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Electric aging behavior of lead-free $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$ piezoelectric ceramics improved by pre-calcined method

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Abstract

In order to improve the piezoelectric and aging properties of the lead-free $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$ piezoelectric ceramics, the conventional solid-state reaction method and the B-side pre-calcined method were achieved and compared in this paper. The physical and electrical properties of the lead-free $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$ piezoelectric ceramics material were investigated and discussed. For the B-side pre-calcined method, the ceramic material exhibited the excellent electrical and piezoelectric parameters. Finally, the electromechanical coupling factors, the resonance frequencies, and the resonance resistances of the lead-free ceramic materials were also discussed.

Keywords: C. Electrical properties; C. Piezoelectric properties; D. Perovskites; E. Capacitors

1. Introduction

Lead-based perovskite piezoelectric ceramics (PZT-based) were widely used as actuators, sensors, transducers, and sonars due to their superior piezoelectric properties in the past. Recent years, lead-free piezoelectric ceramics were important chosen because of the low environment contamination, such as $BaTiO_3$-based materials $(Bi_{1/2}Na_{1/2})TiO_3$-based, Bismuth layered structure materials, and $(K,Na,Nb)O_3$-based (KNN-based) materials [1]. Many reports revealed that the excellent piezoelectricity of KNN-based piezoelectric ceramic materials possible to replace of the PZT-based piezoelectric ceramics [2,3]. However, the high volatility of potassium element for KNN-based ceramics was important reason at high temperature. It was difficult to obtain the dense and well-sintered KNN-based ceramics by conventional solid-state reaction [4]. For PZT based material, lead based piezoelectric ceramic materials were exposed to the bipolar high electric field and high temperature. Bipolar electric field were created huge amount of heating from the relaxation current. The electromechanical properties of ceramic materials, such as piezoelectric coefficient, ferroelectric polarization, and strain hysteresis were changed by high electric field and thermal stresses treatment. Aging effect dependent strain and polarization loops of ceramic material were generated under the high electric field of 1.4 kV/mm [5,6]. Therefore, the aging effects of the piezoelectric ceramics material will be an important parameter for applications in modern electronic devices.

Recently, the pre-calcined technique in conventional solid state reaction was adopted for KNN-based ceramics [7]. The A-site oxides (K_2CO_3, Na_2CO_3, and Li_2CO_3) in the lead-free KNN-based piezoelectric ceramics were easy and first calcined because of the B-site oxides (Sb_2CO_3, Nb_2CO_3, and Ta_2CO_3) were difficult to calcine [4]. For the B-site pre-calcined method, the B-site powders were calcined first and then the A-site powders were added into this calcined powders and calcined again.

2. Experimental

For conventional solid-state reaction method, reagent-grade materials of K_2CO_3, Na_2CO_3, Li_2CO_3, Sb_2CO_3, Nb_2CO_3, and Ta_2CO_3 powders with purity higher than 99.9% were used as

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starting materials and mixed according to the composition of $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$. After ball-milling, drying and grinding, the powder was calcined at 890 °C for 10 h and ground, then polyvinylalcohol (PVA, 5 wt%) was added as a binder. The calcining powders were uniaxially pressed into pellets in a steel die with the size of 1 mm in thickness and 1.3 mm in diameter. After debindering, these pellets were sintered at 1090 °C for 4 h in air. The top and bottom electrode of these pellets were Ag, and then electrodes were curing in an oven (800 °C/10 min).

The resonance resistance (R), resonance frequency (f_r), and anti-resonance frequency (f_a) were measured using the impedance analyzer (HP 4294). The electromechanical coupling factors k_P of ceramic specimens were calculated by Eq. (1) [7,8].

$$\frac{1}{k_P^2} = 0.395 \times \frac{f_r}{f_a - f_r} + 0.574 \quad (1)$$

For the electric aging behavior test, the ceramic specimens were kept in air for a period of 120 days. The variation of the resonance frequencies and resistances were measured and the percentages were calculated by Eqs. (2) and (3).

$$\frac{\Delta f}{f}(\%) = \frac{f_{rd} - f_{r1}}{f_{r1}} \times 100\% \quad (2)$$

$$\frac{\Delta R}{R}(\%) = \frac{R_d - R_1}{R_1} \times 100\% \quad (3)$$

where f_{r1} parameter was the resonance frequency measured. f_{rd} parameter was the resonance frequency measured. R_1 parameter was the resonance resistance measured. The R_d parameter was the resonance resistance measured.

