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Dielectric and ferroelectric properties of lead indium niobate ceramic prepared by wolframite method

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Abstract

The dielectric and ferroelectric properties of lead indium niobate ($Pb(In_{1/2}Nb_{1/2})O_3$, PIN) ceramic prepared by an oxide-mixing method via wolframite route were investigated. The 98.5% perovskite fine-grained PIN ceramics with average grain sizes of 1–2 μm were obtained by sintering at 1050 °C for 2 h. The dielectric properties of the PIN were of relaxor ferroelectric behavior with temperature of dielectric maximum (T_m) ~ 53 °C and dielectric constant (ε_r) ~ 4300 (at 1 kHz). The *P–E* hysteresis loop measurements at various temperatures showed that the ferroelectric properties of the PIN ceramic changed gradually from the paraelectric behavior at temperature above T_m to slim-loop type relaxor behavior at temperature below T_m. Moreover, the *P–E* loop became more open at temperatures much lower than T_m. At −25 °C, the maximum polarization is found to be 8 μm/cm^2 at a field of 30 kV/cm, with P_r value of 2.5 μm/cm^2 and E_c of +7.5 kV/cm.
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1. Introduction

Lead indium niobate $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN) compounds are of interest for the kinetics of compositional ordering investigation [1]. It has been reported that the degrees of ordering on the B-site can be varied by thermal annealing and by forming solid solutions with perovskite compounds that exhibit normal dielectric behavior, such as $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), $PbZrO_3$ (PZ) and $PbTiO_3$ (PT) [2]. With different thermal treatments, the degrees of the In/Nb cation ordering on the B-site in a perovskite structure can be manipulated from a structurally disordered state into various degrees of ordering. The disorder PIN is a relaxor ferroelectric with a pseudo-cubic perovskite structure exhibiting the relaxor behavior with a broad dielectric maximum near 66 °C, when measured at 1 kHz [3,4]. On the other hand, the ordered PIN has the antiferroelectric orthorhombic phase [5–7] with a sharp peak in the dielectric constant at 168 °C [4,8]. However, phase-pure perovskite PIN ceramics free of the pyrochlore phase are very difficult to prepare using a conventional mixed-oxide method [7,9]. This is because the tolerance and the electronegativity difference of PIN are very low compared with other perovskite compounds such as PMN [2,10]. The wolframite method, as used by Groves [11] for the preparation of perovskite PIN ceramic, is not effective in suppressing pyrochlore phase formation. The addition of excess In_2O_3 was shown to yield higher amount of perovskite phase (up to 98%) [11]. Recently, Alberta and Bhalla [7] were able to produce 100% phase-pure perovskite PIN ceramic with the addition of excess indium and/or lithium with wolframite method under oxygen atmosphere. Interestingly, these previous studied employed a mixed-oxide method with a conventional ball-milling technique. However, a vibro-milling technique has recently been employed to produce nano-sized powders which can also be used to fabricate ceramics with fine-grain microstructure that may lead to better resulting properties [12–14]. Therefore, the main purpose of this work is to determine the dielectric and ferroelectric properties of PIN ceramics prepared with the wolframite method via the vibro-milling technique to explore the potential in obtaining fine-grain ceramics, which would in turn lead to superior electrical properties. The dielectric and ferroelectric properties as functions of both temperature and frequency will be presented and discussed.

