Effect of Mn doping on sintering characteristics, microstructure and electrical properties of lead-free potassium sodium niobate ceramics

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The piezoelectric ceramics of $(K_{0.5}Na_{0.5})NbO_3$+x$MnCO_3$ (KNN+xMn) were prepared by the conventional solid-state method, and the effect of Mn doping on the sintering characteristics, microstructure and electrical properties of the ceramics was investigated. The results show that proper Mn doping promotes sintering performance, induces lattice to change from orthorhombic to tetragonal and improves electrical properties of KNN ceramics. When the content of Mn is 2 mol%, the relative density of KNN ceramics is 93.2%, the phase structure is more close to tetragonal and the best electric properties are obtained, such as ε_r is 526, tanδ is 2.3%, d_{33} is 207 pC/N, k_p is 45% and Q_m is 181.

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1. Introduction

Piezoelectric materials play a crucial role in electrical devices such as actuators, accelerators, ultrasonic generators, piezoelectric transducers, filters and sensors. At present, the widely used materials of piezoelectric devices are still mainly lead zirconium titanate based ceramics due to their excellent piezoelectric properties. However, the main raw materials of this kind of ceramics are lead oxide, which will harm human health and cause environmental pollution in the process of production, use and disposal. Therefore, the research and development of lead-free piezoelectric ceramic materials with friendly environment and excellent performance has become an urgent task in the field of piezoelectric ceramics. In lead-free piezoelectric ceramic systems, $(K_{0.5}Na_{0.5})NbO_3$-based piezoelectric ceramics (KNN) which has an ABO_3 type perovskite structure have become a new research hotspot in the field of lead-free piezoelectric ceramics because of its excellent piezoelectric properties and high Curie temperature [1-3]. The traditional solid-phase sintering process is simple and easy to control, and is a common method for the preparation of piezoelectric ceramic materials. However, for KNN-based ceramics, sintering at high temperature by traditional solid-phase method will cause a large amount of volatilization of potassium and sodium, and it is difficult to obtain a dense ceramic body, which greatly limits the application of such materials [4-5].

Doping modification is an important means to promote sintering and improve the piezoelectric properties of KNN-based ceramics [6-12]. As one of the stable doping elements, the Mn doping of multiple systems has been investigated. In 1997, Yoon et al. reported that Mn doping significantly enhanced the mechanical quality factor *Q*m of the PZT-Pb$(Y_{1/3}W_{2/3})O_3$ system while effectively reducing the dielectric loss tanδ [13]. Hou et al. also found in the Mn doping study of PZT-Pb $(Zn_{1/3}Nb_{2/3})O_3$ system that a small amount of Mn doping can significantly improve the piezoelectric properties of the materials, and the piezoelectric transformer made of Mn-doped PZT-Pb$(Zn_{1/3}Nb_{2/3})O_3$ based materials has excellent performance [14,15]. Furthermore, Mn doping also has the effect of improving its piezoelectric properties for the lead-free system $Sr_{2-x}Ca_xNaBi_5O_{15}$ [16]. A number of similar findings were also confirmed in $BaZrTiO_3$, $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$, $(Na_{0.5}Bi_{0.5})TiO_3$-x$BaTiO_3$, $BaTiO_3$-Bi$(Mg_{0.5}Zr_{0.5})O_3$, $BiFeO_3$-$BaTiO_3$ and (1-x)$AgNbO_3$-x$CaTiO_3$ lead-free systems [17-22]. Based on the excellent performance of Mn doping in other systems, it can be predicted that the lattice distortion caused by proper amount of Mn doping can promote sintering and increase the density of KNN ceramics, and the characteristics of its stability additives are also expected to greatly enhance the electrical properties of ceramics.

To sum up, in the absence of research on the Mn doping system of KNN ceramics at present, this paper

selects Mn as doping element to study the modification of KNN ceramics, and systematically studies the effect of Mn on the sintering characteristics, phase structure and electrical properties of KNN ceramics.

