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CHARACTERIZATION OF POWDER-CALCINED $BaZnGeO_4$ BY THERMAL ANALYSIS *

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ABSTRACT

The characterization of powder-calcined $BaZnGeO_4$ has been performed by differential thermal analysis, X-ray diffraction and scanning electron microscopy. The calcination temperature influences the successive phase transitions which are well characterized in DTA. The peak height of the anomaly due to the I–II phase transition is proportional to the fraction of synthesized $BaZnGeO_4$ in the sample. The anomaly due to the IV–V phase transition is not proportional to the fraction of $BaZnGeO_4$, but is dependent on the physical impurities remaining in the specimen. The mechanism of the successive phase transitions is discussed.

INTRODUCTION

In the fabrication of ferroelectric ceramics, the conditions of powder calcination play an important role. The properties of products strongly depend on the conditions, especially in the case of synthesis by solid-state reaction of powder sources. In the course of thermodynamic studies on $BaZnGeO_4$, it has been found that the successive phase transitions are much influenced by the conditions of synthesis from powdered reactants.

Since single crystals of $BaZnGeO_4$ were prepared by Takei et al. [1], the physico-chemical properties have attracted increasing attention over the last few years [2–8]. It has been known that the highest temperature phase I is of the space group $P6_322$. The crystal structures of lower temperature phases are of superstructures derived from phase I, and phase II is of the $P6_3$ group. There are two independent tetrahedral sites for $(Ge,Zn)O_4$, and the occupation by Ge and/or Zn is ordered in phase II, while it is disordered in phase I. The I–II phase transition was theoretically expected to be of first-order [7], which was experimentally observed at 1108 K by DTA and

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* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.

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thermal dilatometry [1,2,4]. The second-order phase transition occurs at 520 K [1,2,4,5], below which (phase III) the crystal structure is incommensurately modulated, and the unit cell dimension is approximately quadrupled [3,4]. The structures of lower temperature phases (IV,V) have not been established yet. Recently, Tanba et al. [7] found a new ferroelectric phase III′ between 232 and 243 K. More recently, Sakashita et al. [8] have reported X-ray diffraction studies and proposed that phase IV (198–232 K) is of incommensurate structure while phase III' is commensurate. However, no DTA experiment has been done below room temperature and little is known about thermodynamic properties of the crystal. Such a situation also prompted us to start thermodynamic studies on this material.

In the present investigation, the properties of $BaZnGeO_4$ synthesized at various temperatures have been studied by differential thermal analysis, powder X-ray diffractometry and scanning electron microscopy.

EXPERIMENTAL

Sample preparation

High purity starting materials $BaCO_3$ (99.99%), ZnO (99.999%) and GeO_2 (99.9999%) were purchased from Rare Metallic Co., Ltd. The starting materials were weighed in the stoichiometric ratio (1 : 1 : 1) and were mixed by the method of wet grinding in ethanol using an alumina mortar. After air-drying at room temperature, the mixture was pressed into tablets (16 mm in diameter and about 10 mm in thickness) at 200 MPa. The scanning electron micrograph of the mixture (see Fig. 2A) showed that the particle size of ZnO and GeO_2 was smaller than 1 μm in diameter while the size of $BaCO_3$ was larger (several μm).

The calcination behavior of the sample tablet was preliminarily studied by TG. On heating at a rate of about 0.15 K s^{-1} in the atmosphere, decomposition of $BaCO_3$ to BaO started at about 750 K and was completed at about 1250 K in 3 ks, which was recorded as a single step of mass loss. No mass loss was observed at the higher temperatures to 1400 K for 100 ks. The synthesis of $BaZnGeO_4$ was expected to be performed above 1250 K.

On the basis of the preliminary experiment, the calcination of the tablets was carried out at various temperatures above 1250 K; for 43 ks at 1260, 1360, 1420, 1470 and 1570 K (named Sample 1 to Sample 5, respectively). Another sample was made by melting the tablet in a platinum crucible at 1690 K (named Sample 6), which was considered to be completely synthesized. For Sample 6, the mass percentages of Ba and Zn were determined as 40.5% (calcd. 40.47%) and 19.0% (calcd. 19.27%) by a gravimetric method and EDTA titration, respectively. The average chemical formula was considered as $Ba_{1.001}Zn_{0.986}GeO_4$.

