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Phasic and Microstructural Developments of $Pb(Ni_{1/3}Nb_{2/3})O_3$ Prepared by the Columbite Precursor Process

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Abstract: The phasic and microstructural developments of perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$ during reaction processes using $NiNb_2O_6$ columbite precursor were investigated. Increasing the purity of $NiNb_2O_6$ in specimens efficiently enhanced the yield of the perovskite phase. Heating 1000°C-calcined $NiNb_2O_6$ with PbO at 880°C resulted in 97.5% perovskite phase. When $NiNb_2O_6$ was over-calcined, the grains of formed $Pb(Ni_{1/3}Nb_{2/3})O_3$ tended to grow significantly. The formation processes of $Pb(Ni_{1/3}Nb_{2/3})O_3$ were elucidated to be a reaction between PbO and $NiNb_2O_6$ to form a pyrochlore phase with a small amount of NiO at above 600°C. Then the pyrochlore phase partially decomposed to generate a trace of PbO from 700°C, and rapidly transformed to a perovskite phase at above 880°C. Pure $Pb(Ni_{1/3}Nb_{2/3})O_3$ was unable to synthesize when no excess of starting materials was added. However, adding excess 1 wt% NiO and 5 wt% PbO induced the generation of the monophasic $Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite. The excess amount of PbO not only increased the grain size markedly, but also enhanced the structural stability of the perovskite phase at elevated temperatures.

1 INTRODUCTION

Lead nickel niobate ($Pb(Ni_{1/3}Nb_{2/3})O_3$) is a member belonging to the lead-containing complex perovskite group with the general formula $Pb(B_1, B_2)O_3$. This material exhibits a perovskite structure and typical relaxor ferroelectric properties. Its dielectric maximum and Curie temperature depend strongly on measured frequencies.[1,2] $Pb(Ni_{1/3}Nb_{2/3})O_3$-based systems, such as $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Fe_{1/2}Nb_{1/2})O_3$[3] and $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$–$PbTiO_3$,[4] have been evaluated to possess low sintering temperatures and high dielectric constants. As a result of the excellent sintering and dielectric characteristics, $Pb(Ni_{1/3}Nb_{2/3})O_3$-based materials can be applied for fabricating multilayer capacitors with low-temperature melting inner electrodes.

In spite of the success in applying $Pb(Ni_{1/3}Nb_{2/3})O_3$ to dielectric devices, the synthesis of monophasic $Pb(Ni_{1/3}Nb_{2/3})O_3$ is difficult. Agranovskaya[5] reported that the conventional mixed-oxide method failed to obtain the pure perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$. After a calcination at 1150°C, a trace of a parasitic pyrochlore phase is coexistent with the perovskite phase. The presence of the pyrochlore phase tends to deteriorate the dielectric properties of $Pb(Ni_{1/3}Nb_{2/3})O_3$. Therefore, the elimination of the pyrochlore phase becomes an important subject. Swartz and Shrout[6] proposed a columbite precursor process to fabricate pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$. In this process, a columbite precursor $MgNb_2O_6$ is prepared first, followed by the consequent reaction between the $MgNb_2O_6$ and PbO. This process can bypass the formation of the pyrochlore phase, resulting in the yield of a pure perovskite phase.[6,7] A similar process was utilized by Veitch,[8] and by Sharama[9] for preparing $Pb(Ni_{1/3}Nb_{2/3})O_3$ by using columbite $NiNb_2O_6$. The former group could prepare pyrochlore-free

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$Pb(Ni_{1/3}Nb_{2/3})O_3$; however, the latter group could not synthesize the pure $Pb(Ni_{1/3}Nb_{2/3})O_3$. In addition, the former group obtained a higher dielectric constant than the latter one, implying the impurity effect on the dielectric properties. The inconsistency in the above results indicates that the influence of processing conditions on the formation of $Pb(Ni_{1/3}Nb_{2/3})O_3$ should be investigated in detail.

In this report the reaction occurring between NiO and Nb_2O_5 for formulating columbite precursor $NiNb_2O_6$ is investigated first. Then the influence of the calcination conditions of $NiNb_2O_6$ on the formation process of $Pb(Ni_{1/3}Nb_{2/3})O_3$ is elucidated. The perovskite yields in the columbite precursor process and the conventional mixed-oxide method are compared. The reaction mechanism of $Pb(Ni_{1/3}Nb_{2/3})O_3$ prepared by the columbite precursor process is explored from the phasic and microstructural developments during heating. Furthermore, the effect of excess amounts of NiO and PbO on the generation of the monophasic perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$ is examined.

