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Fabrication and electrical properties of $Pb(Co_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

$Pb(Co_{1/3}Nb_{2/3})O_3$ (PCN) ceramics have been produced by sintering PCN powders synthesized from lead oxide (PbO) and cobalt niobate ($CoNb_2O_6$) with an effective method developed for minimizing the level of PbO loss during sintering. Attention has been focused on relationships between sintering conditions, phase formation, density, microstructural development, dielectric and ferroelectric properties of the sintered ceramics. From X-ray diffraction analysis, the optimum sintering temperature for the high purity PCN phase was found at approximately 1050 and 1100 °C. The densities of sintered PCN ceramics increased with increasing sintering temperature. However, it is also observed that at very high temperature the density began to decrease. PCN ceramic sintered at 1050 °C has small grain size with variation in grain shape. There is insignificant change of dielectric properties with sintering temperature. The P–E hysteresis loops observed at −70 °C are of slim-loop type with small remanent polarization values, which confirmed relaxor ferroelectric behavior of PCN ceramics.

Keywords: A. Sintering; C. Dielectric properties; PCN

1. Introduction

Lead-based relaxor ferroelectrics, particularly lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) belong to a technologically important class of complex $Pb(B'B'')O_3$ perovskite materials [1]. PMN has advantages of having broader operating temperature range, especially over the room temperature range. This is a direct result of a diffuse paraelectric–ferroelectric phase transition in the vicinity of room temperature. In addition, as a result of their unique microstructure features, PMN ceramics exhibit low loss and non-hysteretic characteristics [2]. However, little attention has been devoted to other lead-base relaxor ferroelectrics, $Pb(A_{1/3}B_{2/3})O_3$ (A is Mg^{2+}, Co^{2+}, Ni^{2+} or Zn^{2+} and B is Nb^{5+} or Ta^{5+}), discovered by Bokov and Myl'nikova [3], with the perovskite structure and the dielectric maximum temperature (T_m) lower than room temperature, except for that of $Pb(Zn_{1/3}Nb_{2/3})O_3$. Although Mg^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} have similar radii, the temperatures at which spontaneous polarization occurs in $Pb(A_{1/3}B_{2/3})O_3$ differ [4].

Therefore, in this study, one of lesser studied ceramics in the $Pb(A_{1/3}B_{2/3})O_3$ system, i.e. $Pb(Co_{1/3}Nb_{2/3})O_3$ (PCN), is investigated. Earlier studies have shown interesting piezoelectric properties of PCN single crystal [3]. Another study also described electrical properties of PZT-PCN ceramics [4]. However, there has been no systematic investigation on the PCN ceramics. Therefore, this study will provide more information about this interesting ceramic. Synthesis method, physical properties, microstructure, dielectric and ferroelectric properties of these ceramics are discussed.

2. Experimental procedure

PCN ceramics were prepared from starting $CoNb_2O_6$ (or CN) and PbO powders by a conventional mixed-oxide method. CN powders were obtained from the columbite method, while PCN powders were prepared by a simple mixed-oxide method. To obtain the perovskite-phase PCN, the cobalt niobate ($CoNb_2O_6$) powders were first prepared by mixing CoO (99.9%) and Nb_2O_5 (99.9%) powders in the proper proportion

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and vibro-milling for 1 h. After drying, the mixtures were calcined at 1100 °C for 4 h to yield so-called columbite powders ($CoNb_2O_6$). Subsequently, the columbite powders were mixed with PbO (99.9%) by the vibro-milling method and calcined at 950 °C for 4 h to form the perovskite-phase PCN powders. Then PCN powders were pressed hydraulically to form disc-shaped pellets 8 mm in diameter and 2 mm in thickness, with 3 wt% polyvinyl alcohol as a binder. The pellets were placed in the alumina crucible. Finally, for optimization purposes, the pellets were sintered at 1050, 1100, 1150 and 1200 °C for 2 h. Optimum sintering conditions for all ceramics were established by identifying the conditions for maximizing both the bulk density and the yield of perovskite. The phase formation of the sintered ceramics was studied by X-ray diffraction (XRD) technique. The densities of sintered specimens were measured by Archimedes method. The microstructure analyses were undertaken by scanning electron microscopy (SEM: JEOL Model JSM 840A). The grain size was determined from SEM-micrographs by a linear intercept method.

