Preparation of needlelike $Sr_{0.5}Ba_{0.5}Nb_2O_6$ particles using molten $SrCl_2$ -Ba Cl_2 salt

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Needlelike $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powder particles were prepared from $SrCO_3$, $BaCO_3$, and Nb_2O_5 in the presence of a mixture of molten $SrCl_2$ and $BaCl_2$. When the composition of the mixture of oxide and carbonate was fixed to be $SrCO_3$: $BaCO_3$: $Nb_2O_5 = 1:1:2$, the phase and morphology of the product particles were dependent on the composition of molten salt. The exchange reaction, $BaO + SrCl_2 = BaCl_2 + SrO$, enriched Sr in the oxide phase. The relation between the compositions of the salt mixture and the reaction product was determined, and needlelike $Sr_{0.5}Ba_{0.5}Nb_2O_6$ particles were obtained by using the molten salt containing 18 mol % SrCl_2.

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1. Introduction

Texture engineering is an important approach to improve properties of polycrystalline ceramics.¹⁾⁻³⁾ One of the preparation methods of textured ceramics is the templated grain growth process. In this process, textured ceramics are prepared by sintering of green compacts containing aligned, large template particles dispersed in a matrix of small particles. Anisometric particles are necessary for the template particles because they are aligned by the application of shear stresses during casting. In many cases, they are prepared by molten salt synthesis, ⁴⁾ In molten salt synthesis, a mixture of starting oxides and/or carbonates is mixed with salt and heated at temperatures above the melting point of the salt. The starting oxides and/or carbonates react under the presence of molten salt. When the reaction product has a highly anisotropic crystal structure, anisometric particles are obtained.

Strontium barium niobate (Sr_xBa_{1-x}Nb₂O₆, abbreviated as SBNx) with x between 0.2 and 0.8 is a ferroelectric material with the tungsten bronze structure.⁵⁾ This material possesses excellent pyroelectric and linear electro-optic properties. Furthermore, it has interesting piezoelectric properties and is one of the candidates for lead-free piezoelectric ceramics.⁶⁾ In the fabrication of textured piezoelectric ceramics with the tungsten bronze structure, needlelike particles have been used.⁶⁾ In the preparation of the needlelike particles by molten salt synthesis, chloride salt has been used.⁷⁾⁻¹¹⁾ However, in many cases, a cation-exchange reaction, such as $PbO + 2KCl = PbCl_2 + K_2O$, is occurred, and alkaline oxide incorporates into the tungsten bronze structure. Therefore, the needlelike particles with the pure SBN composition cannot be obtained by molten salt synthesis using alkaline chloride.^{8)–11)} We have found that the use of SrCl₂ and BaCl₂ can avoid the contamination of alkaline cations in the needlelike particles, and furthermore, that the Sr/Ba ratio in needlelike SBN is dependent on the composition of the chloride mixture. Based on the phase diagram reported by Schei and Flood, 12) the melting points of BaCl₂ and SrCl₂ are 962 and 871°C, respectively, and

the liquid and solid phases have complete miscibility. The liquidus and solidus lines have a minimum at $68 \text{ mol }\% \text{ SrCl}_2$ at 852° C. Because the specimens were heated at or above 1150° C, the salt was completely melted.

2. Experimental procedure

Chemically pure SrCO₃ (Koso Chemical Co., Ltd., Tokyo, Japan), BaCO₃ (Wako Pure Chemical Industries, Ltd., Osaka, Japan), Nb₂O₅ (Mitsui Mining & Smelting Co., Ltd., Tokyo, Japan), SrCl₂ (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and BaCl₂ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used in this experiment. The stoichiometric amounts of SrCO₃, BaCO₃, and Nb₂O₅ (1:1:2) were mixed in a ball mill for 24 h using ethanol as medium, and then the same weight of the SrCl₂ and BaCl₂ mixture with various compositions was added. The mixtures were heated at 100°C/h, soaked for 2 h at various temperatures at or above 1150°C, and cooled in a furnace. The products were washed with water for about 10 times to remove salt.

The phases in the products were determined by X-ray diffraction analysis (XRD) using the Cu K α radiation, and the morphology was observed with a field-emission scanning electron microscope (FE-SEM) attached with an energy-dispersion X-ray analyzer (EDX).

Results and discussion

Figure 1 shows the XRD patterns of the reaction products obtained by using the molten salt containing 50 mol % SrCl₂, heated at various temperatures for 2 h. The crystalline phases in the products at 1150 and 1200°C were $SrNb_2O_6$ and $Sr_2Nb_2O_7$. The diffraction lines of SBN were observed in the 1250 and 1300°C specimens. However, those of $Sr_2Nb_2O_7$ and $SrNb_2O_6$ still remained. The diffraction lines of BaNb₂O₆ were hardly observed.