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2. Experimental procedure

The $Pb(In_{1/2}Nb_{1/2})O_3$ ceramics were prepared from $Pb(In_{1/2}Nb_{1/2})O_3$ powders obtained with the wolframite method via the vibro-milling technique. In this technique, a vibratory laboratory mill (McCrone Micronizing Mill) was employed. A total of 48 polycrystalline corundum milling media with a powder weight of 20 g was kept constant in each batch. The milling operation was carried out in isopropanal inert to the polypropylene jar [12–14]. Initially, phase-pure PIN powders were obtained via a well-known wolframite method [7,15]. With the wolframite method, the single-phase indium niobate ($InNbO_4$) powders were first prepared by mixing starting indium oxide (In_2O_3) and niobium oxide (Nb_2O_5) (Aldrich, 99.9% purity) powders, then calcining the mixed powders at 900 °C for 4 h with heating/cooling rates of 30 °C/min [16]. This yielded a so-called wolframite ($InNbO_4$) powder. The wolframite precursor powders were subsequently mixed with lead oxide (PbO) (Fluka, 99% purity) for 0.5 h. The mixed powders were calcined at 1100 °C for 2 h with heating/cooling rates of 10 °C/min to form a single-phase PIN [17]. It should, however, be noted that to obtain the pure-phase PIN powders 2 mol% excess of In_2O_3 and PbO had to be added to compensate the loss during calcination [17]. The PIN powders obtained were vibro-milled for 0.5, then pressed hydraulically to form disc-shaped pellets 10 mm in diameter and 2 mm thick, with 3 wt.% polyvinyl alcohol as a binder. The pellets were placed on the alumina powder-bed inside alumina crucible and surrounded with atmosphere powders of the same composition. Finally, the pellets were sintered at 1050 °C for 2 h with heating/cooling rates of 5 °C/min. The phase formations of the sintered specimens were examined by the X-ray diffractometer.

The densities of the sintered ceramics were measured by Archimedes method. The microstructure analyses were undertaken by a scanning electron microscopy (SEM: JEOL Model JSM 840A). Grain size was determined from SEM micrographs by a linear intercept method. The dielectric properties were evaluated with a computer-controlled dielectric measurement system consisted of a precision LCR-meter (Hewlett-Packard, model 4284A), a temperature chamber (Delta Design, model 9023), and a sample holder (Norwegian Electroceramics) capable of high temperature measurement. The ferroelectric polarization versus electric field (*P–E*) measurements was made using a standardized ferroelectric test system (RT-66A, Radiant Technologies) with an applied field of 30 kV/cm. More importantly, the temperature dependent ferroelectric properties were also examined.

3. Results and discussion

Fig. 1 shows the XRD pattern of PIN ceramics sintered at 1050 °C for 2 h with heating/cooling rate of 5 °C/min, which indicates $Pb(In_{1/2}Nb_{1/2})O_3$ along with very small amount of pyrochlore phase. The amount of perovskite PIN phase was calculated to be 98.5%, as compared to 90–98% reported in previous investigations [11,18]. The density of the sintered specimen was also determined to be 91% of the theoretical density, similar to that reported earlier [7,19]. SEM micrographs in Fig. 2 reveal fine-grain microstructure (<3 μm) in PIN ceramics with the average grain size of 1.22 μm. However, it should be noticed that the microstructure also represents two distinct grain sizes, i.e. large grains (∼2 μm) and submicron grains. Earlier study on PIN-based ceramics prepared with the conventional ball-milling method has also reported bimodal grain sizes but with large grains over 10 μm and fine-grains about 1–2 μm [20]. Clearly, this shows the advantage of the vibro-milling technique in producing fine-grain PIN ceramics.

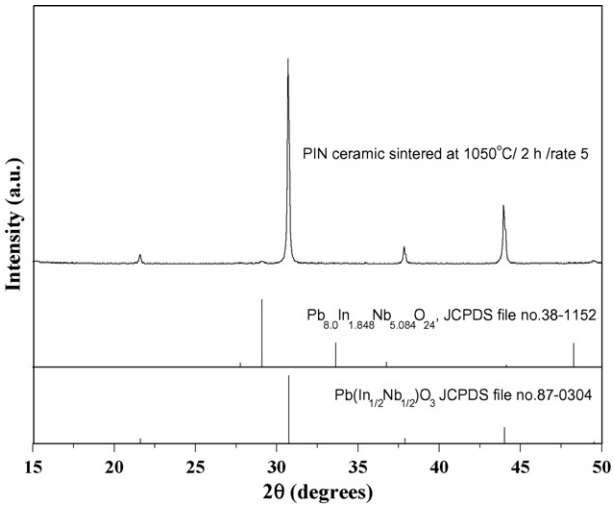

Fig. 1. XRD pattern for PIN ceramic sintered at 1050 °C.

