This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A new ternary ferroelectric crystal of
\[ \text{Pb}(\frac{1}{2}\text{Y}\frac{1}{2}\text{Nb})\text{O}_3-\text{Pb}(\frac{1}{3}\text{Mg}\frac{2}{3}\text{Nb})\text{O}_3-\text{PbTiO}_3 \]

Xiuzhi Li, Zujian Wang, Ying Liu, Chao He, Xifa Long*

Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A ternary piezo-ferroelectric crystal of \( 0.22\text{Pb}(\frac{1}{2}\text{Y}\frac{1}{2}\text{Nb})\text{O}_3-0.44\text{Pb}(\frac{1}{3}\text{Mg}\frac{2}{3}\text{Nb})\text{O}_3-0.34\text{PbTiO}_3 \) (PYN-PMN-PT(22/44/34)) with dimensions of 26 × 26 × 10 mm\(^3\) has been grown by the top-seeded solution growth (TSSG) method for the first time with a purpose of exploring new ferroelectric single crystals with high piezoelectric properties, and which was characterized by structural analysis and electrical measurements. The rhombohedral and tetragonal phases co-exist in the as-grown crystals, which belong to the morphotropic phase boundary (MPB) region. The Curie temperature \( T_C \) and the rhombohedral-tetragonal phase transition temperature \( T_{RT} \) reached 125 °C and 90 °C. The dielectric constant \( \varepsilon' \), dielectric loss tangent \( \tan\delta \), piezoelectric coefficient \( d_{33} \), longitudinal electromechanical coupling coefficient \( k_{33} \), remnant polarization \( P_r \) and coercive field \( E_c \) were found to be 1280, 0.04, 1344 pC/N, 82%, 21.4\(\mu\)C/cm\(^2\), 3.4 kV/cm, for [001]-oriented crystals at room temperature, respectively. These results show that the PYN-PMN-PT(22/44/34) crystals are a promising candidate for uses in electromechanical transducers for

* Corresponding Author: Phone: (86)-591-83710369; Fax: (86)-591-83714946 Email: lxf@fjirsm.ac.cn
applications.

1. Introduction

Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PMN-PT) single crystals have attracted much attention due to their high piezoelectric coefficients, large longitudinal electromechanical coupling factors, high dielectric constants, low dielectric losses and exceptionally high strain levels, with compositions close to or within the morphotropic phase boundary (MPB) region in the past years.\textsuperscript{1-15} However, there are some drawbacks in this system. The Curie temperature ($T_C$) of PMN-PT crystals near the MPB range is only about 150 °C, and even lower is the rhombohedral-tetragonal phase transition temperature ($T_{RT}$) which is about 80°C.\textsuperscript{16-17} The low values of these two temperatures make the materials depoled easily, greatly limiting their applications in the high temperature range. Another drawback is the low coercive field ($E_c = 2 - 3$ kV/cm) of the PMN-PT crystals, which causes the crystals to depole very easily and thereby their piezoelectric performance to degrade, limiting their application in high power field.

More recently, great interest has been paid in introduction of Pb(B’B’’)O\textsubscript{3} (B’ = Yb\textsuperscript{3+}, In\textsuperscript{3+}, Sc\textsuperscript{3+}, ⋯; B’’ = Nb\textsuperscript{5+}, ⋯) into PMN-PT systems, for example,

\begin{align*}
\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{PbTiO}_3 \quad \text{(PYbN-PMN-PT)}, \quad \text{\textsuperscript{18-19}}
\end{align*}

\begin{align*}
\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{PbTiO}_3 \quad \text{(PSN-PMN-PT)}, \quad \text{\textsuperscript{20}}
\end{align*}

\begin{align*}
\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{PbTiO}_3 \quad \text{(PIN-PMN-PT)}, \quad \text{\textsuperscript{21-25}}
\end{align*}

which show promising piezoelectric properties and a higher Curie temperature.

