

AGING BEHAVIOR OF NB-DOPED $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ CERAMICS

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Received: September 06, 2017; Revised: December 01, 2017; Accepted: December 13, 2017

Abstract

In this work, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ PZT ceramics with the addition of x mole% Nb_2O_5 , where $x = 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6 , were prepared by a mixed-oxide technique and solid-state sintering. Poled samples were heated at 500 and 600°C for temperature treatment, and then left for 30 and 60 days aging. To observe the aging behavior, the strain and polarization were measured by modified interferometry technique with a Sawyer-Tower circuit at the time after heat treatment and aging. The results showed that 600°C was required to release the poling effect. The accompanied electrical loss due to heat treatment disappeared when the samples were aged and there was, therefore, less spontaneous polarization.

Keywords: Ferroelectric, optical interferometry, soft doped PZT, aging

Introduction

Lead zirconate titanate (PZT) is well known for ferroelectric devices used in many applications such as high permittivity dielectrics, piezoelectric devices, composite materials, energy harvesters, transducers,

actuators, and sensors. When the perovskite structure of PZT is modified, the character can turn to hard PZT (acceptor doping) or soft PZT (donor doping) (Somwan *et al.*, 2016a; Uchino, 2017). Large piezoelectric properties

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were observed in soft PZT, where the A site or B site of the ABO_3 perovskite structure was replaced by donor ions such as La^{+3} , W^{+6} or Sb^{+5} , Nb^{+5} . At the morphotropic phase boundary (MPB), the phase structure between rhombohedral and tetragonal coexists with the Zr/Ti ratio of 52/48 (Ketsuwan *et al.*, 2007, 2008).

The reliability of a ferroelectric device is necessary and it is related to reproducibility, temperature characteristics, electric field, stress dependence, and the effect of aging. Unfortunately for the long-term use, the ferroelectric properties are degraded by the aging and fatigue phenomena. First, ferroelectric degradation relates to the elapsed time at the equilibrium condition. And secondly, ferroelectric degradation is subjected to the loading process at the use time. Ferroelectric aging is related to composition, structure, and defects after ceramic fabrication in order to release the internal energy (electrical or elastic energy) (Damjanovic, 2005; Somwan and Ngamjarujana, 2015). The aging mechanisms are still discussed in association with charge or defect migration as the volume effect, domain effect, and grain boundary effect. The defect moving over the short-range or long-range is associated to the poled or unpoled state of ferroelectric samples, the AC or DC sample conductivity in terms of space charge migration (Chen *et al.*, 2013; Genenko *et al.*, 2015), where the electrical properties in PZT are related to the doping concentration (Ketsuwan *et al.*, 2008). Recently, aging degradation associated to the heat treatment temperature near the Curie temperature (Promsawat *et al.*, 2017), the degradation of PZT caused by thermal treatment (Alguero *et al.*, 2000), and hard ferroelectric PZT behavior after thermal de-aging has resulted from the poling effect and depends on the PZT phase structure (Kamel and With, 2008).

In this study, lead zirconate titanate in the composition near the morphotropic phase boundary $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ of PZT ceramics, doped with x mole% of Nb_2O_5 , where $x = 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6 , was fabricated. The heat treatment dependence of the polarization and strain behavior at 500°C (fresh) and 600°C

(refreshed) of 20 kV/cm poled samples was investigated and then the frequency dependence of the polarization and strain of the 60 days aging phenomenon was determined to observe the effect of Nb additions to PZT.

Materials and Methods

$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ PZT ceramics with the addition by x wt% of Nb_2O_5 , where $x = 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6 , were fabricated by oxide mixing of solid solution methods and sintered at 1250°C for 2 h. Samples were subjected to 20 kV/cm of poled field at 120°C for 25 min in silicone oil. After that, the first heat treatment at the temperature of 500°C was applied to the fresh samples, and the electric field-induced polarization and strain were measured when the samples were fresh and after 30 days of aging. Next, the second heat treatment temperature of 600°C was applied, and the electric field-induced polarization and strain were measured when the samples were refreshed and after 60 days aging. The measurement was modified by a Sawyer-Tower circuit with the Michelson interferometric technique (Helium-Neon laser; $\lambda = 632.8$ nm) (Somwan and Ngamjarujana, 2015) under the influence of various applied electric frequencies. The signals were detected and recorded to a PC to investigate the effects of the heat treatment temperatures to poled samples and the electric field-induced polarization and strain at various frequencies in the aging phenomenon.