2 EXPERIMENTAL

$NiNb_2O_6$ powders were prepared by mixing proportionate amounts of reagent-grade NiO and Nb_2O_5. Both oxides were ball-milled thoroughly using zirconia balls in a polyethylene jar. Ball-milling was undertaken for 48 h in ethanol. Following drying in a rotary evaporator under reduced pressure, the mixed powders were calcined from 600°C to 1200°C for 2 h. The $NiNb_2O_6$ powders heated at various temperatures were mixed in proportion with PbO followed by the analogous ball-milling and drying processes as stated earlier. The raw materials of $Pb(Ni_{1/3}Nb_{2/3})O_3$ were also prepared by mixing directly PbO, NiO and Nb_2O_5 via ball-milling for 48 h for examining the difference between $NiNb_2O_6$-precursor method and the conventional mixed-oxide method. These two kinds of raw materials for $Pb(Ni_{1/3}Nb_{2/3})O_3$ were uniaxially pressed into pellets of 8 mm in diameter under a pressure of 196 MPa and calcined from 800°C to 900°C for 2 h. In the case of controlling PbO atmosphere, pellets were heated within a powder-bed of raw materials.

The raw materials containing 1000°C-calcined $NiNb_2O_6$ precursor were examined by differential thermal analysis (DTA) and thermogravimetry analysis (TGA). The heating rate was 10°C/min and alumina powder was used as reference. In an electric furnace specimens were heated at the same heating rate as DTA, and quenched in air at various temperatures. The variation in the phase formation and crystallographic structure in specimens was examined by X-ray powder diffraction (XRD) analysis using CuKα radiation. The perovskite content in the specimens was calculated from the ratio of the diffraction intensity of the perovskite (110) peak to the sum of both the diffraction intensity of the perovskite (110) peak and that of the pyrochlore (222) peak. The microstructural evolution of specimens in reaction was observed via a scanning electron microscope (SEM).

In order to synthesize the pure perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$, excess NiO and PbO were added in the columbite precursor process. Excess amounts of NiO (1 wt%) were added in the mixing process of $NiNb_2O_6$ followed by calcining at 1000°C for 2 h. Next, excess amounts of PbO (up to 5 wt%) were added in the second mixing process with $NiNb_2O_6$. Isothermal calcination was performed at 900°C for 2 h. Nitric acid was used to remove the excess PbO present after calcination. The products and microstructure of obtained specimens were investigated by XRD and SEM.

3 RESULTS AND DISCUSSION

3.1 Heat-treatment and thermal analysis

The XRD patterns for the raw materials of $NiNb_2O_6$ calcined at various temperatures for 2 h are illustrated in Fig. 1. This figure indicates that the formation of $NiNb_2O_6$ did not take place at 600°C. At 800°C a large amount of $NiNb_2O_6$ was formed, but accompanied with a trace of unidentified phase. When the temperature reached 1000°C, pure $NiNb_2O_6$ was generated completely. Its diffraction pattern was the same as that listed in JCPDS (File No. 32-694). At 1200°C the diffraction pattern of $NiNb_2O_6$ remained similar to that at 1000°C, but with improved crystallinity. The microstructures of the raw materials of $NiNb_2O_6$ calcined at 800°C, 1000°C and 1200°C are shown in Fig. 2 (a), (b) and (c). The grain size of powders calcined at 800°C and 1000°C lay in a sub-micrometer range. The former was estimated to be around 0.2–0.3 μm, and the latter 0.3–0.4 μm. Besides the difference in grain size, the 800°C-calcined powders tended to formulate aggregates; in contrast, the 1000°C-calcined powders were formed in a well dispersive state with a more uniform distribution of grain size. When the temperature was increased to 1200°C, the grain size of $NiNb_2O_6$ increased significantly one order of magnitude to become around 2.0–4.5 μm. Consequently, the morphology of $NiNb_2O_6$ powders was substantially altered with heating conditions.

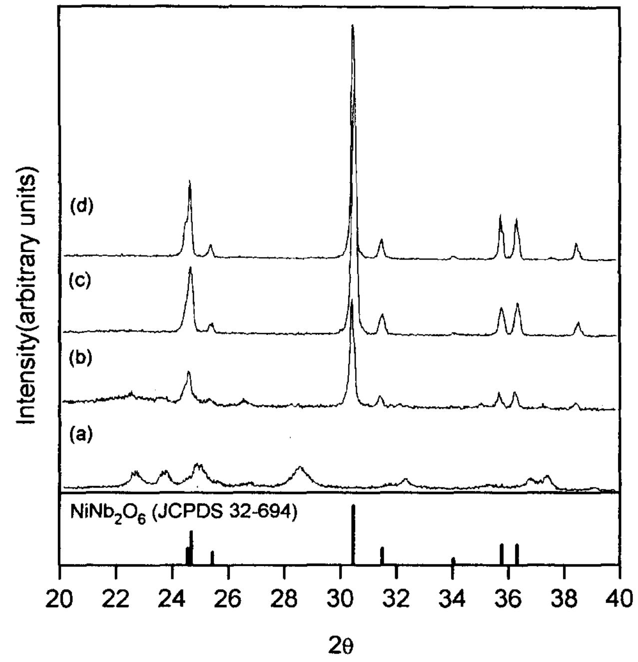

Fig. 1. X-ray diffraction patterns of the mixtures of NiO and Nb_2O_5 calcined at (a) 600°C, (b) 800°C, (c) 1000°C and (d) 1200°C.