2. Experimental procedure

Analytical pure K_2CO_3, Na_2CO_3, Nb_2O_5 and $MnCO_3$ were used as raw materials to prepare $(K_{0.5}Na_{0.5})NbO_3$+x$MnCO_3$ (KNN+xMn) ceramics by traditional solid-phase sintering. According to the stoichiometric ratio of KNN+xMn (molar fraction, x =0%, 1%, 2%, 3%), all kinds of raw materials were weighed and put into ball milling tank, and alcohol was used as medium for milling for 24 hours. The powder after milling was calcined in muffle furnace for 850 °C for 5 h. PVA, accounting for 1% of the total mass of powder, was added for granulation and then pressed into plain body with diameter of 11.5 mm. According to the content of Mn, the ceramic samples were sintered at 1070~1100°C for 2h. The surface of ceramic can be used for observation of phase structure after grinding. The sample was mechanically fractured and then sputtered onto the Au film layer can be used for SEM observation. After plating silver electrode on the upper and lower surfaces, the electrical properties of the samples have been tested. After polarizing at 150°C, by a voltage of 4 kV/mm for 30 min, and ageing for 24 h, samples can be tested for their piezoelectric properties. The XRD test was performed using a Bruker D8 ADVANCE type X-ray diffractometer. The density of the ceramic body was measured by METTLER XS104 balance. The microscopic morphology of the ceramic section was observed using a BCPCAS4800 scanning electron microscope. The dielectric constant and dielectric loss of the sample were measured by an Agilent E4980A LCR measuring instrument. Based on the resonant-antiresonant method, the electromechanical coupling coefficient k_p and the mechanical quality factor Q_m of the ceramic body were acquired with an Agilent 4294A impedance analyzer, and the piezoelectric constant d_{33} was determined by a ZJ-2A quasi-static piezoelectric d_{33} meter.

3. Results and discussion

Fig. 1 shows the XRD patterns of KNN+xMn ceramics. It can be seen from Fig. 1, when x ≤2%, By looking up the JCPDF card, The diffraction peaks correspond to the orthogonal phase of Potassium Niobate (JCPDF No. 71-2171), Which suggests that the system is pure perovskite phase structure, and no diffraction peaks of the second phase appear [23]; when x =3%, there are hetero-peaks in the range of 24~30 °. By looking up the PDF card, it is found that the hetero-peaks correspond to $NNaMnO_2$, which indicates that the solution limit of Mn ions in KNN ceramics is about 2%.

To illustrate the effect of Mn doping on the ceramic phase structure of KNN, the diffraction peaks of XRD patterns in the range of 43.5–47.5° were fitted by Lorentz simulation. The results are shown in Fig. 2 it can be seen that as the Mn ions enter the KNN ceramic lattice, the relative intensity of the (202) peak changes with the (020) peak, which is characteristic of the typical change in the structure of the KNN ceramic phase [2]. The crystal cells of orthorhombic KNN have monoclinic symmetry. The lattice constants of KNN ceramics are analyzed and calculated with based on the method in our previous work [23, 24]. The results are shown in Fig. 3. As can be seen from Fig. 3, when the Mn content is less than 2%, with the increase of Mn content, the lattice constants a_m, c_m, b_m of KNN ceramics all increase, while the β angle decreases. When the Mn content is 2%, the β angle is 90.09°, and the ceramic is closer to the tetragonal phase. When the Mn content is greater than 2%, the lattice constants a_m, c_m, b_m of KNN ceramics decrease with increasing Mn content, while the β angle increases, which indicates that the Mn doping causes the lattice of KNN ceramics to expand first and then contract. Mn ions generally exist in perovskite structures in the way of Mn^{2+} and Mn^{3+} [14]. The ionic radius of Mn^{2+} is 0.072 nm and the ionic radius of Mn^{3+} is 0.067 nm, all of which are close to the ionic radius of Nb^{5+} (0.064 nm) and are easy to replace Nb^{5+}. The substitution of Nb^{5+} by larger radius Mn^{2+} and Mn^{3+} causes lattice expansion, which induces the transition of the KNN ceramic phase structure to the tetragonal phase. When the amount of Mn doping exceeds the solid solution limit of KNN ceramics, the excess Mn will aggregate on the ceramic grain boundaries, which suppresses the lattice distortion of KNN ceramics within the grains, which is consistent with the results of Li-doped KNN ceramics [2].