Results and Discussion

Figure 1 shows the polarization and strain of Nb-doped PZT ceramics at 0.2 Hz of electric field frequency after heat treatment at 500°C (fresh; black line) and 600°C (refreshed; gray line). For the 0.1 Nb-doped PZT sample, the polarization and strain of the 500°C heat treatment temperature had less polarization and strain than at 600°C , and a slim strain-like saturated strain of the hard ferroelectric sample (Jin *et al.*, 2014; Promsawat *et al.*, 2017) was

observed when the positive electric field was increased to maximum, possibly due to the higher energy required to release the electric poling effect. The higher value of the strain and non-slim strain loop is seen when the 600°C heat treatment temperature was applied. In the case of the 0.2 Nb-doped PZT sample, the polarization and strain values were close for the 500 and 600°C of heat treatment due to the soft ferroelectric behavior (Promsawat *et al.*, 2017; Jin *et al.*, 2014), whereas in the case of the 0.3 Nb-doped PZT sample, the higher polarization and strain was obtained when the sample was treated at 500°C and an accompanying high remnant polarization due to electrical loss was dominant especially at the low electric field frequency (Somwan and Ngamjarurojana, 2015). In other cases of x Nb-doped PZT samples where $x = 0.4, 0.5$, and 0.6 , the less spontaneous polarization was dominant due to the higher doping concentrations (Ketsuwan *et al.*, 2008), as the polarization and strain had lower values. Electrical loss was present in the 0.6 Nb-doped PZT sample with the accompanying high strain when heat-treated at 500°C like the 0.3 Nb-doped PZT sample. Finally, for all samples, the symmetry of the strain can be

seen as a result of the heat treatment temperature at 600°C rather than at 500°C.

Figure 2 shows the polarization and strain of the Nb-doped PZT ceramics at 0.2 Hz electric field frequency aged at 30 and 60 days, after 500°C (fresh; black line) and then 600°C (refreshed; gray line) heat treatment temperatures, respectively. In the case of the 0.1 and 0.2 Nb-doped PZT samples, polarization was decreased and the values of polarization of both the 500°C and 600°C heat treatment temperatures were not significantly different due to reduced electrical energy resulting from the aging phenomenon. But higher strain was observed at the 600°C heat treatment temperature, especially for the 0.2 Nb-doped PZT sample. Asymmetry of strain refers to the preferred domain direction according to the reduced elastic energy of the aging phenomenon, whereas in the case of the 0.3 Nb-doped PZT sample, polarization still showed high values after aging at 500°C of heat treatment, like the electrical loss which dominated, but this loss disappeared when the heat treatment was at 600°C. The higher decrease of the asymmetry of the strain was present for both 500°C and 600°C. In the case of the x Nb-doped PZT samples where $x = 0.4$,

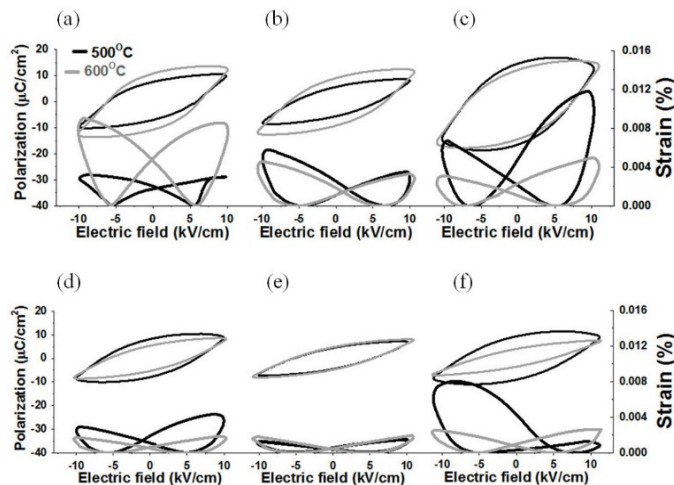


Figure 1. Polarization and strain of Nb-doped PZT ceramics when heat-treated at 500°C (black) and then 600°C (gray) of: (a) 0.1 mol%, (b) 0.2 mol%, (c) 0.3 mol%, (d) 0.4 mol%, (e) 0.5 mol%, and (f) 0.6 mol%

0.5, and 0.6, the polarization and strain were decreased due to the less spontaneous polarization of the aging phenomenon. Therefore, the effect of Nb-doping at a higher content ($x > 0.3$) will not be discussed from now on.

