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Hydrothermal synthesis and piezoelectric property of Ta-doping $K_{0.5}Na_{0.5}NbO_3$ lead-free piezoelectric ceramic

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Abstract

Ta-doping $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ($x = 0.1, 0.2, 0.3, 0.4$) powder was synthesized by hydrothermal approach and its ceramics were prepared after sintering and polarizing treatment in this work. The $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramics near morphotropic phase boundary (MPB), which exhibited optimum piezoelectric properties of $d_{33} = 210$ pC/N and good electromechanical coupling factors of $K_p = 0.3$. The domain structure has been observed from TEM images which indicates that the $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramics have good piezoelectric and ferroelectric properties for it is near the MPB.

Keywords: C. Piezoelectric properties; D. Niobates; Ta-doping

1. Introduction

Lead-free piezoelectric ceramics have received considerable attentions recently from the viewpoint of environmental protection [1]. Ferroelectric–antiferroelectric complex systems are often investigated in order to enhance their piezoelectricity. At room temperature, the crystal structure of $K_{0.5}Na_{0.5}NbO_3$ (KNN) system is orthorhombic, with $KNbO_3$ (KN) being ferroelectric and $NaNbO_3$ (NN) antiferroelectric [2]. KNN, near the morphotropic phase boundary (MPB), possesses much better the piezoelectric and ferroelectric properties than that of pure $KNbO_3$. Although the KNN ceramic shows comparably good piezoelectric properties, it has some disadvantages. The most serious one is the poor sinterability, namely, pure KNN ceramics are known to be difficult to sintering fully by ordinary sintering method. Two main reasons lead to such problem. First, pure KNN is decomposed beyond 1140 °C according to the phase diagram of $KNbO_3$–$NaNbO_3$ [3]. Therefore, the higher sintering temperature is not appreciated. Second, Na_2O and K_2O are easily evaporated at high temperature, which slightly changes the chemical stoichiometry of $K_{0.5}Na_{0.5}NbO_3$ ceramics [4]. So it is very difficult to obtain dense $K_xNa_{1-x}NbO_3$ ceramics using powders prepared from traditional solid state reaction.

One of the methods to obtain dense KNN ceramics is to use refined powders with improved sintering activity. A number of methods such as chemical co-precipitation, sol–gel routine, molten salt synthesis [5] and hydrothermal process have been used to prepare refined ceramic powders. In previous reports, $BaTiO_3$ [6], $Sr_xBa_{1-x}TiO_3$ [7], $Na_{0.5}Bi_{0.5}TiO_3$ [8], $KNbO_3$ [9], and $NaNbO_3$ [10] powders have been successfully prepared by the hydrothermal method. However, $K_xNa_{1-x}NbO_3$ solid solution prepared by hydrothermal synthesis has seldom been reported yet, and further leading to the omitting of the piezoelectric property studies of $K_xNa_{1-x}NbO_3$ ceramics. The hydrothermal method provides a low-temperature process, environmental friendly and an ultrafine powder synthesis method [11]. Accordingly, it is possible to prepare $K_xNa_{1-x}NbO_3$ powders with a small average particles size and then reduce the volatility of Na_2O and K_2O using this method.

$K_{0.5}Na_{0.5}NbO_3$ powders near the MPB had been synthesized by hydrothermal method in our previous work, unfortunately the value of d_{33} achieved is low. In order to improve $K_{0.5}Na_{0.5}NbO_3$ piezoelectric properties, Ta_2O_5 has been doped into the system due to the same chemical valence (+5) of Ta and Nb, similar atomic radius (Ta (0.068 nm) and Nb (0.069 nm)), and electronegativity (Ta (1.5) and Nb (1.6)). In this study, $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ powders have been prepared by hydrothermal method, and $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramic has been obtained by ordinary sintering method. The piezoelectric properties of the ceramic were investigated. The relationship

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between the microstructure and the piezoelectric properties was also discussed in this paper.

2. Experimental

2.1. Hydrothermal synthesis

Analysis-grade Nb_2O_5 and Ta_2O_5 powders, KOH and NaOH were adopted as raw materials. First, both $NaNbO_3$ and $KNbO_3$ were prepared by hydrothermal synthesis in 6 mol/L solutions at 230 °C for 24 h. The experimental details were described as follows.

