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Preparation and Characterization of Lead-free Piezoelectric Ceramics

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Abstract. $(K,Na)NbO_3$-based piezoelectric ceramics are promising candidates for practical applications of lead-free piezoelectric materials due to their excellent piezoelectric properties. In this paper, lead-free piezoelectric ceramics $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (KNL-NTS) were successfully fabricated by traditional ceramics processing. The effects of sintering temperature on the structure, density and electrical properties of KNL-NTS ceramics were investigated. Crystal phases of both calcined powders and KNL-NTS ceramics have orthorhombic structure similar to that of $KNbO_3$ ceramics. The piezoelectric coefficient first increases and then decreases with sintering temperature in the 1100-1180 °C range. KNL-NTS ceramics sintered at 1160 °C shows the maximum piezoelectric coefficient of about 199 $pC\cdot N^{-1}$ and the maximum remnant polarization of 18.75 $\mu C\cdot cm^{-2}$, with the corresponding 10.95 $kV\cdot cm^{-1}$ coercive field and 4.74 g/cm^3 density.

Introduction

Lead-based piezoelectric materials such as $Pb(Zr,Ti)O_3$ (PZT) ceramics are widely used in practical applications due to their superior piezoelectric performance [1]. However, the volatilization of lead in the preparation and disposal processes brings a series of vital environmental problems, since lead is a toxic substance. For the sake of protecting the environment, many lead-free piezoelectric ceramics have been developed to replace the lead-based ceramics. Among various promising lead-free piezoelectric ceramics, potassium sodium niobate $(K,Na)NbO_3$ (KNN)-based ceramics has been considered to be a good candidate for the lead-free piezoelectric ceramics because of its high Curie temperature and large electromechanical coupling factors [2-4]. However, pure KNN ceramics are difficult to fully densify by ordinary sintering methods due to the high volatility of alkaline elements at high temperatures, resulting in non-optimized properties [5-6]. Hot-pressing technique as well as spark plasma sintering have been used to obtain high densities [2], but such processing techniques are not appropriate for industrial applications because of high cost. Thus, introducing modifiers to form solid solutions with KNN by replacing A and/or B site cations of the ABO_3 perovskite structure has been widely used to prepare KNN-based ceramics by conventional solid state sintering methods [7-13].

In this paper, lead-free piezoelectric ceramics $(K_{0.44}Na_{0.52}Li_{0.04})$ $(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (KNL-NTS) were synthesized by traditional ceramics processing. The effects of sintering temperature on the structure, density and electrical properties of KNL-NTS ceramics were investigated.

Sample Preparation

KNL-NTS were prepared by conventional ceramics processing. Analytical grade metal oxides or carbonate powders of K_2CO_3(99%), Na_2CO_3(99.8%), L_2iCO_3(99%), Nb_2O_5(99%), Ta_2O_5(99.99%), Sb_2O_5(99%) and CuO (99%) were used as raw materials. The use of three different powders with carbonate origin requires extra care to be taken against humidity. Thermogravimetric analysis (TGA) shows that the powders lose weight up to 180 °C, equivalent to absorbed water [14]. Therefore, in order to obtain stoichiometric material composition all powders were separately dried in an oven at 200°C for 2 h prior to mixing. Raw materials were mixed according to stoichiometric ratio with the nominal composition of $(K_{0.44}Na_{0.52}Li_{0.04})$ $(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$, followed by ball milling in an ethanol solution in a planetary ball mill using a plastic jar and zirconia grinding balls 3-10 mm in diameter. The batch was ball-milled at 300 rev/min for 5 h. After milling the slurry was dried and kept in an oven at 100 °C.

Calcination was performed in alumina crucible heated to 120 °C before the transfer of the dried powder. After powder transfer it was heated at 3 °C /min rate to 830 °C, 850 °C or 870 °C and kept at that temperature for 5 h. X-ray diffraction (XRD) patterns of calcined powders obtained by this method are shown in Fig.1. Figure 1(a) shows that the reflections of raw materials disappear after calcining at three temperatures and the crystal phase of the sintered powders is orthorhombic, similar to that of $KNbO_3$ (PDF#77-0037M) ceramics. XRD patterns between 20° and 35° were enlarged in Fig. 1(b), implying that there is a second phase in powders sintered at 850 °C and 870 °C, while powder sintered at 830 °C are pure. Therefore, the pre-sintering temperature was set at 830 °C.

