crystals

MDPI

Article

Characterization of Mn-Doped PIN-PMN-PT Single Crystal Grown by Continuous-Feeding Bridgman Method

Kazuhiko Echizenya *, Naoki Noda and Hisato Noro

JFE Mineral & Alloy Company, Ltd., 1, Niihama-cho, Chuo-ku, Chiba-shi, Chiba 260-0826, Japan
* Correspondence: k-echizenya@jfe-mineral.co.jp

Abstract: Mn-doped $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (Mn:PIN-PMN-PT) single crystals are attractive piezoelectric materials owing to their high mechanical quality factor. However, the single crystal boules grown by the conventional Bridgman method show compositional variation along the growth direction. In particular, the Mn content exhibits large variation due to its severe segregation. To improve the compositional uniformity, we applied the continuous-feeding Bridgman method to the growth of a Mn:PIN-PMN-PT single crystal boule. Then, the composition and property distributions of the boule along the growth direction were evaluated. The results showed that excellent composition and property uniformity were carried out over 80mm in boule length. The ranges of the electromechanical coupling coefficient (k_{33}) and the piezoelectric coefficient (d_{33}) were 0.931–0.934 and 1352–1517 pC/N, respectively. The ranges of the mechanical quality factor (Qm_{31}) and the depolarization field (E_d) were 417–535 and 785–859 V/mm, respectively. The Qm_{31} and the E_d values were higher than those of the non-doped PIN-PMN-PT single crystals. The continuous-feeding Bridgman method is therefore an effective technique for improving the uniformity of the Mn content. As a result, the Mn:PIN-PMN-PT single crystal grown by the continuous-feeding Bridgman method possesses excellent property uniformity with characteristics suitable for high power piezoelectric applications.

Keywords: single crystal; PIN-PMN-PT; Bridgman growth; compositional segregation

check for updates

Citation: Echizenya, K.; Noda, N.; Noro, H. Characterization of Mn-Doped PIN-PMN-PT Single Crystal Grown by Continuous-Feeding Bridgman Method. *Crystals* **2022**, *12*, 1183. https://doi.org/10.3390/cryst12091183

Academic Editors: Fapeng Yu and Ana M. Garcia-Deibe

Received: 5 August 2022
Accepted: 19 August 2022
Published: 23 August 2022

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$ (PMN-PT), $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIN-PMN-PT) and Mn-doped $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (Mn:PIN-PMN-PT) single crystals have been found to be excellent piezoelectric materials [1–3]. PMN-PT and PIN-PMN-PT single crystals have been utilized as transducers in medical ultrasound diagnosis systems due to their high electromechanical coupling coefficients ($k_{33} > 0.9$) that contribute to the quality diagnostic images. The Mn:PIN-PMN-PT crystal is a promising candidate for high power applications such as underwater sonar, because it possesses a high mechanical quality factor (Qm ~700).

Most of the single crystal boules have been grown by the Bridgman method. However, since the unidirectional solidification cannot avoid compositional segregation, the composition varies within a boule [4–6]. In particular, Mn content within Mn:PIN-PMN-PT boules severely changes along the growth direction in the elements [7]. Therefore, the Mn:PIN-PMN-PT boules exhibit wide variations of properties, such as the piezoelectric constant (d_{33}) and Qm, which are undesirable from the viewpoint of the industrial applications.

The continuous-feeding Bridgman method is one of the sophisticated crystal growth techniques to overcome the compositional segregation issue. The method controls the melt composition by feeding additional materials into the melt during the crystal growth and substantially improves the composition uniformity on PMN-PT and PIN-PMN-PT boules compared with the conventional Bridgman method [8–11].

In this paper, the growth of a Mn:PIN-PMN-PT single crystal boule was conducted by the continuous-feeding Bridgman method to achieve a stable Mn content within the boule.

The characterization of the single crystal was carried out compared with a non-doped PIN-PMN-PT single crystal.

