Phase Equilibria in the Systems
Rare-Earth Sesquioxide-Beryllium Oxide

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Phase equilibria in systems comprised of a rare-earth or yttrium sesquioxide and beryllia were studied. Two types of beryllates, stable and metastable, with molecular ratios of 1:2 and 3:2, were found; their formation and stability are discussed in terms of crystal chemistry.

I. Introduction

STUDIES of phase equilibria in systems of rare-earth sesquioxides and beryllium oxide are important in understanding their high-temperature physicochemical behavior and in identifying new compounds which may be useful in material applications. In the systems La_2O_3-BeO[1] and Gd_2O_3-BeO,[2] three binary compounds, $La_2O_3 \cdot 2BeO$, $3La_2O_3 \cdot 2BeO$, and $Gd_2O_3 \cdot 2BeO$ have been reported; however, the gadolinium compound is metastable and forms only on quenching of melts. Large single crystals of $La_2O_3 \cdot 2BeO$ with excellent optical quality have been grown.[3,4] When these crystals are doped with Nd, a useful laser material results; the long-pulse and Q-switched laser performance is very good.
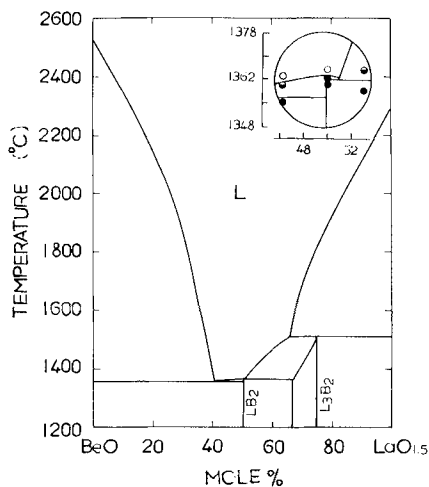
Fig. 1. Phase diagrams of rare-earth oxide-beryllium oxide systems. L=liquid, LB_2=$La_2O_3 \cdot 2BeO$, L_3B_2=$3La_2O_3 \cdot 2BeO$, N_3B_2=$3Nd_2O_3 \cdot 2BeO$, SB_2=$Sm_2O_3 \cdot 2BeO$.
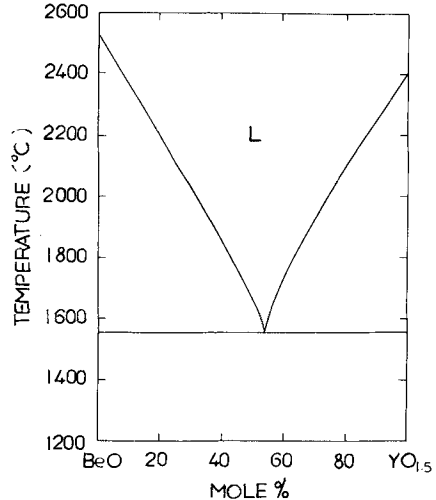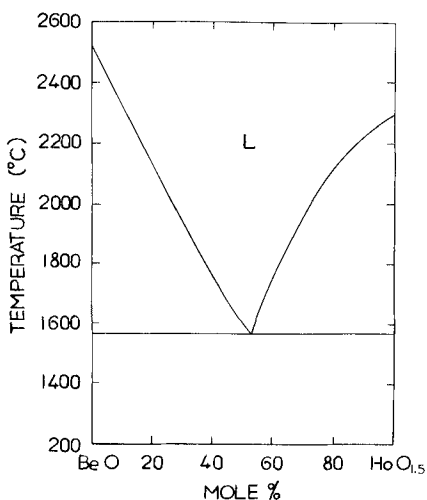
Table II. Stable and Metastable Binary Compounds in the Systems Rare-Earth Oxide-Beryllium Oxide

