Aging rate of dielectric permittivity and loss for PMN–PT based single crystals manufactured by continuous-feeding Bridgman with alternating current poling

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Aging rate (AR) of dielectric permittivity ($\varepsilon_{33}^1/\varepsilon_0$) of ternary Pb(In₁/₂Nb₁/₂)O₃–Pb(Mg₁/₃Nb₂/₃)O₃–xPbTiO₃ (PIN–PMN–xPT, $x = 26$ and 30 mol %) and binary Pb(Mg₁/₃Nb₂/₃)O₃–xPbTiO₃ (PMN–xPT, $x = 30$ mol %) single crystals (SCs) grown by the continuous-feeding Bridgman method (CF-BM) were investigated. The AR of dielectric permittivity was 0.6–2.0 %/decade, whereas that of dielectric loss of the SCs was 1–8 %/decade. Even though the SC growth methods were different, the AR of CF-BM PMN–30PT SCs were similar with that of conventional one-charge Bridgman method (OC-BM) SCs. In this work, the AR of the SCs possessing high $\varepsilon_{33}^1/\varepsilon_0$ more than 8000 by alternating current poling (ACP) was 4 to 7 times larger than that of PZT ceramics. It is noted that SCs with higher $\varepsilon_{33}^1/\varepsilon_0$ tend to exhibit higher AR. Given that the SCs were in an unstable state within 10 h after poling, the AR presented in this paper was calculated from 10 to 100 h after poling. We hope this work provides a new insight for evaluating the properties of the SCs and addresses the fact that SCs for piezoelectric devices should be properly selected by considering whether their AR could let them work normally during their entire lifetime.

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technique, continuous-feeding Bridgman method (CF-BM), was suggested and well succeeded in controlling the compositional uniformity. As a result, large-sized PMN–PT SC ingots (80 mm in diameter, 320 mm in length, and 13 kg of weight) were commercially manufactured since 2011. For ferroelectric-based piezoelectric materials to be macroscopically piezoelectric, poling is an indispensable process to align randomly-distributed domains and thus obtain high piezoelectric and dielectric properties. A direct current poling (DCP) has been widely used for such domain-texturing processes. However, since the first demonstrations of a dynamic alternating current poling (ACP) by Yamamoto and Yamashita et al., it has been of considerable importance due to its further enhancements in dielectric and piezoelectric properties. So far, more than 20 papers relevant to ACP have been reported in the past few years.

Aging is namely a time-dependent spontaneous variation under the absence of external stress and electric field. It is generally accepted that thermodynamic equilibrium states associated with defects are responsible for the aging, and linear correlations with the log time scale are commonly believed in aging behaviors. For medical US probes or other applications, the fast aging of given materials is a critical obstacle and thus deteriorates the qualities of images with their shorter lifetimes. Though the aging rate (AR) of ferroelectric ceramics have been already studied by many researchers, there are few studies on the AR of dielectric permittivity \( (\varepsilon_{33}^T/\varepsilon_0) \) and loss of relaxor-based SCs. It is worthy noted that Chang et al. reported the AR of OC-BM PMN–30PT SC by DCP and ACP were 1.25 and 1.95 %/decade, respectively. However, the AR of loss in PMN–30PT SCs was not primarily investigated and discussed in the aforementioned literature. Therefore, the purpose of the current work is to systematically study the AR of compositionally dissimilar (PIN)–PMN–PT SCs manufactured by the state of art CF-BM SC growth methods. Under different poling conditions including ACP and DCP, comparative experiments were conducted to study how dielectric properties are varied in comparison with commercialized PZT ceramics (\( \varepsilon_{33}^T/\varepsilon_0 > 5000 \)).

2. Experiment

Figure 1 shows the schematic illustrations of (a) the OC-BM in which compositional segregations naturally occur during crystal growth and (b) the CF-BM wherein raw materials are continuously added into a Pt crucible during crystal growth to ensure consistency in properties. The variations of \( \text{TiO}_2 \) contents within the ingot of the OC-BM and CF-BM were reported as ±4 and ±0.5 mol %, respectively.

[001]-oriented PMN–30PT, PIN–PMN–30PT and PIN–PMN–26PT wafers from [011] grown ingots (JFE Mineral Co., Japan) were prepared by the CF-BM method. Furthermore, in order to compare aging properties between high performance PZT ceramics and SCs above, two kinds of PZT ceramics, i.e., PZT 5H and PZT K5500 (Tayca Co., Japan), were also prepared as comparisons.