To B-site pre-calcined method, reagent-grade materials of B-site oxides (Sb_2CO_3, Nb_2CO_3, and Ta_2CO_3) were mixed, ball-milled with deionized water for 10 h, and calcined at 1050 °C for 3 h in air. Then, the reagent-grade materials of A-site oxides (K_2CO_3, Na_2CO_3, and Li_2CO_3) were weighted, added, ball-milled, and calcined at 890 °C for 6 h in the air. To finish the A-site and B-sites mixed, the PVA was added as a binder. The calcining powders were uniaxially pressed into pellets in a steel die. And then the pellets were sintered at 1090 °C for 4 h in air. The top and bottom electrode of these pellets were Ag. Finally, the polarization properties of ceramic specimens were achieved by polarization processes in 100 °C silicon oil. The applied electrical field was about 4 kV/mm for 30 min treatment time. For electric aging behavior test, the average experimental data were carried out the 10–20 ceramic specimens.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the lead-free KNN-based ceramics specimens calcined at 890 °C and sintering in different temperature. The (1 0 0), (1 1 0), (0 0 2), and (2 0 0) peaks were found in Fig. 1. All the lead-free ceramic specimens were perovskite phase and no any secondary impurity were observed. The (1 0 0) peaks of

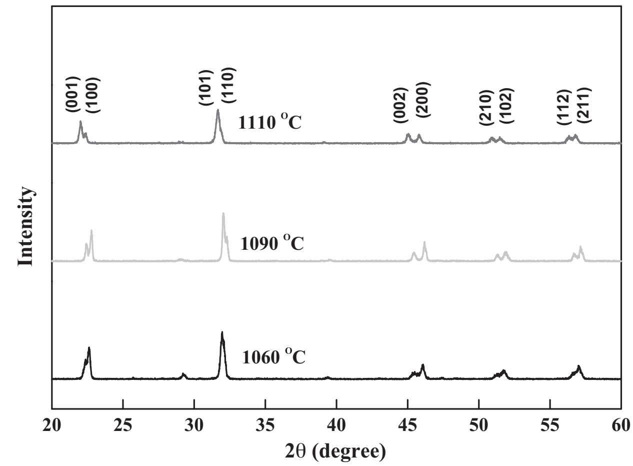

Fig. 1. The XRD of the KNN samples sintered at different temperature.

lead-free KNN-based ceramics specimens increased gradually as the sintering temperature increased. The stronger (1 0 0) peak of lead-free KNN-based ceramics specimens for 1090 °C sintering temperature was observed. All lead-free KNN-based ceramics specimens showed no deliquescence properties in Fig. 1.

Fig. 2 shows the XRD patterns of the lead-free KNN-based ceramics specimens using the conventional solid-state reaction and B-site pre-calcined method. We found that the peak intensity of ceramics specimens using B-site pre-calcined method stronger than those of the conventional solid-state reaction method. The (1 0 1) and (1 1 0) preferred phases of KNN-based ceramics specimens and the crystallization of grains were better than those of other ceramics specimens.

Fig. 3 shows the surface morphology of the KNN-based ceramics specimens with the different method includes the conventional solid-state reaction and B-site pre-calcined. All of KNN-based ceramics specimens using different reaction methods was orthorhombic structure. The B-site pre-calcined technology method significantly affected microstructure of pure KNN-based ceramics specimens were shown in Fig. 3(b). In addition, many distinct pores existed in grain boundary was

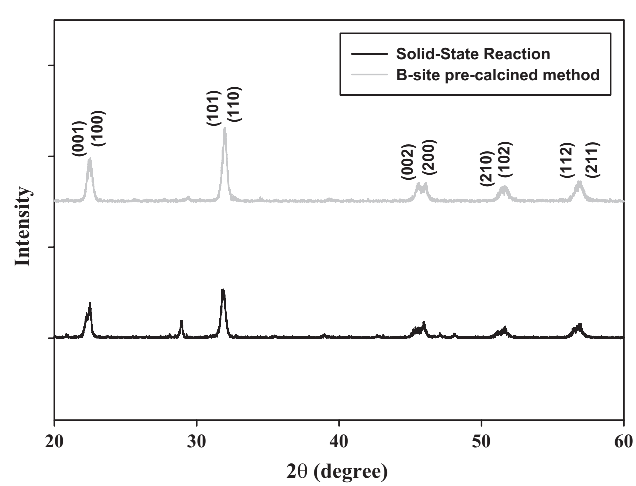

Fig. 2. The XRD of the KNN samples using the B-site pre-calcined method.