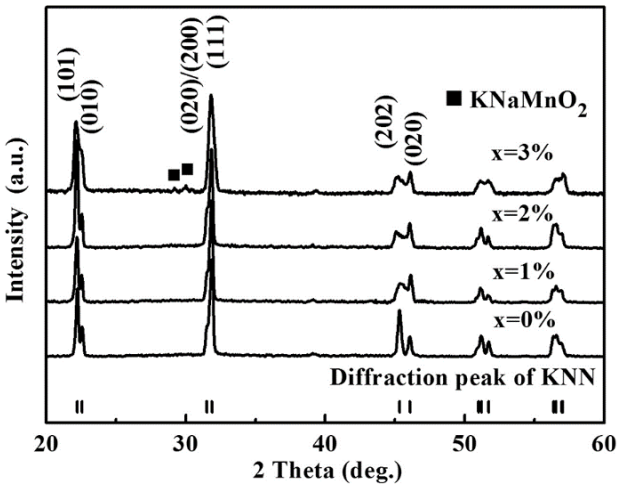

Fig. 1. XRD patterns of KNN+xMn ceramics

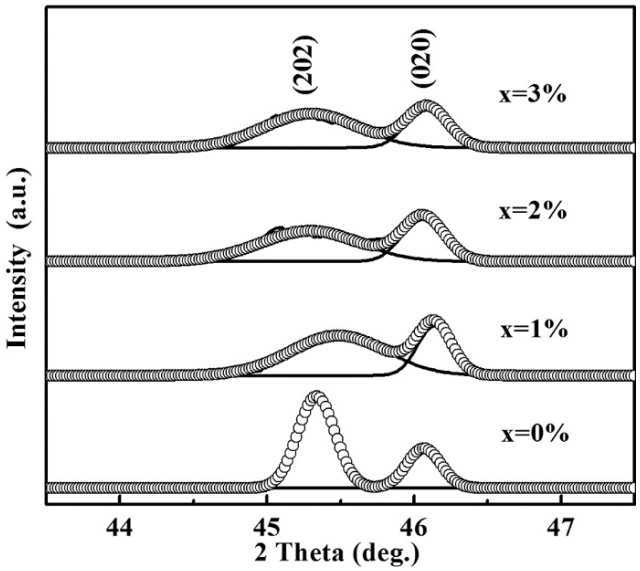

Fig. 2. XRD patterns in range of 43.5~47.5 ° of KNN+xMn ceramics and Lorentz curve simulation

As can be seen from Fig. 4, the relative density of pure KNN ceramics is 90.4%, which shows its low sintering activity. With the increase of Mn content, the relative density of the sample increases, and the relative density reaches 93.2% when the Mn content increases to 2%, which indicates that proper Mn doping is beneficial to sintering densification of ceramics. However, excessive Mn doping leads to a decrease in ceramic compactness. When the Mn doping amount reached 3%, the relative density decreased to 92.8%.

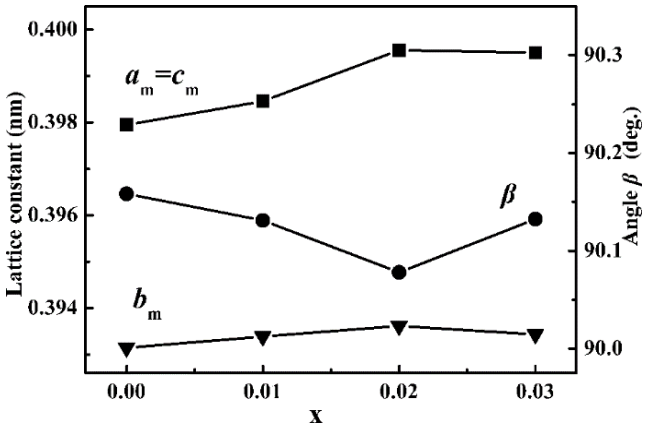

Fig. 3. Variation of lattice constants of KNN ceramics as a function of Mn contents