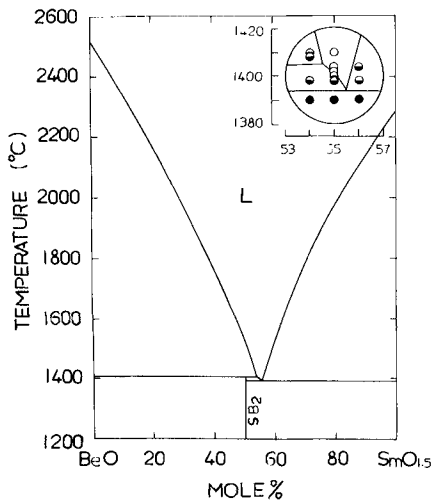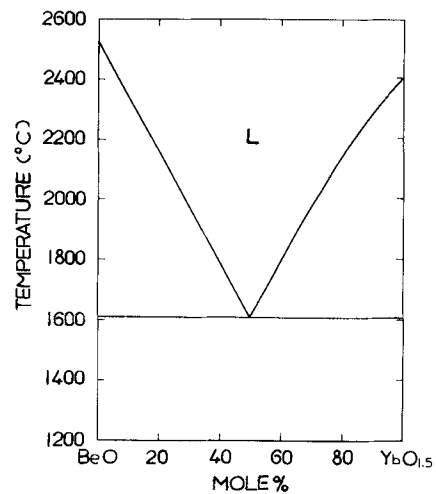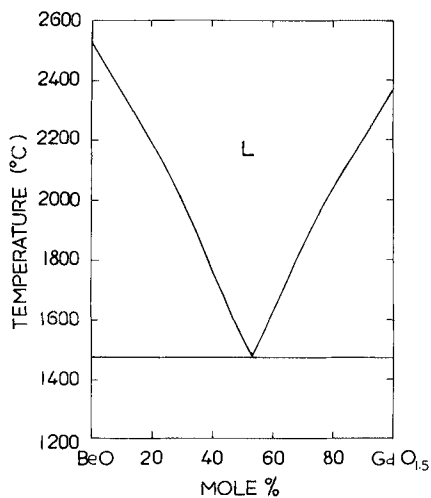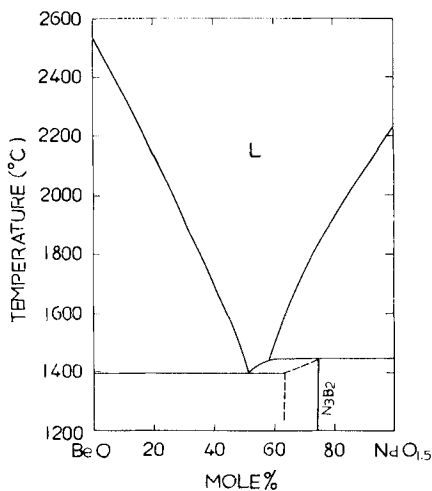| Binary compound	Melting point (°C)	Refractive indices		Symmetry of crystals	Lattice parameters (nm)		
		n_α, n_e	n_γ, n_o		a	b	c
$La_2O_3 \cdot 2BeO$	1363±3, congruent	1.98	2.035	Orthorhombic	0.381±.006	0.995±.001	1.107±.005
$3La_2O_3 \cdot 2BeO$	1510±10, incongruent	2.03	2.055	Hexagonal	0.7306±.0001		1.1456±.001
$Nd_2O_3 \cdot 2BeO$	Metastable	1.99	2.05				
$3Nd_2O_3 \cdot 2BeO$	1440±10, incongruent	2.035	2.06	Hexagonal	0.700±.004		1.107±.003
$Sm_2O_3 \cdot 2BeO$	1405±5, incongruent	1.90	1.95	Orthorhombic	0.3642±.0005	0.9918±.002	1.084±.005
$Gd_2O_3 \cdot 2BeO$	Metastable	1.89	1.94	Orthorhombic	0.3603±.0003	0.985±.003	1.051±.002

