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POLYMORPHIC MODIFICATIONS OF BARIUM METAGERMANATE

J. P. Guha, D. Kolar and A. Porenta

Institute Jožef Stefan, University of Ljubljana, Jamova 39, 61000 Ljubljana, Yugoslavia

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Polymorphic transformations of $BaGeO_3$ were investigated by DTA and X-ray diffraction methods and the data obtained were compared with those previously published. $BaGeO_3$ undergoes a reversible phase transformation at 1100° from a low-temperature hexagonal polymorph to a medium-temperature polymorph having an unknown crystal structure, which undergoes a further reversible transformation at 1200° to a high-temperature orthorhombic polymorph found to be stable up to the melting temperature of 1287°. On cooling from the melt, the high-temperature form can be retained metastably at room temperature, but transforms to the low-temperature form at 900°.

In the course of an investigation of phase equilibrium relations in the $BaO-GeO_2$ system, the stability of various polymorphic forms of barium metagermanate, $BaGeO_3$, was examined. It was found that the results obtained in this investigation did not agree in many respects with those reported in the literature. The work presented in this paper was mainly concerned with the polymorphic transformations of $BaGeO_3$.

$BaGeO_3$ is known to exist in at least two polymorphic forms, a low-temperature α-form having a hexagonal pseudowollastonite-type structure, and a high-temperature β-form having an orthorhombic pyroxene-type structure. Roth [1] has reported that the pseudowollastonite-type of $BaGeO_3$ changes to an entirely different type of structure when heated with 1% Fe_2O_3. Liebau [2], who reported the lattice parameters for both the low- and the high-temperature forms, obtained the high-temperature β-form by melting a $BaGeO_3$ sample with addition of 2% Fe_2O_3. Grebenshchikov et al. [3] have reported that in the absence of mineralizers, $BaGeO_3$ crystallizes only in the low-temperature α-form. They obtained the high-temperature β-form by addition of $BaSiO_3$. Polymorphic transformations of $BaGeO_3$ with additions of Fe_2O_3 and $BaSiO_3$ as mineralizers have been studied by Grebenshchikov et al. [4]. According to these authors, the low-temperature α-form of $BaGeO_3$ remains unchanged at all temperatures without the addition of mineralizers. The β-form was obtained by the addition of 2% Fe_2O_3. The DTA curve of this sample showed an exothermic peak at 870°, representing the conversion of the metastable β-form to the α-form, and two endothermic peaks at 1060° and 1160°, corresponding to the phase transformation from the low-temperature

α- to the high-temperature β-form, and from the high-temperature β-form to an undefined phase designated as the δ-form, respectively. In contrast to these data, Guha et al. [5] observed during an investigation of phase transitions and compatibility relations in the system $BaSiO_3-BaGeO_3$ that the high-temperature β-form of $BaGeO_3$ could be obtained without the addition of mineralizers. The low-temperature α-form was found to transform to the high-temperature β-form at about 1180°.

In this study further evidence was obtained which supports the earlier suggested phase transformations of pure $BaGeO_3$ and provides additional data not presented before.

Experimental

The starting materials used in this study were analytical reagent grade $BaCO_3$ obtained from Riedel-de-Haën, Hannover, G.F.R. and GeO_2 (99.999% pure) obtained from Fluka, Buchs, Switzerland. Three representative batches of $BaGeO_3$ each containing 5 g of the powdered samples were wet-mixed in alcohol, dried in an oven and pressed into cylindrical pellets, which were wrapped in Pt-envelopes and fired at 1050° for a prolonged period with intermittent cooling, crushing and pressing to decompose the carbonate and to ensure the homogeneity of the final product. At the end of the firing, the samples were cooled in air and examined by X-ray diffraction, using a Guinier-type focusing camera and nickel-filtered CuKα radiation. A Linseis DTA unit (Model No. L1040) equipped with a furnace capable of operation up to a maximum temperature of 1500° was used to detect any non-quenchable phase transition and to study the melting behaviour of $BaGeO_3$. The sample size was about 100 mg and the reference standard was α-Al_2O_3. Platinum holders containing the sample and the standard were placed vertically on the tips of Pt-Pt 10% Rh thermocouples and the whole assembly was enclosed in a recrystallized alumina tube. Heating and cooling rates of 10°/min were used and four heating and cooling cycles were repeated in each run from room temperature to 1300°. The DTA apparatus was calibrated against the transition temperatures of K_2CrO_4 and $SrCO_3$ and also periodically checked at the melting points of GeO_2 (1115°) and Diopside, $CaMgSi_2O_6$ (1391.5°). The overall inaccuracy of the DTA data presented here was estimated to be not greater than $\pm 5°$.

