Phase and Chemical Characterization of Perovskite Lead Nickel Niobate Ceramics Fabricated Via a Columbite Precursor Method

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ABSTRACT

Perovskite relaxor ferroelectric lead nickel niobate (PNN) ceramics were fabricated by using B-site precursor method, in which columbite-$NiNb_2O_6$ was employed as key precursor. It has been found that optimization of sintering condition can successfully lead to highly dense PNN ceramics. Although XRD analysis revealed that the ceramics consist of pure perovskite phase, significant fluctuation in chemical composition, precipitation of unreacted precursor and the formation of unwanted phases were found via a combination between SEM EDX and XPS techniques.

Keywords: lead nickel niobate, perovskite, columbite precursor, chemical characteristic.

1. INTRODUCTION

Lead nickel niobate, $Pb(Ni_{1/3}Nb_{2/3})O_3$ or PNN, is one of the significant Pb-based perovskite relaxor ferroelectric materials which has been widely investigated as potential candidates for electroceramic components such as actuator, transducer, capacitor and sensor applications [1-3]. However, as is well-known, a practical limitation to the utilization of this compound in device applications has been the lack of a simple, reproducible preparation technique for a pure perovskite phase with consistent properties. The formation of perovskite PNN is often accompanied by the occurrence of one or more undesirable phases, which significantly

degrade the overall electrical properties of the materials [4-7]. In order to avoid the formation of unwanted phases, several methods have been introduced [6-10]. So far, the columbite method [4-7], in which prefabricated $NiNb_2O_6$ is reacted with an appropriate proportion of PbO, has been widely accepted as one of the promising methods for the preparation of phase-pure PNN-based materials. There has been a great deal of interest in the preparation of single phase PNN powders as well as in the sintering and electrical properties of PNN-based ceramics [3-10]. As is well known, Pb-based perovskite relaxor materials prepared by a mixed oxide method have spatial

fluctuations in their chemical compositions. The extent of the fluctuation depends on the characteristics of the starting powders as well as on the processing schedule [4,5,11]. Interestingly, the study of the chemical characteristic i.e. chemical composition/ distribution especially at the surface of the PNN ceramics has not been widely reported. Thus, in the present study, an attempt has been made to fabricate and characterize the perovskite PNN ceramics by using a columbite-$NiNb_2O_6$ B-site precursor method. Their phase formation and chemical composition were examined by using a combination of several chemical characterization techniques including XRD, SEM, EDX and XPS.

2. MATERIALS AND METHODS

$Pb(Ni_{1/3}Nb_{2/3})O_3$ powders were synthesized by employing *B*-site precursors (i.e. columbite-route) mixed oxide synthetic route, as reported earlier [5]. Starting precursors were as follows: PbO (JCPDS file no. 77-1971), NiO (JCPDS file no. 73-1519) and Nb_2O_5 (JCPDS file no. 30-873) (Aldrich, 99% purity). These three oxide powders exhibited an average particle size in the range of 3.0-5.0 μm. First, an intermediate phase of nickel niobate: $NiNb_2O_6$ was prepared by the solid-state reaction method previously reported [12]. The appropriate amount of PbO was then added to the $NiNb_2O_6$, vibro-milled and calcined in closed alumina crucible. All powders were prepared by using a simple mixed oxide method via a rapid-vibro milling technique for 30 min (instead of 2 [5] or 12 h [3]) with corundum media in isopropyl alcohol, as detail described in earlier works [5,11,12]. Columbite-route mixtures were then calcined at 950 °C for 2 h with heating/cooling rates of 10 °C/min [12]. Ceramic fabrication was achieved by adding 3 wt-% polyvinyl alcohol (PVA) binder, prior to pressing as

pellets in a pseudo-uniaxial die press. Each pellet was placed in an alumina crucible together with an atmosphere powder of identical chemical composition [13,14]. After the binder burn out at 500 °C for 1 h, sintering was carried out with constant heating/cooling rates of 5 °C/min at various temperatures (1100-1250 °C) and dwell time (1-2 h) [3,15].