Table III. Invariant Points in the Systems Rare-Earth Oxide-Beryllium Oxide

System	Phases in equilibrium	Temperature (°C)	Molecular composition
La_2O_3-BeO	$BeO-La_2O_3 \cdot 2BeO$-liquid	1356±2	40.8% $LaO_{1.5}$
	$La_2O_3 \cdot 2BeO-3La_2O_3 \cdot 2BeO(ss)$-liquid	1362±4	51% $LaO_{1.5}$
	$3La_2O_3 \cdot 2BeO-La_2O_3$-liquid	1510±10	66% $LaO_{1.5}$
Nd_2O_3-BeO	$BeO-3Nd_2O_3 \cdot 2BeO(ss)$-liquid	1395±5	51.5% $NdO_{1.5}$
	$3Nd_2O_3 \cdot 2BeO-Nd_2O_3$-liquid	1440±10	59% $NdO_{1.5}$
Sm_2O_3-BeO	$BeO-Sm_2O_3 \cdot 2BeO$-liquid	1405±5	54.5% $SmO_{1.5}$
	$Sm_2O_3 \cdot 2BeO-Sm_2O_3$-liquid	1394±4	55.5% $SmO_{1.5}$
Gd_2O_3-BeO	$BeO-Gd_2O_3$-liquid	1472±2	53.4% $GdO_{1.5}$
Ho_2O_3-BeO	$BeO-Ho_2O_3$-liquid	1565±10	53% $HoO_{1.5}$
Yb_2O_3-BeO	$BeO-Yb_2O_3$-liquid	1610±10	50% $YbO_{1.5}$
Y_2O_3-BeO	$BeO-Y_2O_3$-liquid	1555±15	54% $YO_{1.5}$

Subsequently, the present workers studied systems of representative medium-to-heavy rare-earth oxides with BeO, including Nd_2O_3, Sm_2O_3, Ho_2O_3, and Yb_2O_3, as well as Y_2O_3. The results obtained are reported and the crystal chemistry of these systems is discussed. The phase diagram of the systems rare-earth sesquioxide-BeO may be found in Refs. 1, 2, and 5.

II. Experimental Procedure

The compositions were prepared by blending extra pure, dried $BeO^\dagger$ and rare-earth sesquioxide (99% purity or specified pure, Chinese chemical reagent) in ethanol, and calcining at 1200° for 4 h and at 1300°C for 4 h+4 h, with intermediate grinding and blending.

Quenching experiments were made in a platinum wire-wound furnace and a tungsten or graphite resistor microfurnace (in an argon atmosphere). The accuracies of the temperature measurement and control are within ±1°C at $T<1600$°C and ±10°C at $T>1600$°C. The Pt–Pt10Rh thermocouple and optical pyrometer used in the experiments were calibrated against materials of known melting points, including K_2SO_4 (1069°), CaO·MgO·2SiO$_2$ (1391.5°), Ni (1454°), CaO·SiO$_2$ (1544°), Pt (1773.5°), Rh (1966°), and Ir (2454°C).

Polarizing microscopy and X-ray powder diffraction methods were used for phase identification and morphological observation. For some compositions and temperatures, the attainment of equilibrium was proved by obtaining the same final phase assemblages from different starting materials or by different heat-treatment times.

III. Results and Discussion

(1) Phase Equilibrium Diagrams

The phase diagrams constructed from the data of quenching runs (Table I)[‡] and phase identification are shown in Fig. 1. The melting behavior and crystallographic characteristics of the intermediate compounds found in these systems are reported in Table II, and carefully located invariant points are given in Table III.

These diagrams show that the addition of a rare-earth oxide

rapidly lowers the melting point of beryllium oxide. In systems containing La_2O_3 and Nd_2O_3, where intermediate binary compounds are formed, the melting point depression is striking, with the formation of deep eutectics. The eutectic temperatures of the systems La_2O_3-BeO and Nd_2O_3-BeO are ≈1100°C lower than the melting point of pure BeO.