The hydrothermal synthesis of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramic powders was carried out in a 50 cm^3 stainless Teflon autoclave. The total amount of the Nb_2O_5 and Ta_2O_5 is 1.25 g. The molar ratio of Nb_2O_5 to Ta_2O_5 in the reactant was 0.1:0.9, 0.2:0.8, 0.3:0.7, and 0.4:0.6. And then they were added into the mixed solution of KOH and NaOH whose alkalinity was 6 mol/L under different molar ratios of Na^+ to K^+ of 4:1, 5:1 and 6:1. The resulting suspension was transferred to an autoclave with a filling factor of about 50 vol%, and then stirred for 30 min. Furthermore, the autoclave was put in an oven and heated to 230 °C for 24 h. After cooling, the obtained white powders were washed by deionized water for several times until the pH value was equal to 7. Finally, they were dried at 130 °C for 1 h.

2.2. Piezoelectric ceramic preparation

The as-prepared powders were pressed into pellets of Φ 12 mm × 1.5 mm under 40 MPa pressure, and then followed by a cold-isostatic pressing under 200 MPa for 5 min. The prepared pellets were sintered at 1000 °C for 2 h with a heating rate of 300 °C/h and cooling rate of 600 °C/h.

Before piezoelectric properties measurement, the samples were polarized. Firstly, the sintering pellets were polished and painted with silver paste on the sample surfaces. Then, they were immersed in silicon oil and polarized at 130 °C for 20 min under 5 kV/mm electric field, and the specimens were cooled to room temperature within the electric field. All the polarized pellets were aged for 24 h.

2.3. Piezoelectric and ferroelectric properties measurement

The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (Model ZJ-3, Institute of Academic Sinica). The electromechanical coupling factor was determined by an impedance analyzer (HP 4194) on the basis of IEEE standards. The observation of ferroelectric domains was carried out by TEM (JEOL, 2000FX Japan).

2.4. Phase and microstructure characterization

The phase of obtained powders was characterized by X-ray power diffraction (XRD, Rigaku, Tokyo, Japan). The microstructure of the powders was examined using field-emission scanning electron microscopy (FE-SEM, Model JSM-6480LV).

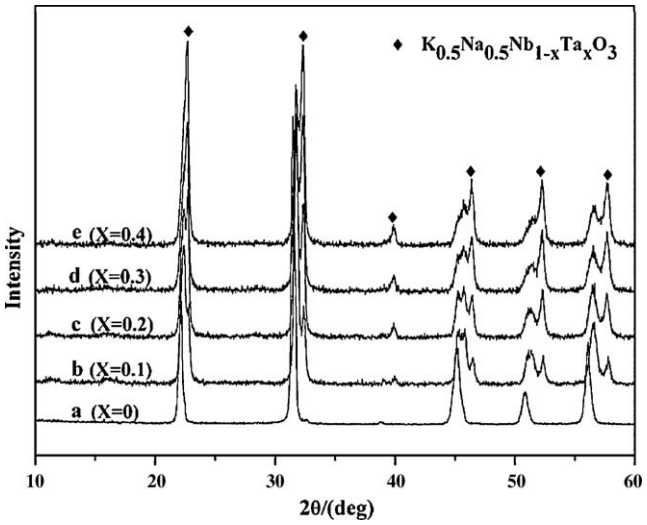

Fig. 1. X-ray diffraction patterns of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ powders of K^+/Na^+ designed molar ratios = 5:1 in precursor with (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, and (e) $x = 0.4$.

The concentrations of K^+ and Na^+ were determined by energy dispersive X-ray (EDS) analysis in SEM. The density of the specimens was measured using the Archimedes method.