Figure 2 provides (a) the as [110]-grown CF-BM PMN–30PT SC (D80 x L320 mm and 13 kg) ingot, (b) a [001]-cut egg-shaped SC wafer [short diameter (SD) 80 and long diameter (LD) 110 x 0.5 mm] and (c) the dimension of PIN–PMN–30PT, PIN–PMN–26PT and PZT ceramics is 7 x 5 x 0.4, 10 x 2.4 x 0.5 and 12 x 3 x 0.5 mm\(^3\), respectively. All samples used in the current experiments were sputtered with Au/NiCr electrodes. The uniformity of \( \text{TiO}_2 \) contents within the ingots and wafers were guaranteed up to ±0.5 mol %.

Since AC voltages in terms of its involved energy vary with respect to the shape of waveforms, we adopted root mean square (rms) voltages for all ACP conditions in order to compare with DC voltages. The term ‘rms voltage’ also known as the effective or heating rate of alternating current is associated with the generation of identical heat at the same time in a capacitor. Therefore, the AC voltages can be properly compared with the DC voltages.
The SCs were ACP using bipolar sine waves in the air from temperature of 40 to 80 °C with electric fields of 3–9 kV rms/cm, 0.1–50 Hz and 12–100 cycles. To compare with the ACP effect of the SCs, we also performed DCP in the air from temperatures of 40–80 °C with electric fields of 3–8 kV cm−1 for 60–300 s. In addition, PZT 5H and PZT K5500 plates were DCP in silicone oil with 20 kV/cm at 80 °C for 600 s. The specific poling conditions for the samples are shown in Table 1.

Their dielectric capacitance and loss were measured 0.1h after poling at 23–27 °C. The free $\varepsilon_{33}^T/\varepsilon_0$ and clamped dielectric permittivity ($\varepsilon_{33}^S/\varepsilon_0$) were calculated from the capacitances measured by an impedance analyzer (HP 4194 A, USA) at 1 kHz and at the two times of anti-resonant frequency ($2f_a$), respectively. Calculated bar mode electromechanical coupling factors ($k_{33}$) were obtained from $\varepsilon_{33}^T/\varepsilon_0$ and $\varepsilon_{33}^S/\varepsilon_0$ according to the following Eq. (1).

$$k_{33} = \sqrt{\frac{\varepsilon_{33}^T/\varepsilon_0 - \varepsilon_{33}^S/\varepsilon_0}{\varepsilon_{33}^T/\varepsilon_0}}$$

As relaxor-PT SCs are very sensitive to external temperatures, we modified $\varepsilon_{33}^T/\varepsilon_0$ values that were not measured at 25.0 °C according to the Electronic Industries Alliance (EIA) 198-1 standard by the following formula (2):

$$MC_{25} = \frac{MC_T}{1 + TDC \times (T - 25.0)}$$

$MC_{25}$ is a material property at 25.0 °C, $MC_T$ is a material property at a measured temperature, and $T$ is a measured temperature according to the EIA standard. TDC is a temperature dependence coefficient and relaxor-PT SCs have usually large TDC reported by Luo et al. and Sun et al.

AR of $\varepsilon_{33}^T/\varepsilon_0$ and dielectric loss for samples were calculated by the following formula (3).
after 1 and 1700 h were measured at the room temperature. This may be the reason why ACP for 2 s had the same AR(0 time) as DCP CF-BM PMN 0 (100 h) and between AR(loss) and dielectric permittivity (TDDP&L) of PZT 5H. Its Curie temperature (Tc) decreased by about 4°C after DCP compared with the unpoled PZT 5H samples.

In order to show the AR properties of all samples in the current experiments, the relationships between AR(©33/©0) and ©33/©0 (100 h) and between AR(loss) and dielectric loss (100 h) are shown in Fig. 6. It is worth noting that the AR(©33/©0) of all samples varies from 0.3–2.0%/decade, and the SCs possessing higher ©33/©0 tend to show faster AR(©33/©0). The PZT K5500 has almost the same ©33/©0 as DCP CF-BM PMN–30PT over 5800, and it has lower AR(©33/©0). We consider that how to decrease the AR of high-performance SCs is our future works.

The AR(loss) of all samples varied from 1–8%/decade. In addition, the AR(loss) of most samples was higher than their AR©33/©0), which is consistent with the conclusions of most cases, i.e., the rate of dielectric loss is higher than that of capacitance.49) In Figs. 4(a) and 4(b), due to the different poling methods, the variational trends of dielectric loss in short time (0.1–1 h) and medium time (1–10 h) were different. As even some samples exhibit drastic
changes, thus we showed all AR(loss) were in the range of the long time (10−100 h).

