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Phase equilibria in the system $BaO-GeO_2$

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Phase equilibria in the system $BaO-GeO_2$ were studied using several complementary methods and a number of modifications made to the previously published phase diagram. The system contains four compounds, Ba_3GeO_5, Ba_2GeO_4, $BaGeO_3$ and $BaGe_4O_9$. Evidence is presented to show that the previously reported compounds $Ba_3Ge_2O_7$ and $BaGe_{19}O_{39}$ do not exist. Four invariant points were established in the system and defined as simple eutectic. A revised phase diagram showing the solid–liquid equilibria existing between the various phases is presented.

1. Introduction

Phase equilibrium relations in the system $BaO-GeO_2$ have been investigated by Grebenshchikov *et al.* [1] who reported the existence of six compounds, namely, Ba_3GeO_5, Ba_2GeO_4, $Ba_3Ge_2O_7$, $BaGeO_3$, $BaGe_4O_9$ and $BaGe_{19}O_{39}$ and the solid–liquid equilibria in the system. The existence of a number of barium germanates has been established earlier by several workers, the data reported being primarily based on the crystal structure of the compounds. Barium metagermanate, $BaGeO_3$, was first prepared by Müller and Gulezien [2] by precipitation from solution. The compound is known to exist in two polymorphic forms: a low-temperature polymorph with a hexagonal structure reported by Liebau [3] and a high-temperature polymorph with an orthorhombic structure reported by Hilmer [4]. Barium orthogermanate, Ba_2GeO_4, was synthesized by Ludekens [5] by the solid-state reaction of $BaCO_3$ and GeO_2 and he also reported the unindexed X-ray data for the compound. Strunz and Jacob [6] determined the crystal structure of Ba_2GeO_4 and proposed an orthorhombic structure. The crystal structure of Ba_3GeO_5 was reported by Eysel [7] who assigned a tetragonal structure for the compound. The crystal structure of barium tetragermanate, $BaGe_4O_9$, was determined from powder data by Robbins and Levin [8] who proposed a hexagonal structure for the compound. The crystallographic data for the compounds $Ba_3Ge_2O_7$ and $BaGe_{19}O_{39}$ reported by Grebenshchikov *et al.* [1] are not available in the literature except for the unindexed *d*-spacings. In a separate publication, Grebenshchikov *et al.* [9] also presented the unindexed X-ray data for the compounds Ba_3GeO_5, Ba_2GeO_4, $BaGeO_3$ and $BaGe_4O_9$.

The phase diagram of the system $BaO-GeO_2$ proposed by Grebenshchikov *et al.* [1] shows several discrepancies. In the diagram, all the intermediate compounds are shown to be stable under normal conditions except $Ba_3Ge_2O_7$, the existence and stability of which seem to be highly improbable. It can be seen from the diagram that $Ba_3Ge_2O_7$ has a temperature stability minimum at 1530° C which apparently forms when a mixture containing primary Ba_2GeO_4 and liquid is heated above this temperature. Furthermore, the solid–liquid equilibria shown to exist between $Ba_3Ge_2O_7$ and Ba_2GeO_4, and also between $Ba_2Ge_3O_7$ and $BaGeO_3$ do not obey the phase rule and, therefore, appear to be highly unlikely. Thus, it is apparent that phase equilibria in the system $BaO-GeO_2$ should be re-examined to resolve the existing discrepancies. In the present investigation, several complementary methods were used and the results obtained were correlated with those previously reported and a revised phase diagram is presented.

2. Experimental details

The starting materials used were $BaCO_3$ (Analar Grade, British Drug House Ltd, UK) and GeO_2

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(99.99% purity, Fluka AG, Buchs, Switzerland). Appropriate mixtures containing variable proportions of the powdered materials were weighed to the nearest milligramme, mixed thoroughly under acetone, dried in an oven and pressed into cylindrical pellets which were wrapped in Pt-envelopes and calcined at 1000° C for 10 h in air to decompose the carbonate. The samples were then fired at 1050° C for longer periods with intermittent cooling, crushing and pressing to promote homogeneity and to attain equilibrium. At the end of firing, the samples were rapidly cooled in air to room temperature and the phases present were analysed by X-ray powder diffraction using a Guinier de-Wolff focusing camera (Enraf-Nonius, Delft, Netherlands) and CuKα radiation. Equilibrium was considered to have been attained when X-ray patterns of successively fired samples showed no further change. The equilibrated samples thus obtained were used for subsequent quenching studies and DTA experiments.

