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Phase equilibria in the system $BaTiO_3$-$BaGeO_3$

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The system $BaTiO_3$-$BaGeO_3$ has been investigated by DTA, metallographic and X-ray diffraction methods. A number of selected samples were also analysed on the electron probe micro-analyser. The system was found to be of the simple binary-eutectic type with partial solid solubility at both ends. The eutectic composition was established as 68 ± 0.5 mol % $BaGeO_3$ and its melting temperature as 1120 ± 5°C. The solid solubility of $BaGeO_3$ in $BaTiO_3$ at 1120°C was found to be 1.8 mol % and that of $BaTiO_3$ in $BaGeO_3$ 2.2 mol %. Additions of $BaGeO_3$ to $BaTiO_3$ did not appear to cause any change in the temperature of the cubic to hexagonal inversion of $BaTiO_3$ but the temperature of the tetragonal to cubic inversion was raised slightly with such additions. The transformation temperature of 1180°C for the low- to high-temperature form of $BaGeO_3$ was not affected by additions of $BaTiO_3$

1. Introduction

In an investigation of the effect of GeO_2 on the dielectric properties of $BaTiO_3$, it has been observed that GeO_2 decomposes $BaTiO_3$ to form $BaGeO_3$ and $BaTi_3O_7$ [1]. This indicates that the join $BaTiO_3$-GeO_2 does not occur in the ternary system BaO-TiO_2-GeO_2, while the joins $BaTiO_3$-$BaGeO_3$ and $BaTi_3O_7$-$BaGeO_3$ occur. Metallographic examination of the fired samples further indicated that a liquid phase was present, and as a result, the density and microstructure as well as the dielectric properties of $BaTiO_3$ were considerably affected. It is not known, however, at what temperature this liquid phase first appears and the amounts which formed in mixtures of given composition.

It is thought, therefore, worthwhile to study the phase-equilibrium relationships in the system BaO-TiO_2-GeO_2. The present investigation, which is a part of the ternary system, deals with the phase equilibria involved in the system $BaTiO_3$-$BaGeO_3$. The effect of $BaGeO_3$ on the tetragonal to cubic, and cubic to hexagonal transitions of $BaTiO_3$ was also studied.

Previous work in this system is not extensive. Plessner and West [2] investigated the influence of small additions of GeO_2 on the dielectric properties of $BaTiO_3$. X-ray analysis of the fired samples revealed a single tetragonal structure without any shift of high-angle reflections indicating that no appreciable solid solubility occurs in the system. As regards the melting points of $BaTiO_3$ and $BaGeO_3$, the most reliable value for $BaTiO_3$ is that of Rase and Roy [3], who reported that $BaTiO_3$ melts congruently at 1618°C. The tetragonal structure of $BaTiO_3$ at room temperature transforms to a cubic form at 120°C and finally to a hexagonal form at1460°C.

The melting point of $BaGeO_3$ is reported by Grebenshchikov *et al* [4] as 1250°C. With additions of a small amount of $BaSiO_3$ and 2% Fe_2O_3, the pseudowollastonite form of $BaGeO_3$ is found to transform to a orthorhombic form at elevated temperatures [5].

2. Experimental

2.1. Starting materials

Both $BaTiO_3$ and $BaGeO_3$ were prepared in this investigation and the materials used were reagent-grade $BaCO_3$, TiO_2 and GeO_2. Appropriate proportions of the materials were weighed, mixed under alcohol in an agate mortar, dried in an oven and pressed into pellets. The pellets thus prepared were calcined at 1100°C in a platinum crucible for a sufficient length of time to ensure complete decomposition of carbonate. The calcined pellets were reground, pressed and refired at higher temperatures to form the respective compounds. A firing temperature of 1550°C was employed to obtain $BaTiO_3$ while a temperature of 1240°C was found to be satisfactory to obtain $BaGeO_3$. High purity $BaTiO_3$, obtained from TAM Division of National Lead Co, USA, was also used in this investigation.

