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Growth and properties of $BaZnGeO_4$ crystals

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Single crystals of $BaZnGeO_4$ have been grown by the Czochralski pulling method from a stoichiometric melt of barium, zinc and germanium oxides. The crystals were colourless, up to 24 mm in diameter and 35 mm length, and their composition corresponded to the formula $Ba_{0.978}Zn_{0.986}Ge_{1.018}O_4$. X-ray diffraction analysis revealed that the crystal structure was a modified $BaAl_2O_4$ type with the hexagonal cell parameters of $a_0 = 92.97$ nm and $c_0 = 352.84$ nm. Phase transitions were observed at 520 K and 1108 K from measurements of DTA, thermal dilatometry and dielectric constants, and by high temperature X-ray precession photography.

1. Introduction

There have been many reports on complex orthosilicates and orthogermanates for the purpose of obtaining useful fluorescent material. They often have polymorphic phase transitions above or below room temperature. In a recent study of the phase relation of BaO–ZnO–GeO_2 ternary system, it was found that the compound $BaZnGeO_4$ melted congruently at about 1400° C in air and large grains of the crystal were easily obtained [1].

$BaZnGeO_4$ was first synthesized by Wallmark and Westgren [2]. This compound is one of the orthogermanates with a stuffed structure [3] derived from the high-tridymite framework, and is reported to be isostructural with $BaAl_2O_4$ [4]. However, the more detailed crystallographic or physical properties of this material have remained unclarified. In the present study, large, transparent and nearly stoichiometric single crystals of $BaZnGeO_4$ were grown, and new data on the crystal structure and polymorphic phase transition between room temperature and 1000° C was obtained.

2. Experimental procedure

2.1. Materials

The starting materials were $BaCO_3$, ZnO (both reagent grade, 99.9% purity) and GeO_2 (electronic grade, 99.99999% purity). They were weighed in stoichiometric proportions and mixed in a polyethylene ball-miller for several hours. The mixture was fired in a platinum crucible in an electric muffle furnace at 1380° C for 3 hours in air.

2.2. Crystal growth

Growth of the $BaZnGeO_4$ crystal was carried out by use of a Czochralski pulling apparatus manufactured by the Kokusai Electric Co (DP-150FOX), which consisted of a r.f. furnace with a pulling mechanism, a 30 kW generator and an electronic controller. The growth furnace was assembled as follows: a platinum crucible of 50 ml capacity was placed in an alumina crucible, zirconia was allowed to flow into the gap between the two crucibles providing thermal insulation, and the whole arrangement was covered by an alumina tube. Seed crystals having the desired orientations were prepared by cutting a large crystalline grain obtained by the modified Bridgman method. The most appropriate conditions for the crystallization are a pulling direction along the $[11\bar{2}0]$ or $[0001]$ axes, with a pulling rate between 2 and $3\,\mathrm{mm\,h^{-1}}$ and a rotation rate of $20\,\mathrm{rev\,min^{-1}}$.

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The maximum power for heating was about 3.5 kW and the melt temperature, measured by an optical pyrometer, was about 1400° C. White smoke due to slight ZnO evaporation was observed. The total loss of ZnO during growth was estimated to be less than 1 gram.

2.3. Analysis of the crystal

The composition of the crystal was determined by wet chemistry techniques. Ba and Zn were analysed by EDTA titration and Ge was analysed by iodometric oxidation–reduction titration. X-ray powder diffraction patterns were obtained with Ni filtered Cu radiation using an internal standard of Si powder. Unit cell parameters were calculated using the U-CELL (II) least square fit program [5]. Single crystal X-ray diffraction pattern analyses were made at room temperature, at 600° C and at 930° C by the Buerger precession method using Zr-filtered Mo radiation. DTA was performed between room temperature and 1500° C in air using heating or cooling at rates of $10^\circ\,\mathrm{C\,min^{-1}}$.