Aqueous polyvinyl alcohol (PVA) solution (9 wt.%) was added into the powder as a binder to improve the quality of green bodies. Pellets with 15 mm diameter were uniaxially pressed at 6 MPa for 50 sec.

The green bodies were sintered at 1100 °C, 1120 °C, 1140 °C, 1160 °C, or 1180 °C in air for 2 h, respectively. The sintering procedure was as follows:

(a) Raising the temperature to 100 ° C at 10 °C/min.
(b) Followed by heating to 600 °C at 5 °C/min with dwell time of 3 h to completely remove organic additives.

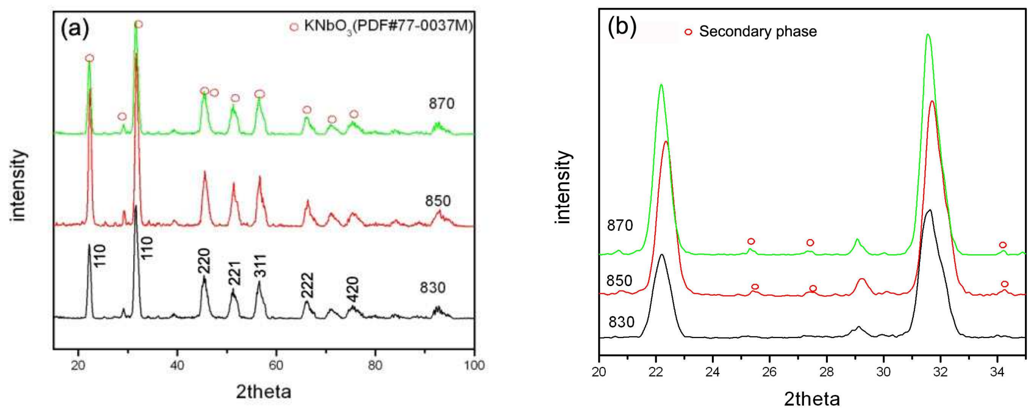

Fig.1. (a) XRD patterns of powders calcined at 830, 850 and 870 °C and (b) enlarged XRD pattern between 20° and 35°.

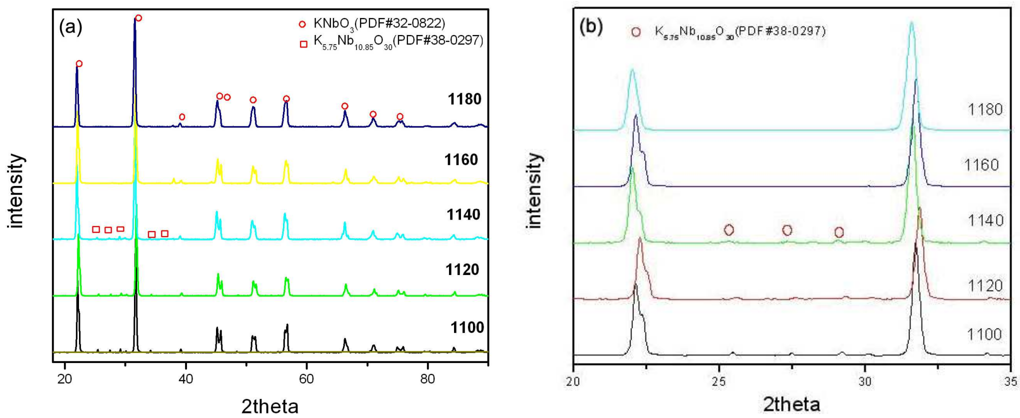

Fig.2. (a) XRD patterns of KNL-NTS ceramics sintered at different temperatures, and (b) enlarged XRD patterns between 20° and 35°.

(c) Finally heating to the sintered temperature at 5 °C/min with 2 h dwell time.