Figure 2 shows the morphology of the reaction products shown in Fig. 1. The 1150 and 1200°C specimens were composed of large block-type particles and small needlelike particles. The amount of the needlelike particles increased in the 1250 and 1300°C specimens. The Sr/Ba ratio was measured at the block-type and needlelike particles in the 1300°C specimen by EDX. The ratio was about 19 at one block-type particle and between 1.3 and 2.3 at four needlelike particles. The results of

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Fig. 1. X-ray diffraction patterns of the reaction products obtained by using molten salt containing $50 \text{ mol }\% \text{ SrCl}_2$, heated at (a) 1150, (b) 1200, (c) 1250, and (d) 1300°C for 2 h.



Fig. 2. Morphology of the reaction products obtained by using molten salt containing 50 mol % SrCl₂, heated at (a) 1150, (b) 1200, (c) 1250, and (d) 1300°C for 2 h.

XRD, SEM, and EDX indicated that the reaction products obtained by using the molten salt containing 50 mol % SrCl₂ were Sr-rich materials.

The above results suggest the exchange reaction between oxide and chloride, $BaO(s) + SrCl_2(l) = BaCl_2(l) + SrO(s)$. The standard free energy change for this reaction, e.g., at 1500 K is -54.889 kJ mol⁻¹.¹³) Therefore, the exchange reaction is possible. The formation of BaCl₂ was confirmed by examining the phases in the reaction product obtained by using only SrCl₂, heated at 1300°C for 2 h. The specimen was not washed with water after the reaction. Figure 3 shows the XRD pattern of this specimen. The diffraction lines of BaCl2 were confirmed, indicating the occurrence of the exchange reaction. The free energy change of reaction is dependent on the activity of each material. In the present case, the activities of Sr and Ba are controlled by the composition of the salt mixture. The phases and morphology of the reaction products were examined by using salt mixtures with various compositions. Figure 4 shows the XRD patterns of the reaction products obtained using the molten salt containing 40, 20, and $0\,mol\,\%$ SrCl_2, heated at 1300°C for 2 h. The heating temperature of 1300°C was selected because the amount of



Fig. 3. X-ray diffraction pattern of the reaction product before washing with water, obtained by heating at 1300°C for 2 h in molten SrCl₂.



Fig. 4. X-ray diffraction patterns of the reaction products obtained by using the molten salt containing (a) 40, (b) 20, and (c) $0 \mod \%$ SrCl₂, heated at 1300°C for 2 h.

impurity $SrNb_2O_6$ and $Sr_2Nb_2O_7$ was the smallest at this temperature as shown in Fig. 1. The specimen obtained by using the molten salt containing 40 mol % $SrCl_2$ still contained impurity phases, but the specimen with SBN single phase was obtained by using the molten salt containing 20 and 0 mol % $SrCl_2$.

From above discussion, it is suggested that the formation of Sr-rich materials can be suppressed by increasing the amount of Ba ions in molten salt. Figure 5 shows the morphology of the reaction products obtained using the molten salt containing 40, 30, 20 and 0 mol % SrCl₂, heated at 1300°C for 2 h. The molten salt containing 40 and 30 mol % SrCl2 gave the mixture of blocktype and needlelike particles, and the products obtained using the molten salt containing 20 and 0 mol % SrCl2 were composed of only needlelike particles. Figure 6 shows the relation between the salt composition and the Sr/Ba ratios of the reaction product (after washing with water). The Sr/Ba ratio of the reaction product was dependent on the salt composition. This relation was expressed by the straight line with slightly scattered data points, as indicated in Fig. 6. The line predicts the salt composition which gives SBN50 contains 19.6 mol % SrCl₂. However, the salt with this composition gave SNB48. By changing the salt

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Fig. 5. Morphology of the reaction products obtained by using the molten salt containing (a) 40, (b) 30, (c) 20, and (d) $0 \mod \%$ SrCl₂, heated at 1300°C for 2 h.



Fig. 6. The relation between the salt composition and the Sr/Ba ratio of the reaction product (after washing with water) heated at 1300° C for 2 h.

composition to 18 mol % SrCl₂, we obtained SBN50. Figure 7 shows the morphology of the reaction product of SBN50. The particles were needlelike with the particle size (long axis) of about $15 \,\mu\text{m}$ and the aspect ratio between 10 and 15.