The temperature dependence of the dielectric constant was measured by means of a wide band capacitance bridge (a "TR-1C" instrument manufactured by the Ando Electric Co.) between room temperature and 600° C. Elastic compliance measurements were made by piezoelectric resonance method. Dilatometric measurements were also carried out using a differential transformer under a load of about $30\,\mathrm{g\,cm^{-2}}$ with a heating rate of about $5^\circ\,\mathrm{C\,min^{-1}}$.

3. Results and discussion

Single crystals of $BaZnGeO_4$ were succesfully grown from the melt of stoichiometric composition. Fig. 1 shows a single crystal of about 60 g pulled along the [0001] direction. As the as-grown crystal was etched by thermal radiation from the melt or the crucible, the surface of the boule was less transparent than the bulk. Cleaved sections are colourless and transparent, as shown in Fig. 2. The polished (0001) sections examined under a microscope in polarized light were found to be free from misorientation, twinning or stress induced birefringence. In some crystals optically visible inclusions were observed under a dark field condition. The most common imperfections were macro-cracks, which originated from the surface of the boule. Good cleavage was found on the (0001) plane. The hardness of this plane was about 6 on Mohs' scale. The crystal was uniaxially negative and dextrorotatory. The refractive index along the [0001] axis was 1.79 ± 0.03 and the birefringence was 0.010 when a W-lamp was used.

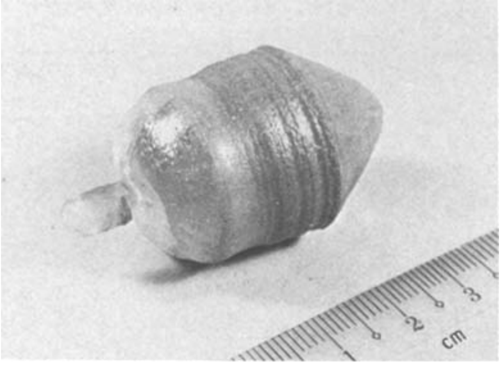

Figure 1 Typical as-grown crystal of $BaZnGeO_4$.

Chemical analyses were performed on four specimens free from the as-grown surfaces and inclusions. Table I shows the results and indicates an average chemical formula of $Ba_{0.978}Zn_{0.986}Ge_{1.018}O_4$.

The X-ray precession diffraction analyses (Figs. 3a and b) and the powder diffraction analyses revealed that the crystal structure belonged to the hexagonal system with the space group

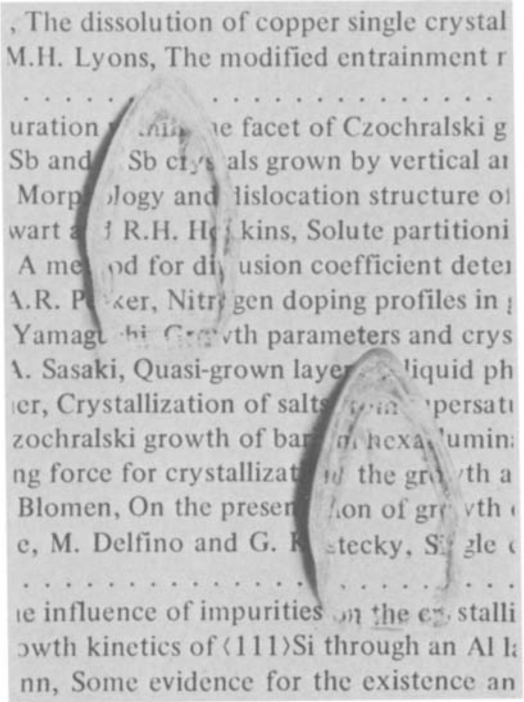

Figure 2 Cross-section of the $BaZnGeO_4$ crystal of thickness about 3 mm.