As the atomic number of the rare-earth element increases, the tendency toward beryllate formation diminishes. From La to Sm, the primary crystallization regions of the beryllates become increasingly narrow; this region for $Sm_2O_3 \cdot 2BeO$ covers a temperature interval of only a few degrees. In systems containing oxides of rare-earth elements with atomic numbers greater than that of Gd, no stable binary compounds were detected.

Intermediate compounds with the molecular ratio of 3:2 were identified in the systems La_2O_3-BeO and Nd_2O_3-BeO, in which excess BeO forms solid solutions. RE_2O_3:2BeO intermediate compounds were found to exist in all the systems studied, but they crystallize as stable phases only in the systems La_2O_3-BeO and Sm_2O_3-BeO. The 1:2 beryllates of Gd, Ho, Yb, and Y occur only as metastable phases obtained when melts of the proper composition are quenched from high temperatures. Careful examination of quenched samples showed no trace of a primary phase region for $Nd_2O_3 \cdot 2BeO$, although the atomic number of Nd is smaller than that of Sm. Judging from the very flat liquidus curve of $La_2O_3 \cdot 2BeO$ and the incongruently melting behavior of $Sm_2O_3 \cdot 2BeO$ in the related systems, it is possible that the phase field of neodymium beryllate rich in BeO can be actually hidden by the crystallization field of $3Nd_2O_3 \cdot 2BeO$.

The metastable beryllates can be distinguished from BeO and rare-earth oxide phases by their characteristic X-ray diffraction pattern, refractive indices, and microhardness values (Table IV). These beryllates appear to have a molecular ratio of 1:2, since almost single-phase crystals with wavy extinction can be obtained from quenched samples containing 50 mol% $REO_{1.5}$. Also, for samples prepared with a rare-earth oxide content slightly greater than 50 mol% $REO_{1.5}$, the rare-earth oxide invariably begins to appear in coexistence with the metastable phase when the batches are melted and quenched.

The metastable beryllates transform into equilibrium phases on heat treatment at temperatures below their eutectic points.

(2) Crystal Chemistry

As predicted from principles of structural chemistry, the small size of the beryllium ion in oxide crystals would result in a rather

Table IV.   Microscopic Characteristics of Metastable Compounds in Rare-Earth Oxide-Beryllium Oxide Systems

Composition	Refractive indices		Microhardness (GPa)
	n_α	n_γ	
$Dy_2O_3 \cdot 2BeO$	1.858	1.890	9.855–13.85
$Ho_2O_3 \cdot 2BeO$	1.882	1.918	11.08 ± 0.39*
$Er_2O_3 \cdot 2BeO$	1.842	1.910	9.807–10.51
$Yb_2O_3 \cdot 2BeO$	1.853	1.878	9.993–10.58
$Lu_2O_3 \cdot 2BeO$	1.837	1.868	11.40 –11.53
$Y_2O_3 \cdot 2BeO$	1.823	1.859	10.51 –11.77
Dy_2O_3	1.955		7.12 – 7.51
Ho_2O_3	1.916		6.91 ± 0.10*
Er_2O_3	1.950		7.41 – 7.78
Yb_2O_3	1.945		7.65 – 8.91
Lu_2O_3	1.923		8.06 – 9.59
Y_2O_3	1.890		7.86 – 8.48
BeO	1.718	1.733	12.18 –17.31

*Mean value.

high polarizing power and inflict large deformations on the oxygen ions. The Be–O bond may thus be expected to exhibit considerable covalent character. It is reasonable that BeO would act as an acid while reacting with rare-earth oxides, since rare-earth ions are much larger than Be^{2+}. The monomers BeO_x^{-2x+2} might be polymerized into complex anions $[(BeO_x^{-2x+2})_n, x > 1]$, which would further combine with rare-earth ions to form beryllates. Investigations by other workers of the crystal structures of La and Y beryllates[6,7] have confirmed this configuration. Each Be atom is surrounded by three or four O atoms, whereas the number of O atoms coordinated with each rare-earth atom is much larger. On the other hand, because of the low strength of the Be–O bond (½ that of the Si–O bond and ½ to ⅔ that of the B–O bond, taking Be as tetrahedrally coordinated), Be–O polyanions would be less stable than the corresponding silicates or borates.