In Figure 3, it can be seen that the polarization and strain were decreased as a function of the frequencies due to the frequency dependence of domain switching (Delibas *et al.*, 2006; Somwan *et al.*, 2014, 2016b), for both the 600°C (refreshed) heat treatment temperature and 60 days aging. After 60 days, the decrease of the polarization and strain referred to the aging phenomenon of soft PZT (Genenko *et al.*, 2015; Somwan and Ngamjarurojana 2015; Horchidan *et al.*, 2016). The same trend can be seen in the 0.2 Nb-doped PZT ceramics (Figure 4) where frequency dependence and aging governed the strain behavior of the ceramics. However, the strain of the aging samples demonstrated higher values as well as an asymmetry strain, indicating the reduced elastic energy of the aging phenomenon for samples at the composition near the MPB (Ketsuwan *et al.*, 2008; Genenko *et al.*, 2015; Somwan and Ngamjarurojana 2015). Figure 5 shows the

strain and polarization of the 0.3 Nb-doped PZT ceramics. The further decreases of polarization and strain still results from the frequency dependence (Delibas *et al.*, 2006; Somwan *et al.*, 2014, 2016b) and aging phenomenon for the 600°C (refreshed) heat treatment temperature. Polarization and strain demonstrated lower frequency dependence in the case of aging because less spontaneous polarization was suppressed to the preferred direction in order to release the energy in the crystal structure (Genenko *et al.*, 2015; Somwan and Ngamjarurojana 2015; Horchidan *et al.*, 2016). In the case of the 600°C (refreshed) heat treatment temperature, when the lower electric frequency was applied (0.1 Hz), the polarization exhibited high remnant polarization (like the electrical loss resulting from conductivity (Jin *et al.*, 2014)) possibly caused by heat treatment, as seen in Figures 1 and 2. At 0.1 Hz of electric field frequency, the electrical polarization was increased but polarization was suppressed at the first and second electric field cycle (red and green lines, respectively) when the samples were left for

60 days for aging, as shown in Figure 6. Domain reorientation was responsible for the

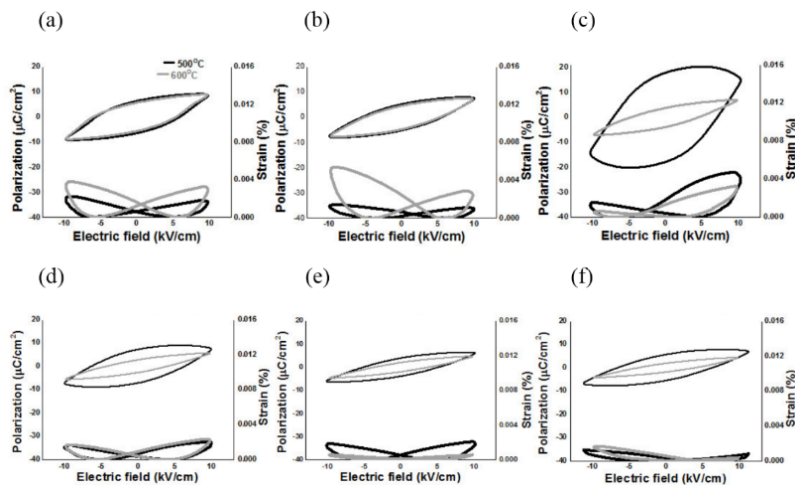


Figure 2. Polarization and strain of Nb-doped PZT ceramics after heat treatment at 500°C (black) and then 600°C (gray) and aging of: (a) 0.1 mol%, (b) 0.2 mol%, (c) 0.3 mol%, (d) 0.4 mol%, (e) 0.5 mol%, and (f) 0.6 mol%

difference of polarization between the first and the second electric field cycles.