The $NiNb_2O_6$ calcined at 800°C was mixed with PbO, followed by heating at temperatures ranging from 800°C to 900°C for 2 h with or without a powder bed. The raw materials of $Pb(Ni_{1/3}Nb_{2/3})O_3$ prepared by the conventional mixed-oxide method were also heated in the same processes. Figure 3 indicates the formation amount of the perovskite phase in different processes. As shown in this figure, no $Pb(Ni_{1/3}Nb_{2/3})O_3$ was generated when the specimens were heated up to 850°C. At 880°C a large amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ was formed in all the specimens with a small amount of pyrochlore phase. After 900°C-calcination, however, the formation amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ for all processes was reduced. The formation amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ in the columbite precursor process was found to be higher than that in the conventional process at all temperatures with or without a powder bed. Therefore, the positive effect on the perovskite yield by using $NiNb_2O_6$ columbite precursor was confirmed. In both processes, the pellets heated within the powder bed contained a higher yield of perovskite phase than those heated without a powder bed. Hence, the powder bed likely created lead atmosphere to efficiently suppress the violation of lead species from specimens. The decline in perovskite content at 900°C is considered to be related directly to the evaporation of lead species, leading to the decomposition of the perovskite phase to the pyrochlore phase.

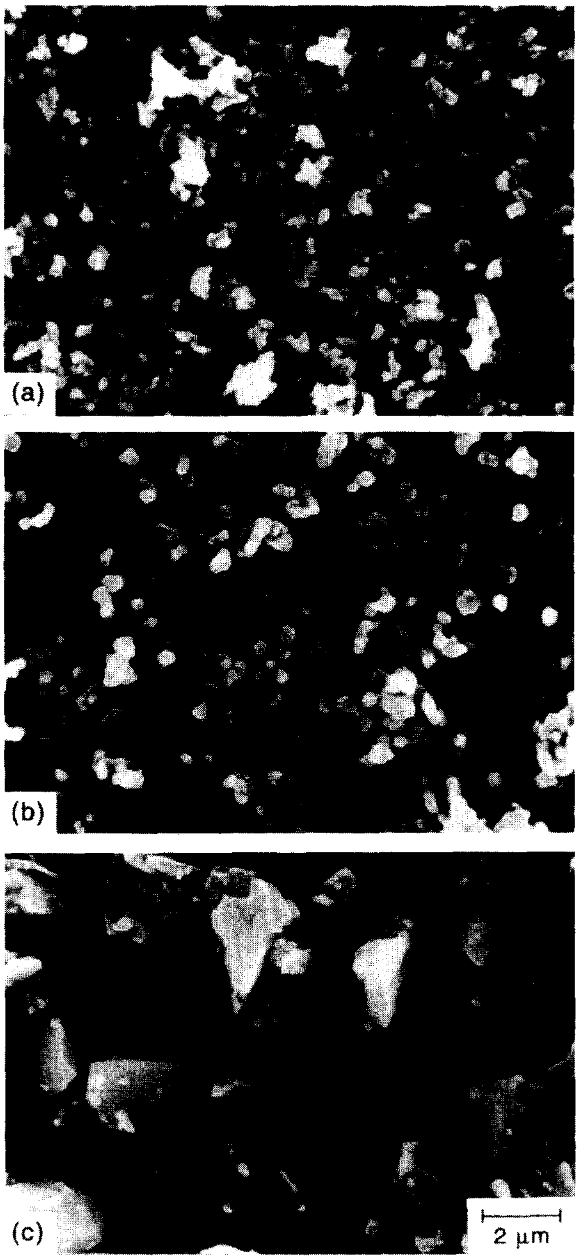

Fig. 2. Scanning electron micrographs of $NiNb_2O_6$ calcined at (a) 800°C, (b) 1000°C and (c) 1200°C.