2. Materials and Methods

2.1. Crystal Growth

The perovskite ceramics were synthesized from Pb_3O_4, MgO, Nb_2O_5, TiO_2, In_2O_3, and MnO powder with 3N-4N purity by the columbite precursor procedure, which synthesizes $InNbO_4$ and $MgNb_2O_6$ as precursors. The mixing ratios for the compositions of the fed ceramics are shown in Table 1. Figure 1 shows the schematic furnace configuration for the continuous-feeding Bridgman method [8–10]. The ceramics were loaded in a platinum crucible with an inner diameter of 80 mm on the support tube, and a <110> seed crystal was set at the bottom of the crucible. The ceramics were melted by the heaters, which surround the crucible at a temperature more than 1300 °C. Then, the crystal growth started after soaking for 16 h. The crucible was lowered at an appropriate speed (less than 1.0 mm/h) with the levitation mechanism, and at the same time, the ceramics were continuously fed into the crucible at a feeding rate with the feeding mechanism. After the continuous-feeding growth of 80 mm in boule length, the remaining melt was solidified without feeding. The boule was grown along the <110> direction, which was the same orientation as the seed crystal. Then, the boule was cooled down to room temperature in the furnace. Finally, the crucible was stripped and the as-grown single crystal boule was obtained. In addition, a non-doped PIN-PMN-PT boule was grown by the same growth method to evaluate the effect of the Mn doping on the properties.

Table 1. Mixing ratios of oxides used for fed ceramics.

Compound	MnO	Pb_3O_4	$InNbO_4$	$MgNb_2O_6$	TiO_2
Mixing ratio (wt%)	0.2	68.4	12.8	11.3	7.3

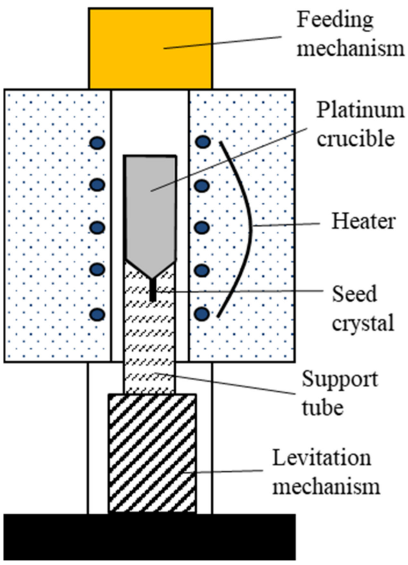

Figure 1. Schematic configuration of growth system for continuous-feeding Bridgman method.

2.2. Characterization

The {001} oriented plates with 0.5 mm in thickness were cut at several locations of the grown boules along the growth direction for evaluation. The composition of the plates was measured with an X-ray fluorescence spectrometer (Rigaku ZSX Primus IV). Gold and nichrome layers were formed on both large surfaces of the plates by sputtering as electrodes. The plates were poled under a direct current field of 1200 V/mm. With an impedance analyzer (HP4192A), the free and clamped dielectric properties were measured at 1 kHz and 6.4 MHz in frequency, respectively. The electromechanical coupling coefficient (k_{33}) was calculated from the free dielectric constant ($\varepsilon_{33}{}^{T}$) and the clamped dielectric constant ($\varepsilon_{33}{}^{S}$) [12]. The piezoelectric coefficient (d_{33}) was measured with a piezo d_{33} meter (ZJ-3D). The mechanical quality factor (Qm_{31}) was calculated by the 3dB down method [13] from the impedance curve measured near the resonance frequency with an impedance gain phase analyzer (HP4294A). The polarization hysteresis loop was taken at 10 Hz in frequency with a ferroelectric characteristics evaluation system (Toyo Corporation FCE-3) to determine the depolarization field (E_d) and the internal bias (Ei).

3. Results and Discussion

Figure 2 shows the Mn:PIN-PMN-PT single crystal boule grown by the continuous-feeding Bridgman method. The boule with the diameter of 80 mm and the length of 145 mm was successfully grown. The boule was black-hued, which was obviously different from the non-doped PIN-PMN-PT single crystal boule [9].

Figure 2. Mn:PIN-PMN-PT single crystal boule grown by continuous-feeding Bridgman method.

