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Short communication

Poling field dependence of ferroelectric domains in tetragonal KNNLN ceramics

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Abstract

In present work, a simple and direct method was proposed, which could be applied for quantitatively calculating the percentage of 90° domain reorientation in the tetragonal phase of KNNLN ceramics. The relationship between 90° domain reorientation and poling field was established through the X-ray diffraction analysis. Experimental results indicate that the poling field of 5 kV/mm is sufficient for the reorientation of 90° domain and while the percentage of 90° domain reorientation 37.9% and piezoelectric constant 232 pC/N are obtained. The general trend of piezoelectric properties corresponds well with that of the percentage of 90° domain reorientation.

Keywords: Poling field; 90° domain reorientation; KNNLN

1. Instruction

Piezoelectricity appears on ferroelectric ceramics when the random ferroelectric domains are aligned through the poling process. It is well known that PZT ceramics contain several kinds' domains. The electric field will force them move toward the direction favorable to the total system energy. The piezoelectric properties of PZT possessing tetragonal phase is affected by both 90° rotation and 180° switching. According to Friedel's law, the reversal of 180° domains during the poling process could not be detected by the X-ray diffraction method. While 90° rotation can be detected by the change in the intensities of the (0 0 2) and (0 0 2) X-ray diffraction (XRD) peaks. Therefore, the domain evolution process could be deduced by the change in the relative peak intensity. Previous works indicate that 90° domain rotation is the main contribution to piezoelectric property, not only in PZT system but also for the other tetragonal phase of Pb-based ceramics. Also lots other efforts were focused on evaluating the degree of 90° domain reorientation of Pb-based piezoelectric ceramics [1–7].

However, similar study has been scarcely carried out on KNN-modified ceramics [8]. An evaluation of the domain structures at various values of E in KNN-based ceramics may be useful for understanding the interrelationship between the dynamic behaviors and the microstructure of ferroelectric ceramics. In this article, a method to investigate the tetragonal phase ferroelectrics KNNLN under different dc poling fields was proposed. The XRD analysis was applied to identify the percentage of the 90° domain reorientation induced by poling.

2. Experimental procedure

Lead-free $Li_{0.058}(Na_{0.51}K_{0.49})_{0.942}NbO_3$ (abbreviated as KNNLN) piezoelectric ceramics were synthesized by a traditional mixed oxide route. The starting powders used in this study were potassium carbonate (K_2CO_3, 99.5%), sodium carbonate (Na_2CO_3, 99.8%), lithium carbonate (Li_2CO_3, 98.5%), and niobium oxide (Nb_2O_5, 99.5%). These powders are all provided by Sinopharm Chemical Reagent Co., Ltd. After being ball milled in a nylon jar with Zirconium balls for 24 h and dried, the stoichiometric KNNLN powder was calcined at 760 °C for 5 h. After the calcination, KNNLN powders were re-milled for 24 h. The powders were dried and pressed into disks, using polyvinyl butyral (PVB) as binder. After PVB was burnt off, the pellets were sintered at 1050 °C for 5 h in air without any protection. The as-sintered samples were all polished and then annealed at 650 °C for 5 h in air in order to eliminate the stress and preferred orientation induced

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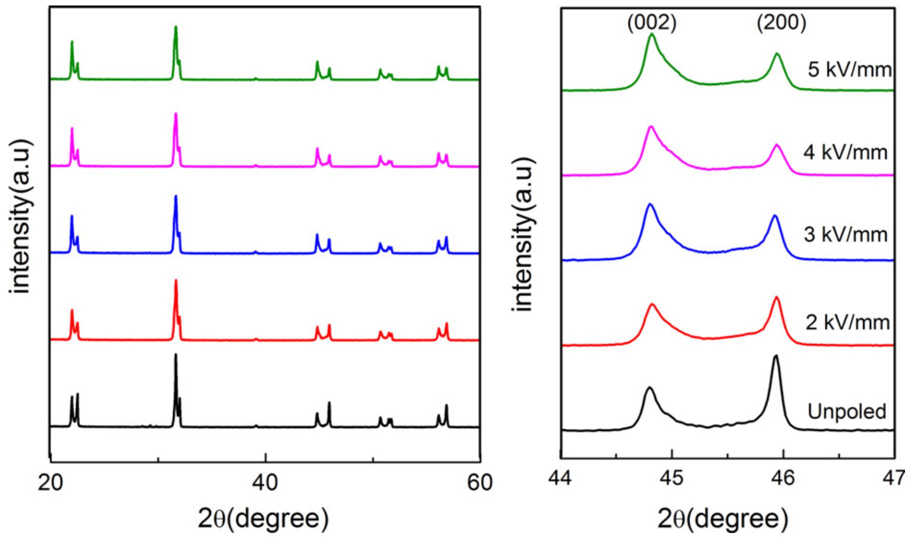