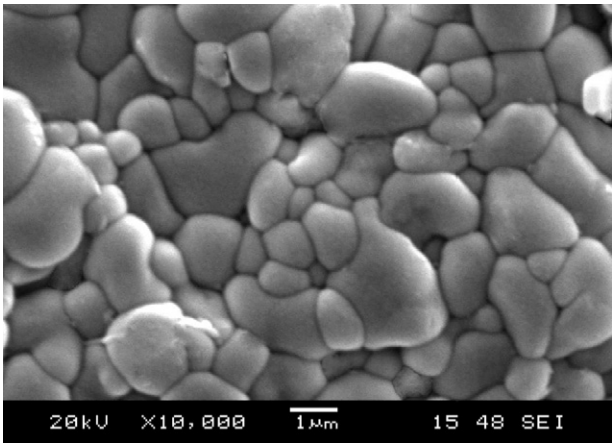

Fig. 2. SEM micrographs of PIN ceramic.

The dielectric properties, e.g. dielectric constant (ε_r) and tan δ, are measured as functions of both temperature and frequency, as shown in Fig. 3. At 1 kHz, the dielectric constant shows a maximum value of 4300 at 53 °C. The value of dielectric constant is higher than those reported earlier by Groves [11] and Park and Choo [18] with similar amount of perovskite phase. This suggests that the fine-grain PIN ceramics obtained exhibit better dielectric properties. However, the dielectric constant is still lower in value than that of phase-pure

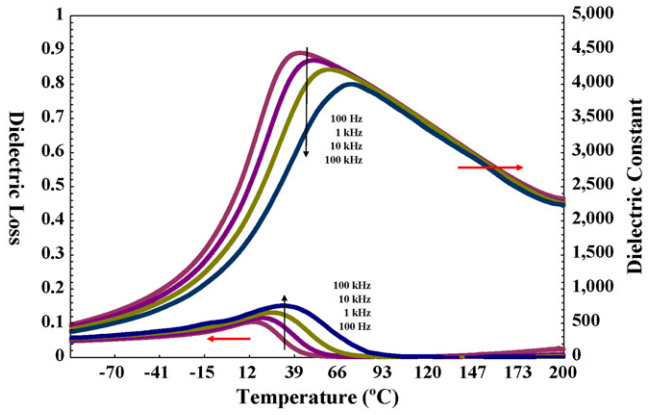

Fig. 3. Temperature and frequency dependent dielectric properties of PIN ceramic.

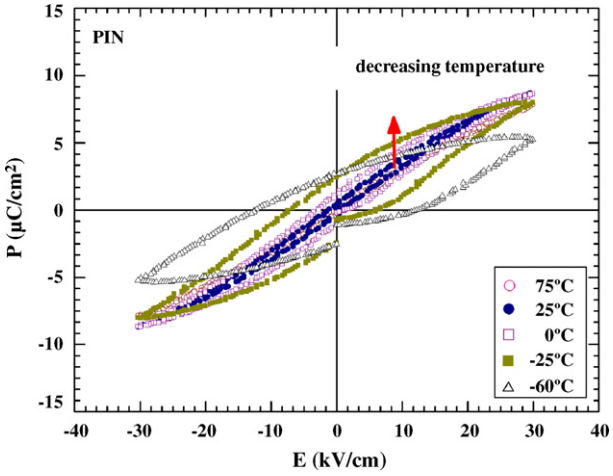

Fig. 4. Temperature dependence of the *P–E* hysteresis loops of PIN ceramic.

