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Synthesis of Ba(Zr,Ti)₂O₅ particles using Zr/Ti-HPA with complexing of Ti-IPA and Zr
using ZrOCl₂

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Abstract

For this study, Zr-substituted BaTi_2O_5 particles were synthesized using an aqueous solution method with peroxidized polytitanic acid as the starting material. After Zr/Ti heteropolyacids were synthesized by complexing Zr with polytitanic acid (Ti-IPA) in aqueous solution using ZrOCl_2 , the obtained Zr/Ti heteropolyacids were mixed with barium hydroxide. Subsequently, the precipitate was dried and heat-treated at $1100\text{ }^\circ\text{C}$ for 10 h. Thereby, we obtained single-phase $\text{Ba}(\text{Zr,Ti})_2\text{O}_5$ powder. Using this method, BaTi_2O_5 was synthesized with up to 6 mol% Zr solid solution on Ti sites. These results were evaluated using XRD and XRF. The crystal structure and structural transition of the resulting $\text{Ba}(\text{Zr,Ti})_2\text{O}_5$ were evaluated using Raman measurements. All $\text{Ba}(\text{Zr,Ti})_2\text{O}_5$ samples showed a structural transition. The Curie temperatures T_c of BaTi_2O_5 , $\text{BaZr}_{0.034}\text{Ti}_{0.966}\text{O}_5$, and $\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$ were, respectively, 480, 450, and $430\text{ }^\circ\text{C}$.

Keywords: BaTi_2O_5 , Raman spectroscopy, solid solution, Zr

1. Introduction

Since BaTi₂O₅ (BT2) was first reported by Akishige et al. as a ferroelectric material with a high Curie temperature (T_c) [1], many investigations of the material have been undertaken [2–12]. In fact, BT2 has a ferroelectric property with the high T_c of 470 °C and a giant dielectric constant of 30,000 at approximately T_c . Therefore, BT2 is a candidate material for producing capacitors and piezoelectric and ferroelectric devices. On the other hand, lots of studies on high Curie point ferroelectrics of non-lead systems have been carried out in addition to BT2 [13–15]. Reportedly, BT2 comes to have relaxor-like properties by substitution of Zr at the Ti site in BT2 [8–10]. Reports have described synthesis of the Zr solid solution BT2 from single-crystal synthesis by arc melting [8] and in thin films using sol-gel method [11]. One study [8] demonstrated that the addition of Zr increased the permittivity of BT2 slightly and decreased its conductivity. In addition to Zr solid solution BT2 particle synthesis, a sol-gel method has been reported using organometallic compounds as starting materials [12].

We earlier synthesized BT2 particles using an aqueous solution method with water-soluble polytitanic acid peroxide (Ti-IPA) and Ba(OH)₂ as a starting material [6]. Furthermore, Sr has been substituted at the Ba site in BT2 using a hydrothermal method

with a Sr nitrate aqueous solution. The structural transition of those materials was evaluated for an earlier study [7]. However, Zr solid-solution application to Ti sites in BT2 is difficult to accomplish using hydrothermal method because of the chemical nature of Zr in aqueous solution medium: ZrO_2 precipitates in aqueous solution under high pressure with a hydrothermal process. Therefore, we attempted to synthesize Zr-doped BT2 using a chemical design: 1. After synthesizing Zr/Ti heteropolyacid (Zr/Ti-HPA) complexing Zr with Ti-IPA using water soluble $ZrOCl_2$, we 2. reacted and fired the obtained Zr/Ti-HPA and $Ba(OH)_2$, thereby producing $Ba(Zr,Ti)_2O_5$ powder. With Zr/Ti-HPA precursor, the $BaTi_2O_5$ (BZT2) particles can be synthesized easily by complexing Ti-IPA and Zr using $ZrOCl_2$. For this study, the structure and structural transition of the obtained $Ba(Zr,Ti)_2O_5$ particles were investigated using Raman measurements.