Fig. 2 shows XRD patterns of KNL-NTS ceramics sintered at different temperatures. It can be concluded that: (1) The crystal phase of KNL-NTS ceramics has orthorhombic structure similar to that of calcined powders. (2) Samples sintered at 1100 °C, 1120 °C or 1140 °C have a second phase, which is $K_{5.75}Nb_{10.85}O_{30}$ (PDF#38-0297). The second phase disappears when the sintering temperature is up to 1160 °C. (3) XRD pattern of ceramics sintered at 1160 °C is more similar to that of $KNbO_3$ (PDF#77-0037M) ceramics than that of other samples. Scanning electron microscopy (SEM) image of ceramics sintered at 1160 °C is shown in Fig. 3.

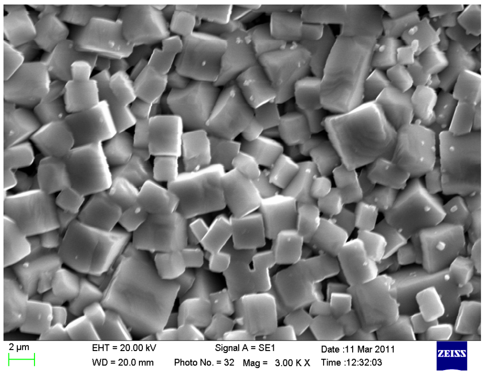

Fig.3. SEM images of KNL-NTS ceramics sintered at 1160 °C.

Table 1. Shrinkage of ceramics sintered at different temperatures.

Sintered temp. [°C]	Diameter [mm]	Shrinkage [%]
1100	12.94	13.7
1120	12.84	14.4
1140	12.76	14.9
1160	12.16	18.9
1180	11.68	22.1

KNL-NTS ceramics density can be characterized by measuring the linear shrinkage of sintered sample's diameter. Table 1 shows the diameter of samples sintered at different temperatures (original diameter of green body is 15 mm). It can be seen that the shrinkage increases with the sintering temperature, implying that the density of sintered ceramics increases with sintering temperature. The density of KNL-NTS ceramics sintered at 1160°C is 4.74 g/cm^3, measured by the Archimedes method using distilled water as a medium. It is difficult to get the theoretical density of KNL-NTS ceramics because of its complex structure. KNL-NTS ceramics has higher density compared with the theoretical density of $(K_{0.65}Na_{0.35})NbO_3$, 4.64 g/cm^3, indicating that the sintered samples are relatively dense.

Characterization

Piezoelectric Coefficient. The d_{33} piezoelectric coefficient was measured by a quasi-static d_{33} meter (ZJ-6A, Institute of Acoustics, Beijing, China). Fig. 4 shows the relationship between the piezoelectric coefficient d_{33} and the sintering temperature, in which each point is an average of 8 data points with an error bar of standard deviation. Fig.4 indicates that the piezoelectric coefficient first increases and then decreases with sintering temperature. The piezoelectric coefficient reaches a maximum of 199 pC·N^{-1} for the KNL-NTS ceramic sintered at 1160 °C. When the sintering temperature was below 1160 °C, the density of KNL-NTS ceramics increased with sintering temperature along with the piezoelectric coefficient increase. Above 1160 °C the piezoelectric coefficient began to decrease with sintering temperature. This may probably be due to the volatilization of alkali components during the sintering, which occurred during KNL-NTS ceramics sintering and caused composition deviation from the starting one.

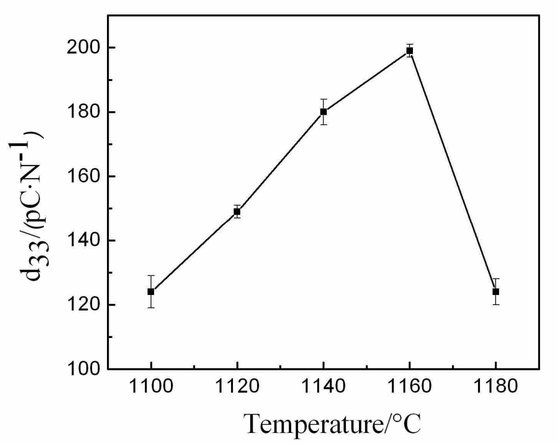

Fig.4. Piezoelectric coefficient d_{33} change with sintering temperature.