Scanning electron microscopy and X-ray diffraction

The fractured surfaces of Samples 1–5 were observed by a scanning electron microscope. The starting mixture before calcination was also observed for comparison.

For the X-ray diffraction, Samples 1–6 were ground in an alumina mortar. The powdered specimens were also used for DTA. The X-ray diffraction patterns were obtained with a diffractometer using Ni-filtered Cu$K\alpha$ radiation.

Differential thermal analysis

For the DTA experiments above room temperature to 1200 K, a TG–DTA apparatus (M-8075, Rigaku Corp.) was used. As a reference material, α-Al_2O_3 was used. The amount of sample used for this experiment was about 60 mg. The rate of heating (cooling) was about 0.17 K s^{-1}.

For the low temperature DTA, an apparatus which works between 90 and 470 K has been newly constructed. A sectional view of the cryostat is shown in Fig. 1. The vessels of sample and reference material C were made of glass (7 mm in outer diameter) with a re-entrant thin well for insertion of thermocouples F and G (type E, 0.13 mm in diameter with double silk insulation, Driver-Harris Co., Ltd.). The vessels were placed in the wells which were bored symmetrically in the copper block D (38 mm in diameter, 70 mm in length). Manganin heater wires E (0.3 mm in diameter, 30 Ω in total resistance) were wound closely on the surface of the copper block. The entire system was hung with two steel cords I (0.3 mm in diameter) from the top flange to which the Pyrex outer tube J (65 mm in diameter, 450 mm in length) was also fixed (vacuum-tight). Prior to experiments, the inside of the Pyrex outer tube was pumped and then filled with dry air at about 50 kPa. The assembly was placed in a Dewar vessel L which was filled with liquid nitrogen for cooling experiments. Before starting the heating experiments, the liquid nitrogen was removed. The electromotive force due to the temperature difference between the sample and the reference material (α-Al_2O_3) was amplified and recorded. About 300 mg of powdered specimen was put into the sample vessel, which was evacuated, filled with helium gas at about 40 kPa, and then sealed off. The DTA experiments were done at rates of -0.01 to -0.1 K s^{-1} for cooling and 0.01 to 0.06 K s^{-1} for heating.

RESULTS AND DISCUSSION

The scanning electron micrographs of the starting mixture and the fractured surfaces of Samples 1–5 are given in Fig. 2. It is clearly seen in the calcined specimens that the solid reaction and the sintering process proceed as the calcination temperature increases.

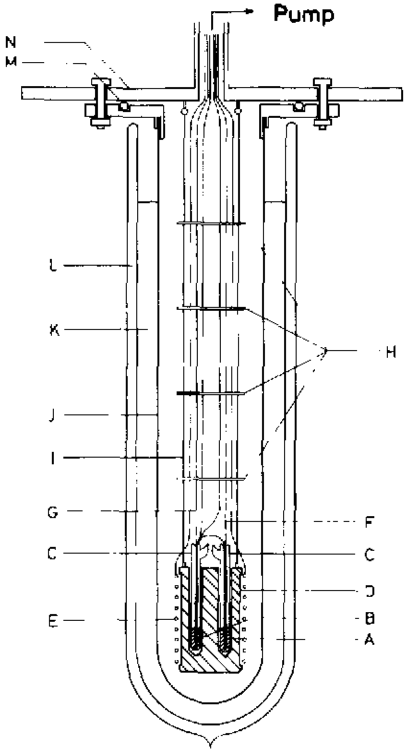

Fig. 1. Sectional view of the cryostat for the low temperature DTA. (A) Sample; (B) reference (α-Al_2O_3); (C) glass vessel; (D) copper block; (E) heater; (F, G) thermocouples; (H) radiation shields; (I) steel cords; (J) glass tube; (K) liquid nitrogen; (L) Dewar vessel; (M) O-ring; (N) flange.