Fig. 1. XRD patterns for KNNLN samples under different dc filed.

in polishing and sintering process. Silver paste was fired on both sides of the samples at 600 °C for 20 min to form electrodes for poling and piezoelectric measurement. The annealed samples were poled in silicon oil bath by applying a direct current electric field of 2, 3, 4, and 5 kV/mm at room temperature for 20 min.

XRD analysis of the pellets was performed on X-ray powder diffraction (D/MAX-2500, Rigaku, Tokyo, Japan) with a CuKα1 radiation (λ = 0.15406 nm). The as sintered surface of the samples were first polished and then scanned at 0.02° intervals of 2θ in the range 20–60°; the scanning speed was 6°/min. The piezoelectric constant d_{33} was measured using a Berlincourt PiezoMeter system. The planar electromechanical coupling factor k_p was determined by the resonance–antiresonance method according to IEEE standards using an impedance analyzer (HP 4194A). The ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technologies Inc., Albuquerque, NM).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of KNNLN samples under different poling field. It was observed that all the samples were pure perovskite phase and no secondary phase was found. In order to accurately identify the room temperature crystal structure of samples, the {2 0 0} reflection lines were measured by slow scanning at 0.5°/min. The results are shown in Fig. 1. It was found that the samples before poling possessed a typical tetragonal phase structure. The samples show evident evolution of (0 0 2) and (2 0 0) diffraction peaks intensity with the poling electric field as a consequence of the reorientation of the ferroelectric domains. Since no preferred orientation exists in the unpoled sample, the relative intensity of (2 0 0) peak should be about twice as that of (0 0 2) peak. The relative intensity of (0 0 2) for the poled samples was promoted to different degrees. The change in the relative intensities of (0 0 2) and (2 0 0) indicates the extent of domain orientation: the higher the difference of the relative intensities of (0 0 2) and (2 0 0) of the samples after poling, the higher the extent of domain orientation.

The lattice parameters obtained using the {2 0 0} XRD data are listed in Table 1. The data reveal that the crystal structures of both the poled and unpoled KNNLN samples remain constant, and the lattice parameters and the *c/a* values change little with poling electric field.

Based on the general principle of X-ray diffraction, the diffractive intensity $I_{(h\,k\,l)}$ for $(h\,k\,l)$ plane can be usually expressed by [9]:

$$I_{hkl} = CAI_0L|F_{hkl}|^2P_{hkl}\,\rho_{hkl} \tag{1}$$

where I_o stands for incident X-ray diffraction, L, Lorentz angle factor; $F_{(h\,k\,l)}$, structure factor for $(h\,k\,l)$ plane; $P_{(h\,k\,l)}$, iterating factor; A, absorption factor and C is known as measuring system constant. Once the measuring conditions and specimens are defined, C can be calculated. $\rho_{(h\,k\,l)}$ is the crystal plane orientation density which is defined as the volume fraction of the crystal grains with $(h\,k\,l)$ plane parallel to specimen surface.

Both 90° and 180° domains exist in the tetragonal phase of KNN-based ceramics, but only 90° rotation can be detected by the change in the relative intensities of the (0 0 2) and (2 0 0) X-ray diffraction peaks, 180° switching is independent of the peak intensities. Therefore, the change rate of $I_{0\,0\,2}$ and $I_{2\,0\,0}$ could reveal some information about the mechanism of the domain reorientations. The percentage of 90° domain reorientation

Table 1
Lattice parameters calculated from XRD patterns for KNNLN ceramics under different poling fields.