3. Results and discussions

3.1. Phase analysis and microstructure of as-prepared powders

Fig. 1 shows the X-ray diffraction patterns of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) ceramic powders synthesized at 230 °C for 24 h. While $x = 0$ the as-prepared powders exhibit an orthorhombic perovskite structure, which was accorded with $KNbO_3$ (JCPDS01-0071-2171). When $x = 0.1$, 0.2, 0.3, and 0.4, the produced powders show a monoclinic perovskite structure, which can be indexed to be $Na_{0.35}K_{0.65}NbO_3$ according to JCPDS 01-077-0038. No peaks of Nb_2O_5 and Ta_2O_5 are observed in the X-ray diffraction patterns, indicating that both Nb and Ta have dissolved into the crystal lattice, and caused a little lattice distortion for the structure phase transition. As shown in Fig. 1 that all the diffraction peaks of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ($x = 0.1$, 0.2, 0.3, 0.4) had slowly shifted to the right due to the substitution of Nb (0.069 nm) by Ta (0.068 nm). The smaller radius of Ta^{5+} doping makes the unit cell size smaller, and as a result, the 2θ of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ patterns increases, according to the Bragg formulary $d = \lambda/(2\sin\theta)$.

SEM images of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ powder along with different amount of Ta-doping were shown in Fig. 2. It can be seen that the as-prepared samples are well crystallized with average grain size about 200 nm.

As shown in Table 1, the molar ratio of K^+/Na^+ of as-prepared powders does not correspond with that of the precursor solution. The reason is that the radius of K^+ (0.133 nm) is much larger than that of Na^+ (0.097 nm), so that it is much more difficult for the bigger K^+ dissolved in the crystal lattice compared with Na^+, which results in the much lower

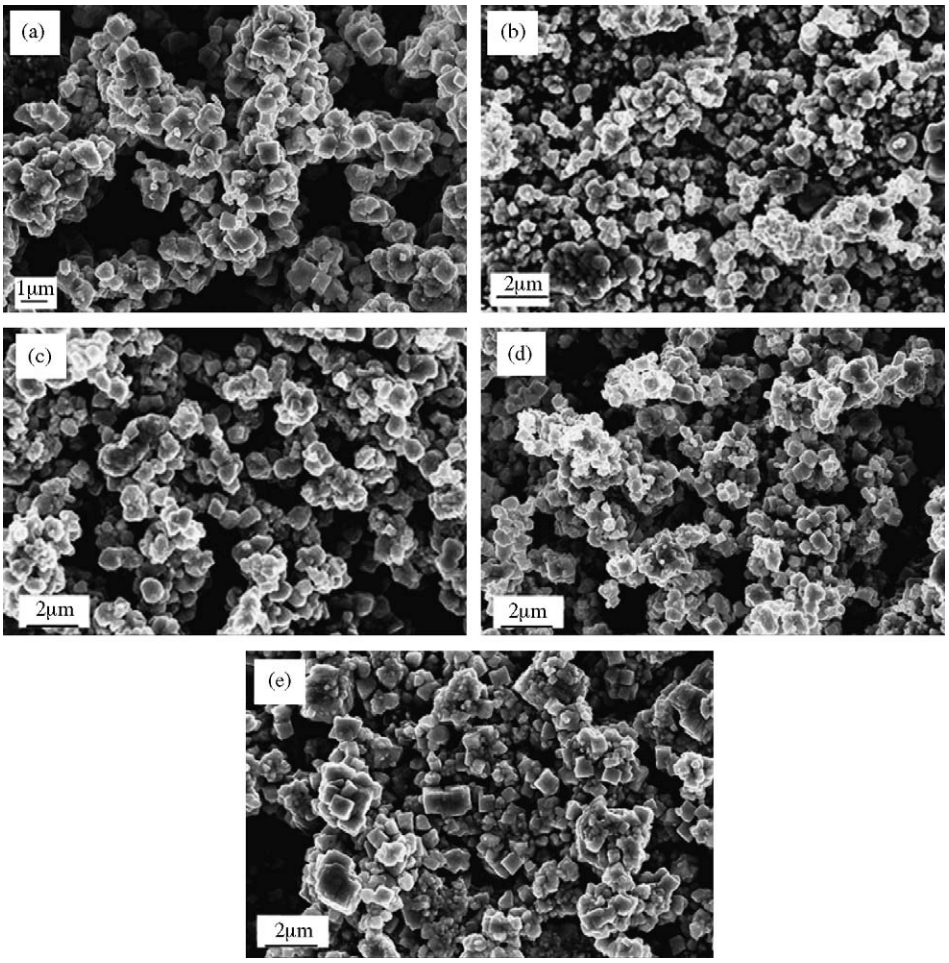

Fig. 2. SEM photographs of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ powders along with different amounts of Ta-doping of x: (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4.