PIN ceramic reported earlier by Alberta and Bhalla [7]. The lower value is attributed to the detrimental effect of the secondary pyrochlore phase. The dielectric properties of PIN ceramic change significantly with temperature and frequency. Both dielectric constant (ε_r) and dielectric loss tangent (tan δ) exhibit strong temperature–frequency dependence below the transition temperature, indication of a typical relaxor ferroelectric behavior. In this case, the temperatures of maximum dielectric constant and dielectric loss tangent are shifted to higher temperature with increasing frequency. The maximum value of the dielectric constant decreases with increasing frequency, while that of the dielectric loss tangent increases. The dielectric properties then become frequency independence above the transition temperature [21]. Interestingly, 98% porovskite PIN ceramic reported earlier [7] showed strong frequency-dependent dielectric properties even above the transition temperature. The degree of broadening or diffuseness in the observed dielectric variation could also be estimated with the diffusivity (γ) using the expression $\ln(1/\varepsilon_r - 1/\varepsilon_{max})$ versus $(T - T_{max})^{\gamma}$. The value of γ can vary from 1, for normal ferroelectrics with a normal Curie–Weiss behavior, to 2, for completely disordered relaxor ferroelectrics [21]. The value of γ of the PIN ceramic is calculated to be 1.89, which confirms that diffuse phase transitions (DPT) occur in the PIN ceramics with a high degree of disorder. It is also observed that the degree of broadening for fine-grain PIN ceramics in this study is larger than that of coarse-grains PIN reported earlier [7], a result of decreased grain size, as reported earlier in other perovskite systems [22,23].

Fig. 4 illustrates a series of polarization (*P–E*) hysteresis loops for the PIN ceramics as a function of temperature from −60 to 75 °C. It is clearly evident that the shape of *P–E* loops and the polarization values vary greatly with the temperature. At 75 °C, which is above the temperature of maximum dielectric constant ($T_m \sim 53$ °C), the *P–E* loop shows a paraelectric behavior. When the temperature was lowered to 25 °C, the *P–E* loop is of a ''slim'' loop type, a characteristic of the suppressed ferroelectric interaction typically found in the relaxor ferroelectrics with polar nano-regions [22,23]. As temperature decreases further, the hysteresis loops of PIN ceramics become more developed and open with increasing remnant polarization (P_r), spontaneous polarization (P_s) and coercive field (E_c). It could be said that the hysteresis loops become more of a typical ''square'' form, a typical characteristic of a phase that contains long-range interaction between dipoles in the ferroelectric micro-domain state [21]. Similar observations have been reported earlier [19,22,23]. At −25 °C, the maximum polarization is found to be 8 μm/cm^2 at a field of 30 kV/cm, with P_r value of 2.5 μm/cm^2 and E_c of 7.5 kV/cm, in the same range as reported earlier [19].

4. Conclusions

The $Pb(In_{1/2}Nb_{1/2})O_3$ ceramics were prepared by a wolframite precursor method via a vibro-milling technique. The 98.5% perovskite fine-grain PIN ceramics with average grain size of 1–2 μm were obtained by sintering at 1050 °C for 2 h. This study suggested the advantage of the vibro-milling technique to lower the optimum calcination temperature and dwell time for formation of single-phase PIN powders and for obtaining fine-grain ceramics. The dielectric and ferroelectric properties of the ceramics were determined. The results indicated that the dielectric properties of PIN ceramics were of relaxor ferroelectric behavior with the maximum dielectric constant of 4300 at 53 °C. Interestingly, the fine-grain PIN ceramics showed slightly better dielectric properties than the coarse grains ceramics in previous investigations. The *P–E* hysteresis loop measurements also demonstrated strong temperature dependent ferroelectric properties. At −25 °C, the maximum polarization is found to be 8 μm/cm^2 at a field of 30 kV/cm, with P_r value of 2.5 μm/cm^2 and E_c of 7.5 kV/cm, in the same range as reported earlier.

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