The X-ray diffraction patterns of Samples 1–6 are shown in Fig. 3. Small amounts of the starting materials remain in Samples 1 and 2 in which by-products such as Ba_2GeO_4 are also detected. As the calcination temperature increases, the synthesis reaction proceeds, and no detectable starting materials or by-products exist in Samples 4–6. Adding known amounts of impurities of ZnO, the relative intensities of the peaks in the diffraction patterns due to the impurities in Samples 1–3 were calculated, and thus the fraction of synthesized $BaZnGeO_4$ was estimated as about 70% in Sample 1, 90% in Sample 2 and 100% in Sample 3. The melted specimen, Sample 6, is expected to be completely synthesized. Another interesting feature in Fig. 3 is that the peaks of (002) and (004) strongly depend on the calcination temperature.

The high temperature DTA curves are given in Fig. 4. The thermal anomaly due to the I–II phase transition is clearly observed at 1093 K, while no anomaly is seen corresponding to the II–III phase transition. These results agree with previous reports [1,2]. Although the I–II transition is of

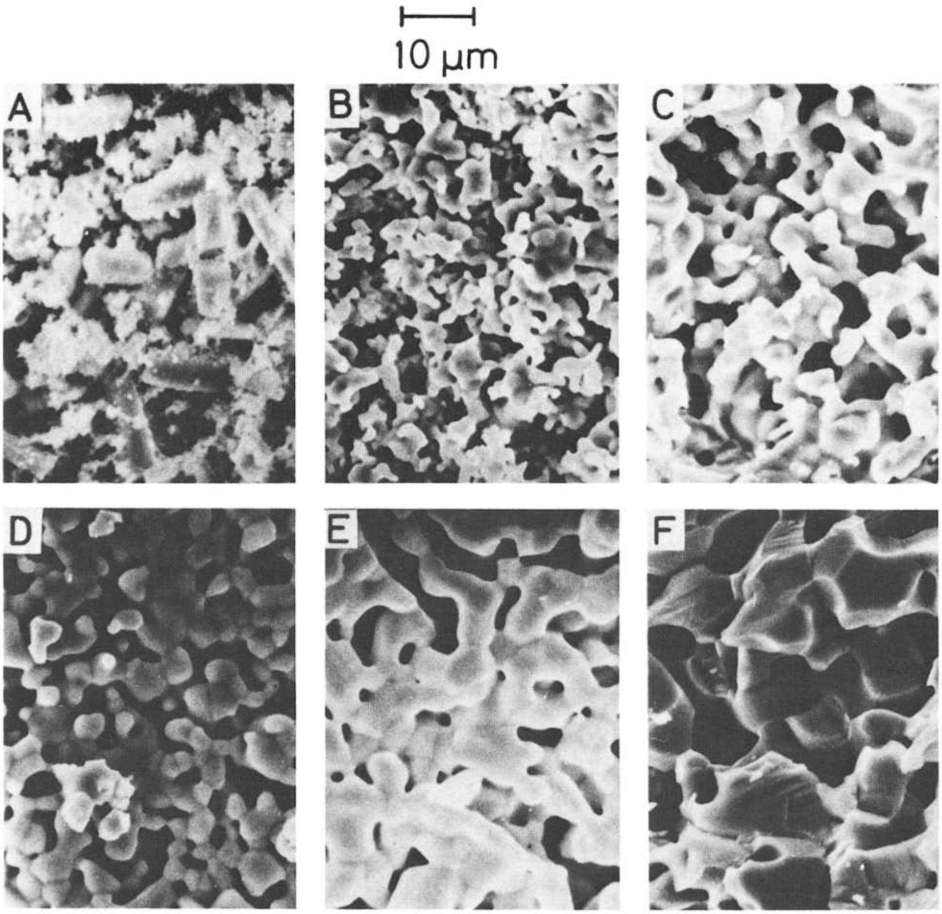

Fig. 2. Scanning electron micrographs of the starting mixture and the fractured surfaces of Samples 1–5. (A) Starting mixture; (B) Sample 1; (C) Sample 2; (D) Sample 3; (E) Sample 4; (F) Sample 5.

first order, no hysteresis phenomenon was detected. For Samples 1–3, the peak height of the anomaly increases as the calcination temperature increases, while little difference is observed among the other three, Samples 4–6. Thus, it seems that the peak height of the anomaly due to the I–II phase transition is proportional to the fraction of synthesized $BaZnGeO_4$ in the calcined specimen, which is also compatible with the results of X-ray diffraction described above.

