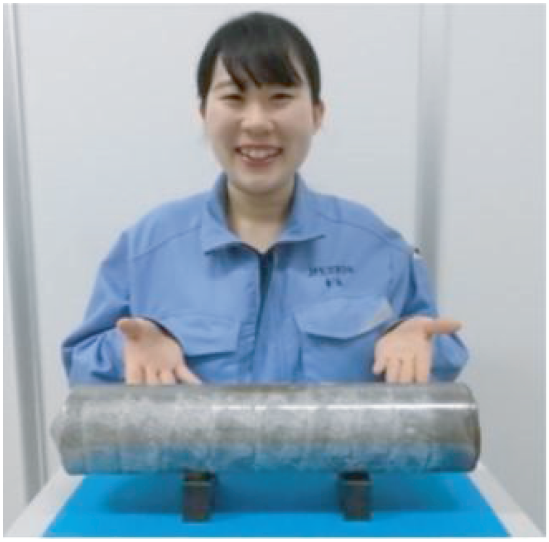


Photo 1 As-grown PMN-PT single crystal ingot

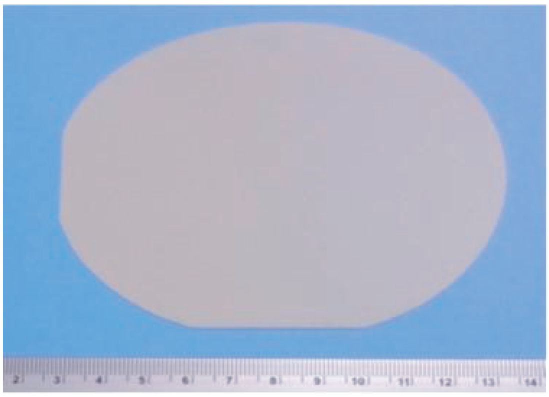


Photo 2 As-sliced PMN-PT single crystal wafer

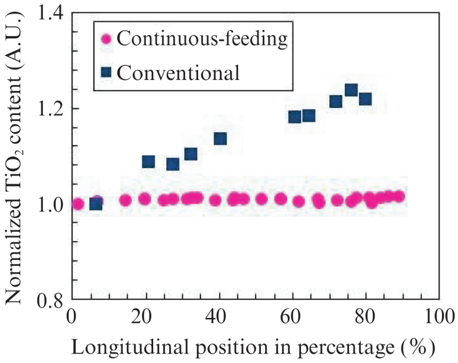


Fig. 4 Normalized TiO_2 content distributions of PMN-PT ingots in growth direction

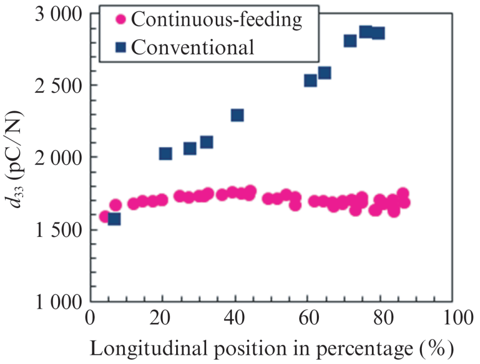


Fig. 5 Piezoelectric constant d_{33} distributions of PMN-PT ingots along growth direction

man growth method enables growth of PMN-PT single crystal ingots with greatly improved compositional uniformity compared to the conventional Bridgman growth method.

Figure 5 shows the piezoelectric constant d_{33} distributions of the ingots shown in Fig. 4. The properties of PMN-PT and PIN-PMN-PT single crystals depend on the crystal orientation to which the electric field is applied in the poling process10). All the properties mentioned in this paper were measured in single crystals poled in the [001] direction. In the ingot grown by the conventional Bridgman growth method, d_{33} increased significantly in the growth direction, reflecting the TiO_2 content distribution shown in Fig. 3, whereas the d_{33} of the ingot grown by the continuous-feeding Bridgman growth method were well controlled in a tight range of less than 300 pC/N due to the improved compositional uniformity. This excellent uniformity not only makes it possible to supply products with stable properties, but also to improve yield substantially. If the d_{33} specification of a product is 1 500 to 2 000 pC/N, 90% of the ingot produced by the continuous-feeding Bridgman growth method is usable, while only 20% of the ingot produced by the conventional Bridgman growth method can be used, indicating that the cost effectiveness of the continuous-feeding Bridgman growth method is also a noteworthy advantage. Although not described here, the PIN-PMN-PT single crystals grown by the continuous-feeding Bridgman growth method also have similar uniformity of composition and properties9).

4. Properties of Single Crystals

Table 1 Typical properties of three single crystals

Property	PMN-PT	PIN-PMN-PT	
	A	B	C
$\varepsilon_{33}/\varepsilon_0$	6 000	5 100	3 400
tan δ (%)	0.5	0.5	0.5
k_{33}	0.94	0.94	0.90
d_{33} (pC/N)	1 780	1 830	1 060
*E*c (V/mm)	220	510	550
*T*rt (˚C)	92	102	142
*T*c (˚C)	143	179	160

Since the continuous-feeding Bridgman growth method enables control of the composition, single crystals with various target compositions can be grown. The composition of the PMN-PT binary system and the PIN-PMN-PT ternary system were studied, and three kinds of single crystals with characteristic properties were developed. Their typical properties are summarized in **Table 1**.

