

Studies of Beryllium Chromite and Other Beryllia Compounds With R_2O_3 Oxides

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Reactions between BeO and R_2O_3 oxides at high temperatures were studied. Compound formation was observed between BeO and the following oxides: B_2O_3 , Al_2O_3 , Ga_2O_3 , Y_2O_3 , Li_2O_3 , and Cr_2O_3 . No reaction was observed with Sc_2O_3 , In_2O_3 , and Fe_2O_3 . Detailed studies were made of $BeO \cdot Cr_2O_3$ which is isostructural with $BeO \cdot Al_2O_3$. $BeO \cdot Cr_2O_3$ is a semiconductor. Optical and X-ray data are given for all reaction products.

1. Introduction

In hydrothermal experiments involving the system $BeO + Al_2O_3 + SiO_2$ with small amounts of added Cr_2O_3 at $850^\circ C$, it was found that X-ray patterns of reaction products persistently showed evidence for an unidentified material. It was found that this material was a compound between BeO and Cr_2O_3 . The compound has been reported earlier to be $BeO \cdot Cr_2O_3$ by Lang, Roth, and Fillmore [1]¹ who studied the system $BeO \cdot Cr_2O_3 \cdot ZrO_2$. They found that it was orthorhombic, isostructural with $BeO \cdot Al_2O_3$, with unit cell parameters $a=10.0 \text{ \AA}$, $b=5.8 \text{ \AA}$, and $c=4.5 \text{ \AA}$. The present report describes the preparation and some of the properties of $BeO \cdot Cr_2O_3$ as well as preliminary studies on the reactions between BeO and the R_2O_3 oxides in group III of the periodic system.

2. Experimental Materials and Methods

All reagents used were oxides of reagent grade except Ga_2O_3 , In_2O_3 , and Y_2O_3 . The former two were made by solution of chemically pure metal in nitric acid followed by thermal decomposition of the nitrate. The available specimen of Y_2O_3 was of commercial origin with a purity of 99.7 percent.

Hydrothermal reactions were carried out in the well-known cold-seal apparatus [2], using platinum containers. Solid state reactions were made through repeated heating and grinding of oxides. Materials were heated to temperatures as high as $1,550^\circ C$ in platinum, while BeO containers were used between $1,550^\circ C$ and $2,100^\circ C$. Temperatures to $1,550^\circ C$ were obtained with platinum wire furnaces and higher temperatures with a carbon resistance furnace using a He atmosphere. Early results indicated the desirability of a rapid screening process. This was accomplished by using a small d-c carbon arc as a furnace. Component oxides were mixed and treated with a sufficient quantity of 10 percent aqueous starch solution to form a paste. The paste was extruded from glass tubing to form small rods $\frac{1}{8}$ in. in diameter, which were dried and melted in the arc using the tubing as a handle. All oxides studied were melted rapidly in the arc and a single

small fused bead was sufficient to permit X-ray and microscopic analysis. The possible reduction and volatilization of the oxides precludes knowledge of the purity or composition of the arc-fused product, but rapid search for reactions is quite simple with this method.

3. Results

3.1. $BeO \cdot Cr_2O_3$

This material formed hydrothermally at temperatures as low as $800^\circ C$ in the presence of water. In this temperature range, however, the reaction rate is very low and crystals are very small.

In the solid state, slow reaction was observed at temperatures as low as $1,400^\circ C$. Microscopic comparisons of the surface with the body of specimens showed that prolonged heating of oxide mixtures at $1,450^\circ C$ produces some surface loss of Cr_2O_3 . The loss accelerates as the temperature is raised so that only BeO crystals remain on the surface after 4 hr at $1,750^\circ C$. Below about $1,600^\circ C$ the rate of loss is believed to be sufficiently low that the bulk composition is essentially unaffected in normal heating periods. That the Cr_2O_3 vapor was at least partially due to vapor pressure of the compound was shown by the fact that $BeO \cdot Cr_2O_3$ sintered in BeO at $1,750^\circ C$ also showed much surface loss of Cr_2O_3 . The competitive processes of reaction of the oxides and vaporization of Cr_2O_3 from the oxide mixture and the compound indicate that there is an optimum temperature for formation of $BeO \cdot Cr_2O_3$. These experiments indicate that this temperature is probably between $1,300^\circ C$ and $1,600^\circ C$. As a result of vaporization of Cr_2O_3 large single crystals would not be expected in open systems; however, crystals as large as 0.05 mm are readily formed under these conditions. The compound forms readily in the arc crystallizing from the liquid phase. Experiments in the arc also showed that the compound $BeO \cdot Cr_2O_3$ was a semiconductor as conductivity of specimens became so high at elevated temperatures that resistance heating could be effected.

