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LEAD PYRONIOBATE PYROCHLORE NANOPARTICLES SYNTHESIZED VIA HYDROTHERMAL PROCESSING

Chung-Hsin Lu and Shih-Yen Lo

Department of Chemical Engineering, National Taiwan University
Taipei, Taiwan, R.O.C.

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ABSTRACT

Ultrafine lead pyroniobate $Pb_2Nb_2O_7$ particles were successfully prepared via hydrothermal processing. When the lead nitrate and niobium hydrogenoxalate solutions were utilized as the starting materials, the PbC_2O_4 precipitates formed hindered the synthesis of $Pb_2Nb_2O_7$. On the other hand, adding ammonia to the lead nitrate solution suppressed the formation of PbC_2O_4 while the formation rate of $Pb_2Nb_2O_7$ was significantly accelerated. Monophasic $Pb_2Nb_2O_7$ was obtained at temperatures as low as $150^\circ C$. The particle size of hydrothermally synthesized powders, compared to that of powders produced by the traditional solid state reaction, was profoundly reduced to the nanometer order (around 10–20 nm). *Copyright © 1997 Elsevier Science Ltd*

KEYWORDS: A. nanostructures, A. oxides, C. electron microscopy, C. infrared spectroscopy, C. X-ray diffraction

INTRODUCTION

The conventional solid state reaction using mixed raw materials to prepare ceramic powders is mainly governed by the diffusion process among solid particles. In order to enhance the diffusivity between solids, heating at elevated temperatures is generally necessary. However, high-temperature heating in an open system leads to the evaporation, and thus escape from the furnace, of volatile species such as lead and bismuth. This vaporization not only causes environmental problems, but renders stoichiometric deviation in the composition of final products. Moreover, high-temperature heating is a very energy-consuming process. On the other hand, using a hydrothermal process for powder synthesis does not pose such problems. The hydrothermal reaction is carried out in a closed system under high pressure; therefore,

the volatile species will not escape into the environment. Since mixed solutions can be directly utilized as starting materials, the diffusivity and mixing of starting materials are enhanced (1). As a result, the synthesis process of powders can be undertaken at temperatures lower than those in the conventional solid state reaction (2–4). The advantages of low-temperature treatment are that the energy required for reaction is reduced and the grain size of synthesized particles can be decreased.

In a previous study (5), an intermediate compound, a pyrochlore phase, was found to form via the hydrothermal process for preparing $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics. Usually in a lead-containing system lead species react rather easily with niobium species to form pyrochlore phases (6,7). Therefore, we presume that utilizing the hydrothermal processing can be an effective approach for preparing the pyrochlore phase of lead pyroniobate $\text{Pb}_2\text{Nb}_2\text{O}_7$, which exhibits interesting dielectric properties (8,9). To our knowledge, this study is the first one attempting to synthesize $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders via hydrothermal processing. The effects of various precursors and reaction temperature on the phase formation and morphology of particles were investigated. The formation and microstructure of the hydrothermally processed powders were compared with those of the powder prepared by the conventional process.

EXPERIMENTAL

Reagent-grade lead nitrate and niobium hydrogenoxalate ($\text{Nb}(\text{HC}_2\text{O}_4)_5$) were used as the raw materials. Each chemical was dissolved in distilled water individually to prepare the aqueous solution containing the specific cation.

Two different hydrothermal processes were carried out in this study. In process I, the aqueous solutions were directly mixed together at a molar ratio of $\text{Pb}^{2+}:\text{Nb}^{5+} = 1:1$. Once the mixing process was undertaken, white precipitates formed immediately. Then the precipitates with solution were introduced into a teflon-lined autoclave apparatus and hydrothermally heated at 200°C and 250°C for 2 h. In order to effectively disperse the precipitates in solution, a mechanical stirrer with a rotation speed of around 200 rpm was used in the hydrothermal reaction. After the hydrothermal treatment, the products were washed with distilled water and dried at around 60°C for several hours. In process II, first an ammonia solution was mixed with the $\text{Nb}(\text{HC}_2\text{O}_4)_5$ aqueous solution, which resulted in an increase in the pH value to around 11. To this was then added the lead nitrate aqueous solution. After adding the Pb^{2+} solution, light-yellow precipitates were formed. The precipitates along with the solution were hydrothermally treated at 150 to 250°C for 2 h and dried as in process I. In the parallel experiment (solid state reaction), PbO was mixed with Nb_2O_5 , at an equal molar ratio, by ball-milling for 48 h. The mixed and dried powder was calcined from 400 to 600°C for 2 h. The compounds present in the obtained powders were identified via X-ray powder diffraction (XRD). The microstructural evolution and particle size of the prepared specimens were examined via scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