The structure of the Pb(Y\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}(PYN) belongs to complex perovskite ABO\textsubscript{3} family with Y\textsuperscript{3+} and Nb\textsuperscript{5+} ordered on the B-site. It is reported that PYN has a
pseudo-monoclinic antiferroelectric phase at room temperature, and varied to paraelectric phase at around 342 °C.\textsuperscript{26-27} Therefore, great interest has been paid in PYN as an end member in Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PZT) in order to improve the ferroelectric and piezoelectric properties.\textsuperscript{28-29} We believe that PYN can form a solid solution with PMN-PT, which should present an MPB and exhibit good electric properties compared with the PMN-PT crystals. In this work, the crystal of PMN-PT doped with PYN was grown by the top-seeded solution growth method for the first time and the ferroelectric and piezoelectric properties were characterized.

2. Experiments

2.1 Crystal growth

The PYN-PMN-PT single crystals were grown by the TSSG method. The starting chemicals, PbO (99.99%), TiO\textsubscript{2} (99.90%), MgO (99.90%), Nb\textsubscript{2}O\textsubscript{5} (99.90%), Y\textsubscript{2}O\textsubscript{3} (99.99%) and H\textsubscript{3}BO\textsubscript{3} (99.90%), were weighed according to the stoichiometric composition of 0.22PYN-0.44PMN-0.34PT (PYN-PMN-PT(22/44/34)). A mixture of PbO and H\textsubscript{3}BO\textsubscript{3} (with a molar ratio of PbO:H\textsubscript{3}BO\textsubscript{3} = 5:1) was used as high-temperature solution. A flux to solute molar ratio of 5:1 was used. The mixed chemicals were heated to 1050 °C at a rate of 100 °C/h in a Pt crucible with a size of $\Phi$60×55 mm\textsuperscript{2} in a vertical tubular furnace, and then slowly cooled down from 1050 °C to 900 °C with a Pt wire was used as seed at a rate between 0.5 and 2 °C/h. At the last stage, the grown crystal was pulled out of the melt surface and then cooled down to room temperature at a rate of 20 °C/h. Finally, PYN-PMN-PT(22/44/34) polycrystal
was obtained, as shown in Fig. 1a.

Then, a small [001]_cub-oriented PYN-PMN-PT single crystal cutting from the grown polycrystal was used as seed and the saturation temperature of the solution was determined accurately by repeated seeding trials. The starting chemicals and the mixture of high-temperature solution were same as above. The crystal growth took place upon cooling from 1020 °C to 920 °C at a rate of 0.2 °C/h. At the end of a slow cooling process, the grown crystal was pulled out of the melt surface and then cooled down to room temperature at a rate of 20 °C/h. A brown quadrate single crystal with dimensions of 26 × 26 × 10 mm³ was obtained, as show in Fig. 1b.

2.2 Characterization procedure

The structural analysis and sample orientation were performed by means of X-ray diffraction (XRD) at room temperature on a Rigaku diffractometer (Rigaku, Japan) equipped with Cu Kα radiation and a graphite monochromator. The data were collected with a scan step of 0.02° (2θ) and an angular range of 10 - 80°. A polarized light microscope (LV100POL, Nikon, Japan) was employed to determined the phase and electric domain of the as-grown PYN-PMN-PT(22/44/34) crystals. The [001]_cub-oriented crystal samples were cut from the as-grown crystal (bar and platelet). All the samples were polished and coated with silver paste on the [001]_cub faces as electrodes. A platelet sample with dimensions of 2.44×2.98×1.18 mm³ was used for dielectric, piezoelectric and ferroelectric measurements. For resonance and anti-resonance measurements, a bar sample with dimensions of 1.13×1.28×3.64
mm$^3$ was prepared. The dielectric constant ($\varepsilon'$) and dielectric loss tangent ($\tan\delta$) were measured at various frequencies as a function of temperature upon heating from –50 °C to 300 °C using a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (Novocontrol GmbH, Germany), with an AC signal of 1V (peak-to-peak) applied. The resonance ($f_a$) and anti-resonance ($f_r$) frequencies of the bar sample at different temperature a step of 5 °C from 20 °C to 150 °C as a function of frequencies were measured. Poling was performed by applying a DC electric field of 1kV and 3kV along the [001] direction for the platelet and bar of the crystal respectively at 120 °C for 15 min, and then keeping the field on while cooling down to room temperature. Piezoelectric coefficient was measured using a quasistatic $d_{33}$ meter (Institute of Acoustics, Chinese Academy of Sciences, model ZJ-4AN). The ferroelectric hysteresis loops were measured using an aix-ACCT TF2000 analyzer (at the frequencies $f=2$Hz).