The effects of calcination temperatures for $NiNb_2O_6$ powders on the yield of $Pb(Ni_{1/3}Nb_{2/3})O_3$ are indicated in Fig. 4. The specimens were calcined within a powder bed of raw materials. At 880°C $Pb(Ni_{1/3}Nb_{2/3})O_3$ began to appear in all the specimens. The formation amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ prepared from 1000°C- and 1200°C-calcined $NiNb_2O_6$ reached to about 97.5%; while the perovskite yield from 800°C-calcined $NiNb_2O_6$ was only 96%. This implies that the low purity of $NiNb_2O_6$ in the 800°C-calcined specimens (see Fig. 1) resulted in the low formation amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$. As the temperature increased to 900°C, the perovskite yield was reduced for all three samples. It is found that the 800°C-calcined

$NiNb_2O_6$ led to the lowest yield of the perovskite phase. The SEM images of the $NiNb_2O_6$-containing samples calcined at 880°C for 2 h are shown in Fig. 5 (a), (b), and (c), respectively. The grain sizes of $Pb(Ni_{1/3}Nb_{2/3})O_3$ using 800°C- and 1000°C-calcined $NiNb_2O_6$ were about 1–2 μm; however, the grain size of $Pb(Ni_{1/3}Nb_{2/3})O_3$ using 1200°C-calcined $NiNb_2O_6$ was increased greatly to around 3–4 μm. This increase in the $Pb(Ni_{1/3}Nb_{2/3})O_3$ grain size is regarded to be caused by the large $NiNb_2O_6$ grains used (see Fig. 2 (c)). From the results shown in Fig. 4, the optimum synthesis process is considered to be heating the precursors containing 1000°C-calcined $NiNb_2O_6$ at 880°C within a powder bed. Nevertheless, the monophasic perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$ was unable to obtain even at the optimum condition.

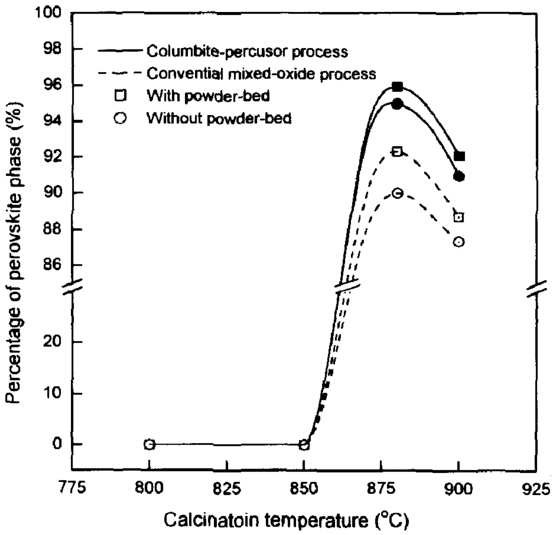

Fig. 3. Formation percentage of the perovskite phase obtained by the columbite precursor process and the conventional mixed-oxide method.

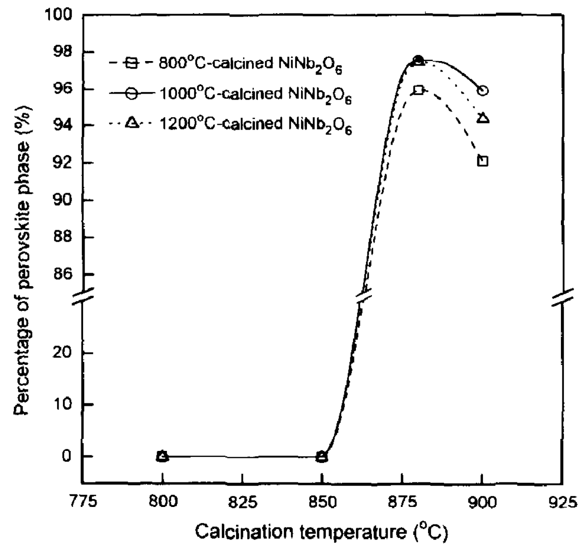

Fig. 4. Formation percentage of the perovskite phase obtained from various $NiNb_2O_6$ precursors.