In process I, after the two starting solutions were directly mixed together, white precipitates were immediately formed. The XRD analysis indicated that the as-dried precipitates were

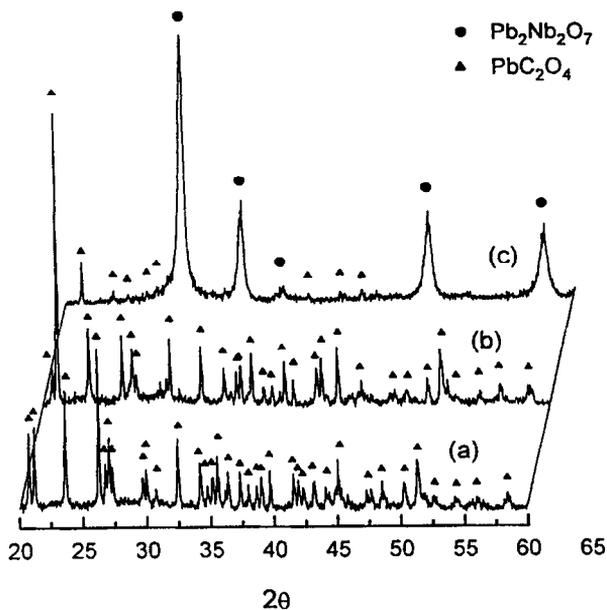


FIG. 1

X-ray diffraction patterns of as-dried precipitates (a) and products of hydrothermal treatment at 200°C (b) and 250°C (c) in process I.

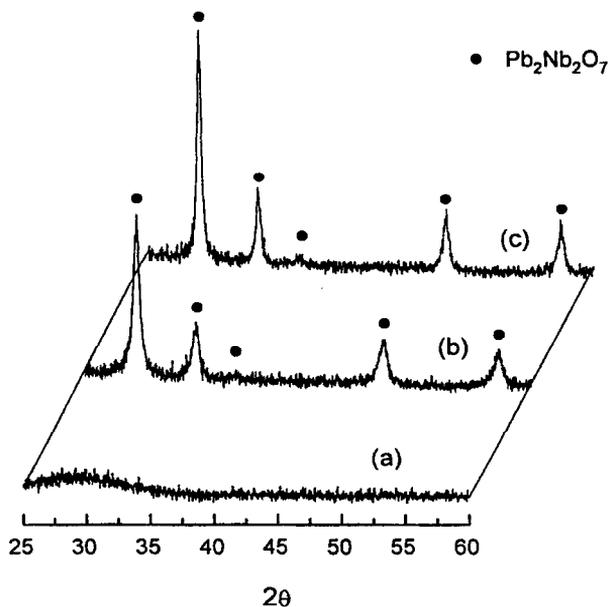


FIG. 2

X-ray diffraction patterns of as-dried precipitates (a) and products of hydrothermal treatment at 150°C (b) and 250°C (c) in process II.

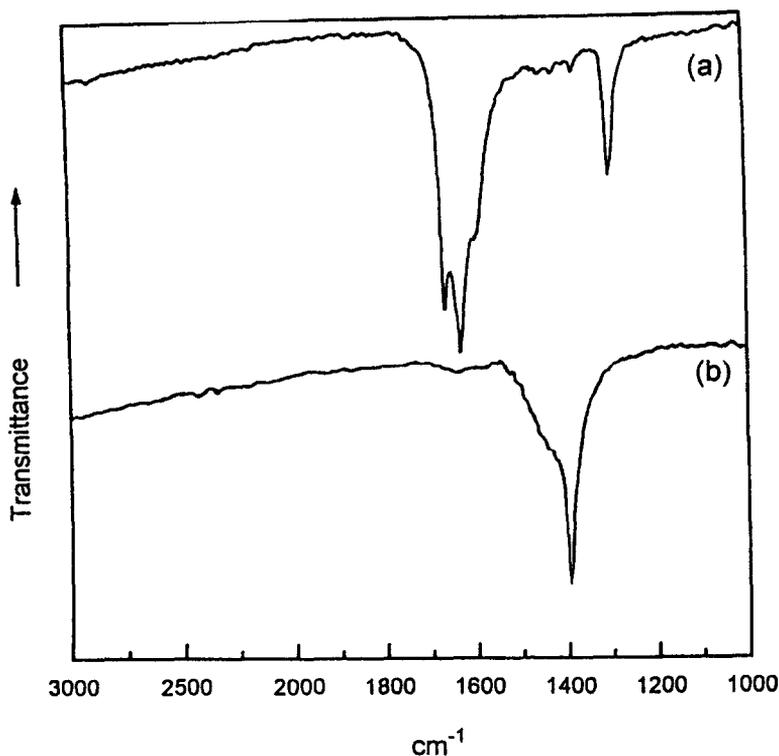


FIG. 3

IR spectra of the precipitates formed in (a) process I and (b) process II.