3. Results and discussion

3.1 Structural analysis and phase of crystals

Fig. 2 presents the powder XRD pattern for grown PYN-PMN-PT(22/44/34) crystal measured at room temperature, showing a pure perovskite phase. In order to accurately study the structure of PYN-PMN-PT(22/44/34) at room temperature in more detail, special attention was concentrated on the (200) reflections around $2\theta = 45^\circ$. It is well known that the XRD profiles of the (200) reflections will show only a single peak R(200) in the rhombohedral structure because all the (200) planes share
the same lattice parameters, whereas in the tetragonal phase the (200) reflections should be split into two peaks, the T(200)/(020) and T(002) profiles. As shown in the insets in Fig. 2, for PYN-PMN-PT(22/44/34) crystal, the (200) reflection is composed of only one single peak, which corresponds to the rhombohedral or pseudo-cubic phase. The lattice parameters of the single crystals were refined to be a = 4.034 Å and α = 89.956 °, based on the XRD data.

Actually, the XRD profiles of the (200) reflections show a little wider peak, which indicate the existence of the tetragonal phase. A polarized light microscope was employed in order to approve this conclusion. The vibration directions of all the domains in the [001]-oriented plate are practically parallel or perpendicular to each other and the extinction angle θ determined as the smaller angle between the domain’s vibration direction and the [100] crystallographic axis is practically the same for all domains, namely, θ =45° in the R phase and θ =0° in the T phase. Fig. 3 shows the electric domain micrographs of the [001]-oriented plate of the PYN-PMN-PT(22/44/34) crystal with a thick of 46µm. When the crossed polar light are in the [100] position as shown in Fig. 3a, the crystal shows some bright regions, labeled for R. The corresponding bright areas appear to be in extinction when θ =45° as shown in Fig. 3b, which indicate the as-grown crystal belongs to rhombohedral symmetry. On the other hand, the black regions in Fig. 3a, labeled for T, become bright when θ =45° in Fig. 3b which indicate the existence of tetragonal symmetry. In conclusion, the rhombohedral and tetragonal phases co-exist in the as-grown crystals, which belong to the morphotropic phase boundary (MPB) region.
3.2 Dielectric Properties

Fig. 4a shows the variations of the dielectric constant (ε’) and dielectric loss tangent (tanδ) of the unpoled [001]-oriented PYN-PMN-PT(22/44/34) crystal sample as a function of temperature at the frequencies of 1 Hz, 100 Hz, 10K Hz and 1000kHz. The maximum of dielectric constant indicates a Curie temperature $T_C$ of 125 °C (at 10 kHz). In order to determine the rhombohedral-tetragonal phase transition temperature $T_{RT}$ of the crystal, the dielectric constant (ε’) and dielectric loss tangent (tanδ) of the poled platelet sample were measured as the function of the temperature, as shown in Fig. 4b. The dielectric anomaly observed around 90 °C in Fig. 4b corresponding to the rhombohedral-tetragonal phase transition temperature $T_{R/T}$. The dielectric constant and loss tangent for the poled sample are 1280 and 0.04, respectively, at room temperature.