Figure 3 shows the MnO, In_2O_3, Nb_2O_5, MgO, and TiO_2 content distributions along the growth direction for the boule shown in Figure 1. All distributions exhibited very small variation in the position ranging from 0 to 80 mm where the continuous-feeding Bridgman growth was operated. The MnO, In_2O_3, Nb_2O_5, MgO, and TiO_2 content were 0.22–0.24 wt%, 6.55–6.66 wt%, 17.73–17.86 wt%, 1.08–1.15 wt% and 7.74–7.90 wt%, respectively. In contrast, obvious composition changes were found in the position over 80 mm. It should be noted that this boule region was grown without feeding. Only the In_2O_3 content distribution showed no large variation over the entire boule length, since the In_2O_3 is not significantly affected by the segregation behavior [7]. The results prove that the continuous-feeding Bridgman method was able to improve the uniformity of the MnO content as well as other content for the Mn:PIN-PMN-PT single crystal boules.

Figure 4 shows the piezoelectric properties of the Mn:PIN-PMN-PT boule along the growth direction, compared with the non-doped PIN-PMN-PT boule. The stable properties were achieved in the position ranging from 0 to 80 mm. However, the properties drastically changed in the position over 80 mm. The region ranging from 0 to 80 mm in length had stable composition as shown in Figure 3 due to the continuous feeding. The property variations in the Mn:PIN-PMN-PT boule were small and almost the same as those of the non-doped PIN-PMN-PT boule. The results indicate that the continuous-feeding Bridgman method can realize Mn:PIN-PMN-PT boules with fewer piezoelectric property variations.

On the other hand, the properties trended along the growth direction were different between the Mn:PIN-PMN-PT and the non-doped PIN-PMN-PT boules. The Mn:PIN-PMN-PT boule exhibited the largest k_{33} and d_{33} at around 40 mm in length. In contrast, the non-doped PIN-PMN-PT boule showed the minimum k_{33} and d_{33} at the same position. This difference was inexplicable only by the composition. The other factors such as domain configuration and residual stress may affect the properties and the contribution to the factors might change with Mn doping. Further study is needed to confirm the reason for the trend difference.