In the case of the 500°C (fresh) heat treatment temperature, the decrease of spontaneous polarization was not the only phenomenon, as the electrical loss (space charge) accompanied it. Especially for the 0.3 Nb-doped PZT ceramics, the electrical loss was still high after 30 days aging, where the spontaneous polarization domain was decreased resulting in the decrease of the strain (Figures 1 and 2), possibly due to the low temperature not being enough to release the

energy to eliminate the poling effect for the 0.1 Nb-doped PZT sample. In the case of the 600°C (refreshed) temperature, the polarization after heat treatment showed values close to the 500°C treatment. The polarization, as well as the electrical loss, of the 0.3 Nb-doped PZT samples still had high values, which possibly resulted from the linkage of the domain and the higher spontaneous domain after the heat treatment, but the electrical loss of the 0.3 Nb-doped PZT samples disappeared when the samples were left for 60 days aging, due to the decreased spontaneous polarization domain

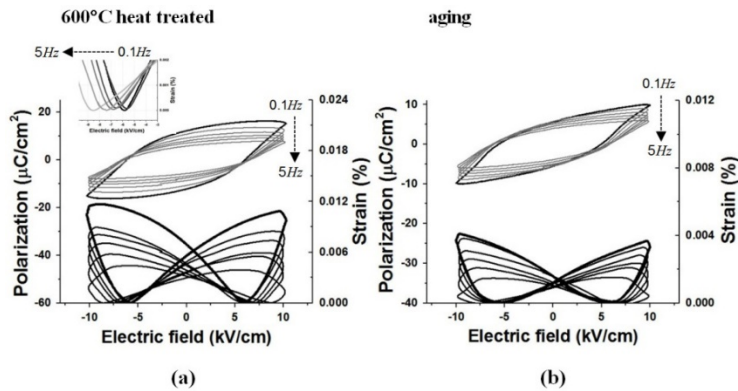


Figure 3. Polarization and strain of: (a) after 600°C heat treatment and (b) 60 days aging of 0.1 Nb-doped PZT ceramics

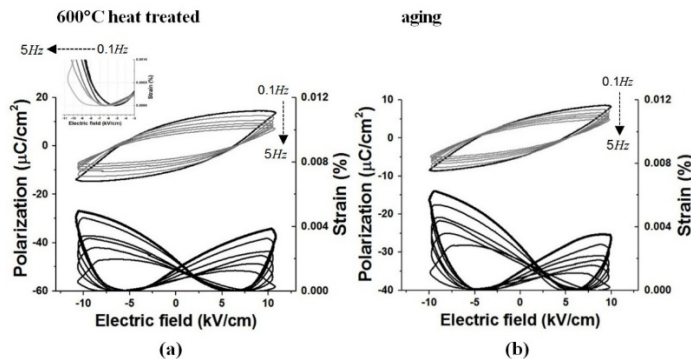


Figure 4. Polarization and strain of: (a) 600°C heat treatment and (b) 60 days aging of 0.2 Nb-doped PZT ceramics

and depolarization in the system (Ma and Wang, 2015; Somwan *et al.*, 2015), as shown in Figures 1, 2, and 5.

Figure 7 shows the electrical loss of the 0.1-2 Hz electric field frequency, after the 600°C (refreshed) heat treatment temperature

(a) and after 60 days left for aging (b), which was calculated by subtracted measured polarization with an amplified 5 Hz value (the lowest electrical loss as a frequency) (Somwan *et al.*, 2015). By subtracting all lower frequencies of polarization by the 5 Hz

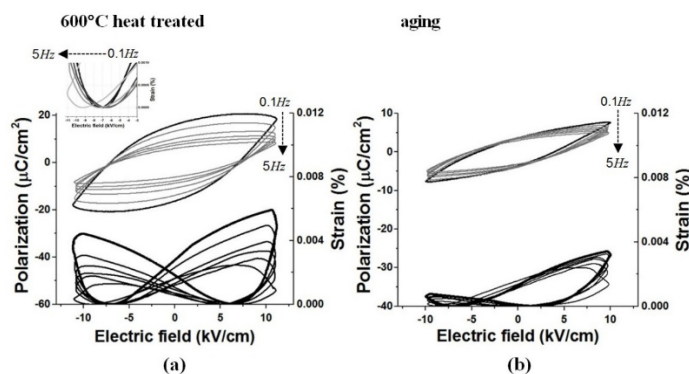


Figure 5. Polarization and strain of: 600°C heat treatment (a) and 60 days aging (b) of 0.3 Nb-doped PZT ceramics