K^+/Na^+ ratio in as-prepared powders. It was reported that $K_{0.5}Na_{0.5}NbO_3$ (KNN) was near the MPB [2], so that a monoclinic phase near the MPB has been obtained when the designed molar ratio in the precursor solution was from 5:1 to 6:1. The molar ratios of Ta^{5+}/Nb^{5+} in the as-prepared powders were similar to the designed one as shown in Table 2, indicating that both Ta^{5+} and Nb^{5+} have dissolved in the crystal lattice of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ according to the molar ratio designed, which corresponded with XRD results.

Table 1
EDS analysis of K^+/Na^+ of as-prepared powders.

K^+/Na^+ (designed molar ratio in the raw alkalinity solution)	K^+/Na^+ (molar ratio of as-prepared powders)
4:1	4:7.11
5:1	5:6.11
6:1	6:5.54

Table 2
EDS analysis of Ta^{5+}/Nb^{5+} of as-prepared powders.

Ta^{5+} doping amount (mol)	Ta^{5+}/Nb^{5+} (molar ratio of as-prepared powders)
0.1	0.08:0.92
0.2	0.23:0.77
0.3	0.26:0.74
0.4	0.38:0.62

3.2. Phase analysis and microstructure of ceramics

Fig. 3 shows the X-ray diffraction patterns of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ (x = 0.1, 0.2, 0.3, 0.4) ceramics. During the process of sintering, the monoclinic perovskite structure of the powders has transferred into the orthorhombic perovskite structure of ceramics, indicating that the higher symmetry has been achieved after the high temperature treatment. They were well agreed with X-ray diffraction patterns of the KNN powders. It also indicated that K^+ and Na^+ did not volatilize during the procession of sintering.

The SEM of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics was shown in Fig. 4. With the increasing amount of the Ta, its density becomes larger. According to Table 3, the relative density increased to the highest of 90.5% while the doping amount of Ta was 0.3 molar, and then followed with little decreasing. As shown in Fig. 2, the finest and most homogenous as-prepared powders have been prepared when Ta-doping amount was 0.3, so that the largest density of the samples has been obtained at same Ta-doping.

In order to investigate the volatility of Na_2O and K_2O after high temperature treatment, the K^+/Na^+ molar ratio in ceramic

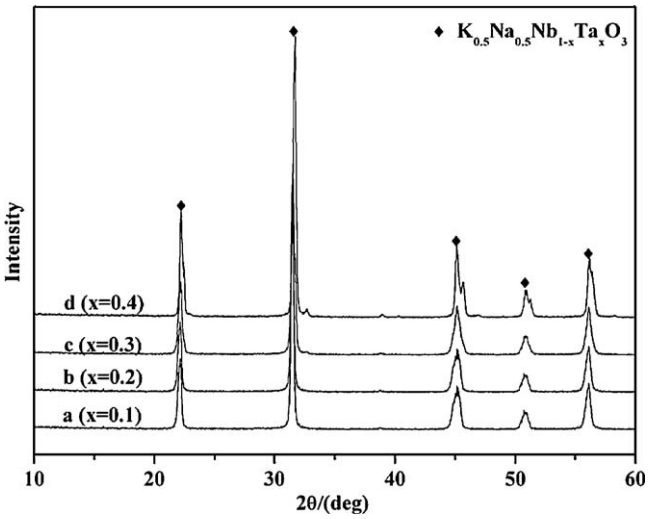

Fig. 3. X-ray diffraction patterns of the $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics of K^+/Na^+ designed molar ratio = 5:1 with (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, and (d) $x = 0.4$.

has been detected by EDS along with different Ta-doping. The EDS analysis of the fracture surface of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics was shown in Table 4. It is shown that K^+/Na^+ molar ratio remained close to 1:1 when the amount of the Ta-doping is about 0.2 or 0.3. In other words, K_2O or Na_2O did not evaporate from the sample and K^+ did not deviate from stoichiometric ratio of KNN ceramics even after 1000 °C sintering, suggesting $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ still near the MPB.