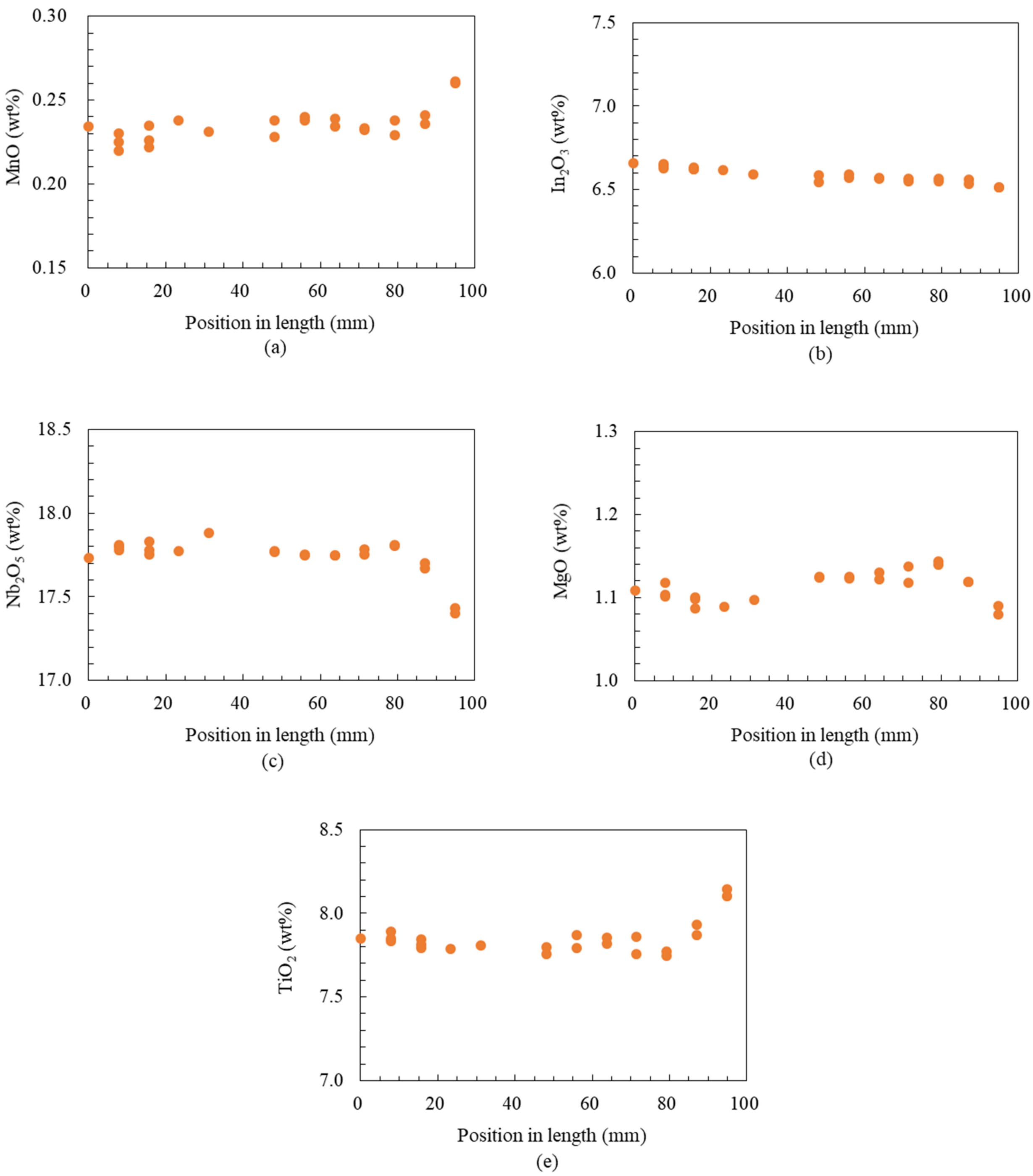

Figure 3. Distributions of (**a**) MnO content, (**b**) In_2O_3 content, (**c**) Nb_2O_5 content, (**d**) MgO content, and (**e**) TiO_2 content for the Mn:PIN-PMN-PT boule along growth direction.

The ranges in the electromechanical coupling coefficient k_{33} and the piezoelectric coefficient d_{33} in the stable property region of the Mn:PIN-PMN-PT boule were 0.931–0.934 and 1352–1517 pC/N, respectively. The ranges were slightly lower than those of the non-doped PIN-PMN-PT boule. Therefore, the Mn doping made a negative contribution to piezoelectric performance.

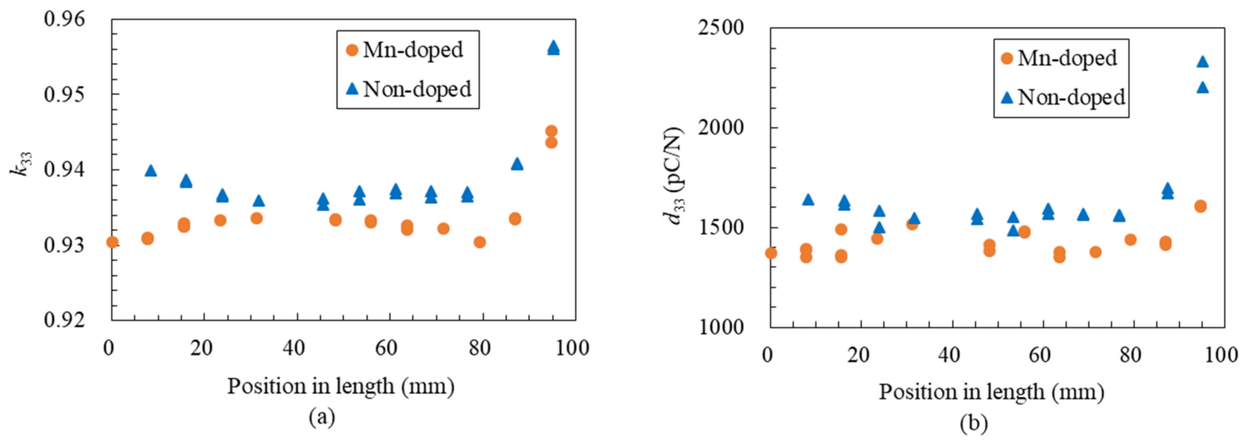

Figure 4. Distributions of (**a**) electromechanical coupling coefficients k_{33} and (**b**) piezoelectric constants d_{33} along the growth direction for Mn-doped and non-doped PIN-PMN-PT boules grown by the continuous-feeding Bridgman method.