TABLE I Comparison of analytical and theoretical data of $BaZnGeO_4$ crystals

	BaO (wt %)	ZnO (wt %)	GeO_4 (wt %)
Analytical	44.88	23.90	31.84
Theoretical	45.19	23.98	30.83

Analytical formula: $Ba_{0.978}Zn_{0.986}Ge_{1.018}O_4$

$P6_3$, and that the unit cell dimensions were $a_0 = 9.297 \pm 0.001$ Å and $c_0 = 35.284 \pm 0.002$ Å. These values are related to the parameters, a' and c', of $BaZnGeO_4$ previously reported by Do Dinh and Durif [4] by the relation $a_0 \sim \sqrt{3}a'$ and $c_0 \sim 4c'$ (see Fig. 4). Similar superstructure reflections were often reported on stuffed derivatives of the β-tridymite structure [6–8]. β-eucryptite ($LiAlSiO_4$) crystals, for example, grown by Winkler [7] showed weak superstructure reflections which required a doubling of the c-axis. Tscherry *et al.* [8] reported that the eucryptite crystal showed additional superstructure reflections which lead to a doubling of all three hexagonal axes of the β-tridymite-like subcell. Such doublings were explained by the ordering of Si and Al atoms for the c-axis [7], and by the ordering of Li and O atoms for the a-axis [7, 9]. In the $BaZnGeO_4$ crystal, it is likely that the superstructures are caused by orderings of Ba, Zn and Ge atoms as well. More precise determination of atom positions is needed to elucidate this problem. Revised powder diffraction data will appear in a separate paper [10]. The X-ray density for $z = 24$ was $5.140\,g\,cm^{-3}$. This is very close to the Archimedean density which is $5.144\,g\,cm^{-3}$ at 20° C, where the analytical formula was used for calculation of the molecular weight. Fig. 5 shows a result of thermal dilatometry between room temperature and 1000° C. On a specimen cut into a cube about 5 mm x 5 mm x 5 mm in size along the directions of $[10\bar{1}0]$, $[11\bar{2}0]$ and $[0001]$, apparent anomalies were observed near temperatures of 247 ± 5° C and 835 ± 5° C. These anomalies were reversible and quite reproducible in several runs and no crack formation occurred during or after dilatometry.

In order to analyse the crystal structure which is stable between 247° C and 835° C, and which is stable above 835° C, high temperature X-ray precession photography was carried out at 500° C and at 930° C. The results are shown in Fig. 6. Fig. 7 is an illustration of the reciprocal planes, where (0001) and $(10\bar{1}0)$ are drawn. At 500° C, the superstructure reflections of the c^*-axis ($4c'$ structure) disappeared, but those of the a^*-axis remained. More simple diffraction patterns were obtained at 930° C, where the $\sqrt{3}a'$ structure disappeared and the simple $BaAl_2O_4$ type structure appeared.

DTA results, as shown in Fig. 8, were obtained from a powdered sample of the crystal free from the as-grown surface or inclusions. No thermal anomaly, such as thermal peak or baseline shift, was detected around 250° C. However, a small sharp peak was reversibly observed at a tempera-