3.3. Piezoelectric properties of KNN ceramic

The values of piezoelectric constant d_{33} of the Ta-doping $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramic along with Ta-doping amount increasing were measured and the results were shown in Table 3. The d_{33} has been increased along with the increasing of Ta-doping, and the highest d_{33} value 210 pC/N was achieved when the doping amount of Ta was 0.3 molar. Because the electronegativity Ta^{5+} is higher than Nb^{5+} and this increases the degree of covalency in the bonds formed. The covalent bonds have sp^3 hybridisation and this leads to increment the existence of a morphotropic phase boundary (MPB), further improvement in the piezoelectric properties of KNN [12]. At same time, the relative density $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ reached the highest one of 90.5%, so that the excellent d_{33} results have been obtained with 0.3 molar Ta-doping.

Table 3
The density and piezoelectric properties of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ with different amounts of Ta_2O_5 at room temperature.

Composition	0 mol	0.1 mol	0.2 mol	0.3 mol	0.4 mol
Theoretical density (g/cm^3)	4.51	4.78	4.98	5.18	5.38
Relative density (%)	86.5	85.7	87.3	90.5	88.7
Piezoelectric constant, d_{33} (pC/N)	78	146	183	210	167

It is reported that the value of d_{33} of $K_xNa_{1-x}NbO_3$ ceramics powders prepared by hydrothermal approach is around 86 pC/N [11]. Recently, modified KNN ceramics have been proved to exhibit good properties. In the system of $K_{0.5}Na_{0.5}NbO_3$–$LiTaO_3$, the value of d_{33} is 134 pC/N [13], while particular KNN ceramics modified by $LiNbO_3$ exhibit piezoelectric constant d_{33} around 200 pC/N [14]. The d_{33} of ZrO_2 addition on the $K_xNa_{1-x}NbO_3$ ceramics is 100 pC/N [3]. The more general system (K,Na,Li)(Nb,Ta,Sb)O_3 seems even more promising, with d_{33} values over 300 pC/N in ceramics with random grain orientation and over 400 pC/N in textured ceramics [15]. In this

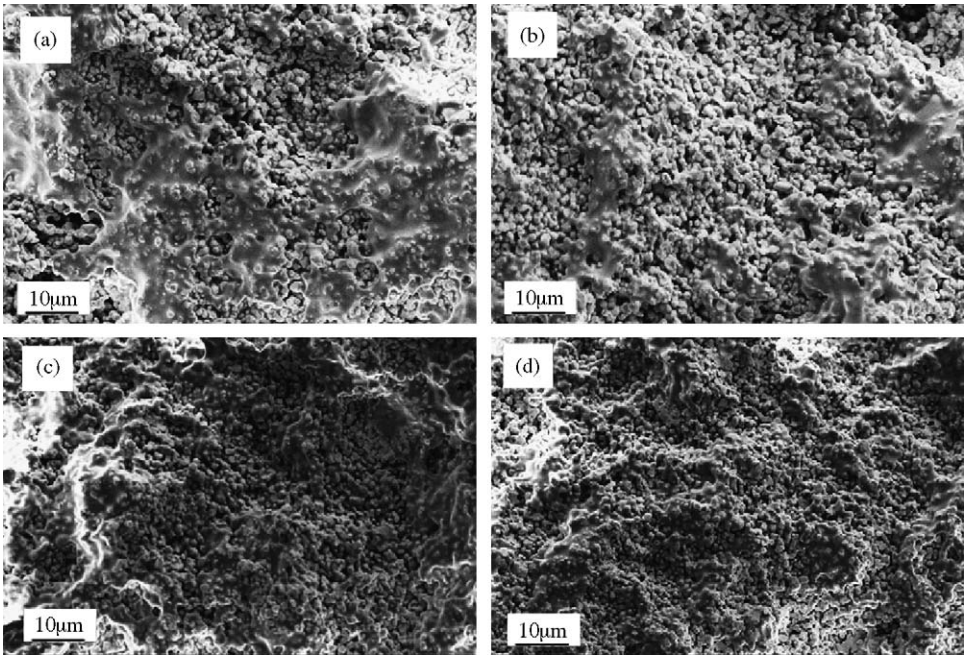

Fig. 4. SEM photographs of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics with x: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4.

Table 4
EDS analysis of the fracture surface of $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ceramics.