Densities of the final sintered products were measured by using the Archimedes principle. Sintered ceramics were examined by room-temperature X-ray diffraction (XRD, Siemen D-500 diffractometer) using CuK_α radiation to identify the phase formed. The microstructural development was characterized using a scanning electron microscopy (SEM, JEOL JSM-840A). Mean grain size of the sintered ceramics was subsequently estimated by employing the linear intercept method [16]. The chemical composition of the ceramic was also elucidated by an energy-dispersive X-ray (EDX) analyzer with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software. In order to evaluate the surface chemistry of the sintered PNN ceramics, XPS spectra were collected using a PHI 5700 X-ray photoelectron spectrometer equipped with PHI 04091 neutralizer and a monochromatic Al Kα X-ray source (hν = 1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated at high resolution with a pass energy of 23.5 eV, a photoelectron takeoff angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. The base pressure in the chamber during measurement was 1×10^{-9} Torr. After collection of the data, the binding energies were referenced by setting the C 1s binding energy to 284.8 eV. All peaks were fit with respect to spin-orbit splitting.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns of columbite-route PNN ceramics sintered at various temperatures for 1 and 2 h are given in Figure 1. (a-c) and 1(e-f), respectively. In general, all XRD patterns show 100% perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$ phase and could be matched with JCPDS file no. 34-103 [17], in agreement with other works [5,7,9]. To a first approximation, this phase has a cubic perovskite-type structure with cell parameter $a = 403$ pm in space group *pm3m* (no. 221). It should be noted that no evidence of either unreacted precursors or pyrochlore-type phases such as $Pb_{1.45}Nb_2O_{6.26}$, $Pb_3Nb_2O_8$, $Pb_3Nb_4O_{13}$, and $Pb_{15}NiNb_{10}O_{41}$ has been found here whereas these phases were found in other works [7,10,18]. Therefore, XRD results clearly show that, in general, the methodology employed in this work provides a simple method for the production of pure perovskite PNN ceramics via a solid-state mixed oxide synthetic route in which columbite-$NiNb_2O_6$ was employed as key precursor together with the optimized sintering conditions without the addition of PbO and NiO in excess [7-8].

The densification data of all samples is shown in Table 1. It is observed that the density of about 93-96% of the theoretical value can be achieved for the columbite mixed-oxide route PNN ceramics. Density increases as sintering temperature increases from 1100 to 1200 °C, consistent with Alberta
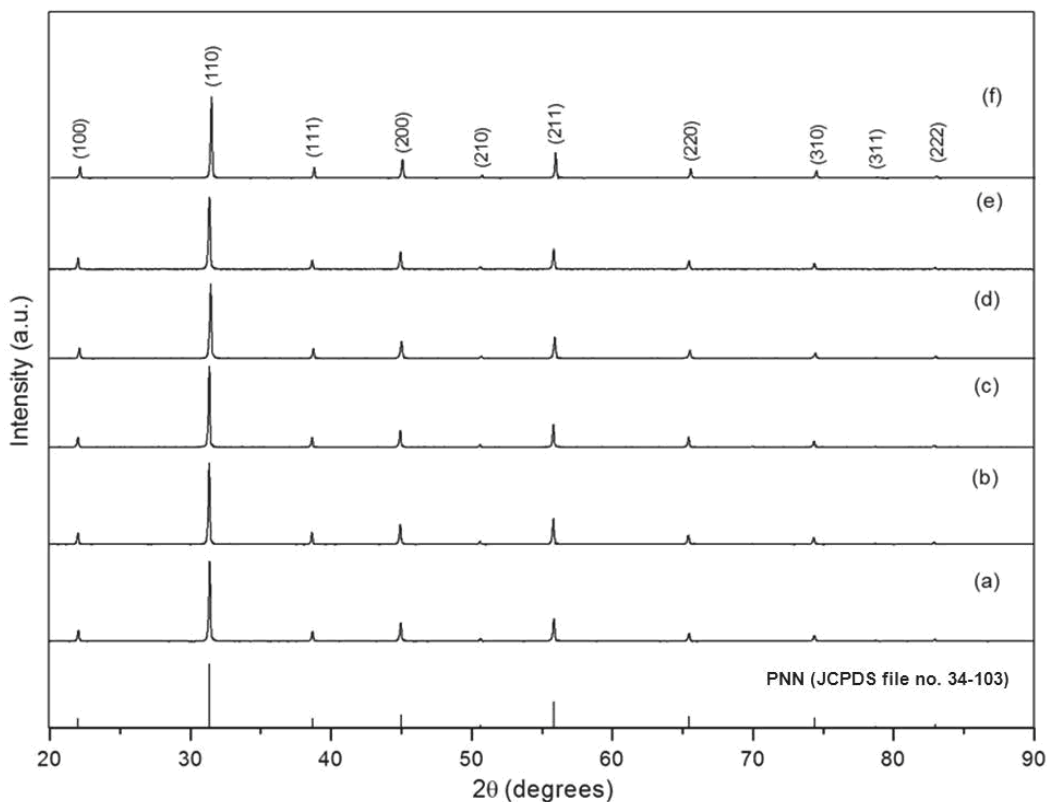

Figure 1. XRD patterns of the columbite-route PNN ceramics sintered for 1 h at (a) 1100, (b) 1150 and (c) 1200 °C, and for 2 h at (d) 1100, (e) 1150 and (f) 1200 °C, with the corresponding JCPDS pattern.

