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HIGH-PRESSURE SYNTHESIS AND CHARACTERIZATION OF EUROPIUM(II) METASILICATE, $EuSiO_3$

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The high-pressure polymorphism of $EuSiO_3$ was studied up to a pressure of 80 kb at 1000 - 1400°C. Two high-pressure phases were obtained in addition to the atmospheric one: α-$EuSiO_3$ was transformed into δ and δ' forms at about 60 and 70 kb, respectively. Their crystal data were determined by means of X-ray diffraction analyses.

Divalent-europium (Eu^{II}) compounds have been synthesized because they are interested in the magnetic and spectroscopic properties. In a binary system EuO - SiO_2, $EuSiO_3$, Eu_2SiO_4, and Eu_3SiO_5 have been obtained, and their magnetic susceptibilities1) and magneto-optical properties2) have been studied at low temperature. For alkaline-earth metasilicates, $CaSiO_3$ and $SrSiO_3$, several high-pressure phases have been prepared: α- or β-$CaSiO_3$ (atmospheric form) transforms into the δ form at about 30 kb and 900°C, and the ε form at about 150 kb and 1000°C, respectively.3) The strontium metasilicate, α-$SrSiO_3$, gives two high-pressure phases at 34 - 120 kb and 750 - 1400°C.4) Consequently, $EuSiO_3$ can be expected to show the same polymorphism as $CaSiO_3$ or $SrSiO_3$ since the ionic radius of Eu^{2+} is similar to that of Ca^{2+} or Sr^{2+}.

The atmospheric-pressure phase, α-$EuSiO_3$, was prepared by heating a mixture of the appropriate amounts of Eu_2O_3 (99.99%), Si (99.999%) and SiO_2 (99.999%) at 1400°C for 3 × 2 h (two times) in Ar. The high-pressure treatments of α-$EuSiO_3$ were carried out with a cubic anvil type apparatus (∿ 60 kb)5) and a split-sphere type apparatus

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(60 - 80 kb).[6)] The powdered sample was packed into boron nitride cups (6 mmϕ × 3.2 mm for the former apparatus or 3.5 mmϕ × 4 mm for the latter one) and was heated by a graphite heater. A Pt/Pt-13%Rh thermocouple was employed to measure a temperature of sample. After maintaining the desired pressure and temperature, the samples were quenched to room temperature and then the pressure was released.

The X-ray powder analysis of resulting phases was performed with the Ni-filtered Cu K$\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) monochromated by a graphite plate on a Rigaku Denki Rotaflex diffractometer, which was calibrated with high purity silicon (99.999%). The accurate lattice parameters were determined by the least-square method. The magnetic susceptibilities of samples were measured with a Shimadzu MB-11 magnetic balance over a temperature range of 80 - 300 K.

Under the pressures of about 60 and 70 kb at 1000 - 1400°C, α-$EuSiO_3$ transformed into two high-pressure phases, which were termed in a similar manner as the calcium analogs, <u>viz</u>. δ- and δ′-$EuSiO_3$. The Eu^{2+} ions tend to be easily oxidized into Eu^{3+} ions in an oxidizing atmosphere, <u>e.g</u>. air, at high temperature. The effective magnetic moments per Eu^{2+} ion for resulting products are shown in Table 1. Since the values of $\mu_{eff.}$ are in good agreement with the theoretical one (7.94 μ_B), the ions of Eu in samples should be in a divalent state.

Table 1. Magnetic moments for the high-pressure polymorphs of $EuSiO_3$

Phase	Treatment		$\mu_{eff.}$ (μ_B)*
	P(kb)	T(°C)	
α			7.95
δ	60	1000	7.72
δ′	70	1200	7.83

*$\mu_{eff.}$ = Magnetic moment per Eu^{2+} ion.

The X-ray powder patterns of resulting products (Tables 2 - 4) were found to be closely similar to those of strontium analogs of which the ionic radius is almost equal to that of Eu^{2+}. The single crystals of $EuSiO_3$ polymorphs could be hardly obtained. Therefore, the crystal data of $EuSiO_3$ polymorphs were determined on the basis of Weissenberg photographs and X-ray analyses with an automated four-circle diffractometer for the single crystals of strontium analogs. The single crystals of $SrSiO_3$ analogs were prepared from a mixture containing KCl as a flux ($SrSiO_3$: KCl = 10 : 1 for mol. wt. ratio) as follows: the samples were maintained under the appropriate pressure (α phase, 35 kb; δ phase, 40 kb; δ′ phase, 55 kb) at 1300 or 1400°C for 1 h and then were cooled to 800°C at a rate of 2°C/min. Transparent crystals (∿ 0.3 mm long) were obtained, of which the crystal habits were plates for the α and δ′ forms, and needles for the δ one. The crystal data of $EuSiO_3$ polymorphs are summarized in Table 5.

