The Dielectric Characteristics of the Lead-free Piezoelectric Ceramics $K_{0.50}Na_{0.50}Nb_{0.95}Ta_{0.05}O_3$

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Abstract

In order to improve the sintering density and dielectric properties of the lead-free $K_{0.5}Na_{0.5}NbO_3$-based ceramics, by the use of solid-state reaction, part of the Nb atoms are substituted by the Ta atoms to form $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics and the dielectric characteristics are detail investigated in this letter. It is found that the phases of $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics are pure perovskite with typical orthorhombic symmetry, in addition, no other secondary phases could be certified. For pure $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics, the shapes of the grains are quadrate and which would due to the increase of the porosity and can not be eliminated easily. Because of the phase stability of pure $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics is limited to 1140 ºC in this study, higher sintering temperature (over than 1140 ºC) is not suitable for the fabrication of $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics. Moreover, the Ta atoms in the $K_{0.5}Na_{0.5}NbO_3$-based ceramics could be used to improve the dielectric properties effectively, and it also reveals lower Curie temperature and lower phase transition temperature than the pure $K_{0.5}Na_{0.5}NbO_3$ ceramics. In this letter, for 1120ºC-sintered $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics, the optimum bulk density is 95.6 % of the theorical density, the Curie temperature is 380 ºC, and the optimum relative dielectric constant is 6107 at 10 kHz.

1. Introduction

Recently, lead-free piezoelectric $(K_{0.50}Na_{0.50})NbO_3$-based (KNN) ceramics [1-3] have been paid much attention because it is environmental friendly and reveal good electrical properties and strong piezoelectricity. In the past, it was reported that Li, Ta, and Sb could improve the piezoelectric properties of the KNN-based ceramics effectively [1, 4, 14], however, these ceramics contain a large amount of Ta (>10 %) [5], and which would limit the applications of the KNN-based ceramics because of the price of Ta_2O_5 is much expensive than that of Nb_2O_5. Moreover, although large amounts of Ta in KNN-based ceramics could improve the piezoelectric properties effectively, the Curie temperature is usually low [6]. On the other hand, the morphotropic phase boundary (MPB) of the KNN-based ceramics is also an important factor affecting the electrical properties [4, 7-10]. However, for pure KNN ceramics, according to the phase diagram for $KNbO_3$-$NaNbO_3$ [12], pure KNN ceramics are difficult to densify by the traditional solid-state method due to the phase stability of that is limited to about 1140ºC [13].

In order to improve the sintering density and piezoelectric properties, in this letter, $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics are developed and the dielectric characteristics are also detail investigated.

2. Experimental

According to the composition $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$, proportional amounts of reagent-grade starting materials of K_2CO_3, Na_2O_5, Nb_2O_5, and Ta_2O_5 were mixed, and ball-milled for 12h with deionized water. After drying, the powder was ground and calcined at 865ºC for 4h. After grinding and drying, the mixed powder was uniaxially pressed into pellets in a steel die. Sintering of these pellets was carried out at temperatures between 1060ºC and 1140ºC under ambient conditions for 3h.

The sintered specimens divided into three parts, the first parts of specimens were analyzed by means of an X-ray powder diffraction method using CuK_α radiation, and the densities of the sintered specimens, as a function of sintering temperature, were measured by the liquid replacement method using deionized water as the liquid (Archimedes's method). By the use of SEM, the second parts of specimens were used to observe the sintered surfaces of the specimens. Finally for the third parts of specimens, after two electrodes were pasted on the two sides of the specimens and firing, an HP4294A impedance analyzer was used for the measurements of the dielectric characteristics and Curie temperatures.