Results

X-ray diffraction studies

Preliminary X-ray diffraction patterns of a pure $BaGeO_3$ specimen fired at various temperatures between 800° and 1275° indicated that the compound exists in two polymorphic forms, one corresponding to the low-temperature α-form stable from room temperature to 1200°, and the other corresponding to the high-temperature β-form stable from above 1200° to the melting temperature of $BaGeO_3$. It was observed that the high-temperature β-form can be retained metastably at room temperature on cooling rapidly from temperatures above 1200°; it transforms to the low-temperature α-form when heated below this temperature.

DTA studies

The DTA curve of a $BaGeO_3$ specimen prepared by the solid-state reaction of appropriate proportions of $BaCO_3$ and GeO_2 at 1050° on the first heating cycle revealed the presence of three clearly-defined endothermic peaks, as shown in Fig. 1a. The peaks were sharp in most cases, so that the onset temperatures could be measured accurately. The first two peaks, at 1098° and 1200°, were attributed to phase transformation, while the third peak, at 1288°, was found to be due to melting. However, on cooling the corresponding peaks due to phase transformation did not appear in the DTA curve. The persistence of the high-temperature β-form far into the stability region of the low-temperature α-form accounted for this anomaly. If the specimen was allowed to cool slowly to room temperature and then reheated through the whole transition region, an exothermic peak appeared in the vicinity of 900°, presumably corresponding to the transformation of the metastable β-form to the α-form, and then the two endothermic peaks identical to those of the first heating reappeared, as shown in Fig. 1b. The only difference

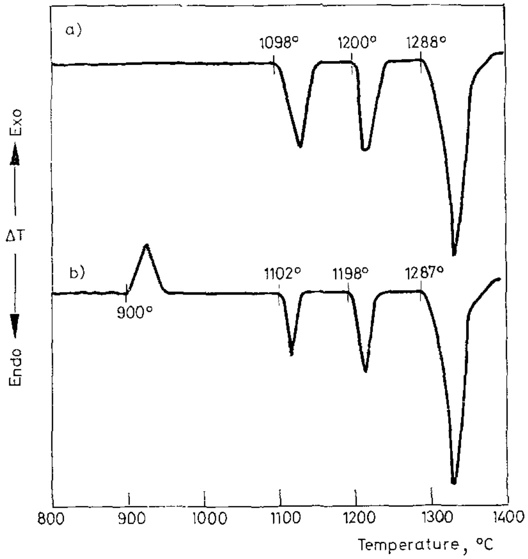

Fig. 1. DTA heating curves of $BaGeO_3$; (a) original sample; (b) sample melted and cooled to room temperature

observed was that the peaks on the second heating had lower areas than previously and were also less defined. The occurrence of the endothermic peaks in the DTA curve in subsequent heating cycles was also observed if the specimen was annealed at temperatures below 1000° for an hour. This point was further verified by interrupting the DTA runs at the appearance of each peak and then repeating the corresponding cooling cycle. This procedure yielded sharp and well-defined peaks in both the heating and cooling curves, with only small variations in the onset peak temperatures, thereby indicating the reversibility in all transitions.

Discussion

X-ray diffraction analysis of quenched specimens consistently showed that the α-form exists up to 1200°, where it undergoes transformation to the β-form, but no trace of the phase transformation occurring at 1100° could be detected. Efforts to obtain this intermediate polymorph of $BaGeO_3$ by quenching the specimen from various temperatures between 1000° and 1200° failed to produce any variation in the X-ray diffraction patterns. It is possible that this phase is unquenchable and therefore cannot be detected by the conventional room-temperature X-ray method.