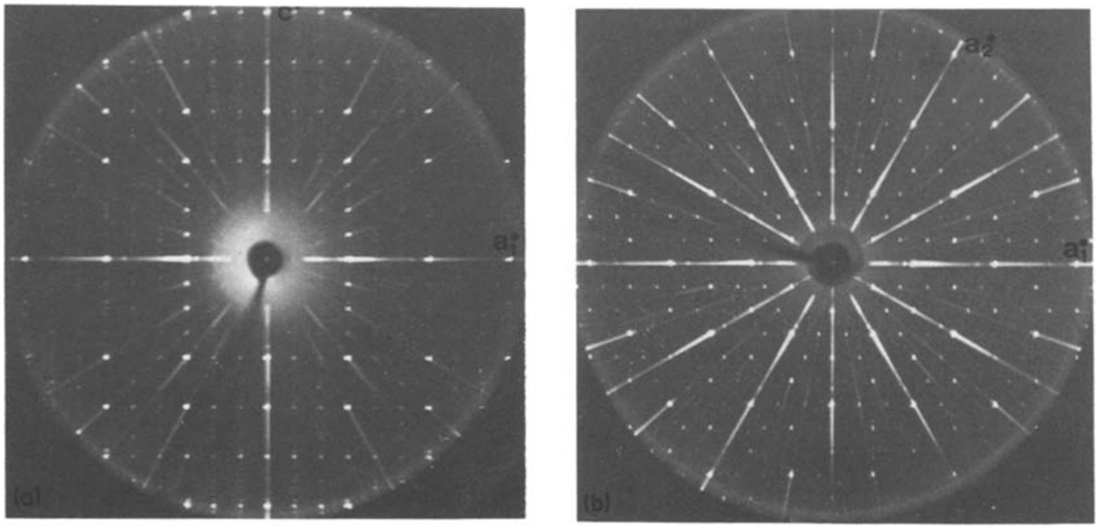

Figure 3 X-ray precession photographs of the $BaZnGeO_4$ crystal. (a) $(10\bar{1}0)$ plane. (b) (0001) plane. $MoK\alpha$ radiation filtered by a Zr foil was used.

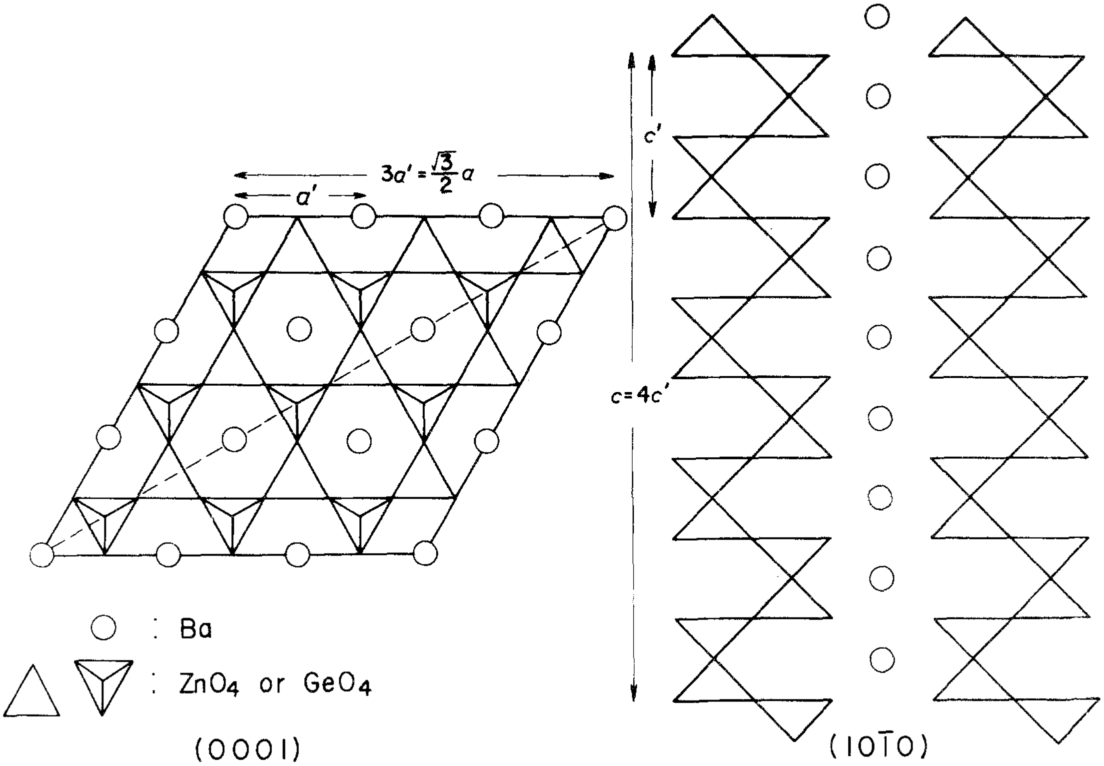

Figure 4 Idealized structure of $BaZnGeO_4$. The triangles represent ZnO_4 or GeO_4 tetrahedra, and the circles represent Ba ions.