Microscopic examination showed that $BeO \cdot Cr_2O_3$ forms well-terminated, transparent, deep green crystals having a reddish pleochroism. The crystals are biaxial negative with $2V \approx 45^\circ$ and indices, $\alpha=2.143$, β not measured, $\gamma=2.230$. Pseudo-hexagonal, highly

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. X-ray powder pattern for BeO·Cr₂O₃

Cu K α , $\lambda=1.5405$		
BeO·Cr ₂ O ₃ ¹		
<i>d</i> _{obs.}	<i>hkl</i>	<i>d</i> _{calc.}
4		4
4.135	101	4.131
3.337	111	3.337
2.653	301	2.654
2.452	220	2.451
2.402	311	2.403
2.335	121	2.335
2.157	401	2.157
1.936	321	1.936
1.715	421	1.715
1.715	511	1.716
1.668	222	1.669
1.539	331	1.538
1.519	003	1.519
1.4159	040	1.4155
1.4140	620	1.4141
1.3765	303	1.3771

¹ Unit cell parameters $a=9.792$ Å, $b=5.663$ Å, $c=4.555$ Å; calculated density 4.654 g/cm³ at 25° C.

twinned crystals similar to those of BeO·Al₂O₃ are obtained on reaction via the liquid phase.

Polycrystalline material appears black and opaque. It has a hardness on the Moh's scale of about 9 by the scratch test. The melting point was not measured but it was found that a eutectic between BeO and BeO·Cr₂O₃ melts below approximately 2,050° C. The measured specific gravity is 4.42 and the principal X-ray powder lines are given in table 1 with the indices and unit cell parameters. X-ray studies conducted on mixtures rich in BeO or Cr₂O₃ showed no appreciable solid solution of the parent oxides in BeO·Cr₂O₃.

X-ray powder patterns show BeO·Al₂O₃ and BeO·Cr₂O₃ are isostructural. Several solid solutions were prepared from the component oxides and the variation of the unit cell parameters with composition is shown in figure 1. Although some curvature is possible in the variation of "a" with composition, the deviations from linearity are probably within the experimental error of determining the cell parameters. In addition the compositions denoted by the points are determined from the known quantities of oxides added and may be subject to some error arising from loss of Cr₂O₃ on firing. This error is believed to be small. From these data it appears that a complete series of solid solutions exists between BeO·Al₂O₃ and BeO·Cr₂O₃. This conclusion differs from that of Gjessing, Larrison, and Major [3] who found only partial substitution of Cr₂O₃ for Al₂O₃ in the BeO·Al₂O₃ structure.

In view of the electrical conductivity of BeO·Cr₂O₃ at elevated temperatures, it was of interest to determine the temperature-resistance characteristics. These measurements were made on polycrystalline sintered bars using platinum electrodes. Specimens were measured in a temperature-controlled furnace using a commercial megohm bridge which applied 500 v across the specimen. Since single crystals were not used, and the bars possessed pores, the resistivities could not be determined, the resulting data