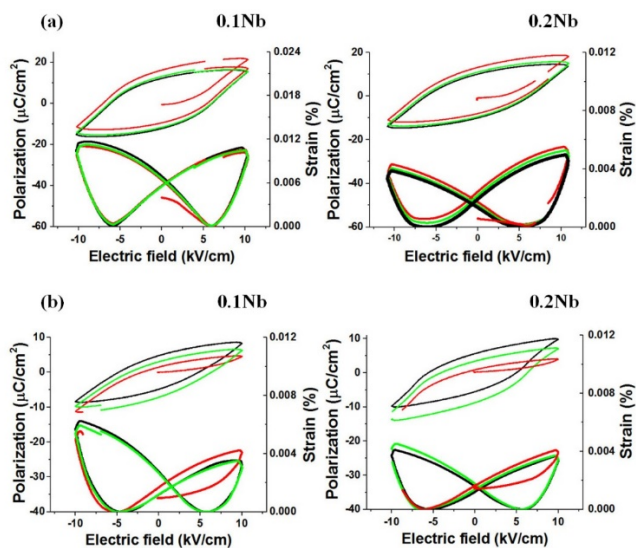


Figure 6. (a) 600°C heat treatment temperature and (b) 60 days aging of 0.1 and 0.2 Nb-doped PZT ceramics for the first (red line) and second (green line) cycle at 0.1 Hz of electric field frequency