Figure 5 shows the ferroelectric hysteresis loops of the Mn:PIN-PMN-PT crystal and the non-doped PIN-PMN-PT crystal. Both crystals show almost the same remnant polarization (~25 C/m^2). The Mn:PIN-PMN-PT crystal exhibited an anisotropic loop and an offset along the x-axis, which indicated the existence of internal bias (E_i) [13]. The E_i was around 90 V/mm. A depolarization field (E_d) is an electric field at which the polarization is zero in the positive field as indicated in Figure 4. The positive field is the reverse polarity for the DC poling. The E_d of the Mn:PIN-PMN-PT crystal and the non-doped PIN-PMN-PT crystal were 785 V/mm and 610 V/mm, respectively. The difference between their E_d was 175 V/mm, which was almost twice the internal bias. Therefore, the Mn:PIN-PMN-PT crystal had a higher E_d than the non-doped PIN-PMN-PT crystal by the internal bias ($E_i \times 2$).

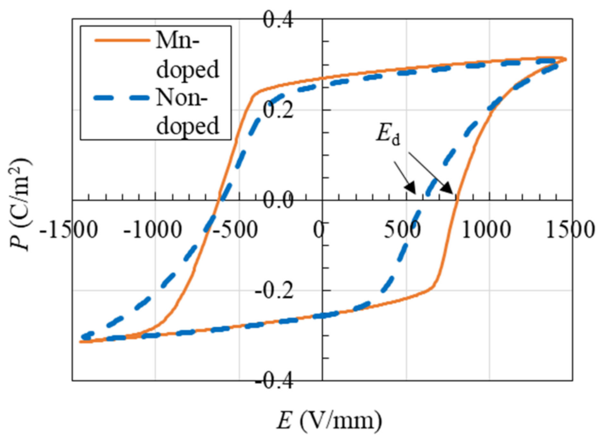

Figure 5. Polarization (P)–electric field (E) hysteresis loops of Mn-doped and non-doped PIN-PMN-PT crystals.

Figure 6 shows the distributions of the E_d and the Ei along the growth direction for the Mn:PIN-PMN-PT boule. The E_d and the E_i ranged from 785 to 859 V/mm (+/−5% in variation) and from 77 to 92 V/mm (+/−9% in variation), respectively. The excellent uniformity of MnO content shown in Figure 3a contributed to the steady E_d and E_i within the boule, since the Ei level was associated with the MnO content [14]. It was demonstrated that the Mn:PIN-PMN-PT boule grown by the continuous-feeding Bridgman method possessed stable electric field stability.

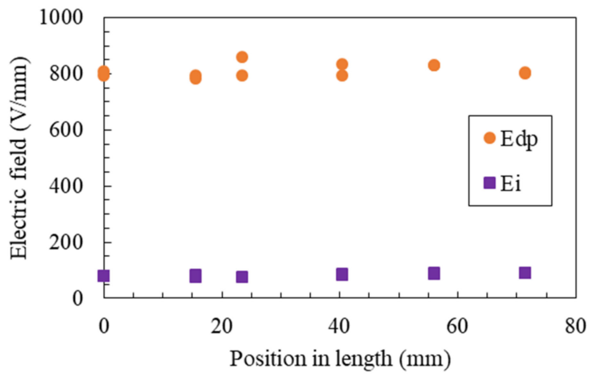

Figure 6. Distributions of E_d and E_i along the growth direction for the Mn:PIN-PMN-PT boule.

Figure 7 shows the distributions of the Qm_{31} along the growth direction for the Mn:PIN-PMN-PT boule. The maximum Qm_{31} and the minimum Qm_{31} were 535 and 417, respectively. The variation was controlled to +/−12% due to the small composition variation. In addition, the Qm_{31} slightly increased along the growth direction. The MnO content also slightly increased along the growth direction, as shown in Figure 3a. Therefore, we think the MnO content strongly relates to the Qm_{31}, and the control of the MnO content is essential for stable mechanical quality factors.

