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Phase Equilibria in the System $BaO-CeO_2$

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The phase equilibrium relationships in the binary system $BaO-CeO_2$ have been investigated by thermal analysis, metallographic and X-ray diffraction methods. The system is characterised by the existence of only one compound, namely, $BaCeO_3$ which is found to melt incongruently at 1480 ± 5° C with formation of solid CeO_2 and a liquid. A eutectic is found to occur between BaO and $BaCeO_3$ at 46 ± 0.5 mol% CeO_2 and its melting point was determined as 1440 ± 5°C. A narrow solid solubility range of BaO in $BaCeO_3$ exists but no solid solubility of $BaCeO_3$ in either BaO or CeO_2 was detected.

1. Introduction

Cerium dioxide is known to react with the alkaline earth oxides to form compounds having the perovskite structure which are of interest in the ferroelectric field. Although data on the crystal structures of these compounds are available in the literature, relatively little is known regarding phase equilibrium relationships involved in the systems between the alkaline earth oxides and CeO_2. In practice, a knowledge of equilibria between the different phases, particularly the nature and extent of solid solubility and temperatures of melt formation in the systems, is of considerable importance in the synthesis of these compounds and in predicting their service behaviour at elevated temperature.

The present investigation deals with phase equilibria in the binary system $BaO-CeO_2$ and describes the melting behaviour of various compositions across the system, with particular reference to $BaCeO_3$ and its compatibility with different phases at high temperatures.

2. Previous Work

The existence of $BaCeO_3$ and data on its crystal structure have been reported in the literature by several workers. Hoffman [1] proposed a cubic structure with a lattice constant $a_0 = 4.386$ Å. Smith and Welch [2], who prepared $BaCeO_3$ at temperatures between 1000 and 1730° C, reported a perovskite structure with a lattice constant $a_0 = 4.397$ Å. The crystal symmetry and positions of the atoms in a perovskite structure as observed in compounds such as $BaCeO_3$ are discussed by Wyckoff [3]. A small departure from perfect cubic symmetry is reported by Roth [4] who prepared $BaCeO_3$ at 1450 and 1525° C and proposed a pseudo-cubic structure with a lattice constant $a_0 = 4.387$ Å. These investigations are, however, mainly concerned with the crystal structure of $BaCeO_3$. Leonov *et al* [5], who investigated the solid-state reactions of cerium oxides with alkaline earth oxides, reported that CeO_2 interacts with oxides having large ionic radius, such as CaO, SrO and BaO, to form compounds of the type $A^{2+}B^{4+}O_3$ and observed limited solid solubility in these systems. Keler *et al* [6] carried out exploratory work on the binary system $BaO-CeO_2$ and confirmed that only one compound, namely $BaCeO_3$, occurs in the system without any solid solubility.

3. Experimental

The starting materials were Analar grade $BaCO_3$ and CeO_2. Mixtures containing various proportions of these materials were weighed, mixed under alcohol, dried in an oven and pressed into small pellets. The pellets were wrapped in platinum foil and prefired at 1000° C for 3 to 4 h in a horizontal-tube resistance furnace to decompose the carbonate. The samples were further fired at higher temperatures with intermittent cooling, crushing and pressing to facilitate homogeneity and attain equilibrium. A platinum/platinum-10% rhodium thermocouple was placed near the sample for accurate determination of firing temperatures. After the end of the firing period, the samples were quenched in air and examined both metallographically and by X-rays for phase identification. X-ray powder diffraction photographs were taken in a 5.7 cm diameter camera using nickel-filtered CuKα radiation.

Although useful, the quenching method was seriously limited in this investigation: firstly, because of the difficulty in reaching equilibrium, so that most compositions after prolonged firing at high temperatures were found to be incompletely reacted, and secondly because the rapid hydration of free barium oxide at room temperature resulted in disintegration of samples after firing. This phenomenon is reported in a previously published phase-diagram study involving BaO [7]. To overcome these difficulties, thermal analysis was carried out on selected samples up to a temperature of 1650°C. A heating rate of 10°C per min was found to be most satisfactory. Results were interpreted from heating curves obtained by repeated runs on each sample, while cooling curves were used only to ascertain the presence of the heat-effects which indicated relatively lower temperatures, mainly due to supercooling.