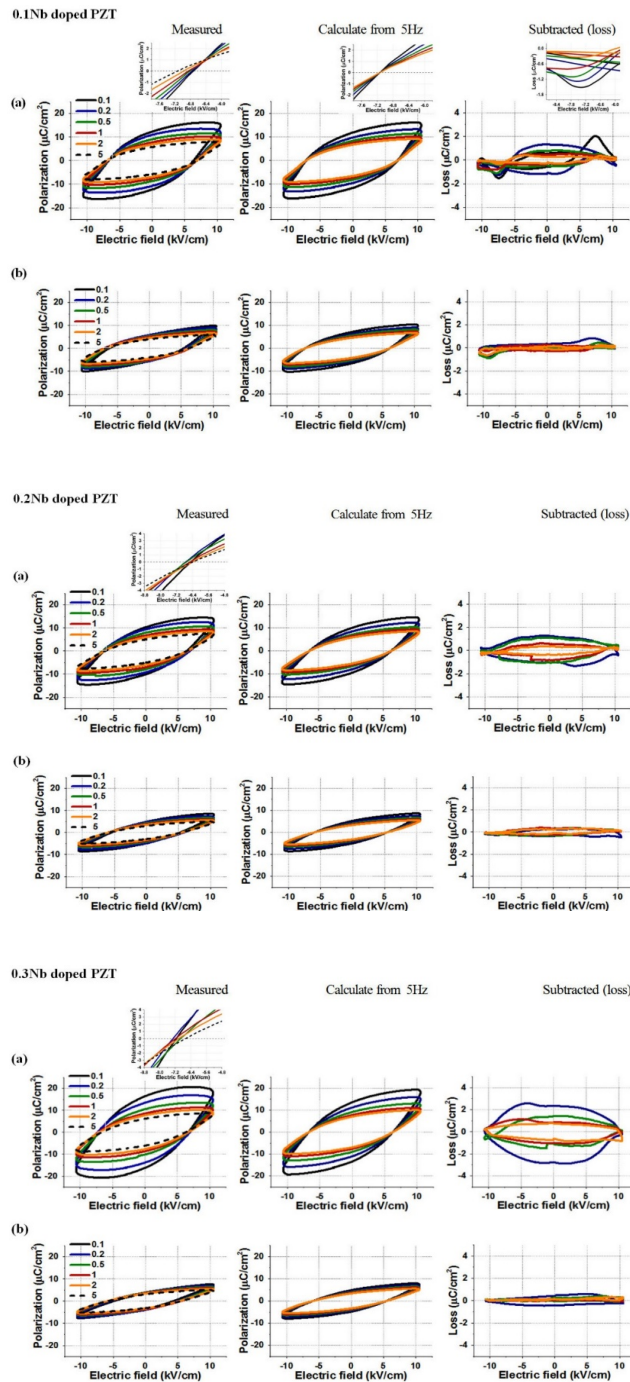


Figure 7. The electrical loss of 0.1-2 Hz compared to gained 5 Hz of polarization: (a) after 600°C heat treatment and (b) after 60 days aging

polarization (Somwan *et al.*, 2015), the 5 Hz of polarization was amplified to equal the maximum polarization of another frequency polarization where, at the maximum electric field, the electrical loss is minimized, resulting in the real values of polarization. In the case of the 0.1 Nb-doped PZT sample, the lower

electrical loss values and different coercive field (like a current density hysteresis loop which relates to the switching polarization of the hard ferroelectric sample (Jin *et al.*, 2014; Genenko *et al.*, 2015)) were represented in all frequencies, indicating that the tetragonal phase was dominant at the lower Nb

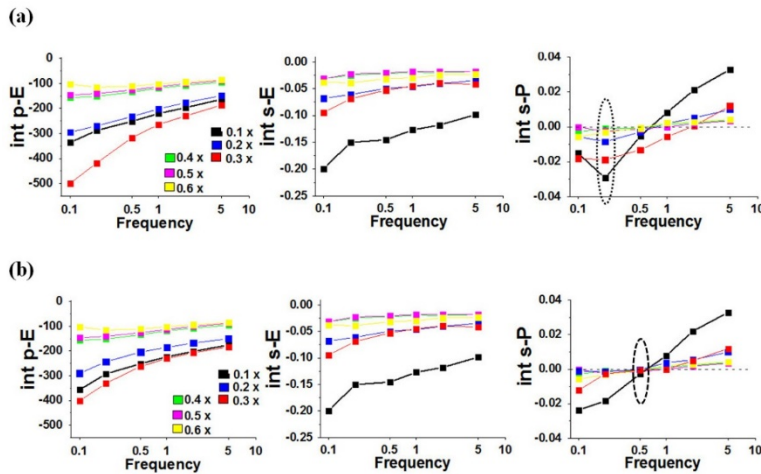


Figure 8. The loop area of P-E, s-E, and s-P of x Nb-doped PZT where $x = 0.1$ to 0.6 , with: (a) before and (b) after electrical loss correction of 600°C heat treatment temperature

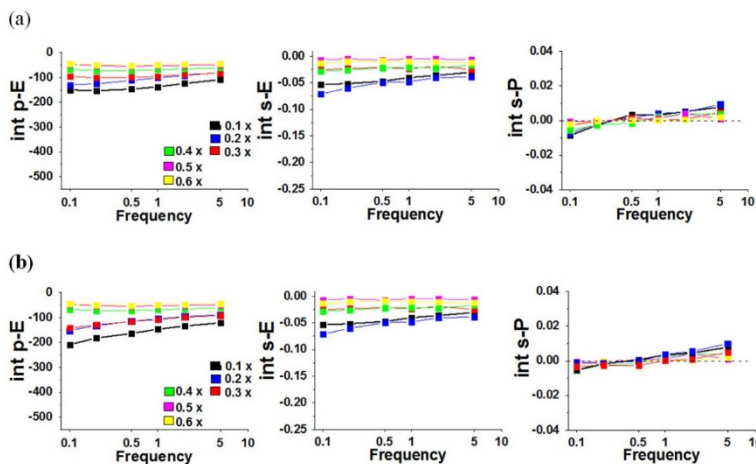


Figure 9. The loop area of P-E, s-E, and s-P of x Nb-doped PZT where $x = 0.1$ to 0.6 , with: (a) before and (b) after electrical loss correction of 60 days aging