The type A PMN-PT single crystal has a high relative permittivity ($\varepsilon_{33}/\varepsilon_0$), a high electromechanical coupling factor (k_{33}) and a high piezoelectric constant (d_{33}). Because these properties offer high sensitivity over a broadband in the probes of ultrasound systems, the type A single crystal is suitable for sector probes, which are used mainly to examine the heart, and convex probes used mainly to examine the abdomen.

The type B PIN-PMN-PT single crystal has a slightly lower relative permittivity, similar piezoelectric properties (k_{33} and d_{33}) and an approximately double coercive field (*E*c) compared to type A. **Figure 6** shows the polarization hysteresis loops of the type A and B single crystals. Polarization (*P*) becomes 0 when the reverse field opposite to the polarization polarity is applied (i.e., if the polarization is +, the reverse field is −). This electric field (*E*) is the coercive field (*E*c) where piezoelectricity is completely lost. Polarization of the type B single crystal is maintained under a larger reverse field compared to type A. It should be noted that the type B single crystal is usable under a high bipolar field that is not acceptable for type A. There-

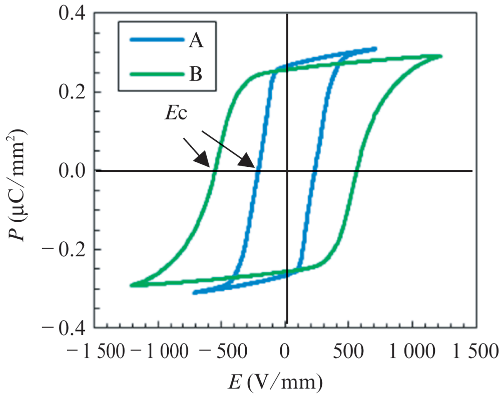


Fig. 6 Polarization hysteresis loops of type A and type B single crystals

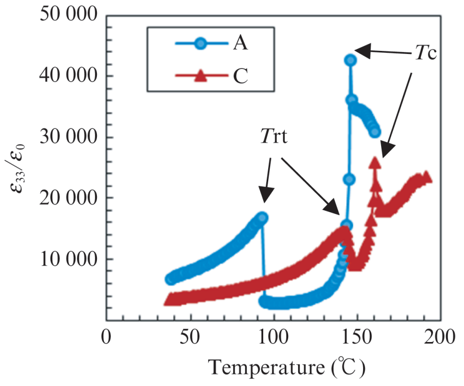


Fig. 7 Temperature dependence of relative dielectric constant for type A and type C single crystals

fore, the type B single crystal is effective for high frequency linear probes, which are mainly used in vascular examinations.

The type C PIN-PMN-PT single crystal has slightly lower piezoelectric properties than type B, but it has the highest phase transition temperature (*T*rt) among the three single crystals. **Figure 7** shows the temperature dependence of $\varepsilon_{33}/\varepsilon_0$ for the type A and C single crystals when heated from room temperature. The $\varepsilon_{33}/\varepsilon_0$ peak observed at the lower temperature for each single crystal is related to the phase transition from rhombohedral to tetragonal. The temperature of this peak is *T*rt. If the temperature exceeds *T*rt, $\varepsilon_{33}/\varepsilon_0$ drops sharply. On the other hand, the temperature of the $\varepsilon_{33}/\varepsilon_0$ peak observed at the higher temperature for each single crystal is the Curie temperature (*T*c), where the phase transition from tetragonal to cubic occurs and piezoelectric performance is completely lost. Because this property abruptly changes at *T*rt, the practical upper limited temperature is *T*rt. The type C single crystal is usable at a 50˚C higher temperature than the type A single crystal. In addition, the property change with temperature for type C is less than that of type A. The change rates of $\varepsilon_{33}/\varepsilon_0$ between 40 ˚C and 80˚C for the type C and type A single crystals are 51% and 81%, respectively. Therefore, the type C single crystal is useful for sonars, which require thermal stability.

5. Conclusion

This paper described the continuous-feeding Bridgman growth method, which was developed by JFE MINERAL and makes it possible to improve the property uniformity within PMN-PT and PIN-PMN-PT single crystal ingots. JFE MINERAL has already commercially produced large, cost-effective single crystal ingots (80 mm in diameter and 320 mm in length) with superior property uniformity (d_{33} variation <300 pC/N) and is supplying single crystal products with stable quality from these ingots worldwide. These single crystals especially contribute to high performance in medical ultrasound diagnostic systems.

Utilizing the excellent composition controllability of the continuous-feeding Bridgman growth method, characteristic PIN-PMN-PT single crystals with a high coercive field (*E*c=510 V/mm) or a high phase transition temperature (*T*rt=142˚C) were also developed. These single crystals are expected to be effective in improving the performance not only of medical ultrasound systems but also sonars and EVs.

Acknowledgment

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