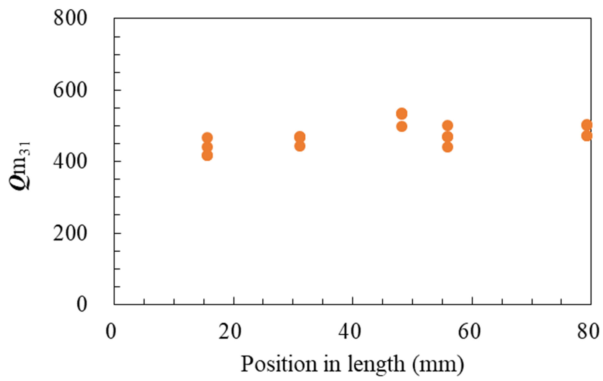

Figure 7. Distributions of Qm_{31} along the growth direction for the Mn:PIN-PMN-PT boule.

Table 2 summarizes the typical properties of the Mn:PIN-PMN-PT single crystal and the non-doped PIN-PMN-PT single crystal. Compared with the non-doped PIN-PMN-PT crystal, the Mn:PIN-PMN-PT crystal exhibited low permittivity $\varepsilon_{33}{}^{T}/\varepsilon_0$, the same dielectric loss (*tan* δ), almost the same k_{33}, low d_{33}, high E_d, and significantly higher mechanical quality factor Qm_{31}. Zheng et al. reported that the polarization rotation restricted by the internal bias enhances the mechanical quality factor [15]. Therefore, we concluded that the internal bias shown in Figure 4 contributed to increasing the Qm_{31} for the Mn:PIN-PMN-PT crystal. The Mn:PIN-PMN-PT crystal is more suitable for high power applications due to its high mechanical quality factor and high depolarization field compared to the non-doped PIN-PMN-PT crystal.

Table 2. Typical properties for Mn-doped and non-doped PIN-PMN-PT single crystals.

Single Crystal	Mn:PIN-PMN-PT	PIN-PMN-PT
$\varepsilon_{33}{}^{T}/\varepsilon_0$	3530	4480
tan δ (%)	0.5	0.5
k_{33}	0.93	0.94
d_{33} (pC/N)	1480	1590
E_d (V/mm)	830	610
Qm_{31}	470	140

4. Conclusions

A Mn:PIN-PMN-PT single crystal boule with a diameter of 80 mm and a length of 145 mm was successfully grown by the continuous-feeding Bridgman method. The composition was controlled in the narrow ranges (0.22–0.24 wt% in MnO content, 6.55–6.66 wt% in In_2O_3 content, 17.73–17.86 wt% in Nb_2O_5 content, 1.08–1.15 wt% in MgO content, and 7.74–7.90 wt% in TiO_2 content) over the boule region of 80 mm in length. The continuous-feeding Bridgman method effectively homogenized the MnO content, which had the severe segregation behavior. As a result of the excellent composition uniformity, the Mn:PIN-PMN-PT single crystal boule showed the narrow property ranges (0.931–0.934 in k_{33}, 1352–1517 pC/N in d_{33}, 785~859 V/mm in E_d, and 417–535 in Qm_{31}).

Compared with a non-doped PIN-PMN-PT single crystal, the Mn:PIN-PMN-PT single crystal possessed the high mechanical quality factor and the high depolarization field.

The Mn:PIN-PMN-PT single crystal boules grown by the continuous-feeding Bridgman method were therefore likely well suited for high power applications, since they possessed stable properties in addition to low loss characteristic and high electrical stability originated from the Mn doping.