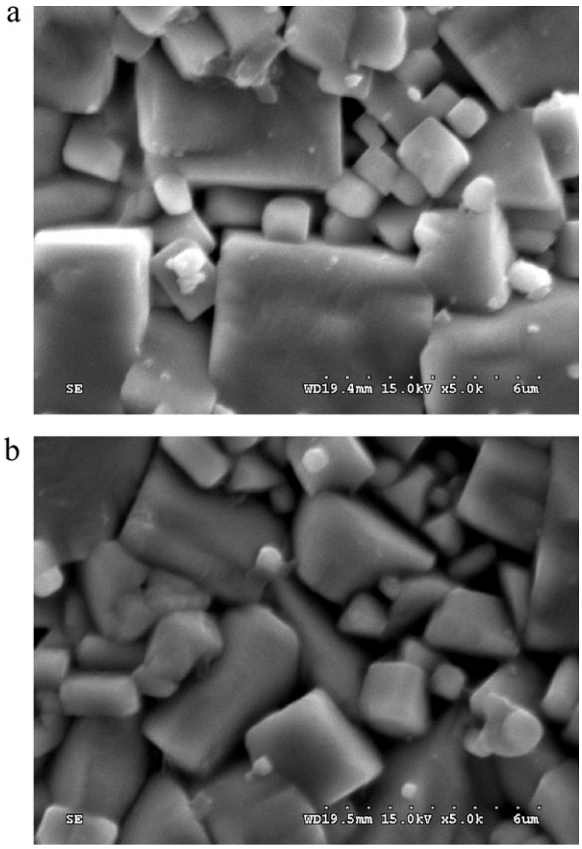

Fig. 3. The surface morphology of the KNN samples with the different method includes (a) the conventional solid-state reaction, and (b) B-site pre-calcined.

also found in conventional solid-state reaction method. The B-site pre-calcined technology method was appropriate and the grains were grown sufficiently because of the lead-free KNN-based ceramics specimens was quadrate.

These electric stresses can changes the electromechanical properties of lead-free KNN-based ceramics materials such as piezoelectric coefficient, ferroelectric polarization and strain hysteresis. For the measurement of electric aging behaviors, the electromechanical coupling factors k_P (%) properties of lead-free KNN-based ceramics specimens were measured and kept in air for 120 days. From the electric aging test, we found that the k_P parameters decreased gradually for two reaction method in Fig. 4. In addition, the k_P parameters of the ceramics specimens using the B-site pre-calcined method were better than those of the conventional solid-state reaction method. For 120 days aging test, the k_P parameters was the value of 39.8 and 30% for two reaction method, respectively. We revealed that B-site pre-calcined method with the better stability characteristics for a long time test.

The resonance frequency parameters were calculated from Eq. (2). Fig. 5 shows the variation of the resonance frequency in the lead-free KNN-based ceramics specimens for 120 days. The resonance frequency of ceramics specimens using B-site pre-calcined method was smaller than those of conventional solid-state reaction method. Therefore, we found that the resonance frequency parameters were attributed by preferred peak and

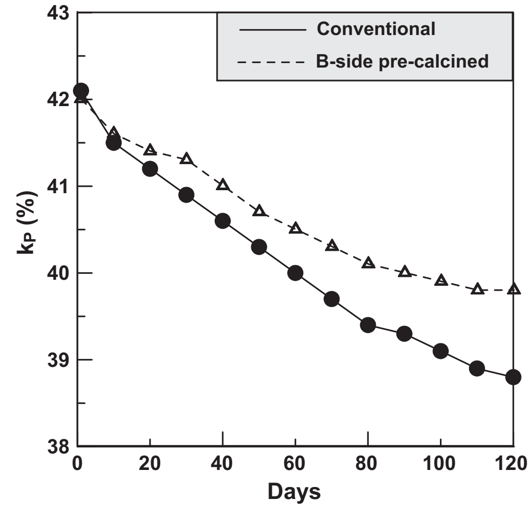

Fig. 4. The variation of k_P for conventional and B-side pre-calcined methods.

crystallization of grain for the lead-free KNN-based ceramics specimens using B-site pre-calcined method.