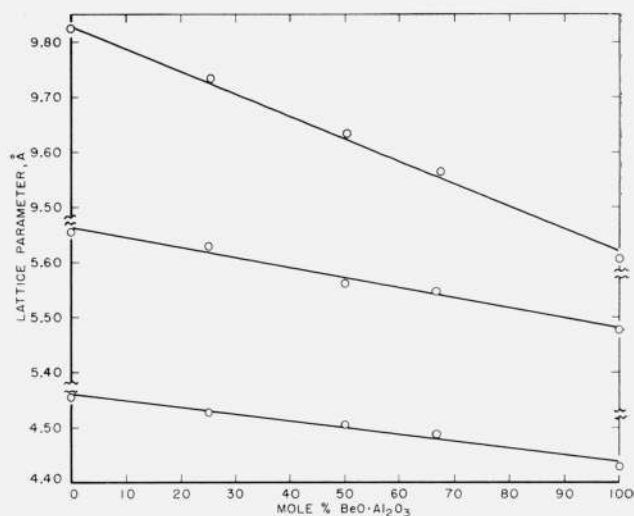


FIGURE 1. Variation of unit cell parameters in the solid solution series BeO·Al₂O₃-BeO·Cr₂O₃.

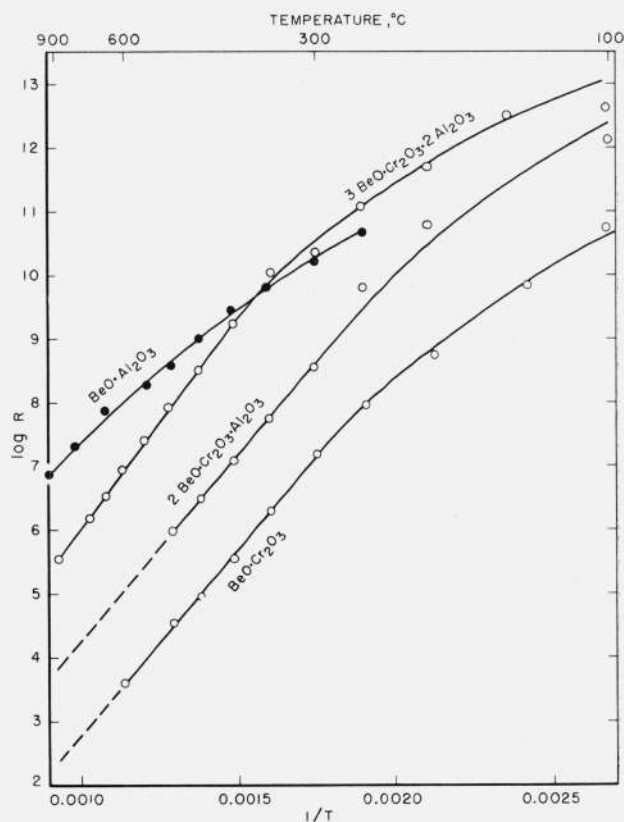


FIGURE 2. Temperature variation of resistance of BeO·Al₂O₃, BeO·Cr₂O₃ and solid solutions.

being valid only for showing the temperature dependence of resistance. The resistance was measured at temperature intervals of approximately 100° C and the data are shown for BeO·Cr₂O₃ as well as BeO·Al₂O₃ and two solid solutions in figure 2. The data are plotted in the usual manner using $1/T$ and $\log R$. From the figure it will be observed that data for

specimens containing Cr_2O_3 are not inconsistent with the interpretation that they are intrinsic semiconductors, above about 300°C . If this interpretation is correct the average energy gap is calculated to be 2.4 eV and appears to be independent of the $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ ratio.

The magnetic characteristics of $\text{BeO}\cdot\text{Cr}_2\text{O}_3$ are being studied by W. E. Henry of the Naval Research Laboratory. Preliminary results show the material to be antiferromagnetic.

3.2. $\text{BeO}\cdot\text{R}_2\text{O}_3$ Reactions

a. $\text{BeO}\cdot\text{B}_2\text{O}_3$

A crystalline product is formed by heating BeO and crystalline B_2O_3 at 800°C . The principal X-ray lines for the material are given in table 2. Crystals are biaxial with $2V \approx 90^\circ$ and indices $\alpha=1.62$, β not measured, $\gamma=1.574$. The material is not isostructural with $\text{BeO}\cdot\text{Al}_2\text{O}_3$. From the X-ray pattern the product can be identified with the compound $3\text{BeO}\cdot\text{B}_2\text{O}_3$ reported by Menzel and Sliwinski [4] and by Mazelev [5].

