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ORNL-TM-94

COPY NO. - 43

DATE - December 22, 1961

EXPERIMENTAL ATTEMPTS TO STABILIZE A CUBIC FORM OF BeO

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Abstract

Binary mixtures of BeO with the oxides Al_2O_3, CaO, Li_2O, MgO, Sc_2O_3, TiO_2, Y_2O_3, and ZrO_2 were fired to temperatures in excess of 2050°C in an attempt to produce a stabilized cubic crystalline modification of BeO. No evidence was observed in microscopic and X-ray diffraction analyses of the cooled specimens that a cubic form of BeO had formed in the experiment.

Introduction

Several investigations of the crystal properties of beryllium oxide at high temperatures[1-3] have shown that a solid state transition occurs below the melting point at approximately 2050°C, although no evidence of this transition has been found in high temperature thermodynamic data.[4,5] No general agreement prevails regarding the nature of the transition. Austerman[3] adopts the view that the change is an order-disorder crystal transition between the space groups C_{6v}^{4} and D_{6h}^{4}, in which induced changes are not discernible by X-ray diffraction data. Miller,[2] in his high temperature X-ray diffraction investigation of BeO, noted the appearance of an unindexed line in the data derived above 2050°C. Rothman and Smith[6] have indexed several lines appearing in X-ray diffraction data taken above 2050°C on the basis of a cubic cell. The discovery that BeO undergoes a solid state transition to a cubic form when heated to temperatures above 2050°C suggests the interesting possibility that the structure might be stabilized by a small amount of another dissolved oxide.

Recent irradiation tests have shown that the hexagonal form of beryllium oxide is subject to radiation damage on long exposure at low temperatures.[7] Damage, attributed to anisotropic expansion of the crystal lattice, is observed in density decrease, as noted in refractive index measurements made on the irradiated material.[8] That a cubic form of BeO might be less vulnerable to radiation damage gives impetus to attempts to stabilize this form. For a cubic form of BeO to prove useful as a stable reactor moderator material, it must necessarily occur as an equilibrium phase at low temperatures. Consequently, it is most desirable that the cubic-hexagonal transition temperature be strongly depressed by small amounts of a dissolved additive. The small free space within the hexagonal crystal of BeO makes it appear that a second non-volatile oxide could not be incorporated within a cubic lattice of BeO unless this form were to be of anomalously low density. Nevertheless, the possibility of achieving fortuitous stabilization by any of several oxides of small cations was a sufficiently interesting goal, that exploratory high temperature experiments were conducted. Binary mixtures of BeO with the oxides Al_2O_3, CaO, Li_2O, MgO, Sc_2O_3, TiO_2, Y_2O_3, and ZrO_2 were heated to temperatures above 2050°C, cooled, and examined using the polarizing light microscope and the X-ray diffractometer. From these examinations, it was evident that each of the binary mixtures had been partially or completely molten. However, no evidence was observed which indicated that a cubic form of BeO had been formed in the experiment.

Experimental

Binary mixtures of BeO with the oxides Al_2O_3, CaO, MgO, Sc_2O_3, and Y_2O_3 were prepared by aqueous precipitation with ammonium hydroxide from mixtures of nitrate solutions, while those containing TiO_2 and ZrO_2 were prepared from chloride solutions. The binary mixture, Li_2O-BeO, was prepared by thermally decomposing a dried mixed residue of $LiNO_3$ and $Be(NO_3)_2$. The coprecipitated oxides were dried at 125°C, heated slowly to 1000°C in a muffle furnace, maintained at 1000°C for 20 minutes, cooled, ground, and pelletized at 20,000 psi to specimens 1/2" in diameter. No binder was used at any stage of the preparation. The pellets were fired for one hour at temperatures of $2075 \pm 30^{\circ}C$ in a graphite resistance vacuum furnace, adapted from a design by Smith.[9] Temperature measurements were made using a Leeds and Northrup optical pyrometer. Furnace temperatures were calibrated against the melting point of pure Al_2O_3.

Chemical and phase analyses of the cooled BeO binary mixtures are shown in Table I.

Discussion

High temperature investigations of BeO systems have been conducted for many years. In the relatively few systems which are known no evidence has been cited for the occurrence of high temperature cubic solid solutions of BeO.[10] The data derived in the experiments reported here also lead to the conclusion that no equilibrium cubic solid solution can be achieved in the usual fusion experiments. Cubic BeO, as well as radiation damaged hexagonal BeO, should be significantly less dense than standard BeO, and contain greater free space into which stabilizing ions might permeate. No attempts to stabilize low density hexagonal BeO were made, because thermal annealing at temperatures 500-1050°C increased the refractive index, and presumably the approximate density, to the usual values for BeO.[8] The possibility remains that other means may be discover-

Table I. Phase Analyses of BeO Binary Mixtures

Composition (mole o/o)	Phase Identification			
	X-Ray Diffraction (I/I$_1$ o/o)			Petrographic
	1000°C	1500°C	2075°C	2075°C
$95BeO-5Al_2O_3$	All BeO, poorly crystallized		Almost entirely BeO; trace $BeAl_2O_4$, trace unid.	Second phase not observed; appreciable BeO grain growth noted
95BeO-5CaO	90BeO, 10 unid.		90BeO, 10 unid.	Well developed BeO crystals; second phase black and dendritic
$95BeO-5Li_2O$	90BeO, 10 unid.		All BeO	Well developed BeO with inclusions; second phase not detected
95BeO-5MgO	70BeO, 30 MgO		90BeO, 10 MgO	Lath-like sintered BeO; second phase observed but not identified
$95BeO-5Sc_2O_3$	90BeO, $10Sc_2O_3$		90BeO, $10Sc_2O_3$	Sintered BeO containing microcrystalline high index cubic material at grain boundaries
82.2BeO-17.8TiO$_2$	$60TiO_2$, Ti_2O_3, 20BeO	50BeO, $50Ti_2O_3$	90BeO, $10Ti_2O_3$	BeO and black opaque phase
$95BeO-5Y_2O_3$	30BeO, $70Y_2O_3$		40BeO, $60Y_2O_3$; BeO well-crystallized	BeO + BeO-Y_2O_3 eutectic growths
$95BeO-5ZrO_2$	50BeO, 30 cubic ZrO_2, 20 monoclinic ZrO_2		80BeO, 15 monoclinic ZrO_2, 5 ZrO_2	BeO + monoclinic and cubic ZrO_2

ed by which stabilizing cations can be retained in a cubic BeO crystal lattice. None of the methods, e.g., introduction of cations via high temperature solid state diffusion, suggests itself as a feasible means for production of laboratory quantities of cubic BeO.

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