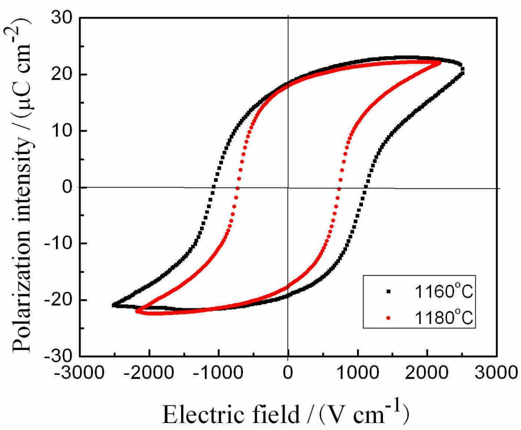

Fig.5. P-E hysteresis loops of KNL-NTS ceramics sintered at 1160 and 1180 °C.

Hysteresis Loops. Generally, the existence of remnant polatization-coercive field (P-E) hysteresis loops is considered as evidence that material is ferroelectric. In this study, saturated P-E hysteresis loops confirm the ferroelectric nature of KNL-NTS ceramics. The coercive field and remnant polarization of KNL-NTS ceramics sintered at different temperatures are shown in Table 2.

Table 2. The coercive field and remnant polarization of KNL-NTS ceramics sintered at different temperatures.

Sintering temp. [°C]	Coercive field E_c [kV·cm^{-1}]	Remnant polarization P_r [μC·cm^{-2}]
1100	8.56	11.10
1120	9.72	12.02
1140	11.30	15.94
1160	10.95	18.75
1180	7.34	17.65

The coercive field E_c increases with sintering temperature in the 1100 °C-1140 °C range. When the sintering temperature is 1140 °C, the coercive field E_c achieves its maximum of 11.30 kV·cm^{-1}, and further decreases with sintering temperature. The trend of remnant polarization P_r is similar to the coercive field E_c, except the maximum value of remnant polarization, 18.75 μC·cm^{-2}, corresponds to the sintering temperature of 1160 °C. Then the remnant polarization P_r drops a little at the sintering temperature of 1180 °C. The P-E hysteresis loops of KNL-NTS ceramics sintered at 1160 °C and 1180 °C are shown in Fig.5.

Discussion

KNL-NTS ceramics were produced using conventional sintering in this study. Although the maximum piezoelectric coefficient of 199 pC·N^{-1} is lower than 290 pC·N^{-1} reported by Liang [15], the nominal composition in their work is $(K_{0.465}Na_{0.465}Li_{0.07})(Nb_{0.95}Sb_{0.05})O_3$, not the same as here. The value of 199 pC·N^{-1} is very close to 195 pC·N^{-1} for $(K_{0.38}Na_{0.52}Li_{0.04})$ $(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_{2.97}$ sintered at 1125 °C for 8 h, and is better than 170 pC·N^{-1} for the sample sintered at 1125 °C for 2 h obtained by Rubio-Macros et al [8]. Moreover, 199 pC·N^{-1} is much higher than 54 pC·N^{-1} and 103 pC·N^{-1} for $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ sintered at 1125°C for 2h and 8h [8], respectively, which nominal composition same as here. Additionally, the piezoelectric coefficient achieved in this paper is higher than that of hot-pressing 115 pC·N^{-1} [6] or spark plasma sintering 148 pC·N^{-1} [2]. This indicates that there is more space to improve piezoelectric properties of lead-free ferroelectric ceramics through optimizing chemical composition and sintering process. In any case improved properties are related to keeping material free of humidity and as close to stoichiometric composition as possible.

Conclusions

A study of lead-free piezoelectric ceramics preparation and characterization using conventional powder synthesis was conducted. Some of the interesting aspects related to preparation and properties can be summarized as the following:

Lead-free KNL-NTS ceramics were produced successfully by sintering at 1100-1180 °C for 2 h under normal pressure. In this temperature range, the piezoelectric coefficient of KNL-NTS ceramics first increases and then decreases with the sintering temperature. KNL-NTS ceramics sintered at 1160 °C shows a maximum 199 $pC\cdot N^{-1}$ piezoelectric coefficient. The sintering temperature was set as 1160 °C in the end. The coercive field Ec and remnant polarization P_r of KNL-NTS ceramics sintered at 1160 °C are 10.95 $kV\cdot cm^{-1}$ and 18.75 $\mu C\cdot cm^{-2}$, respectively.

Acknowledgements

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