The cause of aging is generally believed to be that after the poling electric field be removed, the domain gradually returns to the orientation before poling treatment to eliminate internal stress reported by Schulze and Ogino. The internal bias field could promote domain recovery, so the larger the internal bias field is, the more serious the aging is. And the mechanical quality factor ($Q_m$) of PZT ceramics increase with the increase of internal bias field.
reported by Book “Ferroelectric Physics” edited by W.-L. Zhong.\textsuperscript{56) By investigating the $Q_m$ of all samples in this work, for same composition, the sample with larger $Q_m$ tends to show higher AR, which is consistent with the above description about aging of PZT ceramics K5500.

In order to figure out how phase transition temperatures (Trt) of the samples are changed after different poling conditions and whether ACP has a positive effect on samples, we measured TDDP&L for all SC samples. The TDDP&L of PIN–PMN–30PT SC poled by ACP and DCP is shown in Fig. 7.

The Trt of CF-BM PIN–PMN–30PT was 102 °C before poling\textsuperscript{26) and it increased by 5.5 °C after ACP while it decreased by 0.7 °C after DCP. The Trt shift after the ACP of the CF-BM 24PIN–46PMN–30PT SC in this study and the OC-BM 25PIN–43PMN–32PT SC reported by Ma were similar.\textsuperscript{40) As shown in Fig. 8, the Trt of PIN–PMN–26PT after DCP greatly increased by 7 °C. However, by using 3 kVrms/cm voltage, the ACP samples showed that Trt decreased by 2.7 °C and by using 8 kVrms/cm voltage ACP sample showed Trt decreased by 4.1 °C compared with the unpoled samples Trt of which was 138 °C.\textsuperscript{26} This result indicated that the Trt shift are different between high Trt > 130 °C and low Trt < 110 °C ternary PIN–PMN–xPT SCs.

According to Fig. 9, Trt of the CF-BM PMN–30PT decreased from 92\textsuperscript{26) to 88.3 °C after ACP and to 80.3 °C after DCP.

As we can see in Figs. 7–9, the dielectric properties of SCs in the room temperature are correlated with the position of phase change temperature Trt. Therefore, the temperature dependence of dielectric permittivity of each SC is very important to indicate these AR and phase change phenomena.

We suspected that AR was caused by the change of lattice constant of the SCs after poling time. Therefore, the XRD of (004) surface of the PIN–PMN–30PT after poling 1 and 1700 h was investigated.

In Fig. 10, the DC poled PIN–PMN–30PT showed lower peak intensity with lower angle (99.13°), and by ACP method, peak of (004) of PIN–PMN–30PT moved to higher angle (99.30°), considering that it is caused by the decrease of $c$-axis in lattice constant. Besides, the higher dielectric properties are responsible for the higher peak intensity and angle shift, which is consistent with conclusion of Luo et al.\textsuperscript{38,45) However, there are no big differences of XRD between 1 and 1700 h, showing that the AR is not caused by a large lattice constant change after poling.

4. Conclusion

In summary, the aging properties (dielectric permittivity and loss) of [001]-oriented PIN–PMN–PT and PMN–PT SCs manufactured by CF-BM with respect to different poling conditions and compositions were investigated for
the first time. It should be noted that relaxor-SCs possessing higher $\varepsilon_{33}^0/\varepsilon_0$ tend to show higher AR, while PZT ceramics showed low AR, which indicates that PZT ceramics have excellent time stability. We speculated the reason why the ARs of various SC samples were different is due to different propensity in domain recovery after poling. Given that internal bias field $E_i$ can promote domain recovery, the higher the $E_i$, the faster the AR. In addition, $E_i$ and mechanical quality factor $Q_m$ are positively correlated in PZT systems. Therefore, we investigated the $Q_m$ of all samples and found that the SCs with large $Q_m$ tend to show large AR($\varepsilon_{33}^0/\varepsilon_0$). These AR of the CF-BM PMN–30PT SCs were similar with that of conventional OC-BM SCs even though the SC growth method is different. To our best knowledge, the aging of dielectric loss, at present, has not been systematically studied, and we claim that more investigations are still needed. For the SCs, their dielectric losses were quite low (0.2–0.4 %), but their AR were very high (1–8 %/decade). Meanwhile, the dielectric loss of PZT ceramics was much higher (1.3–1.8 %) than that of the SCs. However, their AR were at low level (3 %/decade) and proved good stabilities in this experiment. Although the AR($\varepsilon_{33}^0/\varepsilon_0$) of some SCs were higher than those high performance PZT, the absolute value of $\varepsilon_{33}^0/\varepsilon_0$ decrease is acceptable in the lifetime of practical applications. This experiment may provide a new insight to evaluate the performance of the SCs. As future studies, we will focus on how to reduce the AR of high $\varepsilon_{33}^0/\varepsilon_0$ SC, which stabilizes and prolongs the lifetime of devices. We hope the current work may have a positive impact on ultrasound applications.

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