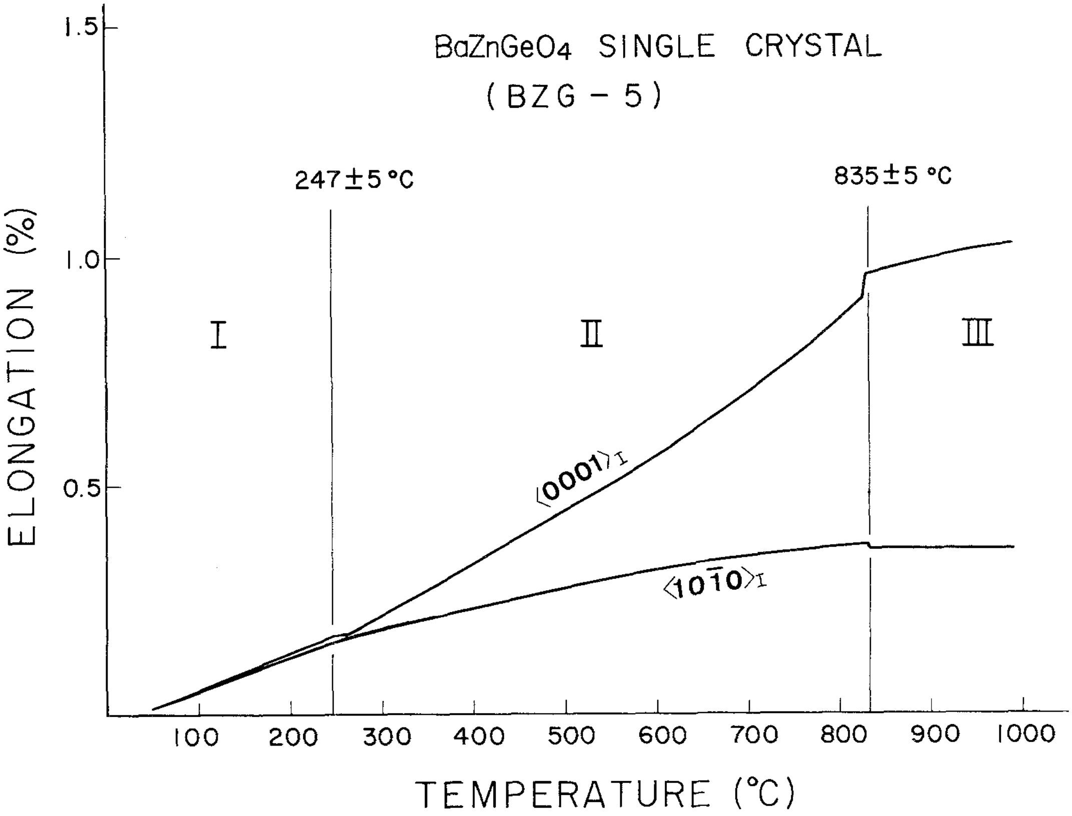

Figure 5 Thermal expansion of the $BaZnGeO_4$ crystal.

