CHEMISTRY LETTERS, pp. 81-84, 1980.

HIGH-PRESSURE SYNTHESIS AND PROPERTIES OF Eu(II)-METABORATES

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High-pressure treatments of Eu(II)-metaborate, EuB_2O_4, were made and several new phases of EuB_2O_4 were obtained. The resulting phases were characterized by X-ray analysis, magnetic susceptibility and luminescent spectral measurements.

Divalent-europium (Eu^{2+}) containing compounds have been synthesized because of their unique magnetic and spectroscopic properties. For example the monoxide, EuO, has been found to be ferromagnetic below about 80 K[1)] and possesses an unusually large magneto-optic effect.[2)] The Eu^{2+}-activated alkaline earth (e.g. Ca, Sr and Ba) compounds give the emissions consisting of a $4f^7$-$4f^6 5d$ band or a $4f^7$-$4f^7$ line spectrum.[3),4),5)]

For M(II)-metaborates, there are two types of chain construction in their structure, namely one of which consists of $(BO_2)_\infty$-chains sharing an oxygen of BO_3 unit (e.g. CaB_2O_4[6)] and SrB_2O_4) and another contains condensed-ring ions of three BO_3 units, $(B_3O_6)^{3-}$, (e.g. BaB_2O_4[7)]). The borates of former type are easily transformed into several high-pressure phases, the triangularly coordinated borons in their units partially or entirely being changed into tetrahedrally coordinated borons by high-pressure treatments.[8),9),10)]

The Eu(II)-metaborate has been synthesized and found to be antiferromagnetic below about 3 K.[11)] It also consists of $(BO_2)_\infty$-chains[12)] and is isostructural with

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the atmospheric phase CaB_2O_4(I) and SrB_2O_4(I). Consequently, it is expected that the similar polymorphism to that of the Ca- and Sr-analogs will be observed on this borate.

An atmospheric pressure phase EuB_2O_4(I) was prepared by heating the mixture of the appropriate amounts of Eu_2O_3 (99.99 %), B(99.5 %, reductant) and H_3BO_3 (99.5 %) at 1000°C for 3 h in vacuum according to the method described elsewhere.[11] The high-pressure treatments were carried out with a cubic anvil type apparatus* in the following way: the powdered samples were packed into boron nitride cups illustrated in Ref.(13). After maintaining the desired pressure and temperature conditions, 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 CuKα radiation (λ=1.5418 Å) monochromated by a graphite plate on a Rigakudenki Rotaflex diffractometer, which was calibrated with high purity silicon (99.999 %). The accurate lattice parameters of samples were determined by the least-squares method. Magnetic susceptibility measurements were carried out with a Shimadzu MB-11 over a temperature range of 80-300 K. The technique of ultraviolet luminescent measurements is described in Ref.(14).

Figure 1 and Table 1 show the phase diagram and lattice parameters for resulting phases of EuB_2O_4. Each phase obtained is termed in a similar manner as the Ca- and Sr-analogs.[10] By high-pressure treatments, EuB_2O_4(I) was found to transform into three additional phases. The two high-pressure phases EuB_2O_4(III) and (IV) crystallize in the orthorhombic system, C_{2v}^{9}-Pna2₁, with twelve molecules per unit cell and in the cubic system, T_h^6-Pa3, with twelve molecules per unit cell, respectively. Under the conditions above 40 kb and 900°C, however, the resulting phase was found to be a decomposed one of two borates, EuB_4O_7 and $Eu_2B_2O_5$, from its X-ray diffraction pattern. This decomposition can be considered to proceed as follows:

$$3\ EuB_2O_4 \longrightarrow EuB_4O_7 + Eu_2B_2O_5$$

According to this scheme the overall mole number reduces from 3 to 2, and hence the volume of samples reduces to 87.5 % and its density increases to Dx = 5.22 g/cm³. Since, as can be seen from Table 1, the value of observed density

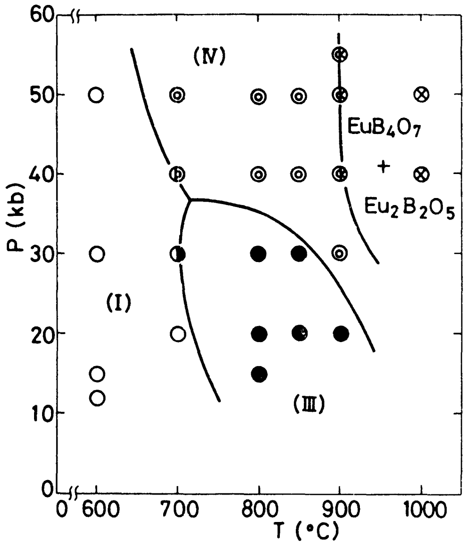

Fig. 1. Phase diagram of EuB_2O_4.