2.2. Experimental methods

Several complementary methods were adopted to eliminate various errors involved in each method. In the quenching method, one gram samples containing $BaTiO_3$ and $BaGeO_3$ were pressed into small pellets, wrapped in platinum foils and fired at predetermined temperatures in an electrically-heated tube furnace. The firing temperatures were measured by a Pt-Pt/10% Rh thermocouple placed near the sample. Specimens were fired several times at the same temperature with intermittent cooling, crushing, mixing and pelleting to ensure homogeneity and to attain equilibrium. After the end of firing, the specimens were quenched and polished sections examined with a reflected-light microscope. The solidus and liquidus temperatures of selected compositions fired at various temperatures were thus determined.

A number of samples were subjected to differential thermal analysis in a Linseis DTA apparatus which could be operated up to 1600°C. Samples containing 0.5 g mixture were used and a heating rate of 10°C/min was found to yield the best result. Platinum containers were used to hold the sample and the reference material. Temperature measurements were carried out using calibrated Pt-Pt/10% Rh thermocouples.

For identification of phases, X-ray powder photographs were obtained in a 57 mm diameter camera, using Ni-filtered CuK_α radiation. X-ray diffraction patterns were compared with the standard values, the intensities being estimated visually.

Selected samples were also analysed on the electron micro-probe, the conventional corrections being made for X-ray absorption, secondary fluorescence and atomic number effects.

The influence of $BaGeO_3$ on the tetragonal to cubic inversion of $BaTiO_3$ was investigated in a Siemens X-ray diffractometer having a MRC high-temperature X-ray attachment. X-ray patterns were obtained from selected mixtures at a series of temperatures at 10°C intervals.

3. Results and discussion

In the present investigation, the melting point of $BaTiO_3$ was found to be approximately 1620°C which is in good agreement with the published data [3]. The melting point of $BaGeO_3$ was found to be somewhat higher than the reported value of 1250°C [4]. Careful observations both by metallography and DTA indicated that $BaGeO_3$ melts congruently at 1285 ± 5°C. This was further corroborated by the fact that a few compositions lying close to $BaGeO_3$ were found to have liquidus temperatures above 1250°C.

Preliminary firing of samples indicated that no new phase other than $BaTiO_3$ and $BaGeO_3$ appeared in the system and the phase diagram was apparently of the binary-eutectic type. The phase diagram with the datum points used in establishing the solidus and liquidus temperatures in the system is shown in Fig. 1.

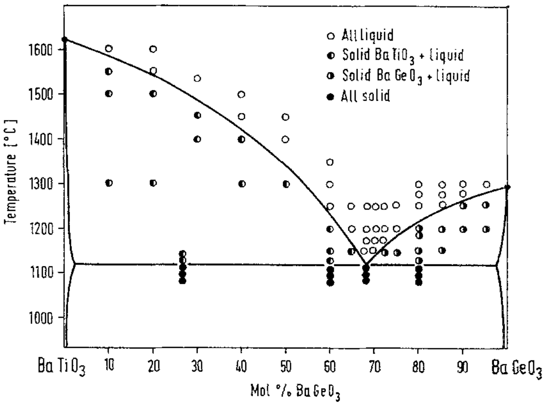

Figure 1 Phase equilibrium diagram of the system $BaTiO_3$-$BaGeO_3$.

The solidus has been drawn in the temperature interval between solid-plus-liquid and solid, and has been placed at 1120 ± 5°C, confirmation of this temperature being obtained from differential thermal analysis. A slightly higher temperature for the solidus was obtained by metallographic examination, perhaps, due to the fact that the amount of liquid which formed in a given composition when heated just above the solidus temperature was insufficient to be detected by microscopy.

