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# Chemical preparation of $Pb(In_{1/2}Nb_{1/2})O_3$ powders

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**Abstract**

A chemical preparation method was applied to the synthesis of lead indium niobate ($Pb(In_{1/2}Nb_{1/2})O_3$, (PIN)) powders from nitrate solutions. As a niobium source, an oxalate-free niobium precursor solution was prepared from niobium hydrogen oxalate. Clear PIN precursor solutions with $Pb^{2+}$, $In^{3+}$ and peroxo–Nb ions were hydrolyzed with aqueous ammonia solutions. Coprecipitates with a high degree of compositional homogeneity were obtained through the control of the hydrolysis conditions. The as-prepared powders were amorphous and consisted of very small particle size (~30 nm). The powders began to crystallize into a cubic pyrochlore phase at 500°C, formed a cubic perovskite phase at 700°C, and yielded a single-phase perovskite at 900°C. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Niobate; Nitrate solution; Perovskites; Powder: chemical preparation; Relaxors

## 1. Introduction

Pb-containing relaxor ferroelectrics are interesting alternative high permittivity materials as they possess broadened phase transitions, high dielectric constants over a wide temperature range, and comparatively low firing temperatures.[1] The compound PIN with a pseudocubic perovskite structure was first prepared by Kupriyanov and Fesenko[2] as part of a synthesis program for the general formula $Pb(B_1,B_2)O_3$ series. They found a diffuse maximum in the dielectric constant measured from a ceramic sample of PIN in its disordered state at about 90°C. Prokopalo et al.[3] and Groves[4] reported that the annealing of PIN at 700°C resulted in an antiferroelectric phase with a pseudotetragonal structure.

Although the PIN compounds are suitable for studying the kinetics of compositional ordering,[5] researchers met difficulties in preparing the single-phase perovskite PIN compounds free of the pyrochlore phase using a conventional mixed oxide method.[6,7] Groves[8] tried a two-step calcination procedure[9] such that $Nb_2O_5$ is first reacted with $In_2O_3$ to form a wolframite phase and then this phase is reacted with PbO to form perovskite PIN (wolframite method). He was able to obtain only a 70% perovskite phase via this route. He also showed that the addition of excess $In_2O_3$ produces a $>95\%$ perovsikte phase. However, the order/disorder transition temperature was reduced by the presence of excess indium on the B site of the structure.

The reasons why the previous attempts to prepare the single-phase perovskite phase of lead-based $A(B_1,B_2)O_3$ type compounds have had only limited success were discussed on the basis of thermodynamic factors (electronegativity difference and tolerance factor) and reaction kinetic factors (purity, particle size and surface area of the staring materials). It was concluded for PIN that the thermodynamics of the system is the controlling factor for stability of the perovskite phase.[10] More recently, single-perovskite phase PIN ceramics were fabricated from stoichiometric mixtures of the $InNbO_4$ precursor and PbO using the wolframite method. These mixtures were calcined in oxygen in a crucible containing an atmosphere powder consisting of a mixture of $In_2O_3$ and PbO,[11] or rapidly heated in a sealed platinum crucible.[12] These alternative processing routes for single-perovskite phase PIN ceramics show that reaction kinetics is critical in suppressing the pyrochlore phase.

In general, chemical powder processing methods can provide a powder with high purity, submicron particle size and high surface area. This allows lower calcining temperature to be used to form perovskite phase by the

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conventional mixed oxide methods. In previous studies, $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Sc_{1/2}Nb_{1/2})O_3$,[13] and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Fe_{1/2}Nb_{1/2})O_3$[14] powders have been successfully prepared from mixed nitrate solutions by a chemical coprecipitation method. In this paper, similar coprecipitation techniques are applied to the synthesis of PIN powders and their properties are described.

## 2. Experimental

Niobium hydrogen oxalate was selected as a starting material of niobium source. By acidifying with nitric acid, a clear aqueous precursor solution for PIN can be prepared from lead and indium nitrates and niobium oxalate. However, coprecipitation of the clear mixed solution by hydrolysis is restricted by the preferential precipitation of lead oxalate. Thus, the oxalate-free niobium precursor solution was prepared from niobium hydrogen oxalate ($Nb(HC_2O_4)_5 \cdot nH_2O$, Soekawa Chemical Co., Ltd., Japan). In the solution, niobium exists as peroxo-complex ions. Details of the preparation method have been described in a previous paper.[13] Precursor solutions of stoichiometric composition of $Pb(In_{1/2}Nb_{1/2})O_3$ containing 0.025–0.047-M PIN were prepared by mixing the niobium precursor solution with lead and indium nitrates ($Pb(NO_3)_2$,99.5%, Koso Chemical Co., Ltd., Japan; $In(NO_3)_3 \cdot H_2O$, 99%, Soekawa Chemical Co., Ltd., Japan). Hydrolysis of the PIN precursor solutions was performed by reverse-strike (addition of PIN precursor solution to 28% ammonia solution) or direct-strike (addition of 28% ammonia solution to PIN precursor solution) methods. The final pH was 9.6–12.2. All the coprecipitates were washed with water and then dried at 80°C for 12 h. Lead, indium and niobium hydroxide (or hydrates) were also prepared from each nitrate solutions with hydrogen peroxide by the reverse-strike method as reference materials of TGA–DTA.