Table 1 Physical properties of the columbite-route PNN ceramics sintered at various conditions.

Sintering condition							
Dwell-time (h)	1			2			
Temperature (C)	1100	1150	1200	1100	1150	1200	1200 [Ref. 3]
Physical properties							
Relative density (%)[a]	93	94	95	94	95	96	94
Grain size range	0.7-3.3	1.2-5.5	1.5-10	1.2-4.2	1.3-5.0	2.0-13	-
(mean) (μm)[b]	(1.7)	(3.2)	(4.2)	(2.2)	(3.3)	(5.5)	(3.7)
Perovskite phase (%)[c]	100	100	100	100	100	100	100

[a] The estimated precision of the relative density density is $\pm$ 0.1%.

[b] The estimated precision of the grain size is $\pm$ 10%.

[c] Calculated from XRD data [11, 12]

and Bhalla [3]. However, further increase in the sintering temperature up to 1250 °C caused the critical damage of the PNN samples (with some melted areas), in contrast to earlier report [3]. This may be attributed to the loss of lead oxide at high sintering temperatures, which is similar to the results found in other Pb-based perovskite systems [14,15,18]. In addition, in the present study, it was found that apart from the sintering temperature, the effect of dwell time was also found to be quite significant for the densification of PNN ceramics (higher density values were observed after longer dwell time applied). Based on the results obtained here, it may be concluded that the optimal sintering condition for the production of columbite-route PNN ceramics with maximum bulk density is 1200 °C for 2 h (in good agreement with other researchers [3,6]), with heating/cooling rates of 5 °C/min.

SEM micrographs of as-fired (i) and fracture (ii) surfaces of columbite-route PNN ceramics sintered at various conditions are compared in Figure 2. The influence of sintering conditions on grain size of these PNN ceramics is also given in Table 1. In general, typical perovskite-type PNN ceramic microstructures consisting of highly dense grain-packing are observed in both samples and in good agreement with literature [3,6,7]. The grain sizes are in the range of 1.5 to 10 mm, which is slightly lower than those observed in the typical columbite-route PNN ceramics [6,7]. The results also indicate that average grain size tends to increase with sintering temperature and dwell time, as also found in other perovskite materials [13,14,19]. Micrographs of fracture surface (Figure 2(ii)) show highly dense microstructures consisting of equiaxed grains, in agreement with other researchers [7]. The PNN ceramics also have an intergranular fracture mechanism, indicating that the grain boundaries are mechanically weaker than the grains [20], similar to the results previously observed in the relaxor perovskite ceramic systems [4,19].

It should be noted that some minor phases can be found in these micrographs (circled), in particular at the grain boundaries and at the triple point junctions. In general, EDX analysis using a 20 nm probe from a large number of areas of these sintered PNN ceramics confirmed the parent composition to be $Pb(Ni_{0.33}Nb_{0.67})O_3$, in agreement with XRD result. However, a combination of SEM and EDX techniques has also demonstrated
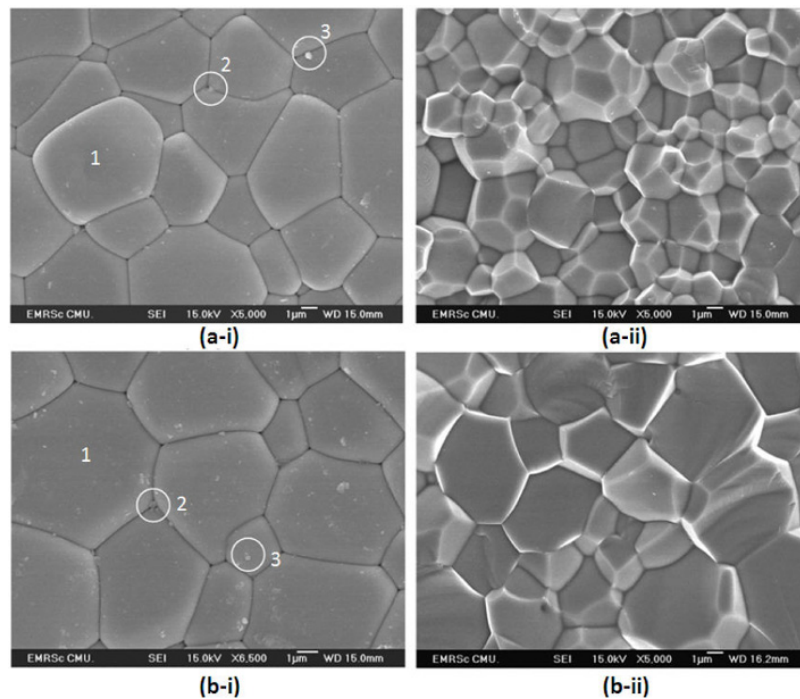
Figure 2. SEM micrographs of (i) as-sintered and (ii) fracture surfaces for columbite-route PNN ceramics sintered for 1 h at (a) 1100 °C and (b) 1200 °C.