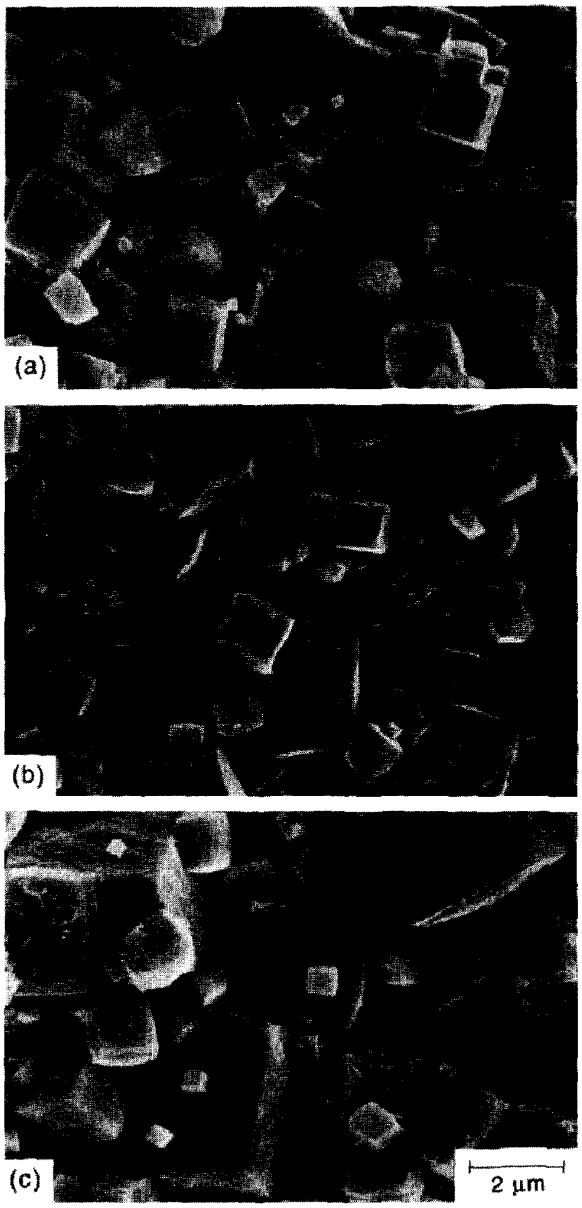

Fig. 5. Scanning electron micrographs of $Pb(Ni_{1/3}Nb_{2/3})O_3$ prepared from the precursors $NiNb_2O_6$ calcined at (a) 800°C, (b) 1000°C and (c) 1200°C.

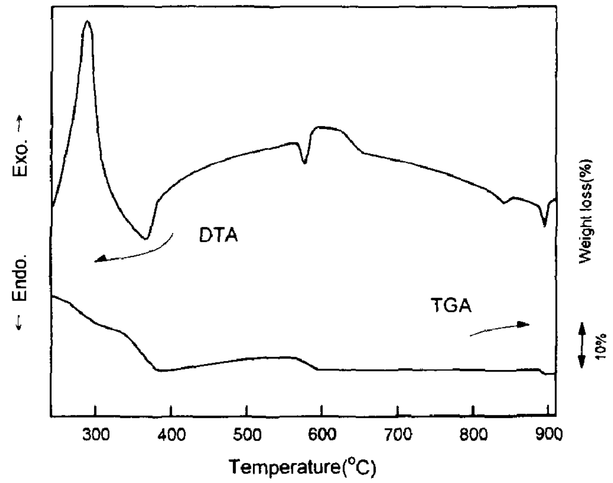

Fig. 6. Differential thermal and thermogravimetric analysis of the mixtures of PbO and 1000°C-calcined $NiNb_2O_6$.

3.2 Formation mechanism

The formation mechanism of $Pb(Ni_{1/3}Nb_{2/3})O_3$ was examined via DTA and TGA. The results are illustrated in Fig. 6. A large exothermic peak occurred at 300°C, associated with a large amount of weight loss. This exothermic peak resulted from the combustion of the contaminant of polyethylene during ball-milling. A slight weight gain began to occur in the TGA curve above 400°C. Then a broad exothermic peak took place from 600°C to 700°C, overlapping with an endotherm peak at 575°C. At the same temperature, a weight loss of about 2.5% was also found. At 840°C and 890°C the other two endothermic peaks were observed.

The starting materials were heated and quenched at expected temperatures to analyse the formation mechanism. The variation of the resultant phases versus quenching temperatures is plotted in Fig. 7. At 500°C Pb_3O_4 was found to be present in specimens. This formation of Pb_3O_4 was related to the weight gain from above 400°C. Above 600°C the pyrochlore phase began to form in specimens, and its amount increased significantly with increasing temperatures. The formation of the pyrochlore phase was associated with the appearance of NiO, and the disappearance of Pb_3O_4 and $NiNb_2O_6$. From the results indicated in Figs 6 and 7, the formation of the pyrochlore phase is considered to cause the broad exothermic peak from 600°C; in addition, the reduction of Pb_3O_4 to PbO led to the occurrence of the 575°C endothermic peak and weight loss. At 800°C orthorhombic PbO was found to appear in specimens. At 850°C this PbO transformed to exhibit a tetragonal structure. A similar phase transformation of PbO was reported in the reaction processes of $Pb(Zr,Ti)O_3$.[10] The endothermic peak at 840°C was attributed to the phase transformation of PbO. The appearance of NiO and PbO during heating was also observed in Sakaki's report.[11] As seen in Fig. 7, $Pb(Ni_{1/3}Nb_{2/3})O_3$ initiated to generate at 880°C, and its amount increased rapidly at 910°C. Therefore, the 890°C endothermic reaction in Fig. 6 is ascribed to the formation of $Pb(Ni_{1/3}Nb_{2/3})O_3$. During heating the diffraction patterns of the pyrochlore phase were found to shift gradually to a high angle side, implying a variation of the chemical composition in the pyrochlore phase.