Sample name	$a = b$ (Å)	c (Å)	c/a
Unpoled sample	3.948	4.041	1.02366
Sample under 2 kV/mm	3.948	4.041	1.02366
Sample under 3 kV/mm	3.949	4.042	1.02365
Sample under 4 kV/mm	3.948	4.041	1.02366
Sample under 5 kV/mm	3.9476	4.041	1.02366

depends on the parameters in the poling process like the intensity of the poling field, the poling time, the poling temperature [8].

Zhang has already established a complete and accurate system to identify the percentage of 90° domain reorientation in the tetragonal phase of PMN–PT ceramics after poling, and the results could explain the change of piezoelectric properties reasonably [7]. On the base of Zhang's result [7], this system was further developed by us to be applied in the KNN-based ceramics. In the tetragonal structure, $P_{0\,0\,2} = 2$ and $P_{2\,0\,0} = 4$. From Eq. (1), we obtain the ratio of intensities:

$$R = \frac{I_{200}}{I_{002}} = \frac{P_{200}|F_{200}|^2 \rho_{200}}{P_{002}|F_{002}|^2 \rho_{002}} = 2\frac{|F_{200}|^2 \rho_{200}}{|F_{002}|^2 \rho_{002}} \quad (2)$$

And the ratio of (2 0 0) and (0 0 2) intensities in a poled sample as follows:

$$R' = \frac{I'_{200}}{I'_{002}} \frac{|F_{200}|^2 [P_{200}\rho_{200} - P_{200}N\rho_{200}]}{|F_{002}|^2 [P_{002}\rho_{002} + P_{200}N\rho_{200}]} = \frac{2|F_{200}|^2 [\rho_{200} - N\rho_{200}]}{|F_{002}|^2 [\rho_{002} + 2N\rho_{200}]} \quad (3)$$

After being poled, the intensities of (2 0 0) and (0 0 2) are indicated as $I'_{2\,0\,0}$ and $I'_{0\,0\,2}$, respectively. Here the N stands for the fraction of domain a changing into domain c via a 90° domain reorientation, standing for the percentage of the 90° domain reorientation induced by poling. We could obtain

$$\frac{R}{R'} = \frac{1 + R\left(|F_{200}|^2/|F_{002}|^2\right)N}{1 - N} \quad (4)$$

and

$$N = \frac{R - R'}{R\left[1 + \left(|F_{200}|^2/|F_{002}|^2\right)R'\right]} \quad (5)$$

It is supposed that the atomic scattering factors for both (2 0 0) and (0 0 2) are equal and $|F_{2\,0\,0}|$ is equal to $|F_{0\,0\,2}|$. Therefore [1,5],

$$N = \frac{R - R'}{R(1 + R')} \quad (6)$$

The N calculated from Eq. (6), d_{33} and k_p are listed in Table 2. The relationship of N and d_{33} with the different poling field was shown in Fig. 2. It could be found that the tendency of N and d_{33} was not exactly same. We suppose that neglecting the difference of structure factors between (2 0 0) and (0 0 2) planes induced this offset of the tendency of N and d_{33}. As no data concerning the ionic coordinates of KNNLN ceramics have been reported so far, hence this condition restrict the accuracy of our results. To exactly determine quantitatively the percentage of 90° domain reorientation is difficult, so the purpose of our research is to establish the relationship between 90° domain reorientation and poling field.

It is known that the 180° domain reversal also contributes to the piezoelectric constant. However, it is also known that 180° domain reversal occurs easily, as it results in no deformation, and that the 180° domain reversal occurs when the poling electric field approaches the coercive field (E_c) [10–12]. In our experiment, E_c was determined by measuring the hysteresis loop as shown in Fig. 3. It is observed that the E_c of the unpoled ceramics is about 2 kV/mm. Therefore, 180° domain would reverse after being poled under the poling field of above 2 kV/mm. The d_{33} value for the samples poled under 2 kV/mm is 141 pC/N, and N is 0.07, which means that the percentage of 90° domain rotation is very low. The d_{33} value for the samples (5 kV/mm) reaches 232 pC/N, with N increasing to 0.379. The d_{33} for 2 kV/mm is 61% of that of 5 kV/mm. Assuming that if the 180° domain reversal totally and it comes to the conclusion that the switching of 180° domain plays a considerable role in

Table 2
Percentage of 90° domain rotation N, piezoelectric constant d_{33} and electromechanical coupling factor k_p for KNNLN samples under different poling fields.