For quenching studies, small quantities of selected samples were placed in Pt-cups and fired in a Pt-wire wound vertical tube furnace at successively higher temperatures until the samples were melted. Temperatures were measured by a calibrated Pt–Pt/10%Rh thermocouple placed adjacent to the sample and assumed to be correct within ± 5° C. At the end of the run, the samples were quenched in air and phases present were examined by petrographic technique using reflected-light and by the conventional room temperature X-ray powder diffraction. A differential thermal analyser (Linseis: L 1040, West Germany) equipped with a furnace capable of operation to 1500° C was used to determine the melting behaviour of the compounds and to establish the solidus and liquidus temperatures in the system. Pt-cups were used to hold the samples and the reference standard material (α-Al_2O_3), and Pt–Pt/10%Rh thermocouples were used for temperature measurements. A heating and cooling rate of $10° C\,min^{-1}$ was found to be most satisfactory. The DTA apparatus was periodically calibrated against the melting point of GeO_2 (1115° C) and Diopside, $CaMgSi_2O_6$ (1391.5° C). The overall reproducibility of the DTA results obtained was assumed to be correct within ± 5° C.

Several problems were encountered during firing of both BaO and GeO_2 rich samples. The reaction of excess BaO with Pt-container material yielded products with deep purple colour and precluded the study in the BaO-rich region of the system. Also, loss of GeO_2 by volatilization, particularly, in the GeO_2-rich samples necessitated correction in the final compositions assuming GeO_2 to be the only volatile constituent. For this purpose, occasional checks were made by following weight changes in the samples during the quenching experiment to ensure that no significant GeO_2 loss occurred by volatilization.

3. Results and discussion

3.1. Compound formation

Approximately 40 compositions were prepared and equilibriated at different temperatures to establish the phase relations existing in the system. In a few cases, reaction of the ingredients was

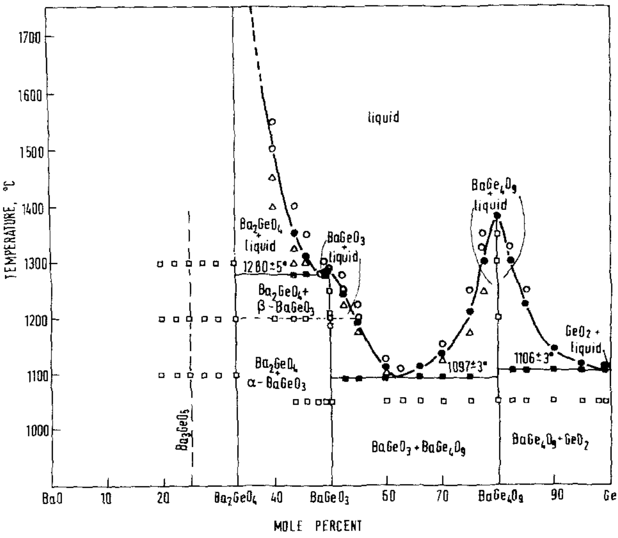

Figure 1 Phase equilibrium diagram of the system BaO–GeO_2 (□ solid, △ solid+liquid, ○ liquid, ■ solidus: DTA, ● liquidus: DTA).

Figure 2 Microstructure of a 30 mol% GeO_2 composition showing small dendrites of Ba_2GeO_4 co-existing with eutectic containing Ba_3GeO_5 and Ba_2GeO_4 (× 200).

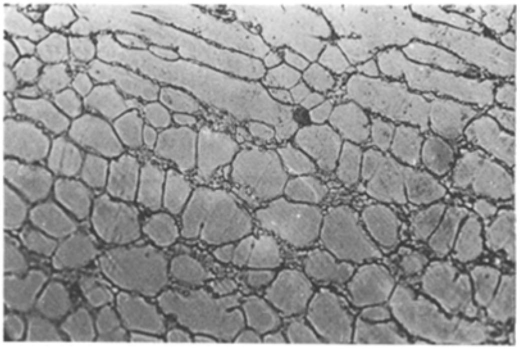

Figure 3 Microstructure of a 40 mol% GeO_2 composition showing dendrites of Ba_2GeO_4 surrounded by a small amount of eutectic liquid containing Ba_2GeO_4 and $BaGeO_3$ (× 300).

found to be incomplete, particularly, at the BaO-rich portion of the system. However, in general, the results were consistent with each other and represented the overall phase equilibrium relations in the system.

