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Preparation of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{--Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ solid solution powder from hydrothermally-treated precursors

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Abstract

Fine $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{--Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ powder was successfully prepared from the hydrothermally-treated precursors. During the calcination process of the precursors, a pyrochlore phase appeared as an intermediate compound. At elevated temperatures, the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{--Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ solid solution having a perovskite phase with a pseudocubic symmetry was formed. The formation rate of the perovskite phase and the morphology of the obtained calcined powder were significantly influenced by the starting materials used in the hydrothermal process. By using the precipitates of constituent species as starting materials, the hydrothermally prepared powder was found to exhibit a better sinterability than that prepared from the solid-state reaction process.

Keywords: Preparation; $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$; $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$; Powder; Hydrothermal process; Sintering; Perovskite

1. Introduction

Lead zirconate titanate ($\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$) ceramics are commercially important piezoelectric materials. They are widely used in displacement transducers, record player pick-ups, high-frequency filters, and actuators. To vary the piezoelectric characteristics and densification behavior of the ceramics, a ternary compound is usually added to $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ for forming a solid solution. Ferroelectric $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has been found to be an appropriate compound for improving the piezoelectric properties of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ [1–3]. However, the densified ce-

ramics of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{--Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ solid solution is difficult to obtain without adding of sintering additives [4,5]. The conventional way to prepare the powder of the above material system is the solid-state reaction process using mixed oxides. However, this process could not well control the microstructural features of the powder, and the sinterability of powder is often insufficient. Recently, the hydrothermal process has been reported to be an effective approach for preparing fine reactive powder having complex perovskite structure [6–9]. The powder prepared by the hydrothermal process has finer grain size and larger surface area than that obtained from the solid-state reaction process; therefore the sinterability of powder is enhanced and the densification of ceramics can be achieved [10,11].

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This study is the first attempt to synthesize $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ powder from the hydrothermally-treated precursors. The reaction process of the precursors after hydrothermal treatment was investigated. The effects of using various starting materials in the hydrothermal process on the formation rate of the perovskite phase and the morphology of the obtained powder were investigated. The sinterability of the calcined powder was also examined, and compared with that of the powder obtained from the solid-state reaction process.

2. Experimental

The chosen chemical composition in $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was $\text{Pb}(\text{Ni}_{1/3}\text{-Nb}_{2/3})_{0.4}\text{Zr}_{0.24}\text{Ti}_{0.36}\text{O}_3$. $\text{Pb}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$, $\text{Ni}(\text{C}_2\text{O}_4)_2$, and $\text{Nb}(\text{HC}_2\text{O}_4)_5$ were used as raw materials to prepare the aqueous solution containing each cation. The Ti^{4+} solution was obtained by dissolving titanium hydroxide precipitates in dilute HNO_3 aqueous solution. Two different processes were performed for obtaining precursors. In process I, the Pb^{2+} , Zr^{4+} , Ti^{4+} , and Nb^{5+} aqueous solutions were mixed together according to the determined amounts, and then ammonia was added to the solution to precipitate all cations. The precipitates were filtered and washed by de-ionized water repeatedly to remove remaining anions. The washed precipitates were added with the Ni^{2+} aqueous solution. Then the mixed slurry was charged into a Teflon-lined autoclave apparatus, and hydrothermally heated at 200°C for 2 h. After the hydrothermal treatment, the products were dried at 100°C for several hours. The dried powder was named as precursor A. In process II, all aqueous solutions were mixed together but without adding ammonia. Then the mixed solution was hydrothermally treated at 200°C for 2 h as in process II. The dried powder was named as precursor B.

The obtained precursors were calcined in air from 600 to 900°C for 2 h. The 900°C -calcined precursors were uniaxially pressed into disks and sintered at 1150°C for 2 h. The compounds present in the calcined specimens were characterized by X-ray powder diffraction (XRD) using $\text{Cu K}\alpha$ radiation. Differential thermal analysis (DTA) was conducted

to analyze thermal variations during heating. Scanning electron microscopy (SEM) was used to examine the microstructural evolution and particle size of the calcined specimens.