Liquidus temperatures were also determined for selected compositions by metallographic examination of quenched samples. The quenching procedure was found to be insufficiently rapid to prevent some crystallization on cooling but the effects observed were utilized to determine the liquidus temperatures of the samples. These

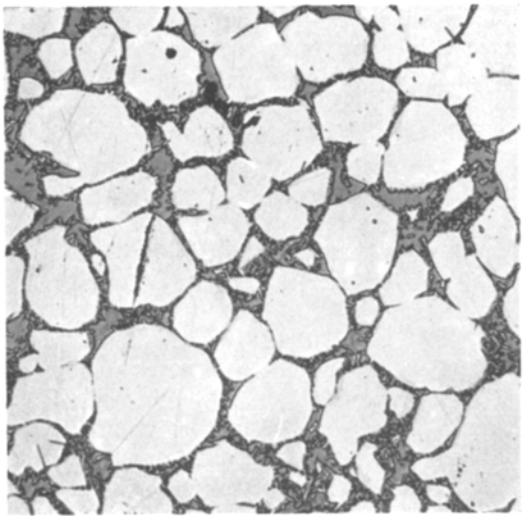

Figure 2 Microstructure of a sample containing 10 mol % $BaGeO_3$. Specimen fired at 1550° C, showing primary $BaTiO_3$ (solid) with eutectic liquid (× 400).

Figure 4 Microstructure of a sample containing 80 mol % $BaGeO_3$. Specimen fired at 1250° C, showing dendrites of $BaGeO_3$ with eutectic liquid (× 400).

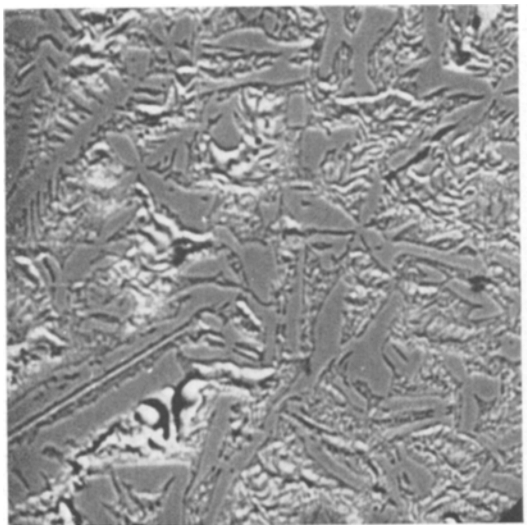

Figure 3 Electron micrograph of a sample containing 40 mol % $BaGeO_3$. Specimen fired at 1450° C, showing dendrites of $BaTiO_3$ with eutectic liquid (× 400).

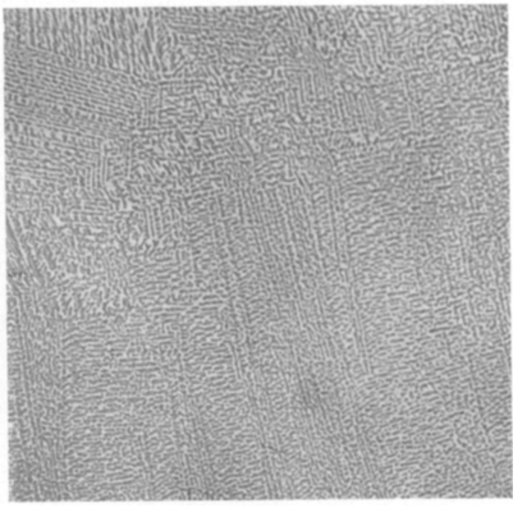

Figure 5 Microstructure of a sample containing 68 mol % $BaGeO_3$. Specimen fired at 1200° C, showing complete eutectic structure (× 250).

effects are illustrated by the micrographs of Figs. 2 to 6.

The microstructure of a composition richer in $BaTiO_3$ quenched from 1550° C as shown in Fig. 2, exhibited solid $BaTiO_3$ in equilibrium with the eutectic liquid, recrystallization being just visible in the liquid phase. This is typical of the microstructure resulting from quenching below the liquidus temperature, the primary phase being present always as rounded massive grains. In contrast, microstructures of compositions which were quenched from above their liquidus temperature show the precipitation within the liquid of the different forms of dendrites of $BaTiO_3$ and $BaGeO_3$ as shown in Figs. 3 and 4, respectively.