PbC_2O_4 (see Fig. 1a). This compound was generated from the reaction between the lead cations and oxalyl ions which were present in the niobium solution. After the hydrothermal treatment at 200°C in process I, no products were formed but the diffraction pattern of PbC_2O_4 became slightly varied (see Fig. 1b). When the hydrothermal temperature was raised to 250°C, a large amount of $\text{Pb}_2\text{Nb}_2\text{O}_7$ began to appear (see Fig. 1c; however, a trace amount of PbC_2O_4 still remained in the products, indicating that the formation reaction was incomplete.

In process II, an ammonia solution was introduced to the $\text{Nb}(\text{HC}_2\text{O}_4)_5$ solution prior to mixing the niobium solution with the $\text{Pb}(\text{NO}_3)_2$ solution. The XRD pattern of the light-yellow precipitates formed after mixing is illustrated in Figure 2a. No diffraction peaks were seen for the precipitates, revealing that the products exhibited an amorphous structure. With the hydrothermal treatment at 150°C, pure $\text{Pb}_2\text{Nb}_2\text{O}_7$ compound was formed. The XRD pattern of this powder was consistent with that reported in JCPDS No. 40-828 (10). With hydrothermal temperature raised to 250°C, the XRD intensity of $\text{Pb}_2\text{Nb}_2\text{O}_7$ was increased and the peak shape became narrower, implying that the crystallinity of formed powders was enhanced. These results show that $\text{Pb}_2\text{Nb}_2\text{O}_7$ can be successfully synthesized with hypothermal process II at temperatures as low as 150°C.

The IR spectra of the precipitates formed in processes I and II are shown in Figure 3. The adsorption bands at around 1300 and 1700 cm^{-1} in Figure 3a indicate the presence of the oxalyl group in the precipitates in process I (11). The XRD results shown in Figure 1a



(a)



(b)



(c)

FIG. 4

Scanning electron micrographs of $Pb_2Nb_2O_7$ powders: (a) powder synthesized in process I at $250^\circ C$ and powder synthesized in process II at (b) $150^\circ C$ and (c) $250^\circ C$, respectively.

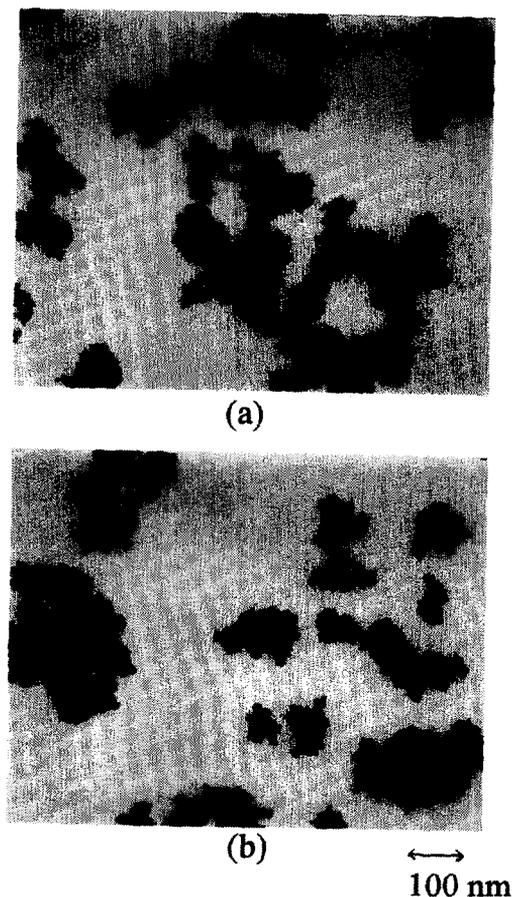


FIG. 5

Transmission electron micrographs of $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders synthesized in process II at (a) 150°C and (b) 250°C.

confirmed the formation of PbC_2O_4 in process I. In Figure 3b the adsorption band at around 1400 cm^{-1} suggests that the hydroxyl group was present in the precipitates formed in process II (12). Although no diffraction peaks are found in Figure 2a, the precipitates in process II are regarded as being amorphous PbC_2O_4 .

Based on the dissociation constants of HC_2O_4^- (6.5×10^{-5}) and NH_3 (5.6×10^{-10}) (13), the concentrations of oxalyl and hydroxyl ions present in solutions after mixing were 1.8×10^{-3} and 3.8×10^{-3} mol/l, respectively. Considering that the solubility products of PbC_2O_4 and $\text{Pb}(\text{OH})_2$ precipitates were 8.51×10^{-10} and 1.42×10^{-20} (14), respectively, the minimum concentration of lead cations required to form $\text{Pb}(\text{OH})_2$ precipitates is 9.8×10^{-16} mol/l, which is much smaller than that for the formation of PbC_2O_4 (4.7×10^{-7} mol/l). Consequently, once the hydroxyl ions are present in the solution, the predominate precipitates formed in solutions will be $\text{Pb}(\text{OH})_2$. The $\text{Pb}(\text{OH})_2$ precipitates will consume most of the lead cations, thereby suppressing the formation of PbC_2O_4 .