4. Results and Discussion

The phase-diagram with the datum points used in establishing the solidus and liquidus temperatures is shown in fig. 1.

The system is characterised by the existence of only one compound, namely, BaCeO$_3$, the crystal structure of which was found to be cubic, with a lattice constant $a_0 = 4.385$ Å. The compound melts incongruently at 1480°C with formation of solid CeO$_2$ and a liquid phase. A typical microstructure indicating the peritectic

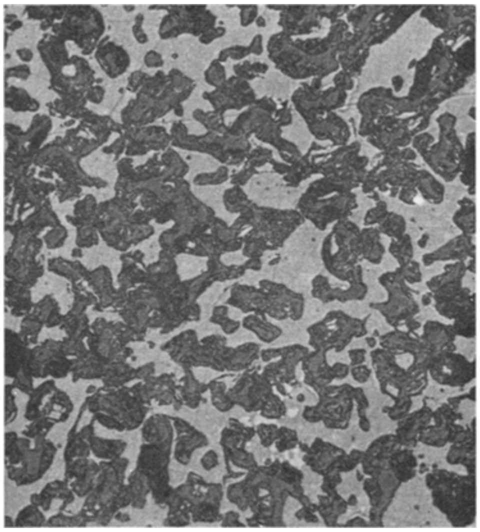

Figure 2 Composition 50 mol% CeO$_2$. Specimen fired at 1500°C. Microstructure showing peritectic reaction. CeO$_2$ + liquid with unmelted BaCeO$_3$ (white) (× 300).

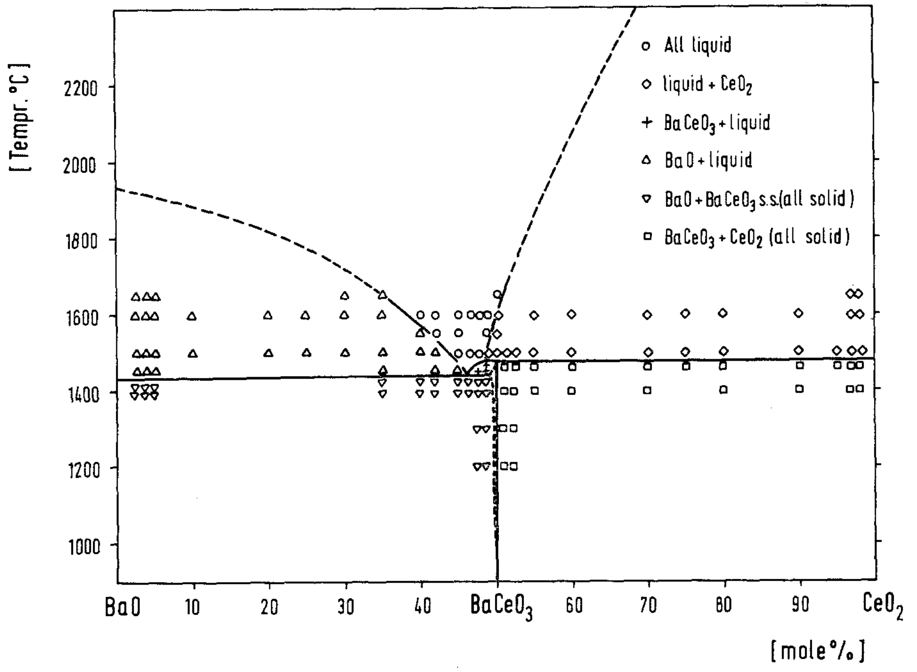

Figure 1 Phase equilibrium diagram of the system BaO-CeO$_2$.

reaction is shown in fig. 2. Compositions having more than 50 mol % CeO_2 were found to contain $BaCeO_3$ and CeO_2, indicating that no other compound richer in CeO_2 exists in the system.

