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

Muangjai Unruan [a], Naratip Vittayakorn [b], Rewadee Wongmaneeruang [a], Anurak Prasatkhetragarn [a], Supon Ananta [a], Rattikorn Yimnirun [a,*]

[a] *Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*
[b] *Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand*

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Abstract

In this study, $Pb(Co_{1/3}Nb_{2/3})O_3$ or 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. The densities of sintered PCN ceramics increased with increasing sintering temperature. However, it was observed that at too high temperature the density began to decrease. Change of dielectric properties with sintering temperature also followed the same trend as the density. Based on X-ray diffraction analysis, density data, SEM micrograph, and dielectric properties, the optimum sintering temperature for a high purity PCN ceramic was found to be about 1100 and 1150 °C. A strongly diffused dielectric peak also showed a typical characteristic of ferroelectric relaxors. The P–E hysteresis loops observed at −70 °C were of slim-loop type with small remnant polarization values, which confirmed relaxor ferroelectric behavior of PCN ceramics.

Keywords: Dielectric properties; Sintering; PCN

1. Introduction

Lead-base 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 rang, especially over the room temperature rang. 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 the 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 Mylnikova [3], with the perovskite structure and the dielectric maxima 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. Synthesis method, physical properties, microstructure, dielectric and ferroelectric properties of the ceramic are discussed.

2. Experimental method

PCN ceramics were prepared from starting PbO and $CoNb_2O_6$ (or CN) powders by a conventional mixed oxide method. CN powders were obtained from the columbite method [5], 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 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 thick, 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. The phase formation of the sintered ceramics was studied by the X-ray diffraction (XRD) technique. The densities of sintered spec-

* Corresponding author. Tel.: +66 53 943 367; fax: +66 53 943 445.
E-mail address: rattikornyimnirun@yahoo.com (R. Yimnirun).

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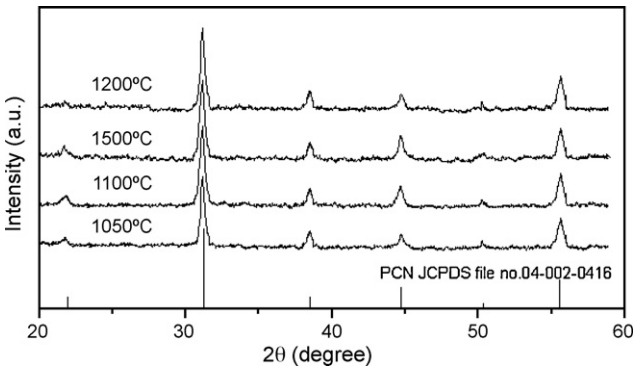

Fig. 1. XRD diffraction patterns of the sintered PCN ceramics.

imens 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 faces. After coating with silver paint as electrode on 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 (dielectric constant (ε_r) and dielectric loss (tan δ)) were measured at temperatures between −120 and 50 °C. The capacitance was measured with a HP4284A LCR meter in connection with a Delta Design 9023 temperature chamber and a sample holder (Norwegian Electroceramics). The dielectric constant (ε_r) 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} Fm^{-1}). Finally, the polarization–electric field (P–E) hysteresis loops at −70 °C were obtained using a standardized ferroelectric tester system (RT66A) with driving 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 perovskite lead cobalt niobate phase. 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 XRD analysis, the optimum sintering temperature for the formation of a high purity PCN phase was found at 1100 °C.

The 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 too high temperature the density begins to decrease. Lead-loss is generally accepted to be the reason for the decreasing density [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 increases 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. Change of dielectric properties with sintering temperature also followed the same trend as the density. The dielectric constant reaches maximum values at sintering temperature of 1150 °C.

Temperature and frequency dependencies of ε_r, as calculated from the capacitance of the sample and its geometry, and tan δ were measured continuously by increasing temperature from −120 to 50 °C and frequency rang from 100 Hz to 100 kHz. The temperature dependence of ε_r and tan δ for the PCN ceramics are plotted in Fig. 3. As the measuring temperature increases the maximum dielectric constant (ε_{max}) appears at −30 °C, this temperature is called dielectric maxima temperature (T_m). It should be noticed that T_m obtained in this study is different from previous studies [3,7–9], which reported T_m of −70 °C for single crystal PCN and stress-dependent T_m for PCN ceramics ranging from −20 to −50 °C. It could be said that the T_m values obtained in this study fall within the previously reported values. This is because in this current study the dielectric properties, which are used to determine T_m, of the PCN ceramic were measured under compressive stress from a rather heavy sample holder used in the measurement system. In addition, the ceramics may also contain internal residual stress. Therefore, the T_m values obtained in this study are slightly lower than the previously reported value under stress-free condition. There is also insignificant change of T_m with different sintering temperatures. The tan δ shows only very small decrease with decreasing temperature below the T_m and tan δ becomes very high above the temperature of maximum dielectric constant. Based on X-ray diffraction analysis, density data, SEM micrograph, and dielectric properties, the optimum sintering

Table 1
Characteristics of PCN ceramics

Sintering temperature (°C)	Density (g/cm^3)	Average grain size (μm)	Dielectric properties	
			ε_{max}	tan δ
1050	7.58	1.83	2178	0.0594
1100	8.06	4.11	2657	0.0592
1150	8.07	6.35	2673	0.0578
1200	7.98	4.58	2248	0.0507