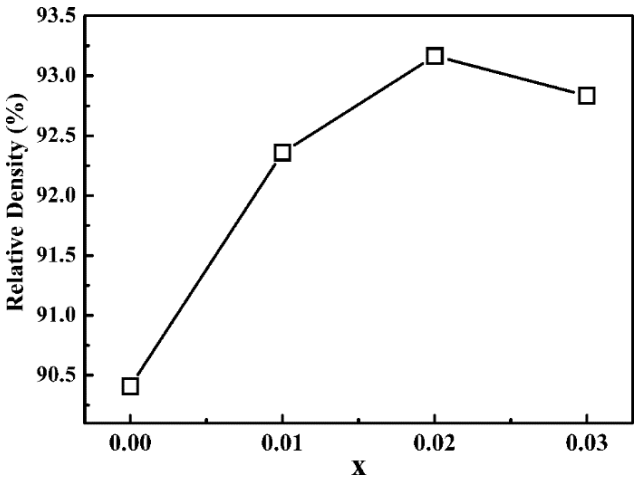

Fig. 4. Variation of relative density of KNN+xMn ceramics

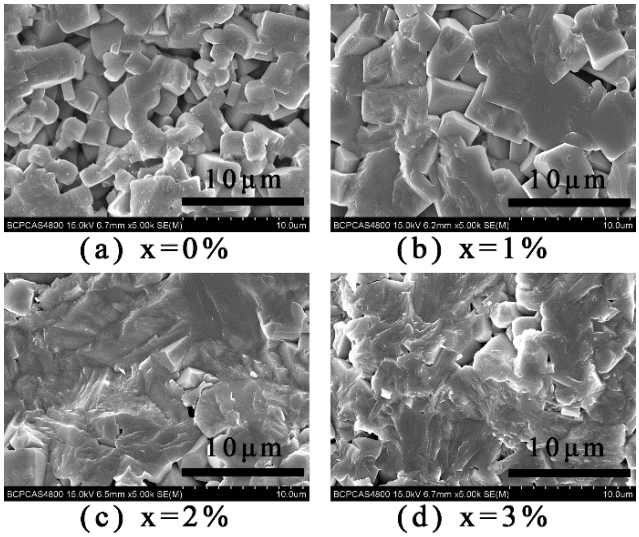

Fig. 5. SEM photograph of the fracture surface for KNN+xMn ceramics

Fig. 5 is a SEM photograph of KNN+xMn ceramic cross-section. As can be seen from the Fig. 5, there are more pores in the undoped KNN ceramic samples. With the increase of Mn content, the grain size of the sample increases and the density is also increased. However, when the Mn content is 3%, the grain shape becomes irregular, the holes gradually increase, and the sintering properties of the ceramics deteriorate. When adding a small amount of Mn, the ceramics display a larger grain size compared with that of the pure KNN ceramics, indicating that the addition of Mn can facilitate the grain growth of the ceramics. The change of the microscopic morphology and density can be explained by the lattice distortion caused by Mn doping. Because the ionic radius of Mn^{2+} and Mn^{3+} is larger than that of Nb^{5+}, it will cause some lattice distortion. It is generally assumed that the presence of lattice distortion is beneficial to promote sintering. This is the main reason for

the grain growth and density increase caused by proper amount of Mn doping. When doped in large quantities, there will be a second phase $KNaMnO_2$ formation. $KNaMnO_2$ belongs to the orthorhombic system, Cccm space group, with lattice constant a =0.9696 nm, b =0.9343 nm, c =0.6936 nm [25-28], which is quite different from the crystal structure of KNN, so the generated second phase $KNaMnO_2$ is mainly aggregated on the grain boundary, which hinders the grain boundary migration, so the relative density of KNN ceramics decreases.

Table 1. Electrical properties of KNN+xMn ceramics

x (mol%)	ε_r	Tanδ(%)	d_{33}(pC/N)	k_p (%)	Q_m
0	215	3.7	132	35	88
1	358	2.7	177	38	158
2	545	2.3	207	45	181
3	525	2.4	184	42	175

The electrical properties of KNN+xMn ceramics are listed in Table 1. It can be seen from Table 1 that the dielectric properties (dielectric constant ε_r and dielectric loss tanδ) and piezoelectric properties (piezoelectric constant d_{33}, electromechanical coupling coefficient k_p and mechanical quality factor Q_m, which obtained by a resonance-antiresonance method) of KNN ceramics increase with increasing Mn content when x ≤2%. When x ≥2%, the dielectric and piezoelectric properties of KNN ceramics decrease with increasing Mn content. The change of dielectric properties of KNN ceramics is mainly effected by the ceramic density. The increase of ceramic density and its grain size caused by proper amount of Mn doping leads to the increase of dielectric constant and the decrease of dielectric loss. However, when the amount of Mn doping exceeds the limit of solution, the appearance of the second phase causes the decrease of ceramic density, which leads to the decrease of its dielectric properties. When the Mn content is 2%, KNN ceramics obtain the optimal dielectric properties: the dielectric constantε_r is 526 and the dielectric loss tanδ is 2.3%. The piezoelectric properties of KNN depend on the change of phase structure in addition to the influence of ceramic density. According to the literature, when KNN ceramics are in the transition region of polycrystalline phase with orthogonal to tetragonal phase transition, the optimal electrical properties will be obtained because of the most possible polarization direction [2]. In the scope of this experiment, when the Mn content is 2%, the phase structure of KNN ceramic is closest to the tetragonal phase, which is in the transition region of the orthorhombic phase and tetragonal phase, so its piezoelectric performance is optimal. The piezoelectric constant d_{33} is 207 pC/N, the electromechanical coupling coefficient k_p is 45%, and the mechanical quality factor Q_m is 181.

4. Conclusions

The traditional solid-phase method was used to prepare KNN+xMn piezoelectric ceramics to investigate the effect of Mn doping on sintering characteristics, microscopic morphology, phase structure and electrical properties of KNN ceramics. It shows that proper amount of Mn doping can promote the sintering of ceramics and cause lattice distortion. When the amount of Mn doping is 2 mol%, the highest relative density of KNN ceramic is 93.2%, and its phase structure is in the transition region of the orthorhombic phase and tetragonal phase. Meanwhile, Mn doping can also obviously improve the electrical properties of KNN ceramics. The best electrical properties were also obtained at doping capacity of 2 mol%: ε_r is 526, tanδ is 2.3%, d_{33} is 207 pC/N, k_p is 45% and Q_m is 181.

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