Metallographic examination of various fired samples indicated that a eutectic occurs between BaO and $BaCeO_3$, the composition of which lies very close to $BaCeO_3$. Compositions richer in $BaCeO_3$, when cooled from below the liquidus, appeared in the form of massive solid phase with liquid of eutectic composition as shown in fig. 3 which could be distinguished readily from the dendritic form when cooled from above the liquidus, as shown in fig. 4. The poorly developed dendrites of $BaCeO_3$ as shown in fig. 4 had apparently crystallised from the liquid in a fine-grained eutectic matrix during cooling. The structures observed above and below the liquidus on the BaO side of the eutectic were somewhat difficult to distinguish from one another because of rapid disintegration of BaO in air at room temperature. Fig. 5 shows an almost complete eutectic structure. The presence of a small amount of BaO in the sample, however, indicates that the composition probably lies slightly on the BaO side of the eutectic. The microstructure of a composition richer in BaO is shown in fig. 6.

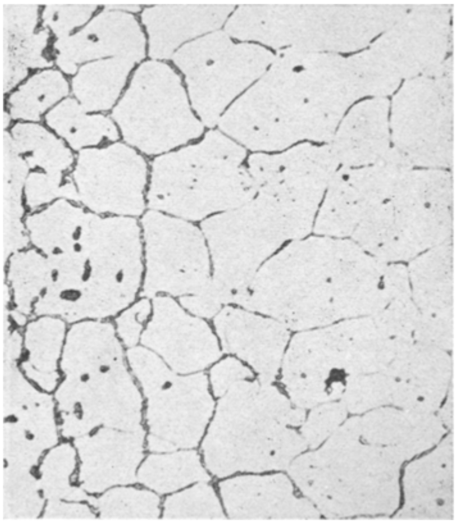

Figure 3 Composition 48 mol% CeO_2. Specimen fired at 1457°C. Solid $BaCeO_3$ + eutectic (solid + liquid) (× 300).

Results obtained by thermal analysis were found to be more reliable in establishing both the solidus line and the composition of the eutectic in the system. A consistent heat-effect was observed in several samples containing BaO and $BaCeO_3$ at 1440° C, indicating the solidus temperature. In contrast, only minor heat-effects due to the liquidus were observed in these samples. This may be due to the formation of only a small amount of liquid at the liquidus temperatures because of sluggish approach to equilibrium in

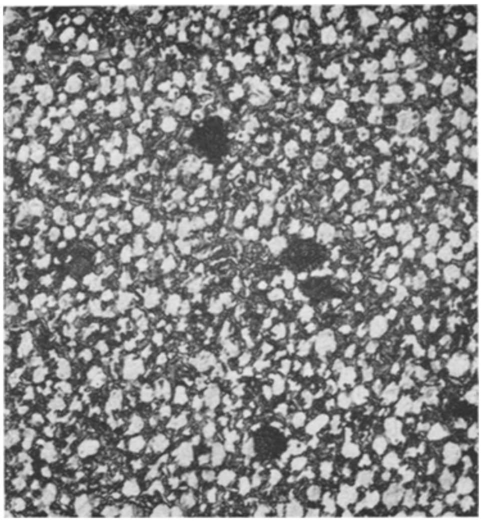

Figure 4 Composition 47 mol% CeO_2. Specimen fired at 1500°C. Dendrites of $BaCeO_3$ + eutectic (all liquid) (× 300).

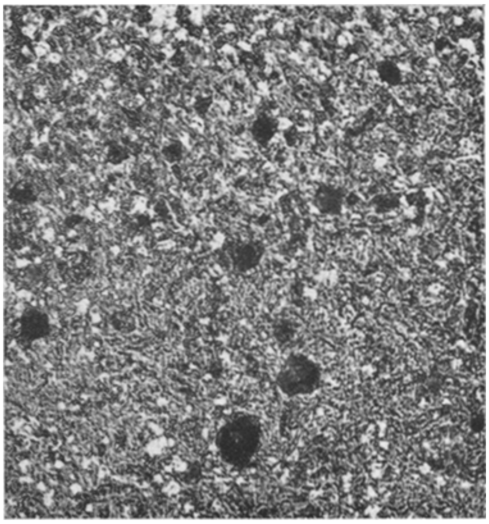

Figure 5 Composition 46 mol% CeO_2. Specimen fired at 1500°C. Eutectic + traces of BaO (all liquid) (× 300).