The resonance resistances parameter was also an important coefficient for ceramics material applications in various electronic devices. In this study, the resonance resistances parameters were calculated from Eq. (3). We found that the resonance resistance parameter was about 20% using conventional solid-state reaction method. In addition, the resonance resistance parameter was about 10% for B-site pre-calcined method. In Fig. 6, the resonance resistance parameter of lead-free KNN-based ceramic material using B-site pre-calcined method was decreased about 50%.

Electric aging behaviors and dielectric constant characteristics of ceramics specimens were discussed. The dielectric constant of ceramics specimens for conventional solid-state reaction and B-site pre-calcined method were 1193 and 1209, respectively. The loss tangent was 2.8 and 1.8, respectively. For 120 days, the dielectric constant for conventional solid-state

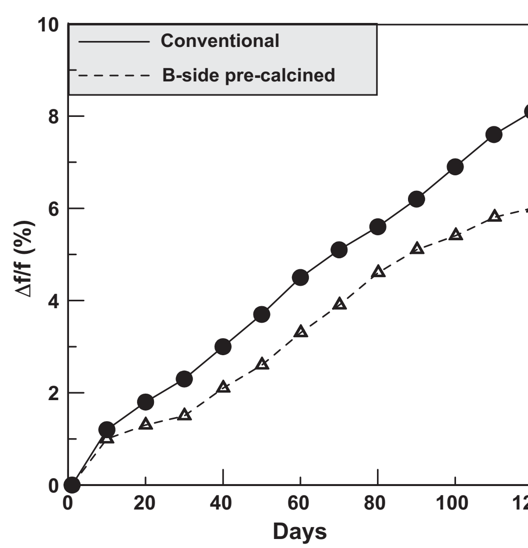

Fig. 5. The variation percentage of the resonance frequency for a period of 120 days.

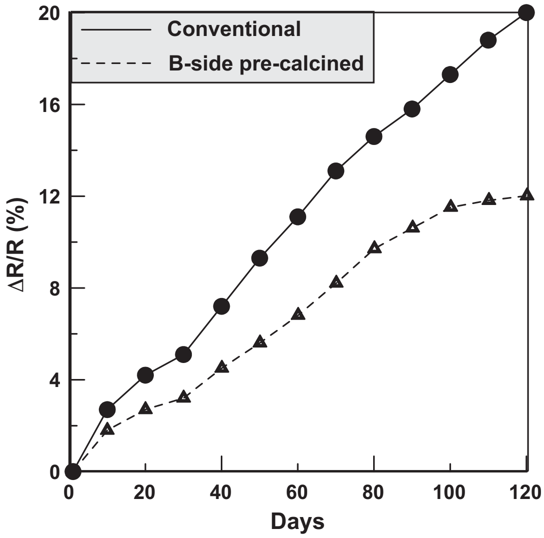

Fig. 6. The variation percentage of the resonance resistance for a period of 120 days.

reaction and B-site pre-calcined method were 1117 and 1153, respectively. We found that the dielectric constant parameters using B-site pre-calcined method methods were a little changed.

According above the experimental results, the polarization inversion of lead-free KNN-based ceramics specimens by external field applied were not induced aging behavior of materials.

4. Conclusion

In this study, the electric aging behaviors of the lead-free $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$ piezoelectric ceramic materials using conventional solid-state reaction and B-site pre-calcined methods were compared and investigated. From the experimental results, the electromechanical coupling factors, the resonance frequencies, and the resonance resistances of the lead-free KNN-based ceramic materials prepared by using the B-site pre-calcined method were better than those of the conventional solid-state reaction method.

Aging effect dependent piezoelectric coefficient of lead and lead-free ceramic material was generated under the high electric field. In this study, we found that the better electrical and physical properties of the $Li_{0.06}(K_{0.48}Na_{0.52})_{0.94}(Nb_{0.86}Ta_{0.08}Sb_{0.06})O_3$ ceramic material improved by the B-site pre-calcined method. Finally, the electric aging effects of the piezoelectric ceramics material will be an important parameter for applications in modern electronic devices.

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