2. Experiment procedure

Metallic Ti powder (Kojundo Chemical Lab. Co. Ltd., Japan) was mixed into a 30% H_2O_2 (Fujifilm Wako Pure Chemical Corp., Japan) and 28% NH_3 (Fujifilm Wako Pure Chemical Corp., Japan) aqueous solution. Then the obtained mixture suspension was stirred and reacted to obtain Ti-IPA solution. The synthesis method was reported

earlier in the literature [6]. After $ZrOCl_2$ aqueous solutions (Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan) having molar ratios of $Zr/(Ti+Zr)=0.02, 0.05,$ and 0.10 were added to the resulting Ti-IPA solution, the solutions were stirred and reacted for 1 h at $10\text{ }^\circ\text{C}$ to obtain the Zr/Ti heteropolyacid peroxide (HPA). After $Ba(OH)_2$ solution was added to the resulting Zr/Ti-HPA solution to produce $Ba/(Ti+Zr)$ with the molar ratio of $1/2$, the mixed solution was reacted for 7 days. Then, after the obtained precursor powder was filtered, dried, and ground, the resultant powder was heat-treated at $1100\text{ }^\circ\text{C}$ for 10 h.

The crystal structures of the powders were confirmed using X-ray diffraction (XRD) analysis (Miniflex; Rigaku Corp., Japan) with $Cu\ K\alpha$ irradiation. Then the microstructure was observed using scanning electron microscopy (SEM, JCM-6000 Plus; JEOL, Japan). The compositions of the resulting BZT2 powders were ascertained using an X-ray fluorescent analyzer (XRF, EDX-700HS; Shimadzu Corp., Japan). Raman scattering measurements were taken using a single monochromator (Lucir Co. Ltd., Japan) with a 532 nm line from an Nd:YAG laser at $200\text{--}500\text{ }^\circ\text{C}$. Details of the instruments have been presented in an earlier report [5]. The obtained Raman spectrum was standardized at a peak of 868 cm^{-1} .

3. Results and Discussion

To synthesize Zr/Ti heteroperoxopolyacid (HPA) using $ZrOCl_2$, precipitation was observed when the reaction temperature was higher than 10 °C. When the reaction temperature of $ZrOCl_2$ and Ti-IPA was set as 10 °C, the final product after calcination was a mixed phase when the combined reaction time was less than 30 min. When the reaction time of $ZrOCl_2$ and Ti-IPA exceeded 2 h (at 10 °C), the precipitation of a mixture of TiO_2 -derived and ZrO_2 -derived products was observed. From these findings, the optimal reaction conditions for reacting Ti-IPA and $ZrOCl_2$ were inferred as 10 °C for 1 h. As described above, $Ba(Zr,Ti)_2O_5$ powder was prepared by reacting Zr/Ti-HPA synthesized with $Ba(OH)_2$ and by heat-treatment of the reacted precursor at 1000 °C for 10 h. The Zr/Ti ratios in the Zr/Ti-HPA were 0 (without Zr), 0.02, 0.05, and 0.10. The samples obtained from heat-treatment were designated respectively as BT, BZT2, BZT5, and BZT10. The resulting Ba-Ti-Zr-O powders were characterized using XRD, XRF, and Raman spectroscopy.

Figure 1 exhibits XRD patterns for the powders of BT, BZT2, BZT5, and BZT10. Actually, BT, BZT2, and BZT5 were almost a single phase of $BaTi_2O_5$ (JCPDS 85-0476) with monoclinic structure; BZT10 showed mixed phases of BT2 and $BaZrO_3$. A $BaZrO_3$ phase was observed in the resulting BZT10 sample, suggesting that Zr and

Ti-IPA did not fully complexate in the precursor Zr/Ti-HPA with the Zr contents of Zr/Ti of 0.10. The cell volumes of the resulting BT, BZT2, and BZT5 were, respectively, 647, 650, and 658. Using XRF, the Zr/(Zr+Ti) molar compositions of BZT2, BZT5, and BZT10 were evaluated respectively as 0.034, 0.059, and 0.180. The BZT10 sample contained considerably large amounts of Zr, suggesting that the Zr/Ti HPA precursor was not well synthesized. These results demonstrated that Zr can be complexed with the precursor Zr/Ti-HPA up to about 0.5 ($\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$). We therefore evaluated the SEM, Raman measurements, and the structural transitions for single-phase BT, BZT2, and BZT5.

Figure 2 depicts SEM images of the BT, BZT2, and BZT5 powders. We also evaluated the particle sizes of the respective powders from SEM images using ImageJ™ image analysis software. The powder particles were spherical and granular. The respective particle sizes of the samples BT, BZT2, and BZT5 were 1.20, 1.33, and 1.69 μm . Results show that the BZT2 particle size increased slightly with increasing Zr contents in the BZT2.