The microstructures of quenched specimens observed via SEM are shown in Fig. 8. Large

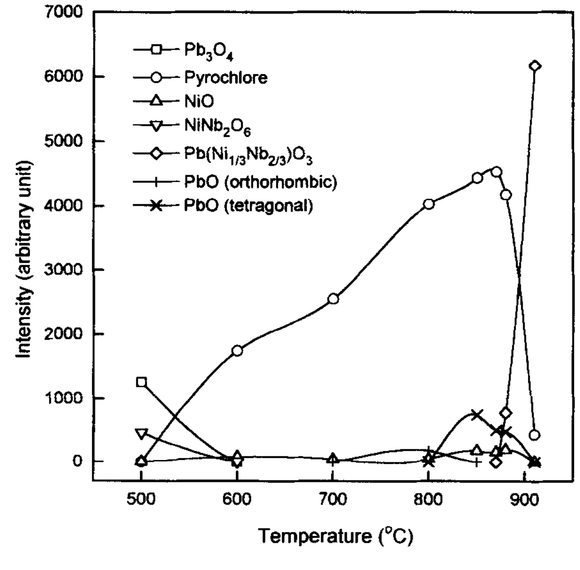

Fig. 7. The variation of resultant phases versus the quenching temperature during the reaction process of $Pb(Ni_{1/3}Nb_{2/3})O_3$.

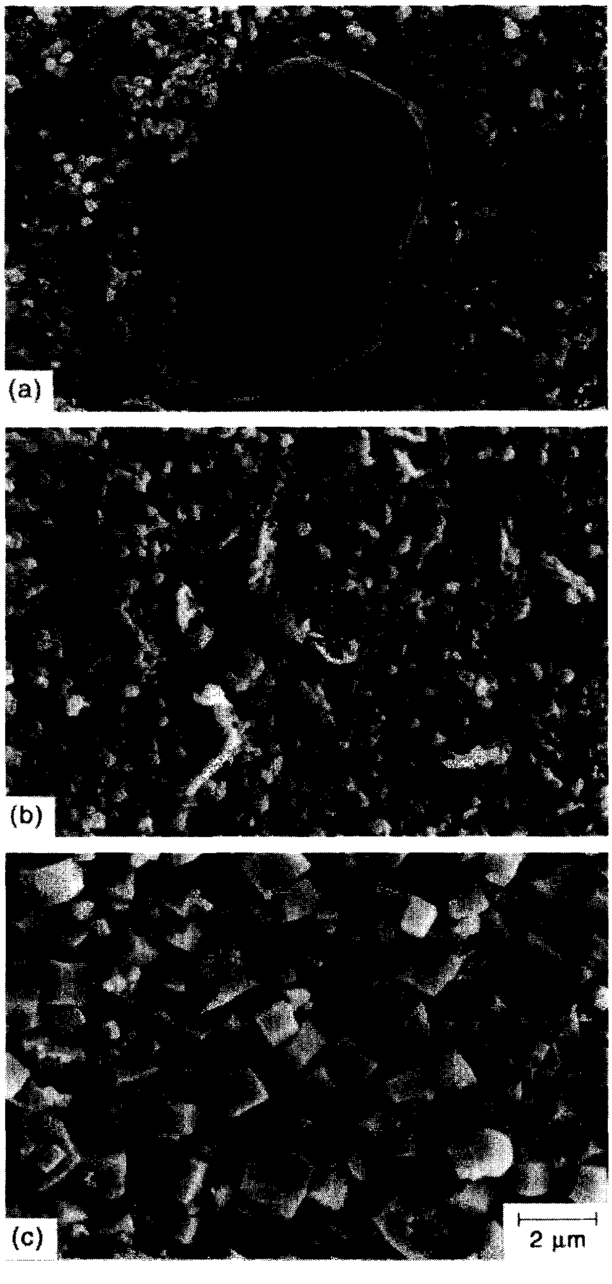

Fig. 8. Scanning electron micrographs of the raw materials of $Pb(Ni_{1/3}Nb_{2/3})O_3$ quenched at (a) 800°C, (b) 880°C and (c) 910°C.