3. Results and Discussion

Fig. 1 shows the XRD patterns of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics, it is found that $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics reveal orthorhombic structures. Comparing to the SEM micrographs of the $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics in Fig. 2, it could be observed easily that as the sintering temperature increases (S_T) from 1060ºC to 1120ºC, the grains become dense and uniform gradually. However, as the sintering temperature (S_T) up to 1140ºC, big grains and more pores could be found in Fig 2(e), this means that the proper sintering temperature of the $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics is about 1100~1120ºC. Fig. 3 shows the bulk density of the $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics, it is found that as the sintering temperature increases from 1060ºC to 1140ºC, the bulk density first increases (1060ºC to 1120ºC) and then decreases (1120ºC to 1140ºC), the maximum relative density is 95.6 % of the theoretical density and happened at S_T=1120ºC, this also prove that the proper sintering temperature of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics is 1120ºC.

The relative dielectric constants of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics is shown in Fig. 4, in addition, the test temperature is 25~500ºC and the test frequency is 10 kHz. It is found that the morphotropic phase boundary (MPB) is about 200ºC, and as the sintering temperature increases from 1060ºC to 1140ºC, the Curie temperature first increases from 375ºC (S_T=1060ºC) to 395ºC (S_T=1080ºC), and finally saturated on 380ºC (as $S_T \geq 1080$ ºC). The relative dielectric constant first increases (1060ºC to 1120ºC) and then decreases (1120ºC to 1140ºC), the maximum relative dielectric constant is 6107 and happened at S_T=1120ºC, which reveal the same tendency as the bulk density do. The detailed characteristics of the $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics are listed and concluded in Table 1.

4. Conclusion

In this letter, the dielectric characteristics of the lead-free piezoelectric $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics are presented, the crystal phase is orthorhombic structure and the maximum relative density is 95.6 % of the theoretical density and which is happened at its proper sintering temperature (1120ºC). The maximum dielectric constant is 6107 (S_T=1120ºC and the Curie temperature is 380ºC) and the morphotropic phase boundary is about 200ºC. For the purpose of environment pollution, in the feature, the KNN-based lead-free ceramics would play an important role for the applications of piezoelectric materials and could be used to substitute for the PZT-based piezoelectric ceramics.

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Table 1. The properties of $K_{0.5}Na_{0.5}Nb_{0.95}Ta_{0.05}O_3$ ceramics.

Sintering temperature (°C)	1060	1080	1100	1120	1140
Bulk density (g/cm^3)	3.53	3.74	4.18	4.31	3.95
Relative density (%)	78.2	82.9	92.7	95.6	87.6
Curie temperature (°C)	375	395	380	380	380
Dielectric constant	4403	4720	5191	6107	5625

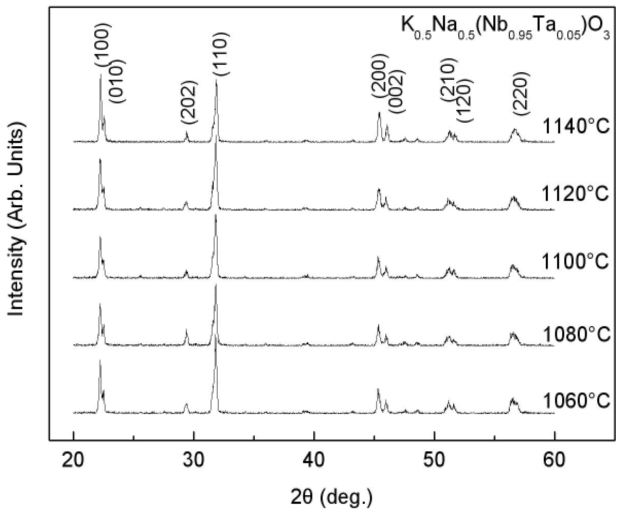

Fig. 1. The X-ray diffraction patterns of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics with the different sintering temperature.