Raman spectra were measured from 200 to 500 °C for the BT (BaTi_2O_5), BZT2 ($\text{BaZr}_{0.034}\text{Ti}_{0.966}\text{O}_5$), and BZT5 ($\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$) samples. Figure 3 presents the Raman spectrum at 400 °C for the BZT5 powder as a representative Zr solid-soluted

BZT2 sample. The resulting spectrum was consistent with the spectra of BT2 described in earlier reports [5–7]. Lattice vibrations related to quasi-elastic scattering around 0 cm^{-1} are frozen at the Curie point. Consequently, the full width at half maximum (FWHM) of the quasi-elastic scattering peak of BT2 is minimal around the Curie point. The quasi-elastic scattering peak and its FWHM were determined 1. by cutting off the peak from -10 to 10 cm^{-1} , 2. by Lorentz fitting the spectrum with the peak at 0 cm^{-1} , and 3. by evaluating FWHM from the fitting curve. Details of the evaluation method were presented in earlier reports [5].

The temperature dependence of the FWHM of the quasi-elastic scattering was measured for each of the BT, BZT2, and BZT5 samples. The results are presented in Figure 4. The FWHM minimum point (Curie temperature T_c) is indicated by an arrow in each figure. The T_c of BT (BaTi_2O_5), BZT2 ($\text{BaZr}_{0.034}\text{Ti}_{0.966}\text{O}_5$), and BZT5 ($\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$) were, respectively, 480, 450, and 430 °C. Also, the T_c of non-doped BT2 was approximately equal to the T_c reported earlier in the literature [1,5–7]. The T_c of BZT2 decreased concomitantly with increasing Zr contents in BZT2. Here, T_c decreased by 50 °C per Zr 5.9 mol% in BZT2.

Shiga et al. used arc melt method to synthesize Zr solid-solution single-crystal BaTi_2O_5 [8]. The T_c of the resulting BZT2 was decreased by 42 °C at 10 mol% Zr in

BZT2. The decrease of T_c found from this investigation was slightly greater than the decrease reported by Shiga et al. The degree of lowering in T_c of BZT might vary depending on the method of BZT synthesis or the oxygen defect in the resulting BZT. For this study, the structural transition and T_c of the BZT2 were evaluated using Raman (optical) measurements. However, they were evaluated in an earlier study using electrical measurements [8]. Because BaTi_2O_5 exhibits a relaxor behavior [9, 10], a difference between the earlier study and the present study was assumed to exist in terms of the lower T_c for the Zr solid solution in BT2.

4. Conclusion

By reacting ZrOCl_2 with Ti-IPA, Zr/Ti heteropolyacid (HPA) was synthesized. Then Zr/Ti HPA and Ba(OH)_2 were reacted and were heat-treated to synthesize Zr solid solution BaTi_2O_5 particles. Through these operations, Zr/Ti HPA was synthesized with Ti-IPA and Zr using ZrOCl_2 . In addition, Zr was composed to about 6% in Zr/Ti HPA. Furthermore, the findings indicate that the Zr/Ti-HPA obtained using this method can synthesize BaTi_2O_5 (or $\text{Ba(Zr,Ti)}_2\text{O}_5$) as well as isopolytitanic acid. The mean particle size of the obtained BZT2 particles was 1.20–1.69 μm , as confirmed from SEM observations. Moreover, greater Zr contents in the precursor Zr/Ti-HPA are associated

with a larger particle size of the obtained BZT2 particles. Single-phase $\text{Ba}(\text{Zr,Ti})_2\text{O}_5$ particles in which Zr was solid-soluted up to 6% at the Ti site were synthesized using a Zr/Ti HPA aqueous solution. Those findings were confirmed using XRD and XRF. The temperature dependence of the structure of the resulting BZT2 was evaluated using Raman spectroscopy. Findings indicate the T_c of BaTi_2O_5 , $\text{BaZr}_{0.034}\text{Ti}_{0.966}\text{O}_5$, and $\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$, respectively, as 480, 450, and 430 °C. Results confirmed that T_c of BT2 decreased concomitantly with increasing Zr contents in the BZT2. In conclusion, we clarified that Zr-substituted BaTi_2O_5 can be synthesized easily using Zr/Ti-HPA as a raw material, with complexed Ti-IPA and ZrOCl_2 .

Acknowledgments

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Ethical approval

The authors declare that no ethical approval was necessary for this study.

Competing interests

The authors declare that they have no competing interests.

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Figure captions

Fig. 1. XRD patterns for the BT, BZT2, BZT5, and BZT10 powders.

Fig. 2. SEM images of the BT, BZT2, and BZT5 powders.