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*Dia 15, Kobe Steel, Ltd., Kobe.

(Dm = 5.22 g/cm^3) agrees with the calculated one, the above decomposition scheme is reasonable. The second phase EuB_2O_4(II) was not obtained in analogy with SrB_2O_4(II). It can be, therefore, concluded that the crystallographic properties of polymorphism of EuB_2O_4 are completely equal to those of SrB_2O_4. This is due to the similarity of ionic radius values of Eu^{2+} and Sr^{2+} ions. However their transition pressures and temperatures differ from each other: EuB_2O_4(I) transforms into other phases at higher temperature than SrB_2O_4(I). This suggests that the bond strength of Eu-O must be stronger than that of Sr-O.

Table 1. High-pressure polymorphism of EuB_2O_4

Phase	Lattice parameters (Å)			S.G.	Z	Density (g/cm^3)	
	CaB_2O_4*	SrB_2O_4*	EuB_2O_4			Dm**	Dx
I	a= 6.214 b=11.604 c= 4.284	a= 6.589 b=12.018 c= 4.337	a= 6.593(1) b=12.063(2) c= 4.343(1)	D_{2h}^{14}-Pnca	4	4.61	4.57
	↕ 12kb	↕ 8kb					
II	a= 8.369 b=13.816 c= 5.007			D_{2h}^{10}-Pccn	8		
	↕ 15kb						
III	a=11.380 b= 6.382 c=11.304	a=12.426 b= 6.418 c=11.412	a=12.44(1) b= 6.43(1) c=11.42(1)	C_{2v}^{9}-Pna2$_1$	12	5.22	5.18
	↕ 25kb	↕ 15kb					
IV	a= 9.008	a= 9.222	a= 9.240(1)	T_h^6-Pa3	12	5.57	6.00
EuB_4O_7 + $Eu_2B_2O_5$			—	—	—	5.40	5.22

*Ref.(10). The treatment temperature is 600°C for SrB_2O_4 and 900°C for CaB_2O_4.
**Data were obtained on the sintered samples with the dimensions: ca 4 ϕmm × 3 mm.

The magnetic and luminescent data obtained on the phase I (untreated), III (20 kb, 800°C), IV (50 kb, 850°C) and the decomposed phase (50 kb, 1000°C) are summarized in Table 2. Since the value of effective magnetic moment per Eu^{2+} ion ($\mu_{eff.}$) of each phase is in agreement with the theoretical one 7.94 μ_B, the Eu ion exists in divalent state. The paramagnetic Curie temperature (θ_c) was about -5 K for the phase III, about 0 K for the phase IV and about -10 K for the decomposed phase, respectively. The magnetic properties of compounds can be approximately discussed on the basis of the sign of θ_c value. In general the θ_c value is a negative one for antiferromagnets while positive for ferromagnets, and hence paramagnets should have the value of zero. The phase EuB_2O_4(I) has been found to be an antiferromagnet with T_N= 3 K and θ_c= -5 K. It can be, therefore, presumed from the θ_c values that the phase III and the decomposed phase are antiferromagnetic and the phase IV is paramagnetic at low temperature.

Table 2. Magnetic and luminescent data for the various phases of EuB_2O_4

Phase	Treatment P (kb)	 T (°C)	$\mu_{eff.}(\mu_B)$*	θ_c(K)**	λ_{max}(nm)***	I****
I	—	—	7.88	-5	370	very weak
III	20	800	7.42	-5	370	very weak
IV	50	850	7.62	0	410	weak
$EuB_4O_7 + Eu_2B_2O_5$	50	1000	7.54	-10	368,395	weak

*$\mu_{eff.}$ = Magnetic moment per Eu^{2+} ion. **θ_c = Paramagnetic Curie temperature. ***λ_{max} = Position of the maximum of emission band. ****I = Emission intensity.

The high-pressure phases of EuB_2O_4 were found to give the band emissions based on the $4f^7$-$4f^65d$ transition of Eu^{2+} ion, and the peak positions of their emissions shifted to longer wavelength and their light outputs slightly increased with transforming into the phase IV and the decomposed phase. The emission of the phase IV and the decomposed phase consist of a band at about 410 nm and two bands at about 368 and 395 nm, respectively, whereas the phase I and III give a very weak emission at about 370 nm. The emission at about 370 nm of the decomposed phase must be attributed to one of resulting products of decomposition, EuB_4O_7, since it gives a relatively strong emission at about 370 nm.14)

The magnetic and luminescent properties of Eu^{2+} ion closely relate to the crystal structure, e.g. the Eu coordination to oxygen and the structural framework. The detailed discussion of the relationship between the structures and properties of the high-pressure phases of EuB_2O_4 will be made elsewhere.

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(Received November 5, 1979)