TABLE 2. X-ray powder patterns for $\text{BeO}\cdot\text{R}_2\text{O}_3$ compounds
Cu $K\alpha$, $\lambda=1.5405$

$3\text{BeO}\cdot\text{B}_2\text{O}_3$		$\text{BeO}\cdot 2\text{Ga}_2\text{O}_3$				$\text{nBeO}\cdot\text{Y}_2\text{O}_3$		$\text{nBeO}\cdot\text{La}_2\text{O}_3$	
<i>d, A</i>	<i>I</i>	<i>d, A</i>	<i>hkl</i> ¹	<i>I</i>	<i>d_{calc.}</i>	<i>d, A</i>	<i>I</i>	<i>d, A</i>	<i>I</i>
7.302	vw	6.717	100	m	6.716	7.190	w	3.768	vs
6.067	w	3.875	110	m	3.877	5.196	w	3.718	m
5.921	w	3.379	200	s	3.358	4.607	vw	3.673	m
3.957	m	2.728	101	s	2.723	4.469	s	3.296	m
3.872	vs	2.539	210	vs	2.538	3.146	m	3.063	m
3.826	m	2.230	202	s	2.228	2.922	vs	3.008	s
3.635	m	1.938	220	w	1.939	2.838	m	2.681	m
3.188	s	1.934	211	w	1.932	2.786	m	2.628	m
2.901	s	1.863	310	w	1.863	2.765	w	2.620	m
2.863	w	1.791	301	m	1.790	2.600	w	2.612	s
2.718	w	1.626	221	w	1.625	2.479	w	2.494	m
2.480	m	1.579	311	w	1.579	2.412	w	2.465	w
2.446	w	1.541	320	w	1.541	2.213	w	2.224	w
2.365	w	1.489	002	w	1.495	2.193	w	2.167	m
2.204	w	1.465	410	w	1.466	2.060	w	2.127	m
2.168	w	1.369	321	m	1.369	1.979	m	2.055	w
2.061	w	1.316	411	w	1.316	1.975	w	2.030	w
1.932	w	1.286	212	w	1.286	1.945	w	1.980	m
1.901	w	1.269	420	vw	1.269	1.888	w	1.965	w
1.751	w	1.207	510	vw	1.206	1.767	m	1.883	m
1.737	w	1.183	222	vw	1.182	1.705	w	1.838	w
1.656	w	1.169	421	vw	1.168	1.682	w	1.820	w
1.430	w					1.631	w	1.785	m
1.275	w					1.460	w	1.763	m
						1.455	w	1.740	w
						1.289	w	1.700	w
								1.698	w
								1.678	w
								1.652	w
								1.647	w
								1.638	w
								1.627	w
								1.610	w
								1.608	w
								1.542	w
								1.515	w
								1.483	w
								1.446	m
								1.209	w
								1.201	m

¹ Indexed on the basis of a hexagonal unit cell with parameters $a=7.78\text{A}$ and $c=2.98\text{A}$.

b. $\text{BeO}\cdot\text{Al}_2\text{O}_3$

In addition to $\text{BeO}\cdot\text{Al}_2\text{O}_3$, the product $\text{BeO}\cdot 3\text{Al}_2\text{O}_3$ is readily formed by arc fusion of the 1:3 oxide mixture. This material is identified with the X-ray powder pattern given originally by Foster and Royal [6] and extended by Budnikov et al. [7].

c. $\text{BeO}\cdot\text{Sc}_2\text{O}_3$

Mixtures of BeO and Sc_2O_3 can be fused with difficulty in the arc. However, despite numerous attempts no evidence for reaction was observed. X-ray powder patterns of fused beads showed only BeO and Sc_2O_3 lines.