Before studying the dielectric properties, the specimens were lapped to obtain parallel face. After coating with silver paint as electrode at the faces, the specimens were heated at 750 °C for 12 min to ensure contact between the electrode and the surface of the ceramic. The dielectric properties were measured by LCR-meter at temperatures between −125 and 50 °C with a frequency of 1 kHz. The dielectric constant was then calculated from a parallel-plate capacitor equation, e.g. $\varepsilon_r = Cd/\varepsilon_o A$, where C is the capacitance of the specimens, d and A are, respectively, the thickness and the area of the electrode and ε_o is the dielectric permittivity of vacuum (8.854×10^{-12} F m^{-1}). Finally, the polarization–electric field (P–E) hysteresis loops at −70 °C were obtained using a standardized ferroelectric tester system (RT66A) at a frequency of 4 Hz.

3. Results and discussion

The phase formation behavior of the sintered ceramics is revealed by an XRD method. The XRD patterns are presented in Fig. 1, with the corresponding JCPDS pattern also shown. In general, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of lead cobalt niobate phases. These can be matched with JCPDS file number 04-002-0416 for the $Pb(Co_{0.33}Nb_{0.67})O_3$. Based on the JCPDS file, the optimum sintering temperature for the formation of a high purity PCN phase was found at 1050 and 1100 °C. The PCN ceramics sintered at 1150 °C showed a small peak of pyrochlore near $2\theta \sim 30°$, while the peak of PCN ceramics sintered at 1200 °C at $2\theta \sim 22°$ disappeared.

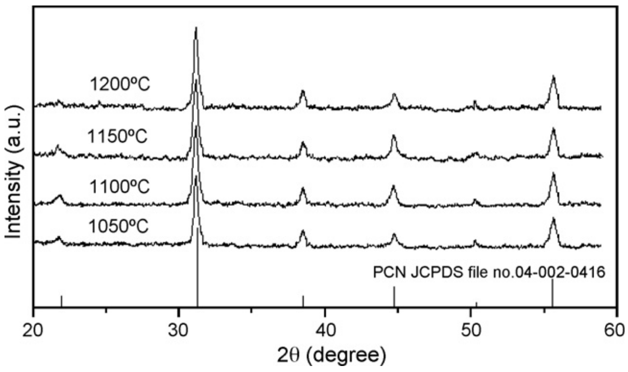

Fig. 1. XRD diffraction patterns of the sintered PCN ceramics.

Table 1
Characteristics of PCN ceramics

Sintering temperature (°C)	Relative density (%)	Average grain size (μm)	Dielectric properties	
			ε_{max}	tan δ
1050	89.39	1.83	2178	0.0594
1100	95.05	4.11	2657	0.0592
1150	95.16	6.35	2673	0.0578
1200	94.10	4.58	2248	0.0507

The relative densities of PCN ceramics sintered at different temperatures are listed in Table 1. It is clear that the density usually increases with increasing sintering temperature. This is believed to be a result of more completed solid-state reactions at higher sintering temperatures. However, it is also observed that at very high temperature the density begins to decrease. Lead-loss is generally accepted to be the reason for the decreasing density [5,6].

The SEM-micrographs of fractured surfaces of all PCN ceramics are shown in Fig. 2. PCN ceramic, sintered at 1050 °C, has small grain size with variation in grain shape. However, the other ceramics exhibit different morphology showing a possible pyrochlore formation (with pyramidal-shaped grains) and also over-sintered specimens. Table 1 also shows that the average grain size of PCN ceramics sintered at 1050 °C is relatively small, as compared to those sintered at higher temperatures. The average grain size seems to increase with increasing sintering temperatures. However, it is also observed that at very high temperature, the grain size begins to decrease, which is similar to the trend observed for the density.