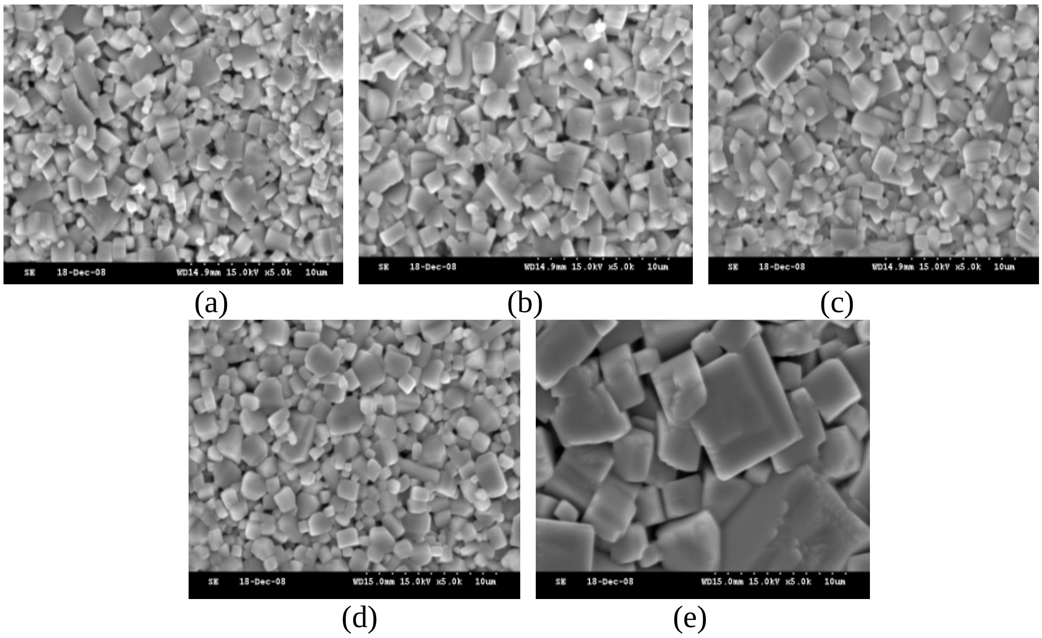

Fig. 2. The SEM micrographs of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics. (a) 1060ºC (b) 1080ºC (c) 1100ºC (d) 1120ºC (e) 1140ºC

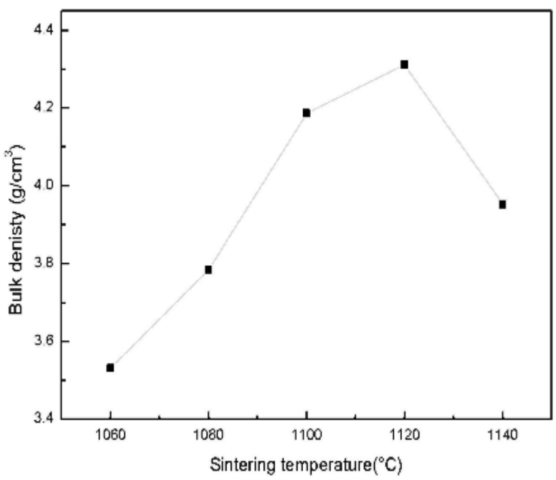

Fig. 3. The bulk density of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics.

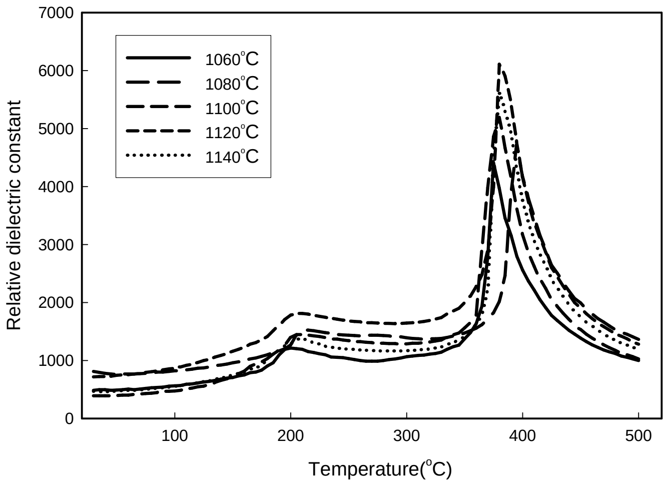

Fig. 4. The relative dielectric constant of $K_{0.5}Na_{0.5}(Nb_{0.95}Ta_{0.05})O_3$ ceramics (at 10 kHz).