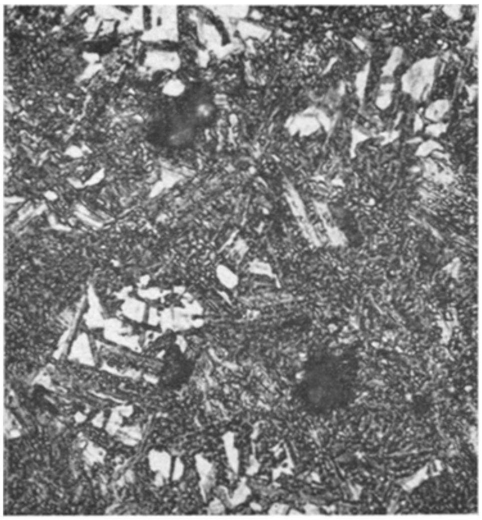

Figure 6 Composition 42 mol% CeO$_2$. Specimen fired at 1500°C. Solid BaO + eutectic (solid + liquid) (× 300).

the system. Further, the eutectic composition is located very close to BaCeO$_3$ and the solidus and liquidus temperatures of compositions richer in BaCeO$_3$ follow one another within a few degrees. Therefore, only a narrow BaCeO$_3$ primary phase field exists in the system, which under equilibrium conditions implies that a small proportion of crystals would actually be involved between the solidus and the liquidus, and this would result in a minor liquidus heat-effect which is difficult to detect. The steep rise of the liquidus above 1650°C on the BaO primary-phase field side, on the other hand, limited the number of thermal runs to only a few samples, However, on the basis of the above observations, the composition of the eutectic between BaO and BaCeO$_3$ is established as 46 ± 0.5 mol% CeO$_2$ and its melting point as 1440 ± 5°C.

X-ray diffraction patterns of fired samples containing BaO and BaCeO$_3$ revealed a slight increase in the lattice constant of BaCeO$_3$ which is attributed to solid solution of BaO in BaCeO$_3$. Earlier workers [2, 4] who obtained higher lattice constant values for BaCeO$_3$, employed firing temperatures above 1480°C, whereby, partial incongruent melting of BaCeO$_3$ resulted in the formation of solid CeO$_2$ and a liquid which contained BaO. Free BaO thus formed might have entered into solid solution with remaining unmelted BaCeO$_3$ during cooling, causing slight expansion of the lattice. The extent of the solid solubility was very small and could not be determined accurately by the conventional room-temperature X-ray method. No solid solubility of BaCeO$_3$ either in CeO$_2$ or in BaO was detected. Further, the reaction of BaO with platinum above 1200°C gave spurious X-ray diffraction lines in powder photograph which made it increasingly difficult to investigate any solid solubility in the high BaO portion of the system.

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References

1. A. HOFFMAN, *Z. Physik. Chem.* **28B** (1935) 65.
2. A. J. SMITH and A. J. E. WELCH, *Acta Cryst.* **13** (1960), 653.
3. R. W. G. WYCKOFF in "Crystal Structures", Vol. 2 (Interscience Publishers, New York, 1967) p. 390.
4. R. S. ROTH, *J. Research NBS*, **58** (1957) 75.
5. A. I. LEONOV, A. B. ANDREEVA, V. E. SHVAIKO-SHVAIKOVSKII, and E. K. KELER in "Chemistry of high-temperature materials" ed. N. A. Toropov (Consultants Bureau, New York, 1969) p. 99.
6. E. K. KELER, N. A. GODINA, and A. M. KALININA, *Zh. Neorg. Khim*, **1** (1956) 2556.
7. D. E. RASE and R. ROY, *J. Amer. Ceram. Soc.* **38** (1955) 102.

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