Temperature dependencies of the dielectric constant (ε_r), as calculated from the capacitance of the sample and its geometry, and dielectric loss (tan δ) were measured continuously by increasing temperature from −125 to 50 °C. The temperature dependence of the dielectric constant and dielectric loss for the PCN ceramics are plotted in Fig. 3. As the measuring temperature increases, the maximum dielectric constant (ε_{max}) appear at −30 °C, this temperature is called dielectric maxima temperature (T_m). There is also insignificant change of ε_{max} with different sintering temperatures. The dielectric loss shows only very small decrease with decreasing temperature below the T_m and its value is much higher than that above the temperature of maximum dielectric constant. A strongly diffused dielectric peak is characteristic of ferroelectric relaxors. Frequency-dependent dielectric properties below T_m (not shown here) are also observed, further indicating relaxor behavior of PCN ceramics. Based on X-ray diffraction analysis, density data, SEM-micrograph, and dielectric properties, the optimum sintering temperature for a high purity PCN ceramic is found to be about 1050 and 1100 °C.

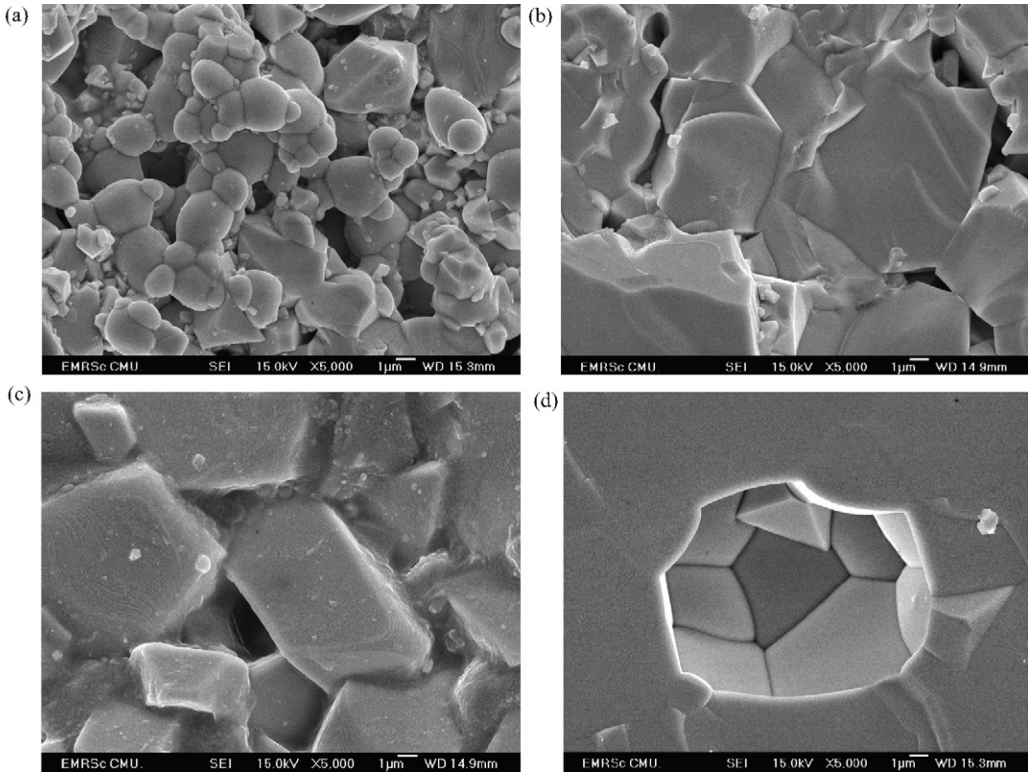

Fig. 2. SEM-micrographs of PCN ceramics at different sintering temperature: (a) 1050 °C; (b) 1100 °C; (c) 1150 °C; (d) 1200 °C.