The as-dried powders were characterized by scanning electron microscopy (SEM) (Model JSM-6301F, Jeol, Japan), X-ray diffractometry (XRD) (Cu$K\alpha$ radiation, Geigerflex SG-9, Rigaku, Japan), thermogravimetric analysis and differential thermal analysis (TGA–DTA) (Thermoflex, TG-DTA 8112H, Rigaku, Japan). About 50 mg of the as-dried powders was placed in a platinum holder and measured at a heating rate of 10°C /min in air with alumina powder as a reference. The specific surface areas were determined by the BET method (Quantasorb, Quantachrome CO, USA). Fifty milligrams of the as-dried powders were dissolved in mixed hydrofluoric and nitric acids and the cation ratios were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) (SPS-1000, Seiko Electronic Co., Japan). For calcining, an electric furnace was allowed to equilibrate at the desired calcining temperature (400 to 900°C). One gram of the as-dried powders was heated in the furnace for 1 h in air. The relative content of the perovskite and pyrochlore phases for the calcined powders was determined from the relative intensities of the (110) perovskite peak and (222) pyrochlore peak, respectively.

## 3. Results and discussion

The XRD analysis revealed that the yellow coprecipitates obtained from the PIN precursor solutions were all amorphous. SEM observations showed that the as-dried powders consisted of agglomerates of small particles ranging in diameter from 20 to 30 nm (Fig. 1). The results of ICP analyses of the as-dried powders are shown in Table 1. The cation ratios are in agreement with the assumption that all components were completely precipitated by the coprecipitation method.

The TGA–DTA curves of precipitates (hydroxides or hydrates) from each nitrate solutions with hydrogen peroxide are shown in Fig. 2. The weight loss occurs stepwise for all the hydroxides. Exothermic peaks appear at about 300°C for the lead hydroxide and the indium hydroxide. The TGA–DTA curves of coprecipitates from PIN precursor solutions are shown in Fig. 3. The TGA curves of the powders by the direct-strike and reverse-strike methods show 10.1 and 7.8% weight losses, respectively, below 500°C due to the physical desorption of water and dehydration with endothermic

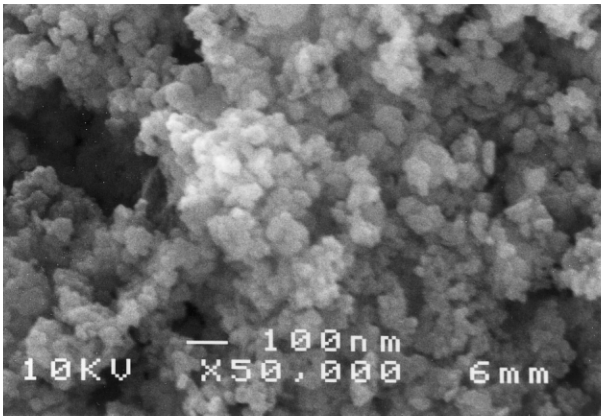

Fig. 1. SEM photograph of as-dried powder from 0.025-M PIN precursor solution by reverse-strike method.

Table 1
Chemical analysis of as-dried powders from 0.025-M PIN precursor solution by reverse-strike method (normalized molar ratio)

| | Pb | In | Nb |
|---|---|---|---|
| Formula | 1.00 | 0.50 | 0.50 |
| Measured | 1.00 | 0.50±0.01 | 0.50±0.01 |