In process I, after the PbC_2O_4 precipitates were generated, the following reactions took place between PbC_2O_4 and niobium cations. The decomposition temperature of PbC_2O_4 is 300°C at ambient atmosphere (15). Although the hydrothermal treatment might reduce the



FIG. 6

Scanning electron micrographs of $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders synthesized in solid state reaction at 750°C .

decomposition temperature, the decomposition process of PbC_2O_4 tends to delay the formation of $\text{Pb}_2\text{Nb}_2\text{O}_7$. In contrast, amorphous $\text{Pb}(\text{OH})_2$ precipitates were formed in process II. The amorphous precipitates exhibit a loose bonding structure and do not require high activation energy for breaking bonds to generate new compounds. Therefore, the amorphous precipitates can react with niobium cations at low temperatures to facilitate the formation of $\text{Pb}_2\text{Nb}_2\text{O}_7$.

The microstructures of the obtained $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders were examined by SEM (Fig. 4). The $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders synthesized by process I exhibited a spherical shape. The particle size was estimated to be around $0.5\ \mu\text{m}$ and the size distribution was narrow (see Fig. 4a). Along with spherical particles, a small region exhibited a fluffy morphology, which may be related to unreacted species. On the other hand, both batches of $\text{Pb}_2\text{Nb}_2\text{O}_7$ particles obtained from process II had a very small particle size (Figs. 4 b and 4c). TEM observation (Fig. 5) confirmed that the particle size was reduced to nanometer range (around $10\text{--}20\ \text{nm}$) and the particles exhibited a fairly good dispersion state. Increasing the hydrothermal temperature from 150°C to 250°C did not significantly vary the particle size of $\text{Pb}_2\text{Nb}_2\text{O}_7$. The finer grain size of $\text{Pb}_2\text{Nb}_2\text{O}_7$ obtained via process II implies that during the hydrothermal reaction more nuclei were formed from the amorphous precipitates than from the PbC_2O_4 precipitates.

In the parallel experiment, $\text{Pb}_2\text{Nb}_2\text{O}_7$ was prepared by the conventional solid state reaction using mixed oxides. A small amount of $\text{Pb}_2\text{Nb}_2\text{O}_7$ appeared at 400°C , but the heating temperature had to be raised to 750°C for the complete reaction. In the solid state reaction, the low reactivity of PbO with Nb_2O_5 particles results in the slow formation of $\text{Pb}_2\text{Nb}_2\text{O}_7$. The microstructure of the $\text{Pb}_2\text{Nb}_2\text{O}_7$ particles obtained at 750°C is depicted in Figure 6. The morphology of these particles was irregular and tended to form agglomerates with a rather wide size distribution ranging from 0.3 to $1.0\ \mu\text{m}$. Comparison of the hydrothermal processes and the solid state reaction indicates that hydrothermal processing can reduce both the synthesis temperature and the particle size of $\text{Pb}_2\text{Nb}_2\text{O}_7$ powders. However, the selection of precursors for the hydrothermal process is a key factor for controlling the reaction processes and morphology of particles.

CONCLUSIONS

1. Directly mixing lead nitrate with $\text{Nb}(\text{HC}_2\text{O}_4)_5$ in process I resulted in the formation of PbC_2O_4 precipitates. The presence of PbC_2O_4 tended to hinder the formation of lead pyroniobate $\text{Pb}_2\text{Nb}_2\text{O}_7$. After hydrothermal treatment at 250°C , pure $\text{Pb}_2\text{Nb}_2\text{O}_7$ could not be obtained.
2. Adding ammonia to the lead nitrate solution in process II suppressed the formation of PbC_2O_4 , and the formation rate of $\text{Pb}_2\text{Nb}_2\text{O}_7$ was greatly elevated. Monophasic $\text{Pb}_2\text{Nb}_2\text{O}_7$ was synthesized at temperatures as low as 150°C .
3. The precursors used in the hydrothermal process significantly influenced the microstructure of obtained powders. The morphology of the powders in process I exhibited a spherical shape with a submicron size, and the particle size in process II was reduced to nanometer range.
4. In comparison with the conventional solid state reaction, hydrothermal processing markedly reduced not only the synthesis temperatures but also the particle size of $\text{Pb}_2\text{Nb}_2\text{O}_7$ particles when certain precursors were utilized as starting materials.

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