Fig. 3. Raman spectra for the source BZT5 powder ($\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$) measured at 400 °C.

Fig. 4. Temperature dependence of FWHM using the QE-scattering peak of the Raman spectra for the source BT2, BZT2 ($\text{BaZr}_{0.034}\text{Ti}_{0.966}\text{O}_5$), and BZT5 ($\text{BaZr}_{0.059}\text{Ti}_{0.941}\text{O}_5$) powders.

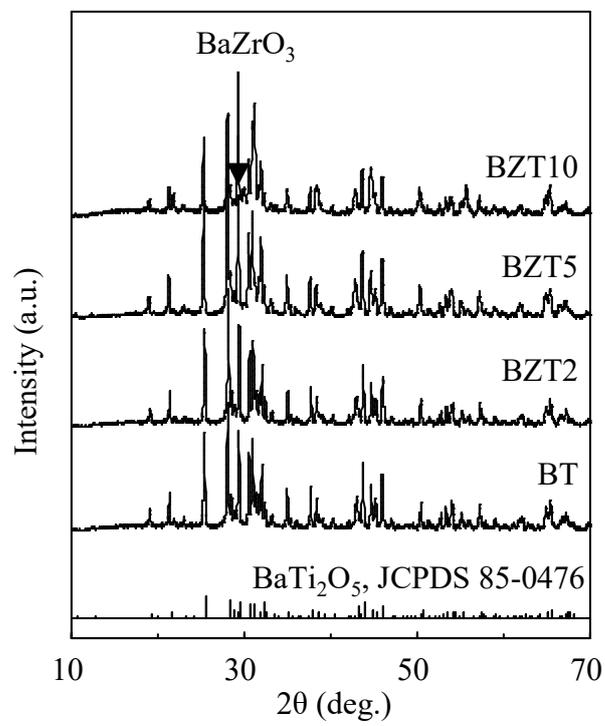


Fig. 1.
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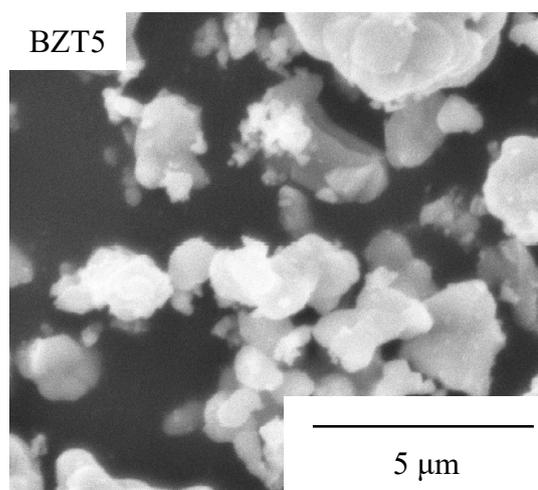
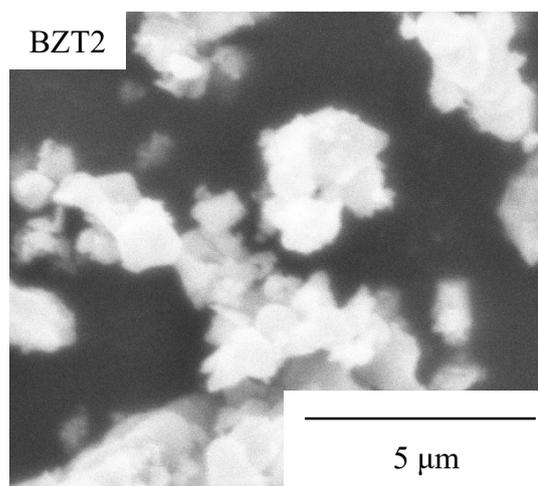
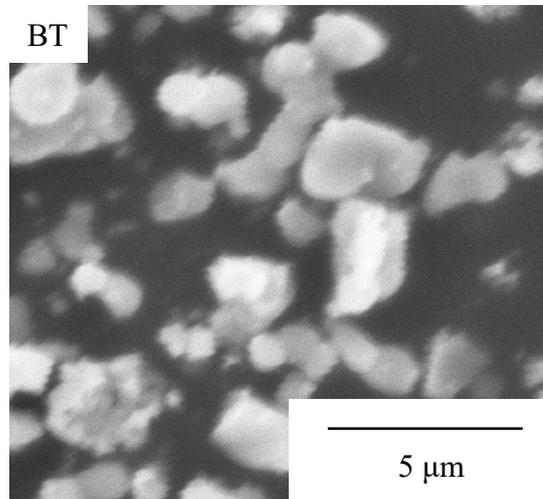