that the chemical compositions of the minor phases, neighbouring the parent PNN phase (marked as "1"), are identified as pyrochlore-type $Pb(Ni_{0.12}Nb_{1.66})O_{3.33}$ (dark area; marked as "2"), and unreacted precursor NiO (bright area; marked as "3"). As expected, based on the SEM-EDX data, it may be concluded that, single-phase perovskite PNN ceramics cannot be straightforwardly fabricated by sintering pure PNN powders derived from a well-known mixed oxide columbite B-site precursor method. However, these minor phases could not be detected by XRD technique (one of the most widely used techniques to characterize ceramics), suggesting low concentration of those components which is consistent with earlier work [9].

So far, the employed characterization techniques explore both the surface and the bulk information. As is well documented, whether the sample is crystalline or not, the nature of the surface is often important.

Is the chemical composition the same throughout the PNN sample, especially at the surface? In connection with this, X-ray photoelectron spectroscopy (XPS) which is one of the most used surface-sensitive techniques [21-25] was adopted to obtaining data on the chemistry and bonding close to the surface. A wide energy range of XPS spectrum of the PNN ceramics (Figure 3) shows all elementary compositions of the PNN compound including the Auger lines. Carbon peak was found in the spectra due to contamination in the samples, which is generally found in ceramic materials [21-23]. The binding energy of all compositions was referred to C 1s line at 284.8 eV. The core levels of Pb, Ni, Nb and O are presented in Figure 4. The line position of Pb $4f_{7/2}$ (Figure 4(a)) shows at 138.1 eV, which is consistent with Pb in the $Pb(Mn_{1/3}Nb_{2/3})O_3$ ceramics [22]. The binding energy of Ni $2p_{3/2}$ (Figure 4(b)) is 855.3 eV, which is in good