3. Results and discussion

Fig. 1 shows the XRD results of precursor A calcined at various temperatures for 2 h. The as-received precursor A was found to contain a small amount of a pyrochlore phase. The existence of the pyrochlore phase indicates that the starting materials could partially react with each other under the 200°C -hydrothermal condition. After 600°C -heating, a perovskite phase appeared, and the pyrochlore phase was also existent in the specimens as an intermediate compound. When the temperature was raised, the intensity of the perovskite phase increased with a decrease in the intensity of the pyrochlore phase. After 900°C calcination, only the perovskite pattern was observed by XRD, indicating that the formation of the perovskite phase was complete. This result revealed that using hydrothermal process one can successfully synthesize this compound. When XRD analysis was carried out from $2\theta = 10^\circ$ to 60°

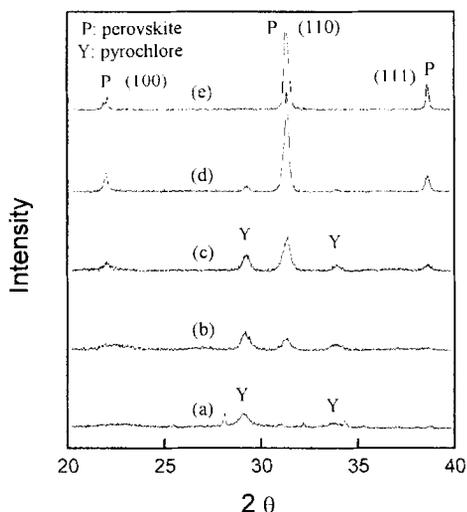


Fig. 1. X-ray diffraction patterns of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ precursor obtained from process I. (a) as-received powder, and the precursor heated at (b) 600°C , (c) 700°C , (d) 800°C , and (e) 900°C for 2 h.

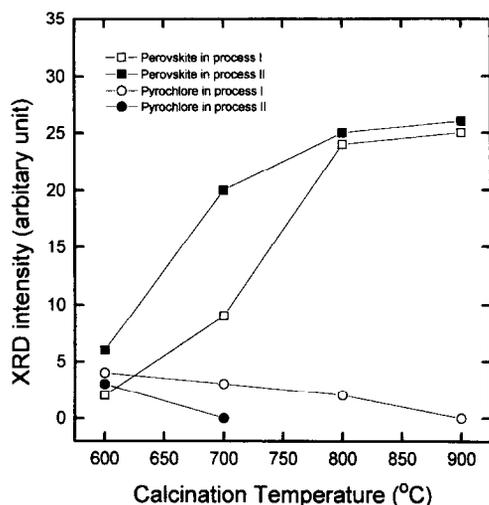
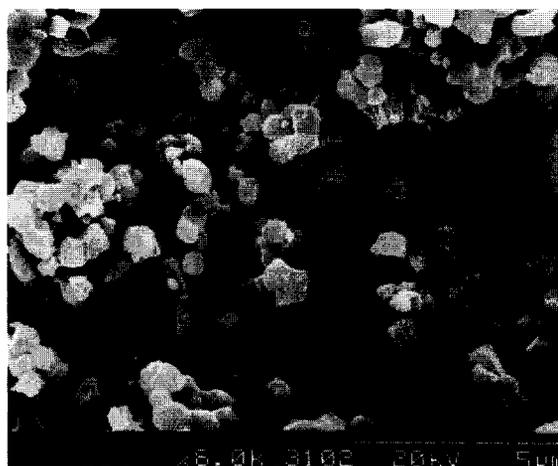


Fig. 2. X-ray diffraction intensity for the perovskite and pyrochlore phases formed in precursors A and B at various calcination temperatures.

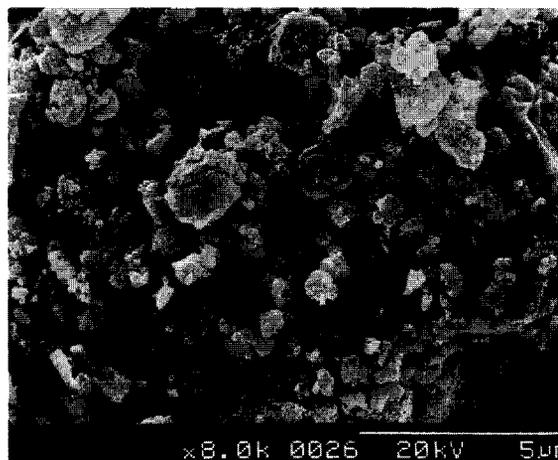
on this compound, only the diffraction peaks corresponding to (100), (110), (111), (200), (210), and (211) planes were observed. Based on these diffraction data, this compound was characterized to have a pseudocubic symmetry with a lattice constant of 4.033 Å. According to the phase diagram of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ [12], when the composition ratio of PbZrO_3 to PbTiO_3 is 2:3, a tetragonal phase will be formed. However, the specimen with a composition of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3 : \text{PbZrO}_3 : \text{PbTiO}_3 = 3.3 : 2 : 3$ exhibited a pseudocubic crystalline structure. This result indicates that the addition of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ modified the structure of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, and also a solid-solution of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3 - \text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was formed.