Furthermore, the dielectric constant shows a relative broad maximum with frequency dispersion, the temperature of which ($T_m$) shifts to higher temperature with the increasing frequency, indicating typical dielectric relaxor behavior\textsuperscript{12,32,33}. In normal ferroelectrics, the temperature dependence of the dielectric constant above the Curie temperature obeys the Curie-Weiss law: $1/\varepsilon’ = (T - T_{CW})/C$, where $C$ is the Curie constant and $T_{CW}$ is the Curie-Weiss temperature. However, in relaxor ones, the dependence relation deviates the Curie-Weiss law due to short-range correlations between polar regions.\textsuperscript{12,34} In a wide range above $T_m$ and below Burns temperature ($T_b$), the temperature dependence of $1/\varepsilon’$ follows the Lorentz-type quadratic
\[
\frac{\varepsilon_\perp}{\varepsilon'} - 1 = \frac{(T - T_A)^2}{2\delta^2}
\]

(1)

where \( T_A \) and \( \varepsilon_A \) are the fitting parameters and \( \delta \) is a measure of the degree of diffuseness of the permittivity peak. Figure 5 shows the temperature dependence of \( 1/\varepsilon' \) (at 100 kHz) for the grown crystal. It can be seen that the data can be well fitted into the Lorentz-type quadratic relationship with parameters of \( \varepsilon_A = 22506, \delta = 50.43 \) ºC, \( T_A = 103.50 \) ºC.

### 3.3 Electromechanical Coupling and Piezoelectric Properties

In order to determine the electromechanical coupling factor \( (k_{33}) \), the resonance \( (f_r) \) and antiresonance \( (f_a) \) frequencies for the crystal sample at various temperature were measured. The longitudinal electromechanical coupling factor \( (k_{33}) \) was derived by the following equation:\(^{38-39}\)

\[
k_{33}^2 = \frac{\pi}{2} \frac{f_r}{f_a} \cot \left( \frac{\pi}{2} \frac{f_r}{f_a} \right)
\]

(2)

Figure 6 shows the impedance and phase angle as functions of frequency for the PYN-PMN-PT(22/44/34) single crystal at the temperature of 55 ºC. It can be seen that impedance spectrum shows two peaks at \( 1.75\times10^5 \) and \( 2.77\times10^5 \) Hz, indicating resonance frequencies \( f_r \) and \( f_a \), respectively. The \( k_{33} \) derived from equation (2) is 80.61% at temperature of 55 ºC.

Figure 7 shows the variation of electromechanical coupling factor as a function of temperature. It can be seen that \( k_{33} \) remains at a high value of 78-82% in the
temperature range of 20 °C up to about 80°C. And then suddenly decrease to 51-53% at the temperature range of 90 °C - 125°C, which is believed to result from the rhombohedral-tetragonal phase transition before dropping down at the Curie temperature of 125°C. The $k_{33}$ steeply drops toward zero at above $T_c$, which indicates the crystal belong to the paraelectric phase. The piezoelectric coefficient $d_{33}$ was measured to be 1344 pC/N at room temperature using a quasistatic $d_{33}$ meter.

3.4 Ferroelectric properties

The ferroelectric properties of the PYN-PMN-PT(22/44/34) crystals were revealed by the well-developed polarization-electric field hysteresis loops measured at room temperatures, as displayed in Figure 8. The saturation of polarization is achieved at an electric field of $\pm 7$ kV/cm and at room temperature. The coercive field $E_c$ and remnant polarization $P_r$ are found to be 3.4 kV/cm and 24.1 $\mu$C/cm$^2$, respectively. The coercive field $E_C$ of the PYN-PMN-PT(22/44/34) crystals is higher than that of PMNT crystals, indicating a higher stability for the poled state.