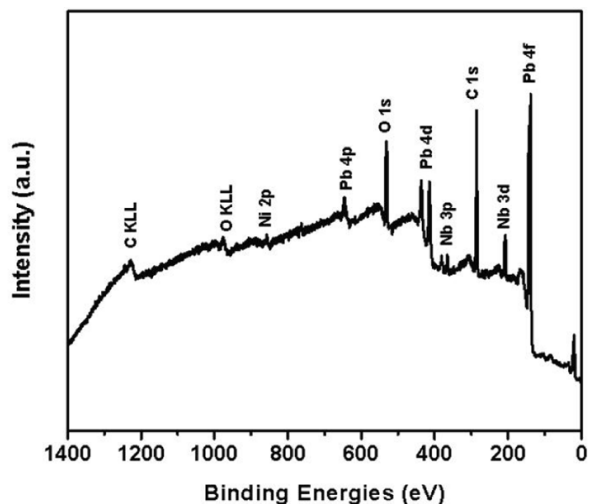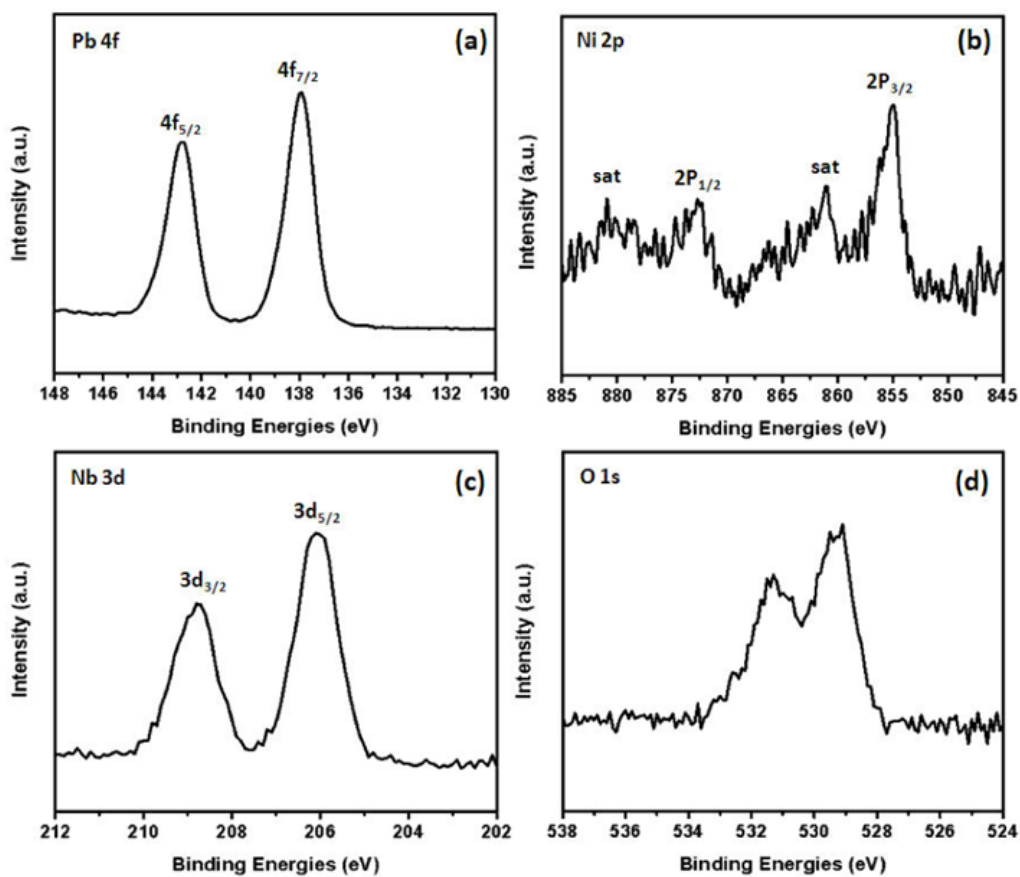**Figure 3.** The XPS spectrum measured in the wide energy range of the surface of $Pb(Ni_{1/3}Nb_{2/3})O_3$ ceramics.

Figure 4. The XPS (a) Pb 4f, (b) Ni 2p, (c) Nb 3d, and (d) O 1s lines of $Pb(Ni_{1/3}Nb_{2/3})O_3$ ceramics.

agreement with Rivas *et al*. [24]. In the present study, the satellite peaks (sat) of Ni 2p which is the typical characteristic of Ni 2p peak, are also found in the PNN spectrum, as shown in Figure 4(b). From Figure 4(c), it is seen that the binding energy of Nb $3d_{5/2}$ is 206.4 eV and the spin-orbit splitting is 2.8 eV. The binding energy of Nb 3d here is slightly lower than those obtained from the typical relaxor perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics (206.8 eV) [25]. This could be attributed to different environment of Nb in the crystal structure. The O 1s core level spectrum of sintered PNN is shown in Figure 4(d) with two peaks, in good agreement with literature [23-26]. The first peak at 529.6 eV is typically assigned to O_2^{2-} and the second peak at 531.6 eV commonly found at the surface of several perovskite ceramics might be attributed to the hydroxyl species [24-26].

To the author's knowledge, the present data are the first results for the surface chemistry analysis of relaxor perovskite PNN ceramics fabricated via a columbite B-site precursor method. The results obtained in this study suggest that a systematic study of the chemical (elemental) distribution for each layer from the ceramic surface deep down into the bulk (chemical depth profile) are further required for better understanding the chemical characteristics and the homogeneity of the well-known mixed-oxide derived PNN ceramics.

4. CONCLUSIONS

Evidence gained from a typical XRD analysis technique revealed that single-phase of perovskite PNN ceramics can be successfully formed by employing a mixed oxide columbite B-site precursor method under optimized sintering conditions. However, fluctuation in chemical composition, precipitation of unreacted precursor and the formation of unwanted pyrochlore phases different from perovskite PNN especially at the surface were detected by a combination of SEM, EDX and XPS techniques.

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