grains with a size of about 5-8 μm were found to distribute among the matrix at 800°C (see Fig. 8(a)). Through EDS analysis, these grains were confirmed to be lead oxide. This result was in agreement with that illustrated in Fig. 7. These large lead oxide grains disappeared at 880°C as shown in Fig. 8 (b). Up to 910°C $Pb(Ni_{1/3}Nb_{2/3})O_3$ grains with a cubic shape were rapidly formed (see Fig. 8(c)). From the results indicated in Figs 6–8, the formation mechanism of $Pb(Ni_{1/3}Nb_{2/3})O_3$ is delineated as follows:

$$PbO + O_2 \xrightarrow{400^\circ C\text{–}550^\circ C} Pb_3O_4 \qquad (1)$$

$$Pb_3O_4 \xrightarrow{550^\circ C\text{–}600^\circ C} PbO + O_2 \qquad (2)$$

$$PbO + NiNb_2O_6 \xrightarrow{600^\circ C\text{–}700^\circ C} PY1 + NiO \qquad (3)$$

$$PY1 \xrightarrow{700^\circ C\text{–}800^\circ C} PY2 + PbO \qquad (4)$$

$$PY2 + PbO + NiO \xrightarrow{880^\circ C\text{–}910^\circ C} Pb(Ni_{1/3}Nb_{2/3})O_3 \qquad (5)$$

where PY1 and PY2 indicate pyrochlore phases with different compositions.

3.3 Effects of excess lead and nickel oxides on the formation of $Pb(Ni_{1/3}Nb_{2/3})O_3$

As illustrated in the previous section, during the formation of the pyrochlore phase, NiO is formed from the decomposition of $NiNb_2O_6$. Then the pyrochlore phase will be decomposed to form a small amount of PbO from above 700°C. EDS results also indicated that the lead and nickel contents in impure $Pb(Ni_{1/3}Nb_{2/3})O_3$ were less than the stoichiometric values. In order to obtain the monophasic perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$, 1 wt% excess amounts of NiO were added in the synthesis process of $NiNb_2O_6$. Then various excess amounts of lead oxide were added in the mixing process of lead oxide and $NiNb_2O_6$. The resultant XRD patterns of specimens calcined at 900°C for 2 h are illustrated in Fig. 9. Under the condition of 1 wt% excess NiO, the perovskite content was increased significantly with the amount of PbO. When no excess PbO was added, the calcined specimens were only composed of 88% of the perovskite phase (as seen in Fig. 9 (a)). With

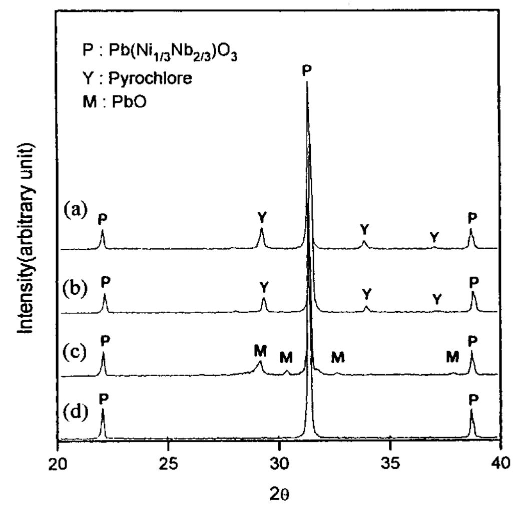

Fig. 9. X-ray diffraction patterns of the specimens heated at 900°C for 2 h. The excess amount of NiO for all specimens is 1 wt%, and the excess amount of PbO for (a) is 0 wt%, (b) 2.5 wt% and (c) and (d) 5 wt%. Specimen (d) is specimen (c) washed by nitric acid to remove residual PbO.