X-ray powder diffraction results of samples equilibriated at various temperatures showed that in the range of compositions studied, only four compounds, namely, Ba_3GeO_5, Ba_2GeO_4, $BaGeO_3$ and $BaGe_4O_9$ exist in the system. The compounds $Ba_3Ge_2O_7$ and $BaGe_{19}O_{39}$ reported by Grebenshchikov *et al.* [1] apparently do not exist. Present attempts to prepare these compounds either by solid-state reaction or by cooling from the melt resulted in two-phase mixtures. Further evidence against the existence of these compounds was found in the X-ray diffraction patterns reported by Grebenshchikov *et al.* [1]. For example, the pattern of $Ba_3Ge_2O_7$ can be interpreted as a mixture of Ba_2GeO_4 and orthorhombic $BaGeO_3$, and that of $BaGe_{19}O_{39}$ as a mixture of $BaGe_4O_9$ and hexagonal GeO_2. Thus after repeated examination of several compositions by solid-state reaction technique and comparing the X-ray powder diffraction data with the reported unindexed data for these compounds, it was concluded that the previously reported compounds $Ba_3Ge_2O_7$ and $BaGe_{19}O_{39}$ apparently resulted from non-equilibrium conditions and misinterpretation of X-ray data.

DTA and X-ray powder diffraction results indicated that only $BaGeO_3$ exhibits polymorphic transformation. A detailed study of polymorphism in $BaGeO_3$ was reported by Guha *et al.* [10] who observed that a low-temperature hexagonal polymorph of $BaGeO_3$ undergoes transformation at 1200° C to a high-temperature orthorhombic polymorph via an intermediate phase change at 1100° C, which was apparently evident in the DTA curve but could not be detected by the conventional room-temperature X-ray diffraction. It was concluded that the intermediate phase was unquenchable and, therefore, high-temperature X-ray data was needed to confirm its existence and to ascertain its crystal structure.

3.2. Phase equilibrium relations

The revised phase diagram for the system $BaO-GeO_2$ with the datum points used for establishing the solidus and the liquidus temperatures, and various phase fields occurring in the system are shown in Fig. 1. Altogether, four invariant points were established and defined as simple eutectic between the juxtaposed pair of compounds. The compounds Ba_3GeO_5 and Ba_2GeO_4 form a eutectic between themselves at a temperature above 1700° C and at 28 mol% GeO_2, approximately. The high temperature involved in melting the compositions in this

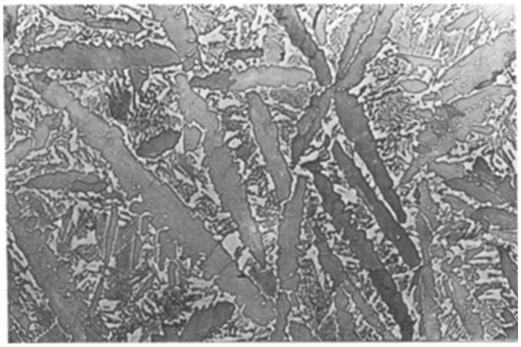

Figure 4 Microstructure of a 55 mol% GeO_2 composition showing large dendrites of $BaGeO_3$ surrounded by eutectic containing Ba_2GeO_4 and $BaGeO_3$ (× 300).

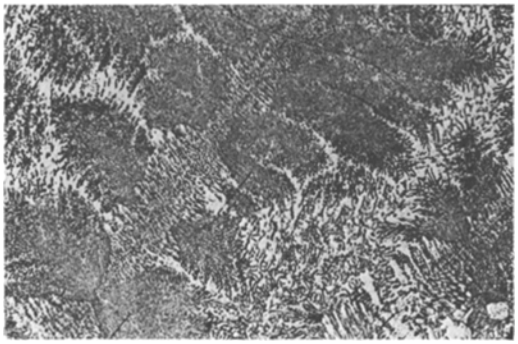

Figure 5 Microstructure of a 61.5 mol% GeO_2 composition exhibiting a complete eutectic structure between $BaGeO_3$ and $BaGe_4O_9$ (X 200).

region precluded a detailed study of the solid–liquid equilibria existing between the compounds and, therefore, are not shown in the diagram.