Fig. 2.
H. Miyazaki

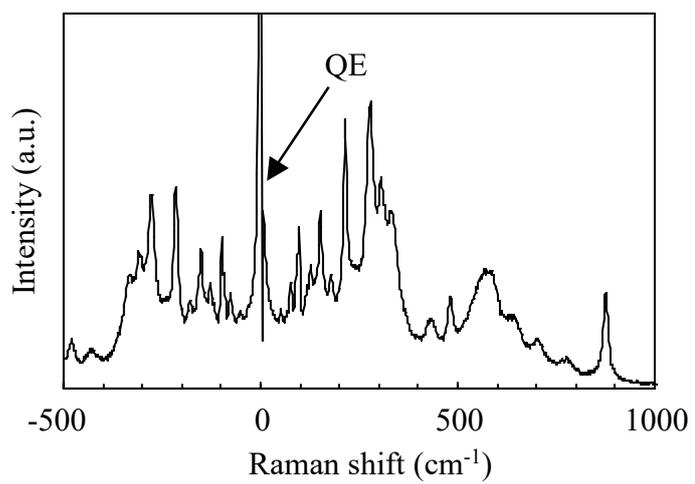


Fig. 3.
H. Miyazaki

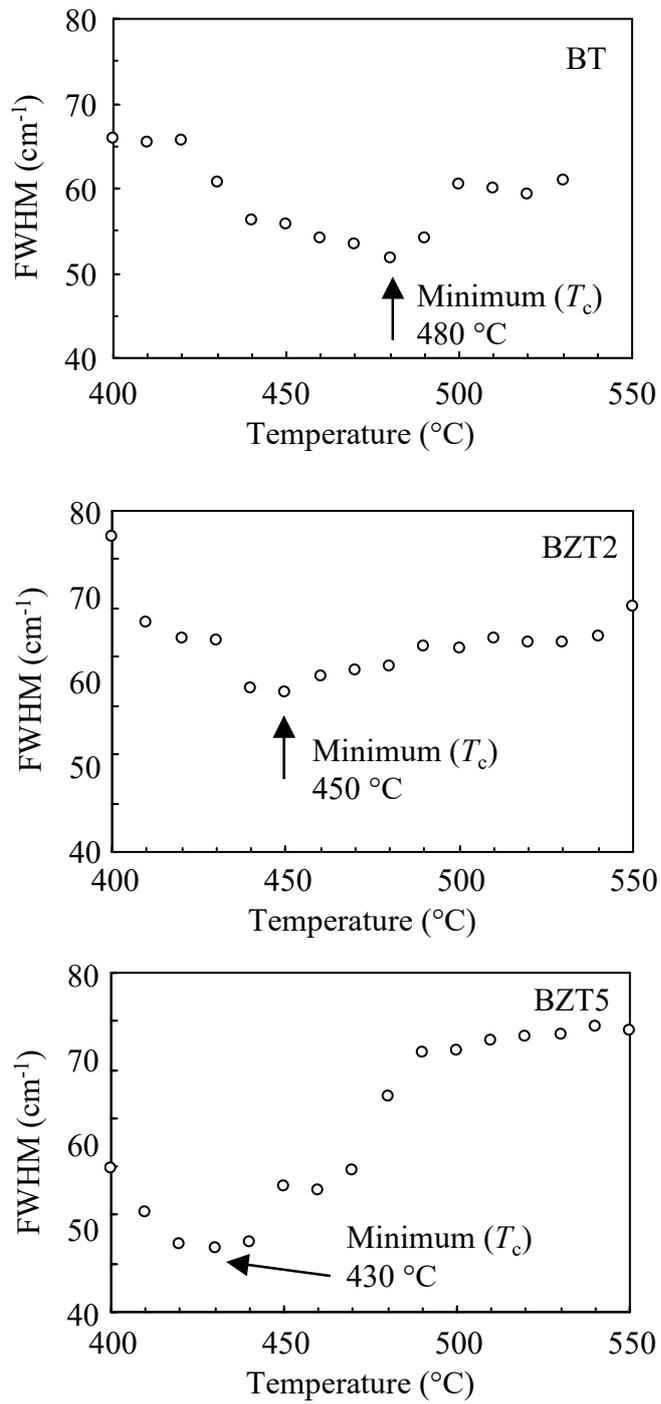


Fig. 4.
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