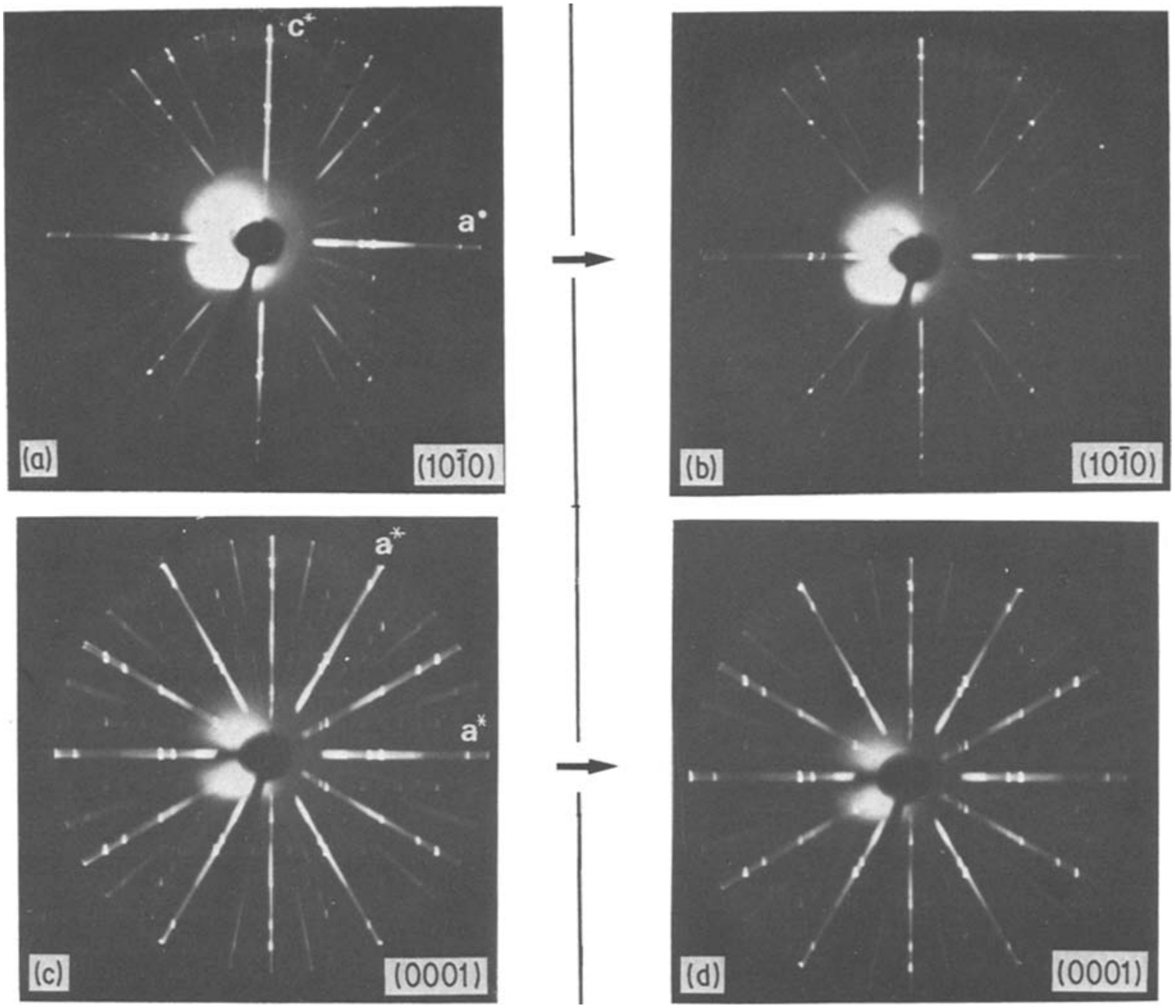

Figure 6 High temperature X-ray precession photographs. (a) and (c) at a temperature of 550° C and (b) and (d) at a temperature of 930° C.

ture of 835 ± 5° C. This indicates that a first order phase transformation occurs at this temperature. The congruent melting point temperature of $BaZnGeO_4$ was 1394 ± 5° C.

Apparent piezoelectricity was observed at room temperature. The elastic compliance of shear component S^{e}_{44} was obtained from the piezoelectric constant d_{14} measured on a square thin (10$\bar{1}$0) plate. Fig. 8 is a plot of S^{e}_{44} as a function of temperature, where a sharp bend of the curve appears at 247° C. The dielectric properties were measured between room temperature and 500° C. As also shown in Fig. 8, the curve of the dielectric constant along the c-axis, $\epsilon_{\parallel c}$, against temperature has a sharp maximum at 247° C. These results and the fact that no exothermic or endothermic effect was detected around 250° C imply that the phase change at 247° C is a second order one. No hysteresis relation between electric field and polarizability could be found along the [10$\bar{1}$0] and [0001] axes under an applied field of 6 kV cm^{-1} at room temperature. Thus it remains uncertain whether the anomalies in the dielectric constant and the elastic compliance at 247° C are due to ferroelectricity or not.