The microstructure of a Ba_2GeO_4-rich composition is shown in Fig. 2. This is typical of the microstructure resulting from quenching above the liquidus in which the primary phase crystallized in the form of dendrites within the liquid phase. In these samples, the quenching procedure was found to be insufficiently rapid to prevent some crystallization on cooling. However, samples containing a higher proportion of GeO_2 on quenching above the liquidus temperature were obtained in the form of a clear glass. As a result, petrographic examination of quenched samples in the GeO_2-rich region of the system could not be used effectively and the delineation of phase boundaries was primarily based on the DTA results. The eutectic between Ba_2GeO_4 and $BaGeO_3$ was located close to $BaGeO_3$ at 1280 ± 5° C and 48 ± 0.5 mol% GeO_2. The $\alpha \rightarrow \beta$ transformation temperature of $BaGeO_3$ at 1200° C remains unchanged in the presence of either Ba_2GeO_4 and $BaGe_4O_9$.

The microstructure of a composition rich in Ba_2GeO_4 is shown in Fig. 3 exhibiting massive primary dendrites of Ba_2GeO_4 co-existing with a small amount of eutectic liquid. The eutectic composition between $BaGeO_3$ and $BaGe_4O_9$ was located at 61.5 ± 0.5 mol% GeO_2 and its melting temperature was established at 1097 ± 3° C. This is the lowest temperature at which the first sign of melt formation was observed in the system.

The microstructure of a composition lying in the primary phase field of $BaGeO_3$ is shown in Fig. 4 exhibiting massive dendrites of $BaGeO_3$ surrounded by a small amount of eutectic liquid. The occurrence of a steep liquidus curve at the $BaGeO_3$ end of the system gave rise to some inaccuracies in ascertaining the exact liquidus temperatures of the samples when examined petrographically. DTA results were extensively used in establishing the liquidus curve in this region. The microstructure of the eutectic composition between $BaGeO_3$ and $BaGe_4O_9$ is shown in Fig. 5 exhibiting a fine-grained eutectic structure with partial separation of $BaGe_4O_9$ in a few isolated areas.

Fig. 6 shows the microstructure of a $BaGe_4O_9$-rich composition in which crystallization of primary $BaGe_4O_9$ in the shape of long needles is visible in a eutectic matrix. The eutectic composition between $BaGe_4O_9$ and GeO_2 was located close to the GeO_2 end of the diagram at 98 ± 0.5 mol% GeO_2 and its melting temperature was established at 1106 ± 3° C. Samples quenched or cooled from liquid were obtained in the form of

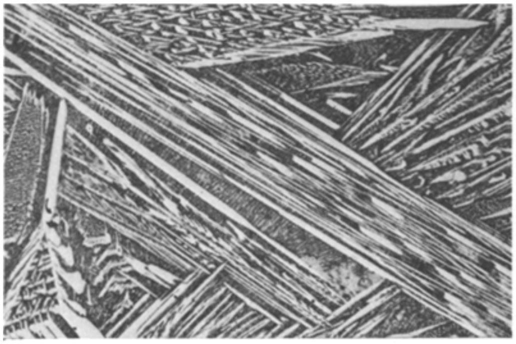

Figure 6 Microstructure of a 70 mol% GeO_2 composition showing crystallization of primary $BaGe_4O_9$ in a eutectic matrix containing $BaGeO_3$ and $BaGe_4O_9$ (X 250).

Figure 7 Microstructure of a 95 mol% GeO_2 composition showing crystallization of primary $BaGe_4O_9$ in a eutectic matrix containing $BaGe_4O_9$ and GeO_2 (X 250).

a clear glass with hardly any sign of crystallization of the primary phase. The solid–liquid equilibria in this region were established mainly by DTA results. However, by slowly cooling the samples from above the liquidus, the primary phase in the $BaGe_4O_9$ could be partially crystallized. Fig. 7 shows a typical microstructure representing such an effect in which the small dendrites of $BaGe_4O_9$ can be found to have crystallized in a large area of the eutectic containing $BaGe_4O_9$ and GeO_2.

Finally, it is interesting to note that due to the large difference between the melting temperature of $BaGe_4O_9$ and GeO_2, the samples in the GeO_2-rich region of the system readily segregate during melting and give rise to non-equilibrium conditions at which one or more of the barium germanates were formed and identified by X-ray diffraction. This might be one of the reasons why Grebenshchikov *et al.* [1] misinterpreted their X-ray data which led to the erroneous identification of the compound $BaGe_{19}O_{39}$. In the present investigation, the problem of segregation was encountered by slowly heating the samples above the solidus temperature until melting was completed and repeating the same procedure several times with intermittent cooling and crushing before they were finally cooled or quenched to room temperature to identify the equilibrium phases.

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