4. Conclusions

The ternary piezoelectric single crystals of PYN-PMN-PT(22/44/34) with dimensions of $26 \times 26 \times 10$ mm$^3$ have been successfully grown for the first time by the TSSG method, which presents pure perovskite structure. The dielectric/piezo-/ferroelectric properties of the grown crystals were investigated. The Curie temperature $T_C$ and the rhombohedral-tetragonal phase transition temperature $T_{RT}$
reached 125 °C and 90 °C. The piezoelectric coefficient $d_{33}$ is about 1344 pC/N and the longitudinal electromechanical coupling coefficient $k_{33}$ remains consistently high (78 – 82%) from room temperature up to 80 °C. The remanent polarization $P_r$ and coercive field $E_c$ were found to be 21.4µC/cm$^2$, 3.4 kV/cm, for [001]-oriented crystals at room temperature, respectively. These results demonstrate that the PYN-PMN-PT(22/44/34) crystals are a promising candidate for uses in electromechanical transducers for high-power applications. PYN-PMN-PT(22/44/34) crystals are a promising candidate for uses in electromechanical transducers for applications.

Acknowledgments

This work was supported by the Fund of Key Laboratory of Optoelectronic Materials Chemistry and Physics, Chinese Academy of Sciences (2010KL007), the National High Technology Research and Development Program of China (863 Program) under grant No.2011AA030208, the National Natural Science Foundation of China under Grant No. 91122020.

References


11. A. Sehirlioglu, D.A. Payne, P. J. Han, Appl. Phys. 2006, 99, 064101.


Figure captions

Fig. 1 Photograph of as-grown PYN-PMN-PT(22/44/34) crystals.

Fig. 2 X-ray powder diffraction patterns of the grown PYN-PMN-PT(22/44/34) crystals; (200) reflections composed of one single peak, suggesting rhombohedral symmetry at room temperature as shown in the insets.

Fig. 3 Electric domain micrographs of (001) plate of PYN-PMN-PT(22/44/34) crystal under crossed polar (a) Polarization direction; (b) 45° extinction direction.

Fig. 4 Variations of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) of (001)-oriented PYN-PMN-PT(22/44/34) crystals as a function of temperature measured at 1 Hz, 100 Hz, 10K Hz and 1000kHz: (a) unpoled; (b) poled.

Fig. 5 Temperature dependence of $1/\varepsilon'$ at 1 kHz for the PYN-PMN-PT(22/44/34) crystal; The insets show the fitting to the Lorentz-type quadratic relationship.
**Fig. 6** Frequency dependences of the impedance and phase angle of the PYN-PMN-PT(22/44/34) crystals measured at room temperature.

**Fig. 7** Temperature dependence of the electromechanical coupling factor $k_{33}$ of a (001)-oriented PYN-PMN-PT(22/44/34) crystal bar.

**Fig. 8** Ferroelectric hysteresis loop of (001)-oriented PYN-PMN-PT(22/44/34) single crystals at room temperature.
Fig. 2

Fig. 3
Fig. 4

Fig. 5

Fig. 6
Fig. 7

Fig. 8
Abstract

A ternary piezo-/ferroelectric crystal of 0.22Pb(Y_{1/2}Nb_{1/2})O_3-0.44 Pb(Mg_{1/3}Nb_{2/3})O_3-0.34PbTiO_3 (PYN-PMN-PT(22/44/34)) with dimensions of 26 × 26 × 10 mm³ has been grown by the top-seeded solution growth (TSSG) method for the first time with a purpose of exploring new ferroelectric single crystals with high piezoelectric properties, and which was characterized by structural analysis and electrical measurements. The rhombohedral and tetragonal phases co-exist in the as-grown crystals, which belong to the morphotropic phase boundary (MPB) region. The Curie temperature $T_C$ and the rhombohedral-tetragonal phase transition temperature $T_{RT}$ reached 125 °C and 90 °C. The dielectric constant $\varepsilon'$, dielectric loss tangent $\tan\delta$, piezoelectric coefficient $d_{33}$, longitudinal electromechanical coupling coefficient $k_{33}$, remnant polarization $P_r$ and coercive field $E_c$ were found to be 1280, 0.04, 1344 pC/N, 82%, 21.4µC/cm², 3.4 kV/cm, for [001]-oriented crystals at room temperature, respectively. These results show that the PYN-PMN-PT(22/44/34) crystals are a promising candidate for uses in electromechanical transducers for applications.