On the other hand, the low temperature DTA gave very different results as shown in Fig. 5. It is surprising that no anomaly is seen in Samples 1 and 2. Only one anomaly, probably due to the IV–V phase transition, is observed in Samples 3–6 at about 200 K on heating, and the peak height increases as the calcination temperature increases. It is supposed that only

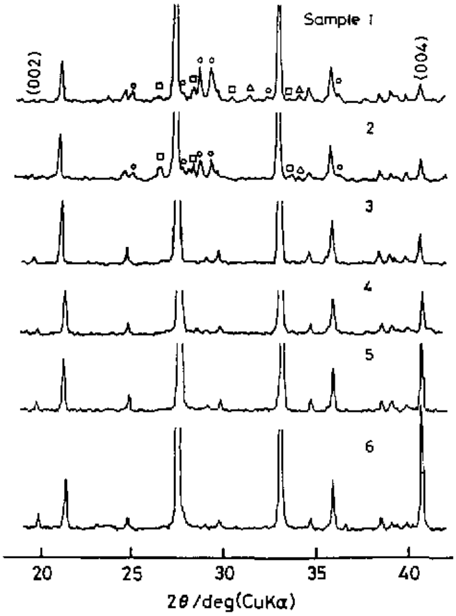

Fig. 3. Powder X-ray diffraction patterns of Samples 1–6. (○) Ba_2GeO_4; (△) ZnO; (□) unknown.

Sample 6 has the intrinsic behavior of the $BaZnGeO_4$ crystal. In this case, abnormal hysteresis phenomena are observed as seen in Fig. 5.

The behavior described above is expected to reflect the mechanism of the phase transition. The I–II phase transition is not influenced by the existence of any impurities and thus the peak height of the anomaly due to the transition is proportional to the fraction of $BaZnGeO_4$. As the I–II phase

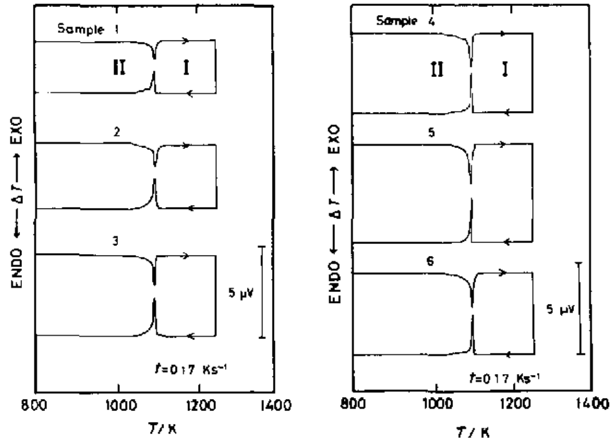

Fig. 4. High temperature DTA curves.

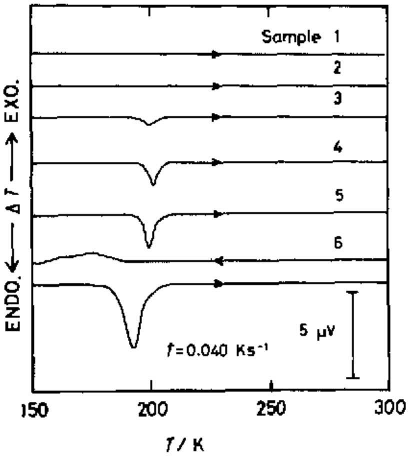

Fig. 5. Low temperature DTA curves.

transition is of order–disorder type, the strong interactions between the two tetrahedral sites must be weakly affected by any impurities. On the other hand, the IV–V phase transition is strongly influenced by the impurities. Even if $BaZnGeO_4$ is chemically synthesized, as in Samples 4 and 5, the transition is affected by possible existence of physical impurities such as defects, dislocations and lattice strain, etc. This is probably ascribed to a transition mechanism of displacive type. The behavior depends on the delicate balance of interactions between the different ions.

More detailed thermodynamic studies of the crystals of $BaZnGeO_4$ are in progress.

SUMMARY

The properties of $BaZnGeO_4$ synthesized from powdered reactants at various temperatures are well characterized by the successive phase transitions in DTA. Abnomal behavior has been observed at the IV–V phase transition, while the peak height of the anomaly due to the I–II phase transition is proportional to the fraction of synthesized $BaZnGeO_4$ in the calcined specimen. Such behavior reflects the mechanism of the phase transitions.

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