Ta^{5+} doping amount (mol)	K^+/Na^+ (molar ratio of as-prepared powders)	K^+/Na^+ (molar ratio of ceramics)
0.1	1:1.22	1: 2.2
0.2	1:1.22	1:1.3
0.3	1:1.22	1:1.17
0.4	1:1.22	1:1.52

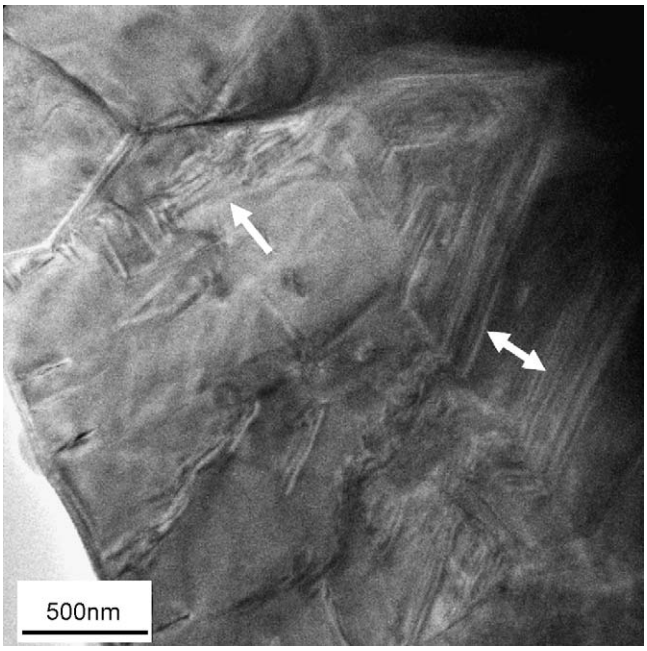

Fig. 5. The well discernible ferroelectric domains in $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic from TEM image.

study, good d_{33} of 210 pC/N can be achieved by simply Ta-doping and ordinary sintering.

The electromechanical coupling factors K_p of 0.3 have been measured on the $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic which possess optimal d_{33} value. It is reported [16] that the range of K_p for pure KNN was about 0.29–0.40, and the hot pressed KNN (~99% of the theoretical density) has been reported to possess a high K_p of 45% and d_{33} of 160 pC/N [14]. However, the hot pressed technique was not benefit to its wide application. Hence, $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic, possess higher d_{33} and satisfied K_p value, is one of the potential lead-free piezoelectric materials for its simple preparation process.

3.4. Domain structure observation

The morphology of ferroelectric domains of the $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic is highlighted in Fig. 5. This observation is in agreement with an earlier study of KNN ceramics sintered at 1100 °C [17] and a TEM study of $0.95K_{0.5}Na_{0.5}NbO_3$–$0.05BaTiO_3$ sintered at 1060 °C [18]. It can be seen that the herringbone domain distributed around the grain boundary attributed to its ferroelectric properties. Because $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic was near the MPB, it showed good piezoelectric and ferroelectric properties. Moreover Ta-doping increased its unsymmetry, induced the aberrance of crystal lattice, so that ferroelectric properties of $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic have been enhanced. The typical domain structure has been observed in it.

4. Conclusion

The $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ($x = 0.1$, 0.2, 0.3, 0.4) powders have been hydrothermally synthesized at 230 °C for 24 h. The $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ powders exhibit the monoclinic perovskite structure and grain sizes are very homogeneous and fine, being on the order of 200 nm. The morphotropic phase boundary (MPB) has been formed when the molar ratio of K^+/Na^+ in precursor was about 5:1. The $K_{0.5}Na_{0.5}Nb_{1-x}Ta_xO_3$ ($x = 0.1$, 0.2, 0.3, 0.4) ceramics exhibit orthorhombic perovskite structure. With the increasing amount of the Ta-doping, the grains become denser, when $x = 0.3$ the relative density is highest than the others. And the EDS analysis of the fracture surface of ceramics showed that $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic remained near the MPB. After sintering and polarizing treatment, it was found that the value of d_{33} increased with the increase of amount of Ta-doping and the $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ showed the highest value of d_{33} 210 pC/N and the electromechanical coupling factors K_p are 0.3. The obvious domains structure has been observed, which indicated that the $K_{0.5}Na_{0.5}Nb_{0.7}Ta_{0.3}O_3$ ceramic had good piezoelectric and ferroelectric properties for it's near the MPB.

Acknowledgements

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