4. Conclusions

Large and transparent single crystals of $BaZnGeO_4$ with nearly stoichiometric composition have been grown and their physical properties have been measured. The data indicate that $BaZnGeO_4$ is piezoelectric and possesses three polymorphic phases above room temperature. The first phase

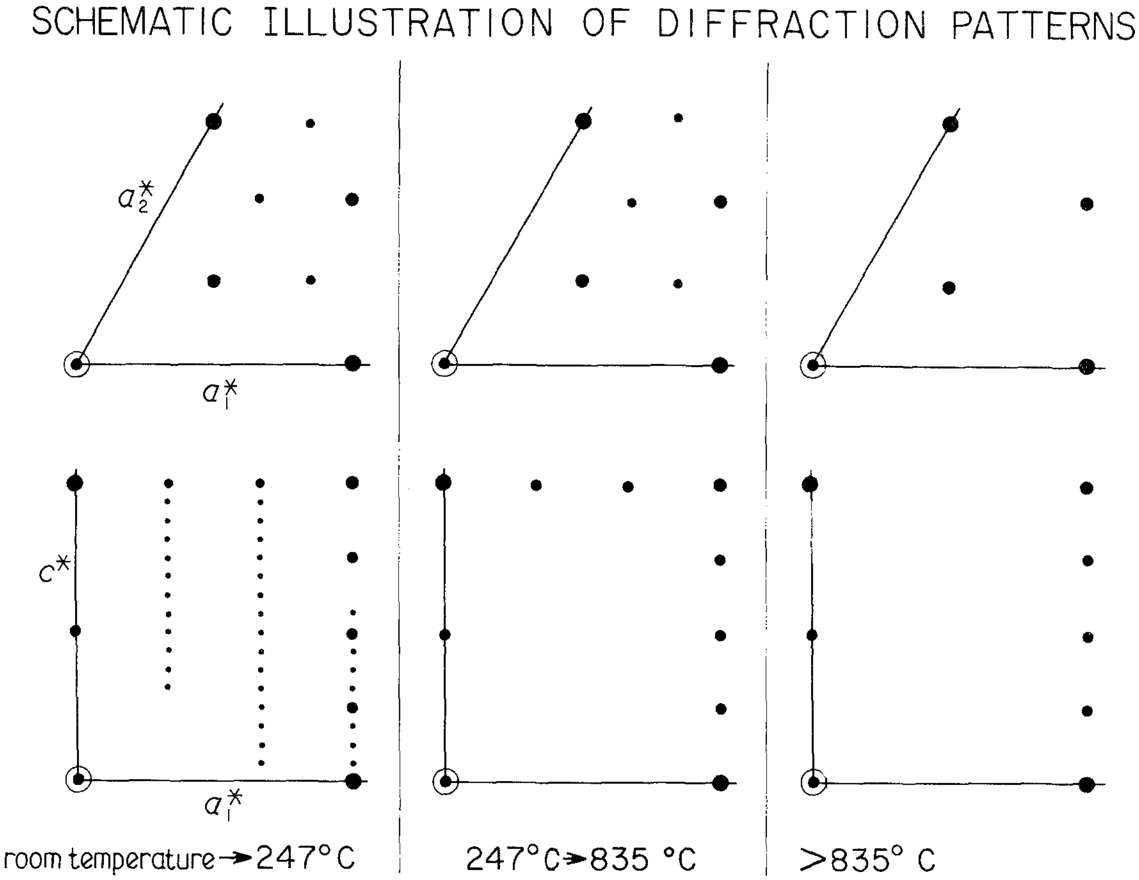

Figure 7 Schematic illustration of the diffraction patterns of $BaZnGeO_4$ produced by the precession method.

(I-phase or room temperature phase) is hexagonal with a superstructure of $BaAl_2O_4$ to the *a*- and *c*-axes. This phase is stable below 247° C. The I-phase reversibly changes in a second order transition into the second phase (II-phase) at 247° C. The II-phase, which also is of hexagonal symmetry with a superstructure to the *a*-axis, existst between 247° C and 835° C. After a reversible first order transition the third and final hexagonal phase (III-phase) appears above 835° C. This phase is the same in crystal structure as $BaAl_2O_4$. Table II is a summary of the properties.