Author Contributions: Conceptualization, K.E.; investigation, N.N.; writing—original draft preparation, K.E.; writing—review and editing, H.N.; supervision, H.N.; project administration, K.E.; funding acquisition, K.E. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Office of Naval Research, grant number N62909-21-1-2065.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors appreciate the help of Yuuko Echizenya with XRF measurements.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Park, S.E.; Shrout, T.R. Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *J. Appl. Phys.* **1997**, *82*, 1804. [CrossRef]
2. Hosono, Y.; Yamashita, Y.; Sakamoto, H.; Ichinose, N. Growth of Single Crystals of High-Curie-Temperature $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Ternary Systems near Morphotropic Phase Boundary. *Jpn. J. Appl. Phys.* **2003**, *42*, 5681. [CrossRef]
3. Luo, J.; Hackenberger, W.S.; Zhang, S.; Shrout, T.R. The Progress Update of Relaxor Piezoelectric Single Crystals. In Proceedings of the 2009 IEEE International Ultrasonics Symposium, Rome, Italy, 20–23 September 2009; pp. 968–971.
4. Luo, H.; Xu, G.; Xu, H.; Wang, P.; Yin, Z. Compositional Homogeneity and Electrical Properties of Lead Magnesium Niobate Titanate Single Crystals Grown by a Modified Bridgman Technique. *Jpn. J. Appl. Phys.* **2000**, *39*, 5581–5585. [CrossRef]
5. Zawilski, K.T.; Custodio, M.C.; DeMattei, R.C.; Lee, S.G.; Monteiro, R.G.; Odagawa, H.; Feigelson, R.S. Segregation during the vertical Bridgman growth of lead magnesium niobate–lead titanate single crystals. *J. Cryst. Growth* **2003**, *258*, 353–367. [CrossRef]
6. Tian, J.; Han, P.; Huang, X.; Pan, H.; Carroll, J.F., III; Payne, D.A. Improved stability for piezoelectric crystals grown in the lead indium niobate–lead magnesium niobate–lead titanate system. *Appl. Phys. Lett.* **2007**, *91*, 222903. [CrossRef]
7. Tian, J.; Han, P. Crystal growth and property characterization for PIN–PMN–PT ternary piezoelectric crystals. *J. Adv. Dielectr.* **2014**, *4*, 1350027. [CrossRef]
8. Echizenya, K.; Matsushita, M. Continuous feed growth and characterization of PMN-PT single crystals. In Proceedings of the 2011 IEEE International Ultrasonics Symposium, Orlando, FL, USA, 18–21 October 2011; pp. 1813–1816. [CrossRef]
9. Echizenya, K.; Nakamura, K. Piezoelectric single crystals grown by continuous feeding growth method. In Proceedings of the 17th US-Japan Seminar on Dielectric and Piezoelectric Ceramics, Matsumoto, Japan, 15–18 November 2015; pp. 227–230.
10. Echizenya, K.; Nakamura, K.; Mizuno, K. PMN-PT and PIN-PMN-PT single crystals grown by continuous-feeding Bridgman method. *J. Cryst. Growth* **2020**, *531*, 125364. [CrossRef]
11. Baasandorj, L.; Chen, Z. Recent Developments on Relaxor-$PbTiO_3$ Ferroelectric Crystals. *Crystals* **2022**, *12*, 56. [CrossRef]
12. Zhang, S.; Li, F.; Sherlock, N.P.; Luo, J.; Shrout, T.R. Recent developments on high Curie temperature PIN–PMN–PT ferroelectric crystals. *J. Cryst. Growth* **2011**, *318*, 846–850. [CrossRef] [PubMed]
13. Luo, N.; Zhang, S.; Li, Q.; Yan, Q.; Zhang, Y.; Ansell, T.; Luo, J.; ShroutL, T.R. Crystallographic dependence of internal bias in domain engineered Mn-doped relaxor-$PbTiO_3$ single crystals. *J. Mater. Chem. C* **2016**, *4*, 4568. [CrossRef]

14. Zheng, L.; Sahul, R.; Zhang, S.; Jiang, W.; Li, S.; Cao, W. Orientation dependence of piezoelectric properties and mechanical quality factors of $0.27Pb(In_{1/2}Nb_{1/2})O_3$-$0.46Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.27PbTiO_3$:Mn single crystals. *J. Appl. Phys.* **2013**, *114*, 104105. [CrossRef]
15. Zheng, L.; Yang, L.; Li, Y.; Lu, X.; Huo, D.; Lü, W.; Zhang, R.; Yang, B.; Cao, W. Origin of Improvement in Mechanical Quality Factor in Acceptor-Doped Relaxor-Based Ferroelectric Single Crystals. *Phys. Rev. Appl.* **2018**, *9*, 064028. [CrossRef]