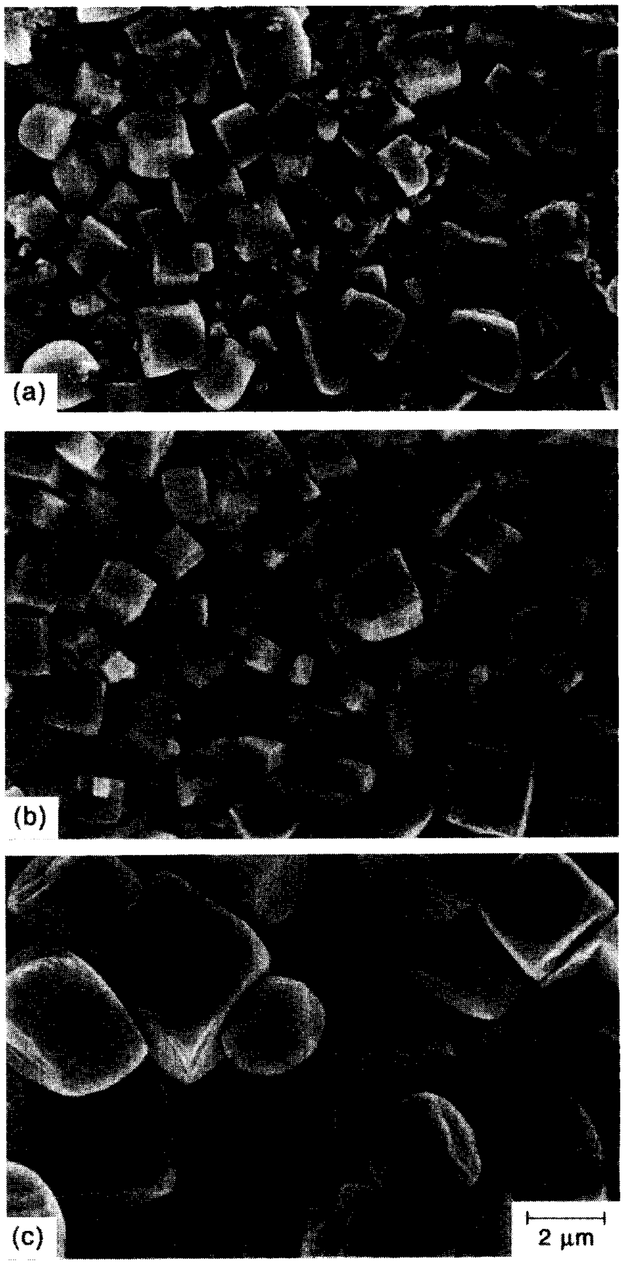

Fig. 10. Scanning electron micrographs of 900°C-calcined $Pb(Ni_{1/3}Nb_{2/3})O_3$. The excess amount of NiO for all specimens is 1 wt%, and the excess amount of PbO for (a) is 0 wt%, (b) 2.5 wt% and (c) 5 wt%.

2.5 wt% excess amount of PbO, the perovskite content was increased to 91%. When the excess amount of PbO increased to 5 wt%, pure perovskite phase was formed without the presence of the pyrochlore phase, as seen in Fig. 9(c); however, a small amount of PbO was left. After residual PbO was moved by nitric acid, monophasic $Pb(Ni_{1/3}Nb_{2/3})O_3$ without the presence of the pyrochlore phase was yielded (see Fig. 9(d)).

The microstructures of obtained specimens are shown in Fig. 10. Diphasic microstructures were observed in the specimens when the excess amounts of PbO were zero and 2.5 wt% (see Fig. 10 (a) and (b)). The $Pb(Ni_{1/3}Nb_{2/3})O_3$ grains had a cubic shape, while the pyrochlore grains were formed as a powder-form. As the excess amount of PbO was increased to 5 wt%, no presence of pyrochlore phase can be found in the microstructure (see Fig. 10 (c)); further, the grain size of $Pb(Ni_{1/3}Nb_{2/3})O_3$ was increased rapidly to 3–4 μm. The rapid grain growth is considered to be related with the liquid phase sintering through the melting of residual PbO. The PbO melt is also considered to facilitate the formation of perovskite phase to be complete. Without utilizing excess amounts of PbO, the perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$ tended to decompose at 900°C, as indicated in Fig. 4. However, $Pb(Ni_{1/3}Nb_{2/3})O_3$ can maintain its perovskite structure at 900°C, when excess amounts of PbO are coexistent with $Pb(Ni_{1/3}Nb_{2/3})O_3$. This phenomena implies that the stability of $Pb(Ni_{1/3}Nb_{2/3})O_3$ at elevated temperatures is enhanced through the presence of excess PbO. Consequently, the excess PbO present not only accelerates the formation of $Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite, but also increases its structural stability.

4 CONCLUSIONS

Lead nickel niobate was synthesized through the columbite precursor process. This process was confirmed to produce higher yield of $Pb(Ni_{1/3}Nb_{2/3})O_3$ than the conventional mixed-oxide method. Heating 1000°C-calcined $NiNb_2O_6$ with PbO at 880°C resulted in 97.5% perovskite phase. When $NiNb_2O_6$ was calcined at 1200°C, the grains of $Pb(Ni_{1/3}Nb_{2/3})O_3$ formed tended to grow significantly. Through thermal analysis and XRD examination, the formation mechanism of $Pb(Ni_{1/3}Nb_{2/3})O_3$ was characterized to be a reaction between PbO and $NiNb_2O_6$ to form the pyrochlore phase with a small amount of NiO at above 600°C. From 700°C the pyrochlore phase decomposed partially and generated PbO. At above 880°C, the pyrochlore phase transformed rapidly to the perovskite phase. The appearance of NiO and PbO in the complicated reaction processes seems to be responsible for the failure in synthesizing pure perovskite when no excess of starting materials was added. However, adding excess 1 wt% NiO and 5 wt% PbO resulted in the formation of the monophasic $Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite. The excess amount of PbO not only significantly increased the grain size through the mechanism of liquid-phase sintering, but also enhanced the structural stability of the perovskite phase at elevated temperatures.

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