Precursor B was also calcined and characterized by XRD. The reaction scheme of precursor B was similar to that of precursor A. The pyrochlore phase was also present as an intermediate compound and disappeared at elevated temperatures. The XRD intensities of the perovskite and pyrochlore phases in precursors A and B at each calcination temperature are compared in Fig. 2. This figure shows that the formation amount of the perovskite phase in precursor B was higher than that in precursor A, and the temperature for the pyrochlore phase to disappear in

precursor B was reduced to be as low as 700°C. Differential thermal analysis (DTA) was performed to examine the reaction process of these two precursors. In precursor B, an endothermic peak was observed at 680°C. A large amount of the perovskite phase was found after the 680°C endotherm, indicating that the endothermic peak was attributed to the reaction of the pyrochlore phase converting into the perovskite phase. On the other hand, no distinct DTA peak was found in precursor A, and only a



(a)



(b)

Fig. 3. Scanning electron micrographs of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3 - \text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ powder derived from (a) precursor A and (b) precursor B after 900°C calcination for 2 h.

small amount of the perovskite phase was formed in the 700°C-quenched specimens. These results also indicate that the formation of the perovskite phase was accelerated in precursor B. Considering that precursor B was prepared from the solution of constituent species, the distribution of the chemical species in precursor B should be more homogeneous than that in precursor A which was prepared from precipitates. Therefore, the improved compositional homogeneity in precursor B led to the enhanced formation of the perovskite phase.

The microstructures of the precursors A and B calcined at 900°C are shown in Fig. 3 a and b. In the former sample, the perovskite grains were formed in a dispersed state, and the grain size was estimated to be around 0.8–1.0 μm. On the other hand, in the latter specimen the grain size had a wider distribution from 0.5 μm to 2.0 μm; in addition, these grains tended to form agglomerates of the fine particles. It was found that the different preparation procedures not only influenced the formation process, but also the morphology of the obtained powder. Sintering at 1150°C for 2 h was performed on the 900°C-calcined specimens. The sintering densities of the sintered specimens from the two kinds of precursors were found to be 7.9 g/cm³ and 6.2 g/cm³, respectively. The low density of the specimen prepared from precursor B was ascribed to the reduced sinterability of large grains, and the low packing efficiency of the agglomerates. In the other parallel experiment, the powder of Pb(Zr, Ti)O₃–Pb(Ni_{1/3}Nb_{2/3})O₃ with the same composition was prepared by the solid-state reaction process using mixed oxides. Sintering at 1150°C was carried out on the 900°C-calcined sample. The sintering density was found to be 6.9 g/cm³ which was lower than that of the specimens prepared from precursor A. Densified ceramics can be obtained by using precursor A rather than the powder prepared from mixed oxides. These results indicate that hydrothermal processing is a potential method to improve the sinterability of Pb(Zr, Ti)O₃–Pb(Ni_{1/3}Nb_{2/3})O₃ materials

when the agglomeration state of the powder is controlled.

4. Conclusion

(i) Fine Pb(Zr, Ti)O₃–Pb(Ni_{1/3}Nb_{2/3})O₃ powder was prepared from the hydrothermally-treated precursors. The hydrothermal condition was 200°C for 2 h.

(ii) During the reaction process, a pyrochlore phase was formed as an intermediate compound. At elevated temperatures, the Pb(Zr, Ti)O₃–Pb(Ni_{1/3}Nb_{2/3})O₃ solid solution having a perovskite structure with a pseudocubic symmetry was formed.

(iii) The formation rate of the perovskite phase and the morphology of the obtained calcined powder were influenced by the starting materials used in the hydrothermal process. By using the precipitates of constituent species as starting materials, the hydrothermally prepared powder exhibited better sinterability than that prepared from mixed oxides via the solid-state reaction process.

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