The point of intersection of the extrapolated liquidus curves on the solidus isotherm gave the eutectic composition as 68 mol % $BaGeO_3$. This was further confirmed by metallographic exam-

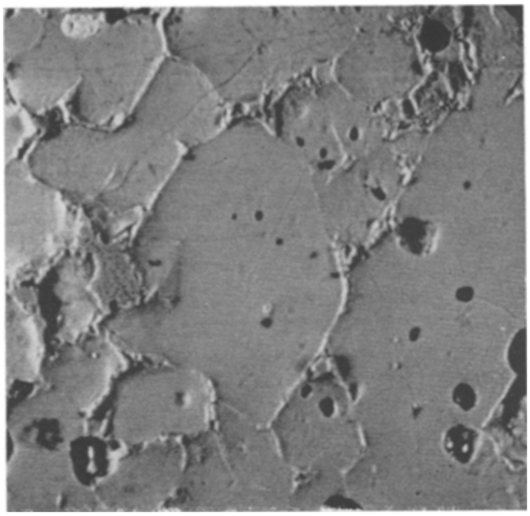

Figure 6 Electron micrograph of a sample containing 95 mol % $BaGeO_3$. Specimen fired at 1250°C, showing unmelted $BaGeO_3$ with eutectic liquid (× 400).

ination of several closely spaced compositions ranging from 65 to 75 mol % $BaGeO_3$ which were cooled from above their liquidus temperature. Fig. 5 shows the microstructure of the eutectic composition. An electron micrograph of a sample containing 95 mol % $BaGeO_3$ quenched from a temperature of 1250°C is shown in Fig. 6 indicating solid $BaGeO_3$ co-existing with a small amount of eutectic liquid. The occurrence of $BaGeO_3$ as solid in this sample at 1250°C apparently indicates a higher melting temperature for pure $BaGeO_3$.

The solid solubility occurring in this system was found to be very small. This was indicated by the absence of any appreciable shift in the characteristic X-ray diffraction lines. Selected samples were subjected to electron probe microanalysis, which indicated that the solubility of $BaGeO_3$ in $BaTiO_3$ was only 1.8 mol % and that of $BaTiO_3$ in $BaGeO_3$ was 2.2 mol %. The absence of any appreciable solid solubility between $BaTiO_3$ and $BaGeO_3$ may be due to the differences in their crystal structures. While $BaTiO_3$ belongs to the well-known perovskite type structure, $BaGeO_3$ possesses a pseudo-wollastonite type hexagonal symmetry. According to Roth [6], $BaGeO_3$ cannot form a perovskite-type structure, the Ge^{+4} ion being too small to occupy an octahedral position with respect to oxygen. Further the differences in ionic radii of Ge^{+4} (0.53) and Ti^{+4} (0.68) indicate that extensive solid solubility between these two compounds is unlikely.

The effect of additions of $BaGeO_3$ on the transition temperatures of $BaTiO_3$ has also been investigated. A series of X-ray diffraction patterns were obtained at temperatures ranging from 70 to 180°C and the transition from the tetragonal to cubic form was ascertained by satisfactory resolving of the (200) peak in the pattern. The result indicated that transition temperature of $BaTiO_3$ at 120°C does not change appreciably with additions of $BaGeO_3$. This is consistent with the findings of Baxter *et al* [7] and of Plessner and West [2]. These workers measured the temperature characteristics of the dielectric constant of $BaTiO_3$ with various oxide additions and observed that the permittivity peak at the transition temperature of 120°C was depressed without being appreciably displaced with addition of $BaGeO_3$. The cubic to hexagonal transition of $BaTiO_3$ with additions of $BaGeO_3$ was studied by quenching the samples from temperatures above 1460°C and the phases present were identified by the conventional room-temperature X-ray method. It was observed that the transition temperature of $BaTiO_3$ at 1460°C does not change appreciably with additions of $BaGeO_3$. Traces of hexagonal $BaTiO_3$ lines were identified with the cubic lines in all the samples quenched from above this temperature.

The quenching method was also used to investigate the effect of $BaTiO_3$ on the transition temperature of $BaGeO_3$. As reported earlier [8], the present authors observed that $BaGeO_3$ undergoes a crystallographic transformation at 1180°C. With small additions of $BaTiO_3$, no change in this transition temperature was detected.

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