d. $\text{BeO}\cdot\text{Ga}_2\text{O}_3$

Arc fusion studies showed reaction between BeO and Ga_2O_3 , but X-ray patterns showed the product was not isostructural with $\text{BeO}\cdot\text{Al}_2\text{O}_3$. Gjessing, Larrison, and Major [3] have previously reported a compound, $\text{BeO}\cdot 2\text{Ga}_2\text{O}_3$, which is not isostructural with $\text{BeO}\cdot\text{Al}_2\text{O}_3$. Solid state reactions indicated that the material was readily formed at $1,350^\circ$ from a mixture of oxides. Although complete reaction was not obtained in short periods at this temperature as shown by X-ray lines of unreacted BeO or Ga_2O_3 the product is believed to be identical with the $\text{BeO}\cdot 2\text{Ga}_2\text{O}_3$ reported earlier [3]. Microscopic examination showed the material to be uniaxial positive with indices 1.747 and 1.774. The X-ray powder pattern lines given in table 2 were obtained by deleting the known lines of BeO from the pattern. This pattern has been indexed in the hexagonal system with $a=7.78\text{A}$ and $c=2.98\text{A}$, with the indices given in table 2.

e. $\text{BeO}\cdot\text{Y}_2\text{O}_3$

Arc fusion studies showed reaction between BeO and Y_2O_3 . All attempts to produce a similar material by solid state reactions at temperatures as high as $1,600^\circ\text{C}$ were unsuccessful. Therefore the composition as well as the purity of the material are not known. Microscopic examination showed biaxial crystals with $2V \approx 90^\circ$ and indices, $\alpha=1.84$, β not measured, $\gamma=1.85$. The X-ray powder pattern lines are listed in table 2 but it should be noted that extraneous lines from impurities introduced by the arc may be present. This material is obviously not isostructural with $\text{BeO}\cdot\text{Al}_2\text{O}_3$ and does not appear to have been reported previously.

f. $\text{BeO}\cdot\text{In}_2\text{O}_3$

Repeated efforts at high and low temperatures, in open and closed systems, both with and without water present failed to give any evidence for reaction. Ensslin and Valentiner [8] reported $\text{BeO}\cdot\text{In}_2\text{O}_3$ as having the same lattice constant as In_2O_3 . Gjessing, Larrison, and Major [3] found no reaction. On the basis of the present work it is concluded that reaction between the oxides does not occur to $1,600^\circ\text{C}$.

g. $\text{BeO}\cdot\text{La}_2\text{O}_3$

These oxides react readily in the arc. Solid state reactions may be carried out at $1,300^\circ\text{C}$ and indicate that the product is probably $2\text{BeO}\cdot\text{La}_2\text{O}_3$. Microscopic examination shows biaxial crystals with $2V \approx 90^\circ$ having indices, $\alpha=1.995$, β not measured, $\gamma=2.047$. X-ray powder pattern lines are given in table 2.

h. BeO-Cr₂O₃

In addition to the compound BeO·Cr₂O₃ the question of a 1:3 compound analogous to BeO·3Al₂O₃ was investigated. Evidence was found that only the 1:1 compound was formed, X-ray patterns showing lines for BeO·Cr₂O₃ and Cr₂O₃ only.

i. BeO-Fe₂O₃

Several experiments were performed to prepare the BeO·Fe₂O₃ analog of BeO·Al₂O₃ starting from the oxides. None were successful. In most instances Fe₃O₄ was formed. The question of the existence of BeO·Fe₂O₃ from previous work is not clear [9, 3]. However, from the present experiments it appears that such a compound does not form from the oxides at temperatures up to the liquidus.

4. Summary

High temperature reactions of BeO with the R₂O₃ oxides have been studied. The compound BeO·Cr₂O₃ has been studied in some detail. It is isostructural with BeO·Al₂O₃ and a continuous series of solid solutions forms between these compounds. The unit cell parameters in the solid solutions show nearly ideal behavior. BeO·Cr₂O₃ is a semiconductor.

Compound formation was verified between BeO and the following oxides: B₂O₃, Ga₂O₃, Y₂O₃, and La₂O₃. Powder X-ray diffraction patterns are given for all compounds and that for BeO·2Ga₂O₃ is indexed in the hexagonal system. No reaction was observed between BeO and Sc₂O₃, In₂O₃, and Fe₂O₃.

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5. References

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