The DTA results obtained in this study were found to be in reasonably good agreement with those reported by Grebenshchikov et al. [4]. The reason for the apparent lack of agreement in the initiation temperatures of the peaks, however, is not clear, but it is possible that the lowering of the transition temperatures in the DTA curve shown by Grebenshchikov et al. was mainly due to the presence of Fe_2O_3 in the starting material used by them. This is further corroborated by the fact that Grebenshchikov et al. [4] obtained entirely different data on the polymorphic behaviour of $BaGeO_3$ with additions of $BaSiO_3$ as a mineralizer. One major difference between the present results and those of Grebenshchikov et al. is, however, the temperature stability of the various forms of $BaGeO_3$. They reported that the low-temperature α-form transforms directly to the high-temperature β-form, which again undergoes a further transformation to an undefined δ-form. The transition temperatures were given for $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \delta$ as 1060° and 1160°, respectively. However, they also reported that $BaGeO_3$ crystallizes in the β-form on cooling from the melt. In contrast to these data, we have observed, after repeated DTA runs on different batches of $BaGeO_3$ and performing rigorous X-ray diffraction analysis of the quenched specimens as well as comparing our X-ray data with those reported, that the high-temperature β-form of $BaGeO_3$ exists only above 1200° and remains stable up to the melting temperature. Below this temperature only the α-form was detected in the X-ray patterns. We conclude from this investigation that the α-form does not transform directly to the β-form, but that the transformation proceeds via an intermediate phase change, which although evident in the DTA curve cannot be distinguished by the room-temperature X-ray method. It is assumed that the phase change in this region is nonquenchable and therefore high-temperature X-ray data are needed to confirm the existence of the proposed phase transformation and to ascertain the crystal structure of this polymorph.

The melting point of pure $BaGeO_3$ as observed in a heating microscope was found to be in excellent agreement with the DTA result and is given as $1287 \pm 5°$. The sharp reversal of the DTA peak on melting indicated that the compound melts congruently. The result was further supported by X-ray analysis of the melted specimen, which showed a pattern identical to that of the unmelted compound.

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RÉSUMÉ — On a étudié les transformations polymorphiques de $BaGeO_3$ par ATD et diffraction des rayons X et comparé les résultats avec ceux obtenus antérieurement. A 1100° C $BaGeO_3$ subit une transformation de phase réversible de la forme hexagonale stable à basse température à la forme stable à moyenne température, de structure cristalline inconnue, qui se transforme réversiblement à 1200° C en une phase orthorhombique qui reste stable jusqu'à 1287° C. Au refroidissement, la forme stable à haute température peut être maintenue à l'état métastable à la température ambiante, mais elle se transforme à 900° C en la forme stable à basse température.

ZUSAMMENFASSUNG — Polymorphe Umwandlungen von $BaGeO_3$ wurden unter Anwendung der DTA- und Röntgendiffraktionsmethoden untersucht und die erhaltenen Angaben mit den früher veröffentlichten verglichen. Bei 1100° vollzieht sich eine reversible Phasentransformation der $BaGeO_3$ von der hexagonalen Struktur bei niedrigen Temperaturen in eine Verbindung unbekannter Kristallstruktur bei mittleren Temperaturen, welche wiederum bei 1200° eine weitere reversible Umwandlung in eine orthorhombische Struktur erfuhr und sich bis zur Schmelztemperatur von 1287° als stabil erwies. Beim Abkühlen der Schmelze kann die Form bei hohen Temperaturen bei Zimmertemperatur in metastabilem Zustand erhalten bleiben, wird jedoch bei 900° in die Form bei niedrigen Temperaturen umgewandelt.

Резюме — Были исследованы методами ДТА и дифракцией рентгеновых лучей полиморфные превращения $BaGeO_3$ и полученные данные сопоставлены с ранее опубликованными. $BaGeO_3$ подвергается обратимому фазовому превращению при 1100° из низко-температурной гексагональной полиморфной формы до средне-температурного полиморфа с неизвестной кристаллической структурой и который подвергается дальнейшему обратимому превращению при 1200° до высоко температурной орторомбической формы, которая стабильна до температуры плавления 1287°. При охлаждении расплава высоко-температурная форма может остаться метастабильной при комнатной температуре, но превращается в низко-температурную форму при 900°.