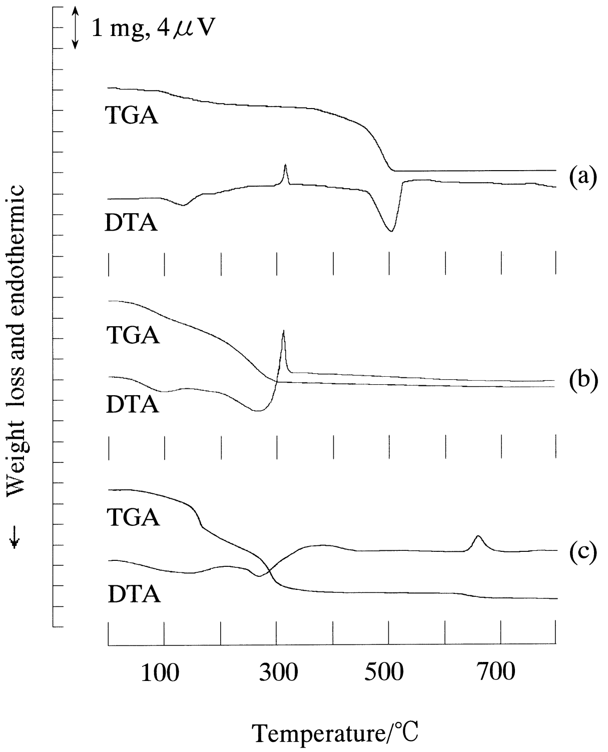

Fig. 2. TGA and DTA curves of hydroxide powders from nitrate solution with hydrogen peroxide: (a) lead hydroxide; (b) indium hydroxide; (c) niobium hydroxide.

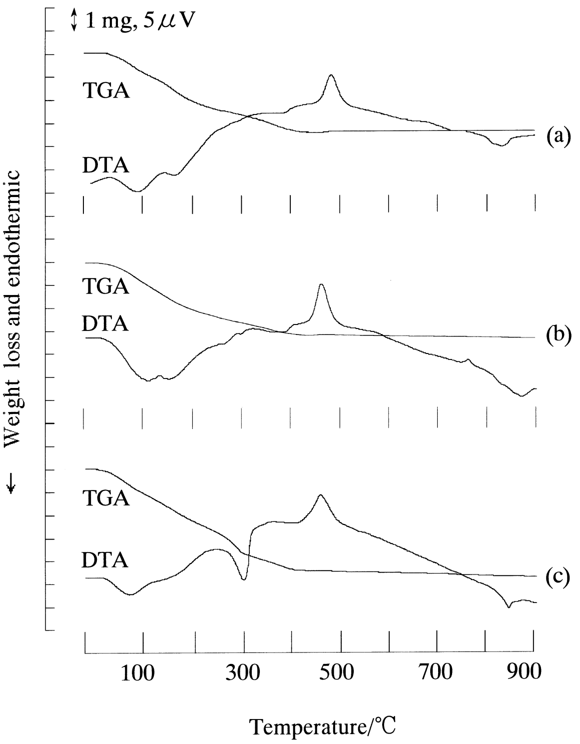

Fig. 3. TGA and DTA curves of as-dried powders: (a) 0.025-M PIN precursor solution and reverse-strike method; (b) 0.047-M PIN precursor solution and reverse-strike method; (c) 0.047-M PIN precursor solution and direct-strike method.

effects on the DTA curves. For the reverse-strike samples [Fig. 3(a) and (b)], the TGA curves of weight loss are smooth. No exothermic peak appears below 450°C. Therefore, these TGA–DTA curves are not a superposition of the individual decomposition of the three hydroxides. This means a high degree of chemical homogeneity in the coprecipitates. On the other hand, the TGA–DTA curves from high concentration PIN precursor solutions by the direct-strike method [Fig. 3(c)] are not smooth below 450°C. One can consider each dehydration reaction of the hydroxides to occur in a stepwise manner in the powders. The pH at which each hydroxide can deposit from their solution corresponding to the 0.025-M PIN precursor solutions were experimentally determined, The pH values were 7.3, 7.0 and 0.15 for $Pb^{2+}$, $In^{3+}$ and $Nb^{5+}$, respectively, indicating the preferential precipitation of niobium hydroxide. Thus, the reverse-strike method should be effective for the PIN precursor solutions and indeed, increased the degree of compositional homogeneity in the coprecipitates as observed in the TGA–DTA curves.

All samples have an exothermic peak at 460–490°C immediately after the dehydration reaction is finished. An XRD analysis was performed for the samples heated in the TGA–DTA apparatus to the temperatures before and after the exothermic peak. The XRD pattern of the powders heated to the temperatures before the peak showed only a broad peak around $2\theta = 29°$; the XRD pattern of the powders quenched immediately from the temperatures after the peak showed a cubic pyrochlore phase. This exothermic effect essentially represents a crystallization from amorphous powder, since the weight loss reaction was finished in the relevant temperature range.