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TABLE II Properties of $BaZnGeO_4$ crystals

Analytical formula	$Ba_{0.978}Zn_{0.986}Ge_{1.018}O_4$
Melting point	1394 ± 5° C (congruent)
Crystal structure	hexagonal ($P6_3$)
a_0	9.297 ± 0.001 Å
c_0	35.284 ± 0.002 Å
V_x	2640.92 Å^3
z	24
Density	5.140 g cm^{-3} (X-ray), 5.144 g cm^{-3} (Archimedean)
Optical property	uniaxially negative and dextrorotatory
Refractive index	1.79 ± 0.03 (using a W-lamp, along *c*-axis)
Birefringence	0.010
Piezoelectric	yes
Elastic compliance of shear component, S_{44}^e	~ 3 × 10^{-11} m^2 N^{-1} at 20° C
Firstphase transition	247° C (2nd order)
Secondphase transition	835° C (1st order)
Hardness on Mohs scale	~ 6 for (0001)
Cleavage	mainly (0001).

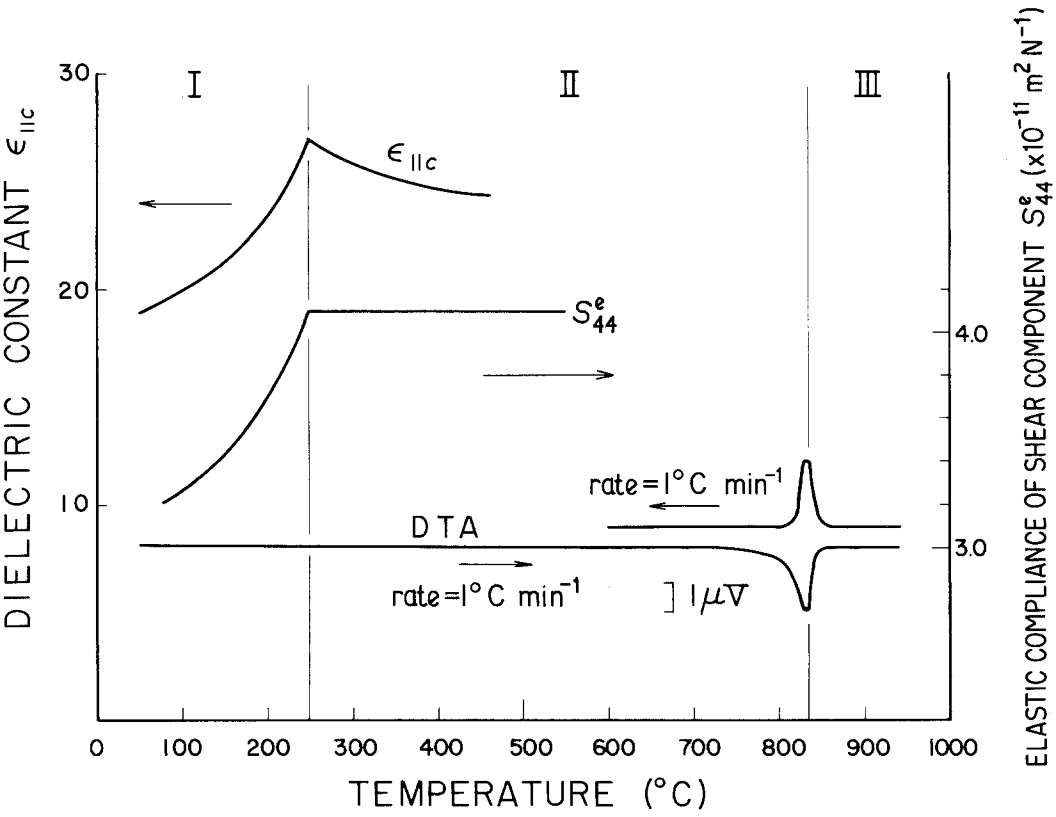

Figure 8 Result of DTA, dielectric and elastic measurements.

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