The incongruent melting behavior of many rare-earth beryllates might be accounted for by the tendency for Be-O polyacidic ions to dissociate at high temperatures, with the exception of $La_2O_3 \cdot 2BeO$, which is the only congruent-melting compound found in all such systems studied. However, the liquids curve also appears to be very flat. In Ref. 5, $La_2O_3 \cdot 2BeO$ is shown as an incongruent phase in the system La_2O_3-BeO and is located at the corner of the primary BeO crystallization region. The very narrow $La_2O_3 \cdot 2BeO$ crystallization field shown in Fig. 1 might account for this discrepancy, since it might be easily missed in quenching studies. However, the fact that large crystals with optical quality have been prepared by the Czochralski technique seems to confirm the congruent melting behavior of $La_2O_3 \cdot 2BeO$. Similarly, the very small primary phase field of $Sm_2O_3 \cdot 2BeO$ and its incongruent melting behavior might also be the reason why this compound was not detected in the study of the binary system by the thermal analysis method.[5]

(3) Formation of Metastable Beryllates

In addition to the metastable beryllates identified in the Nd, Gd, Ho, Yb, and Y oxide systems, metastable beryllates of Dy, Er, and Lu were also prepared (Table IV). These beryllates are similar to the metastable phases in the other systems, in that they can be obtained only by quenching of melts and are transformed into the corresponding oxides during heat treatment at temperatures below the solidus temperature (Fig. 2).

Crystallization of nonequilibrium phases in glasses or melts of systems involving high-temperature oxides is common. Similar phenomena have been found with alkaline-earth as well as Y beryllates.[7-10] In the formation of beryllates of rare-earth elements from La to Lu, it could reasonably be expected that the effect of the size of the rare-earth ion would be a determining factor. As the ionic radius decreases, the covalent nature of the rare-earth–oxygen bond increases, due to the increasing polarizing power of the cation, thereby reducing somewhat the stability of the Be-O polyanion and, consequently, the tendency toward formation of stable beryllates.

Furthermore, it was shown that during the formation of the metastable $Gd_2O_3 \cdot 2BeO$ phase, the eutectic point of compositions in the region $Gd_2O_3 \cdot 2BeO$-Gd_2O_3 is only $\approx 4°C$ lower than that of BeO and Gd_2O_3 in equilibrium.[2] It is obvious that the difference between the equilibrium and nonequilibrium liquidus is rather trivial.

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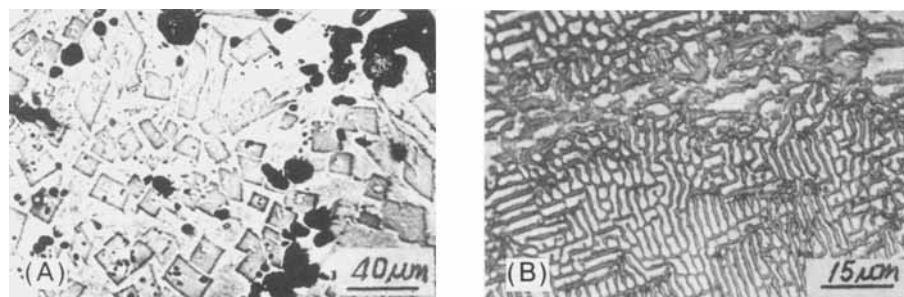

Fig. 2. (A) Metastable $Y_2O_3 \cdot 2BeO$ crystals and (B) BeO and Ho_2O_3 equilibrium phases formed by decomposition of metastable compound at 1495°C for 10 min.