Name	$I_{2\,0\,0}/I_{0\,0\,2}$	N	d_{33} (pC/N)	k_p
Unpoled sample	1.906			
Sample under 2 kV/mm	1.413	0.07	141	0.35
Sample under 3 kV/mm	0.805	0.292	179	0.42
Sample under 4 kV/mm	0.706	0.343	223	0.47
Sample under 5 kV/mm	0.642	0.379	232	0.50

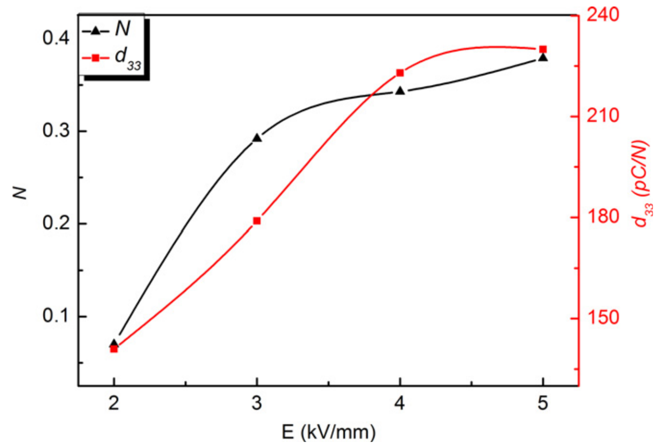

Fig. 2. The degree of 90° domain rotation N and piezoelectric constant d_{33} with the increase of external poling field.

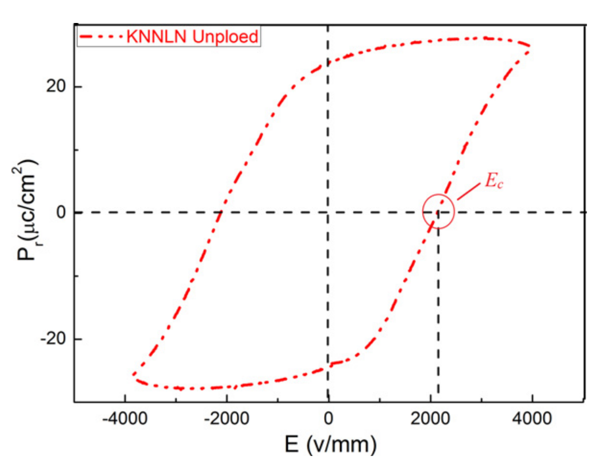

Fig. 3. The room temperature hysteresis loop of the unpoled KNNLN sample.

the contribution of macroscopic piezoelectric property of KNNLN samples. It is not the same case in PMN-PT ceramics. In Zhang's result, the reorientation of 90° domain makes main contribution to the increase of d_{33} and the switching of 180° domain just possess just one fourth of the max macroscopic piezoelectric property [7].

Fig. 2 also indicated that when the dc poling field increased above 4 kV/mm, both the percentage of 90° domain reorientation N and piezoelectric constant d_{33} of the samples change little, indicating that the poling in these samples approaches saturation. Therefore, samples poled under 5 kV/mm can be regarded as sufficiently poled, with a 90° domain reorientation percentage of 37.9%.

4. Conclusions

KNNLN ferroelectric ceramics under different dc poling fields have been examined. From the measurement of the intensities of (2 0 0) and (0 0 2) diffraction lines before and after poling, we can quantitatively determine the percentage of 90° domain reorientation. The degree of 90° domain reorientation (N) and piezoelectric constant (d_{33}) both increase with increasing poling field. The percentage of 90° domain reorientation in a well-poled sample is 37.9%, under which condition its d_{33} equals 232 pC/N.

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