concentration (Ketsuwan *et al.*, 2008). In the case of the 0.2 Nb-doped PZT sample, the electrical loss also represented the lower in all frequencies (maximum for a low Nb concentration (Haccart *et al.*, 2003)), but the coercive field was closed, referring to the relaxor or soft doping in the structure when the Nb concentration was increased (the rhombohedral phase increased) (Jin *et al.*, 2014; Promsawat *et al.*, 2017). In the case of the 0.3 Nb-doped PZT sample, the higher electrical loss was due to the increased Nb doping (Jin *et al.*, 2014), but all electrical loss disappeared when the samples were aged. The electrical losses of the samples after aging are shown in Figure 7(b). All samples show a lower electrical loss at all frequencies, and the higher decrease of electrical loss of the 0.3 Nb-doped PZT ceramics was due to the long range migration of defects which can be observed as electric DC conductivity or space charge motion (Genenko *et al.*, 2015), resulting in a decrease of the strain and polarization after aging, as shown in Figure 5. It can be seen in this work that Nb affects the electrical loss by means of soft doping where it changes the dielectric and ferroelectric properties of PZT. The increase of B-site vacancies and disorder accompanying the change of the crystal structure (Ketsuwan *et al.*, 2008) are the main factors which cause the change of the strain and polarization.

Figure 8 shows the loop area of the polarization-electric field (int p-E), strain-electric field (int s-E), and strain-polarization (int s-p), of x Nb-doped PZT before and after electrical loss correction (the electric loss correction is the means to calculate the real polarization after eliminating the electrical loss) of the 600°C (refreshed) heat-treated temperature. Before the electrical correction, especially in the 0.3 Nb-doped PZT, the int p-E loop area had a higher value accompanied with electrical loss, which differs from the int s-E loop area where spontaneous polarization switching behavior was observed when an alternate electrical field was applied. A non-linear relationship as a function of the frequency of the int s-p loop area at a lower frequency (inside the dotted circle) is observed,

where the loop of the strain as a function of polarization is referred to the switching domain dominant as 180° or non-180° (Somwan *et al.*, 2014; Uchino, 2017). After the correction of the electrical loss, the int s-p loop area demonstrates a linear relationship as a function of the electric field frequency, and the slim loop s-p is seen at 0.5 Hz (inside the dashed circle of Figure 8(b)) of the electric field frequency, referring to the slim s-p loop and less than 180° domain switching (Somwan *et al.*, 2014, 2015). Figure 9 shows the loop area of the polarization-electric field (int p-E), strain-electric field (int s-E), and strain-polarization (int s-p) of x Nb-doped PZT before and after electrical loss correction of 60 days aging. There is shown to be a little electrical loss for all electric field frequencies. The higher decrease of the int p-E and s-E loop area of 0.3 Nb-doped PZT is related to the disappearance of electrical loss or DC conductivity or space charge motion (Genenko *et al.*, 2015; Horchidan *et al.*, 2016). However, for the 0.2 Nb-doped PZT sample, the int p-E and s-E loop area was still high because it is near the MPB composition (Ketsuwan *et al.*, 2008). The slim loop s-p is shown for all samples due to the less spontaneous polarization after the second aging (Somwan *et al.*, 2014, 2015).

Conclusions

The induced strain and polarization of aging of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ PZT ceramics with the addition of x mole% of Nb_2O_5 , where x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6, were studied. The heat treatment temperature at 500°C (fresh) resulted in electrical loss at a lower electric field frequency (0.1-2 Hz). The heat treatment temperature at 600°C (refreshed) was enough to eliminate the poling effect, and lower electrical loss was demonstrated. The high electrical loss affected especially the 0.3 Nb-doped PZT, and the heat treatment effect disappeared when samples were aged, resulting in less spontaneous polarization. The sample showed a tetragonal phase at a low Nb (0.1 Nb) concentration and the switching field of the

sample was relaxed at 0.2 Nb due to the increase of the rhombohedral phase.

Acknowledgements

This work was supported by Rajamangala University of Technology Lanna Chiang Mai (RMUTL), and the Department of Physics and Materials Science, Faculty of Science, Chiang Mai University. The authors would like to thank Dr. Apichart Limpichaipanit for fruitful discussion and proofreading of this manuscript.

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