The crystal data of α- and δ-$SrSiO_3$ have been reported as follows: α form, hexa-

Table 2. X-ray powder diffraction data for α-$EuSiO_3$

hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0
002	5.08	5.07	50	004	2.540	2.533	20	$\bar{1}34$	1.7841	1.7826	20
020	3.571	3.571	85	023	2.456	2.453	5	$\bar{6}22$		1.7818	
$\bar{3}11$		3.571		222	2.399	2.403	10	224	1.7819	1.7807	20
$\bar{2}03$	3.536	3.533	15	$\bar{4}22$	2.299	2.304	25	$\bar{4}25$	1.7770	1.7760	15
$\bar{3}10$	3.370	3.371	25	313	2.070	2.073	40	$\bar{4}06$	1.7615	1.7665	5
021		3.368		024	2.068	2.066	45	332		1.7627	
$\bar{3}12$	3.353	3.352	15	223		2.065		006	1.6875	1.6884	15
202	3.242	3.250	15	421	2.064	2.063	50	620	1.6852	1.6856	15
$\bar{1}13$	3.223	3.229	70	$\bar{3}31$	2.061	2.060	35	042	1.6835	1.6837	20
220	3.026	3.031	10	132	2.058	2.060	25	$\bar{6}24$	1.6761	1.6761	5
311	2.926	2.927	85	600	1.9109	1.9120	40	$\bar{5}33$	1.6671	1.6685	20
022	2.915	2.918	100	331		1.9118		$\bar{5}16$	1.6428	1.6429	15
$\bar{3}13$	2.897	2.902	20	$\bar{3}33$	1.9056	1.9048	30	333	1.6016	1.6022	15
400	2.877	2.868	15	040	1.7871	1.7852	35	710	1.5979	1.5974	15
$\bar{2}22$	2.868	2.857	35					$\bar{3}35$	1.5926	1.5941	5

Table 3. X-ray powder diffraction data for δ-$EuSiO_3$

hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0
$1\bar{1}0$	5.18	5.20	30	120	2.705	2.708	45	$\bar{1}24$	2.050	2.052	15
$\bar{1}11$		5.20		$\bar{1}\bar{2}1$		2.706		$1\bar{2}3$		2.050	
012	3.753	3.768	15	022	2.698	2.699	40	$2\bar{2}2$	2.023	2.023	15
$0\bar{1}2$		3.761		201	2.693	2.695	50	$\bar{2}24$		2.023	
111	3.485	3.481	70	$0\bar{2}2$		2.694		032	2.008	2.005	10
$\bar{1}\bar{1}2$	3.477	3.471	70	$\bar{2}03$	2.686	2.688	30	$0\bar{3}2$	2.002	2.002	10
020	3.346	3.347	15	$2\bar{1}1$		2.687		130	1.9646	1.9660	20
$\bar{2}01$	3.328	3.336	15	210	2.615	2.620	15	$\bar{1}\bar{3}1$		1.9648	
$\bar{1}21$	3.276	3.278	25	$\bar{2}\bar{1}2$		2.616		$\bar{3}\bar{1}1$	1.9586	1.9619	20
$1\bar{2}0$		3.277		$2\bar{2}0$	2.602	2.601	15	$\bar{3}\bar{1}2$		1.9607	
102	3.215	3.201	25	$\bar{2}22$		2.600		$\bar{1}33$	1.9388	1.9392	20
$\bar{1}03$		3.194		$1\bar{1}3$	2.348	2.347	15	$1\bar{3}2$		1.9369	
021	3.146	3.143	70	$\bar{1}14$		2.346		221	1.9296	1.9242	20
$0\bar{2}1$	3.138	3.139	90	$2\bar{2}1$	2.327	2.331	10	$\bar{2}33$	1.9108	1.9108	10
200	3.127	3.135	80	$\bar{2}23$		2.331		$2\bar{3}1$		1.9102	
$\bar{2}02$	3.121	3.130	65	004	2.274	2.277	15	123	1.8855	1.8886	25
$2\bar{1}0$	3.116	3.124	45	$\bar{1}31$	2.271	2.272	30	024	1.8841	1.8842	25
$\bar{2}12$		3.121		$1\bar{3}0$		2.271		$\bar{1}\bar{2}4$	1.8815	1.8833	30
003	3.039	3.035	100	$\bar{3}11$	2.266	2.265	20	203		1.8827	
$1\bar{1}2$	3.023	3.025	80	$\bar{3}12$		2.264		$\bar{2}05$	1.8800	1.8782	20
$\bar{1}13$		3.024		$2\bar{1}2$	2.248	2.243	15	$\bar{2}15$	1.8756	1.8770	20
112	2.768	2.767	20	$\bar{3}01$	2.213	2.209	25	$\bar{3}\bar{1}3$	1.8735	1.8746	15
013		2.767		$\bar{3}02$		2.207		114	1.8288	1.8284	15
$0\bar{1}3$	2.755	2.762	15	031	2.167	2.168	15	$\bar{1}\bar{1}5$	1.8253	1.8242	20
$\bar{1}\bar{1}3$	2.750	2.759	10	$\bar{2}\bar{2}1$	2.127	2.120	25	$\bar{3}24$	1.8209	1.8195	15
$\bar{2}21$	2.715	2.714	25	$\bar{3}21$	2.087	2.088	15				
				$\bar{3}22$		2.087					