The XRD patterns of the calcined powders from the reverse-strike and 0.025-M PIN precursor solutions are shown in Fig. 4. The powders began to crystallize into a cubic pyrochlore phase with broad peaks at 500°C and a cubic perovskite phase at 700°C. As the heating proceeded to 800°C, below 888°C which is the melting point of lead oxide, more perovskite continued to form without any liquid phases. The powders calcined at 900°C for 1 h did not have any detectable amount of pyrochlore. This is significantly lower calcining temperature than that required for conventional mixed oxide process (e.g. 1200°C for 24 h[12]). Low temperature calcining can provide a highly reactive powder of submicron particle size. This would lead to lower sintering temperatures which reduce PbO vaporization in the PIN ceramics and avoid the thermal conditions leading to exaggerated grain growth.

Table 2 shows the percent of perovskite in the calcined powders and the specific surface area of the as-dried powders. The percent of perovskite is dependent upon not only the calcining temperatures, but also the precipitation conditions. The reverse-strike method has

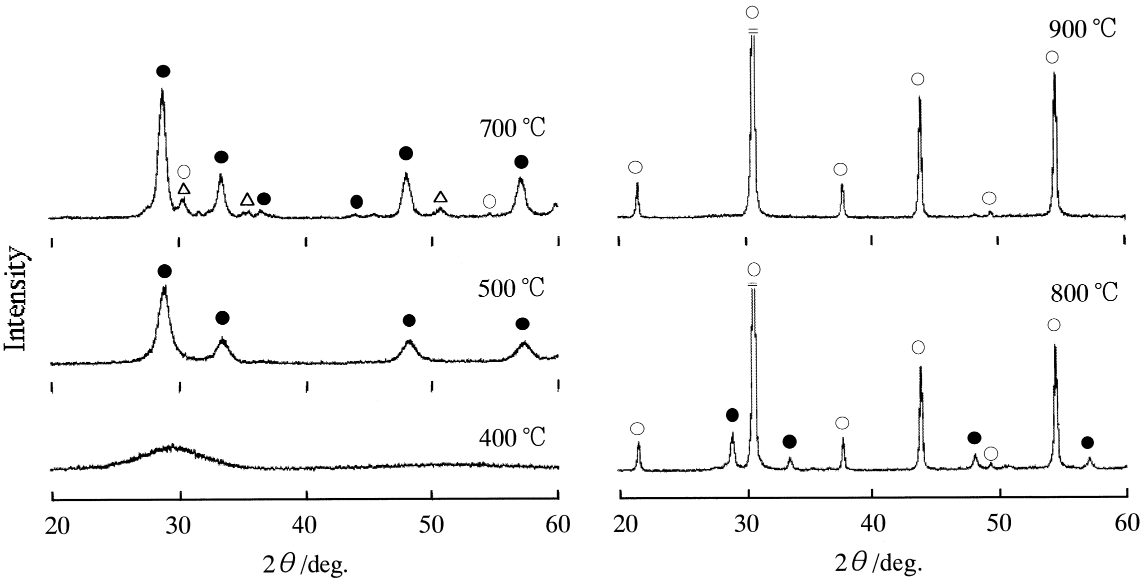

Fig. 4. XRD patterns of calcined powders from 0.025-M PIN precursor solution by reverse-strike method: ○, perovskite; ●, pyrochlore; △, indium oxide.

Table 2
Percent of perovskite phase and surface area of as-dried powders

| Sample | Solution concentration (mol/l) | Percent of perovskite | | Surface area ($m^2$ / g) |
|---|---|---|---|---|
| | | 800°C | 900°C | |
| No. 1 direct-strike | 0.047 | 24.4 | 94.2 | 80 |
| No. 2 reverse-strike | 0.047 | 59.1 | 97.2 | 88 |
| No. 3 reverse-strike | 0.034 | 91.4 | 100 | 102 |
| No. 4 reverse-strike | 0.025 | 93.6 | 100 | 109 |

the effect of increasing the chemical compositional homogeneity with consequent increase of the perovskite phase content, but only resulted in a powder containing 97% of the perovskite phase for 0.047-M PIN precursor solution. Lowering the concentration of the PIN precursor solutions had also the effect of increasing the degree of compositional homogeneity and surface area. Under the present conditions, the specific surface area is an indicator of the probable calcining behavior.

## 4. Conclusion

Lead indium niobate ($Pb(In_{1/2}Nb_{1/2})O_3$) powders have been prepared from nitrate solutions with $Pb^{2+}$, $In^{3+}$ and peroxo-Nb ions by hydrolysis. Coprecipitates with a high degree of compositional homogeneity were obtained through the control of the reaction conditions. Combination of the reverse-strike method and lowering the concentration of PIN precursor solutions had the effect of increasing the degree of compositional homogeneity of coprecipitates. They can be converted into a single perovskite phase at 900°C by calcination in an air for 1 h.

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