The sequence of reaction is deduced as follows. The formation of particles with clear facets (Fig. 2) suggests that the solid particles (Sr-rich materials and SBN) precipitate from the liquid phase.⁴⁾ In an early stage of reaction, Nb₂O₅ dissolves in molten salt and reacts mainly with dissolved SrO to form SrNb₂O₆ and Sr₂Nb₂O₇. The reaction with BaO is sluggish or a part of BaCO₃ is consumed by the exchange reaction $BaO + SrCl_2 = BaCl_2 +$ SrO. After the formation of the Sr-rich materials, Ba ions start to participate in the reaction. The facts that the amount of Sr-rich materials decreases as the heating temperature is increased and the SBN particles have smaller size than the Sr-rich materials (Figs. 1 and 2) indicate that the Sr-rich materials dissolve in the molten salt and react with dissolved BaO to form SBN particles. The amount of Ba ions in these particles is dependent on the amount of Ba ions in molten salt (Fig. 6). When the Ba-rich salt is used, the amount of Sr-rich materials is reduced at the same temperature (Fig. 5). Probably, the rate of reaction from the Sr-rich materials to SBN is promoted and/or the tungsten bronze phase directly precipitates in the Ba-rich salt.

The particle shape (habit) is determined by the surface energy and/or the growth rate of each crystal face.¹⁴⁾ The growth rate is determined by the surface structure at an atomic level; a rough



Fig. 7. Morphology of the reaction products obtained by using the molten salt containing $18 \mod \%$ SrCl₂, heated at 1300° C for 2 h.

surface has a high growth rate than a smooth surface. In the present case, we cannot judge which factor determines the particle shape, because the quantitative data on the surface energies and the surface structure are not available.

Conclusions

Needlelike $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN50) particles were prepared by molten salt synthesis. When the mixture of $SrCO_3$, $BaCO_3$, and Nb_2O_5 with the ratio of 1:1:2 was used as the starting materials for SBN and the mixtures of $SrCl_2$ and $BaCl_2$ were used as molten salt, the phase and morphology of the product particles were dependent on the salt composition, for which the exchange reaction $BaO + SrCl_2 = BaCl_2 + SrO$ was responsible. The Sr/Ba ratio in the reaction product was controlled by selecting the salt composition, and needlelike SBN50 particles were obtained by using the molten salt containing 18 mol % $SrCl_2$.

References

- G. L. Messing, S. Trolier-McKinstry, E. M. Sabolsky, C. Duran, S. Kwon, B. Brahmaroutu, P. Park, H. Yilmaz, P. W. Rehrig, K. B. Eitel, E. Suvaci, M. Seabaugh and K. S. Oh, *Crit. Rev. Solid State Mater. Sci.*, 29, 45–96 (2004).
- 2) T. Tani and T. Kimura, Adv. Appl. Ceram., 105, 55-63 (2006).
- 3) T. Kimura, J. Ceram. Soc. Japan, 114, 15–25 (2006).
- 4) T. Kimura and T. Yamaguchi, "Ceramic Powder Science", Ed. by G. L. Messing, K. S. Mazdiyasni, J. W. McCauley and R. A. Haber, American Ceramic Society, Westerville (1987) pp. 169–177.
- 5) Y. Xu, "Ferroelectric Materials and Their Applications", North-Holland, Amsterdam (1991) pp. 247–276.
- C. Duran, S. Trolier-McKinstry and G. Messing, J. Am. Ceram. Soc., 83, 2203–2213 (2000).
- T. Kimura, M. Machida, T. Yamaguchi and R. E. Newnham, J. Am. Ceram. Soc., 66, C-195–C-197 (1983).
- C. Duran, G. L. Messing and S. Trolier-McKinstry, *Mater. Res. Bull.*, 39, 1679–1689 (2004).
- J. Xu, L.-H. Zhu, Q.-W. Huang and H. Gu, J. Mater. Sci., 39, 3445–3447 (2004).
- L.-H. Zhu, Q.-W. Huang and H. Gu, J. Cryst. Growth, 267, 199–203 (2004).
- W. Chen, S. Kume, C. Duran and K. Watari, J. Eur. Ceram. Soc., 26, 647–653 (2006).
- 12) A. Schei and H. Flood, *Acta Chem. Scand.*, 14, 2067–2070 (1960).
- "NIST-JANAF Thermochemical Tables, Forth Edition", Ed. by M. W. Chase, Jr., American Institute of Physics, New York (1998).
- D. Elwell and H. J. Scheel, "Crystal Growth from High Temperature Solutions", Academic Press, London (1975) pp. 202–236.