Table 4. X-ray powder diffraction data for δ′-$EuSiO_3$

hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0	hkl	d_o(Å)	d_c(Å)	I/I_0
012	4.29	4.27	25	211	2.601	2.600	25	024	2.133	2.136	5
$\bar{1}13$	3.576	3.587	20	$\bar{3}02$	2.477	2.473	5	123	2.094	2.095	30
013	3.350	3.345	35	202	2.462	2.466	5	221		2.089	
200	3.321	3.316	40	023	2.418	2.420	10	$\bar{2}16$	2.093	2.087	20
$\bar{2}12$	3.174	3.164	40	$\bar{3}04$	2.369	2.371	15	$\bar{1}16$	2.082	2.084	15
112	3.157	3.155	50	104	2.363	2.361	15	310	2.078	2.077	10
$\bar{2}11$	3.139	3.130	40	$\bar{2}22$	2.348	2.349	20	$\bar{1}25$	2.011	2.013	25
020	3.020	3.037	35	$\bar{2}21$	2.338	2.335	25	213	2.007	2.003	20
004	3.002	3.005	100	$\bar{3}12$	2.288	2.290	15	031	1.9962	1.9965	20
$\bar{2}13$	2.993	2.994	70	$\bar{2}12$		2.284		$\bar{2}25$	1.9724	1.9696	15
$\bar{1}14$	2.959	2.952	30	$\bar{2}23$	2.275	2.277	10	115	1.8875	1.8891	25
021	2.949	2.945	55	220	2.243	2.240	10	025	1.8831	1.8849	25
210	2.912	2.910	35	$\bar{2}06$	2.227	2.222	15	$\bar{4}04$	1.8500	1.8533	25
120	2.769	2.761	15	$\bar{1}06$	2.221	2.219	10	$\bar{2}04$	1.8483	1.8460	20
$\bar{1}22$	2.705	2.713	15	300	2.206	2.210	10	$\bar{2}17$	1.8340	1.8358	30
$\bar{2}14$	2.696	2.701	20	114	2.196	2.201	5	$\bar{3}25$	1.7845	1.7842	25
113	2.619	2.612	20	$\bar{2}24$	2.140	2.140	10				

Table 5. Crystal data for the polymorphs of $EuSiO_3$

Phase	Symmetry	S.G.	Lattice parameters (Å)	Z	Density (g/cm³)	
					Dm	Dx
α	Monoclinic	C_2^3-C2(5)	a = 12.337(6) b = 7.141(3) c = 10.894(6) β = 111.58(4)°	12	5.12	5.09
δ	Triclinic	C_i^1-$P\bar{1}$(2)	a = 6.877(3) b = 6.898(3) c = 9.727(5) α = 85.01(4)° β = 110.58(4)° γ = 104.00(4)°	6	5.36	5.42
δ′	Monoclinic	C_{2h}^5-$P2_1/c$ (14)	a = 7.455(6) b = 6.074(4) c = 13.513(10) β = 117.19(6)°	8	5.48	5.57

gonal, a = 7.127(1) and c = 10.115(1) Å; δ form, orthorhombic, a = 8.492(6), b = 10.913(7), and c = 36.25(2) Å,4) but these data are not in agreement with our results. The atmospheric phase, α-$EuSiO_3$, crystallizes in the monoclinic system of the space group C_2^3-C2 (systematic absence: h + k = 2n + 1 for hkl) with a cell volume: 892.5(6) $Å^3$ and Z = 12. Two high-pressure forms, δ- and δ'-$EuSiO_3$, belong to the triclinic and monoclinic symmetries of C_i^1-$P\bar{1}$ and C_{2h}^5-P21/c (systematic absences: δ form, no conditions; δ' form, l = 2n + 1 for h0l and k = 2n + 1 for 0k0). Their cell volumes are 419.2(3) and 544.3(6) $Å^3$, and the values of Z are 6 and 8, respectively. The determination of space groups, C_2^3-C2 and C_i^1-$P\bar{1}$, was made on the basis of the Patterson maps for the X-ray intensity data of α- and δ-$SrSiO_3$. Two forms, α- and δ-$EuSiO_3$ ($SrSiO_3$) are approximately isostructural with α- and δ-$CaSiO_3$. However the δ' form is a high-pressure polymorph observed only on $EuSiO_3$ or $SrSiO_3$.

The density of $CaSiO_3$ considerably increases when it transforms into the ε form (Dx: 2.90 g/cm^3, α-$CaSiO_3$7); 3.06 g/cm^3, δ-$CaSiO_3$8); 4.56 g/cm^3, ε-$CaSiO_3$3)) because the silicate units change from SiO_4 tetrahedra to SiO_6 octahedra. The phases, α- and δ-$CaSiO_3$, contain the $(Si_3O_9)^{6-}$ ring of three SiO_4 tetrahedra7,8) while ε-$CaSiO_3$ (perovskite type) consists of a $(SiO_3)_\infty$ network of SiO_6 octahedra.3) However, the density of $EuSiO_3$ is not appreciably changed with the phase transformation. This seems to suggest that δ'-$EuSiO_3$ ($SrSiO_3$) consists of silicate anions of SiO_4 tetrahedra in a similar manner as the α and δ forms.

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