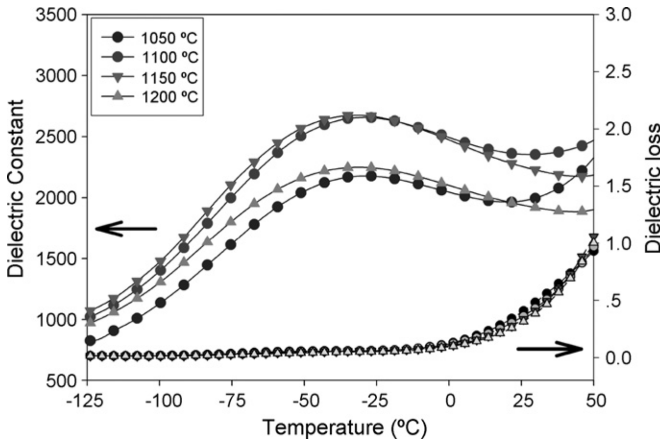

Fig. 3. Temperature dependence of dielectric properties of PCN ceramics at 1 kHz.

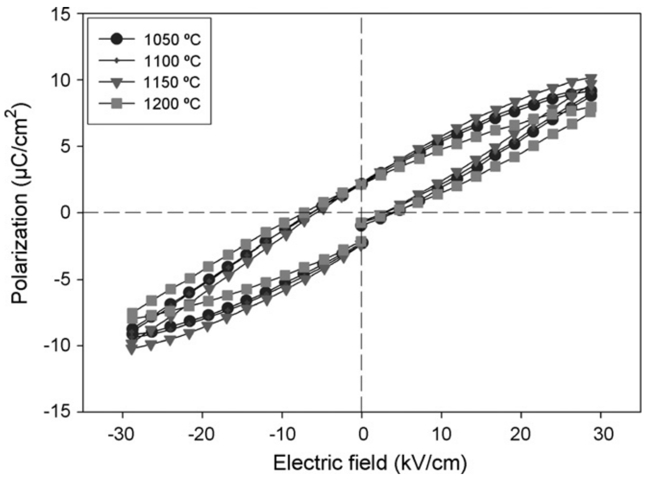

Fig. 4. *P–E* hysteresis loops of PCN ceramics measured at −70 °C and frequency 50 Hz.

The hysteresis loops at −70 °C of PCN ceramics sintered at different temperatures are shown in Fig. 4. It can be seen that slim *P–E* loops with small remanent polarization values are generally obtained for all ceramics. The slim-loop nature of the *P–E* curves suggests that most of the aligned dipole moments switch back to a randomly oriented state upon removal of the field. This behavior has previously been observed in ferroelectric relaxors [7]. In relaxor ferroelectric materials, micro to macro-domain transition occurs. In the absence of any external field, the domain structure of relaxor ferroelectrics contains randomly oriented micropolar regions. However, when an electric field is applied, the micro-domains orient along the field direction and the macro-domains occur [7]. The *P–E* loops observed here also support that the PCN ceramics exhibit relaxor ferroelectric behavior.

4. Conclusions

In this study, PCN ceramics were prepared by the columbite precursor method. The PCN ceramics with perovskite structure and a high purity single phase were obtained. The optimum sintering temperature for the formation of a high purity PCN phase was found to be at 1050 and 1100 °C. Density of these ceramics increases with increasing sintering temperature. However, at very high temperature the density begins to decrease. There is insignificant change of dielectric properties with different sintering temperatures. The samples exhibit a relaxor behavior around the maximum dielectric constant, characterized by a strongly diffused dielectric peak. The hysteresis loops at −70 °C show slim *P–E* loops with small remanent polarization values. This behavior has been observed in ferroelectric relaxors.

Acknowledgements

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