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SYNTHESIS AND MAGNETIC PROPERTY OF EUROPIUM(II) HALOBORATES, Eu_2BO_3X (X=Cl and Br)

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New europium(II) haloborates, Eu_2BO_3X (X=Cl and Br), were prepared by solid state reactions of $Eu_3(BO_3)_2$ and $EuCl_2$ or $EuBr_2$, and were found to be ferromagnets with $4.2<T_c<5$ K. The hexagonal-prismlike single crystals, which have been grown from the molten samples containing a large excess of EuX_2 as a flux, crystallize in the hexagonal system (space group: $P6_3mc$).

Some of europium(II) containing compounds have been synthesized directing toward ferromagnets caused by exchange interactions between neighboring Eu^{2+} ions$^{1)}$ or phosphors giving blue to green emissions based on the $4f^7$-$4f^7$ or $4f^7$-$4f^6 5d$ transition of Eu^{2+} ions.$^{2)}$ These physical properties are closely related to the crystal structures, the distances between neighboring Eu^{2+} ions and the anion environments around Eu^{2+} ions. Recently we have synthesized a ferromagnetic compound, $Eu_3(BO_3)_2$ (T_c=7.5 K), and discussed the magnetism by considering the crystal structure.$^{3)}$ In a ternary system EuO-EuX_2-B_2O_3, $Eu_2B_5O_9X$ type haloborates have been obtained,$^{4)}$ and the alkaline-earth analogs activated by Eu^{2+} ions have been found to be efficient photoluminescence materials.$^{5)}$

Hanic and co-workers$^{6)}$ have obtained a new chloroborate, Ca_2BO_3Cl, as an intermediate phase in a system $Ca_3(BO_3)_2$-$CaCl_2$ and performed the X-ray structural analysis to show that the structure consists of Ca^{2+}, Cl^-, and BO_3^{3-} ions arranged in distinct, mutually alternating anionic and cationic layers. This suggests that the europium(II) analogs, Eu_2BO_3X, also are obtainable in the system EuO-EuX_2-B_2O_3.

The europium(II) haloborates were prepared as follows: the mixtures of $Eu_3(BO_3)_2$ and EuX_2 (mol. ratio=1:1) were pelletized and preheated at 300°C for several hours in

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vacuo, in order to remove the adsorption water, and then the samples were heated at 900°C for 2 h in He. The resulting materials were colored with dark-brown. The preparation method of $Eu_3(BO_3)_2$ is described elsewhere,[3a] and EuX_2 can be easily prepared by heating $EuX_3 \cdot nH_2O$ together with a large excess of NH_4X at 650-700°C for a few hours in a reducing atmosphere. The single crystals were grown from the molten samples containing a large excess of EuX_2 as a flux by cooling at a rate of about 3°C/h from 1050 to 800°C. Their crystal habits were hexagonal-prismatic (∿2 mm) and the color was black.

The cell parameters of resulting materials were determined using a Weissenberg camera and a Rigaku automated four-circle diffractometer, and were refined by the least-square method from X-ray powder diffraction patterns obtained with the Ni-filtered Cu $K\bar{\alpha}$ radiation (λ=1.5418 Å) monochromated by a graphite plate on a Rigaku Rotaflex diffractometer using high-purity silicon as an internal standard. The magnetizations and magnetic susceptibilities of powder samples were measured with a Shimadzu MB-11 over a temperature range of 4.2-300 K.

The cell parameters of Eu_2BO_3X are summarized in Table 1. These haloborates are entirely isostructural with each other: Eu_2BO_3X belongs to the hexagonal system and shows a systematic absence, l=2n+1 for hhl. It is concluded, from the Patterson maps calculated on the basis of the intensity data, that the space group of Eu_2BO_3X is $P6_3mc$. The observed and calculated densities suggest that the value of Z is 6. The X-ray diffraction pattern of Eu_2BO_3Br is given in Table 2.

Table 1. Crystal data for Eu_2BO_3X

	Eu_2BO_3Cl	Eu_2BO_3Br
F.W.	398.18	442.64
Symmetry	Hexagonal	
S.G.	$P6_3mc$ (l=2n+1 for hhl)	
a (Å)	10.585(3)	10.598(1)
c (Å)	6.804(2)	6.845(1)
V (Å^3)	660.3(4)	665.8(2)
Z	6	
Dm (g/cm^3)	5.95	6.55
Dx (g/cm^3)	6.01	6.63

The chloroborate, Ca_2BO_3Cl, has been reported to crystallize in the monoclinic system with cell dimensions: a=3.9484(4), b=8.692(2), c=12.402(2) Å, β=100.27(1)°, and Z=4. These crystal data considerably differ from those of Eu_2BO_3X, and the symmetry of the latter compounds is higher than that of Ca_2BO_3Cl. The structure of Ca_2BO_3Cl consists of distorted BO_3^{3-} ions, but the BO_3^{3-} ion in Eu_2BO_3X seems to be a triangle with high symmetry, e.g. a symmetry of threefold rotation.

The europium(II) haloborates were found to be ferromagnets from the measurements of magnetizations at low temperature. In Figs. 1 and 2, we show the temperature and

Table 2. X-ray diffraction data for Eu_2BO_3Br

hkl	d_{obst}	d_{calcd}	I/I_0	hkl	d_{obst}	d_{calcd}	I/I_0	hkl	d_{obst}	d_{calcd}	I/I_0	hkl	d_{obst}	d_{calcd}	I/I_0
101	5.50	5.49	20	300	3.060	3.059	20	401	2.176	2.176	30	322	1.7939	1.7933	11
110	5.31	5.30	15	301	2.795	2.793	20	222	2.093	2.095	25	330	1.7728	1.7662	25
200	4.60	4.59	25	202	2.745	2.744	100	312	2.043	2.043	20	421	1.6817	1.6813	30
201	3.814	3.812	45	220	2.650	2.649	85	321	2.012	2.013	30	510	1.6483	1.6484	10
002	3.430	3.423	25	310	2.548	2.545	15	411	1.9233	1.9222	10	114	1.6282	1.6284	10
102	3.207	3.207	20	400	2.283	2.294	15	402	1.9058	1.9058	50	204	1.6035	1.6034	25
211	3.096	3.094	65	103	2.214	2.214	35	303	1.8289	1.8290	15	422	1.5467	1.5471	35

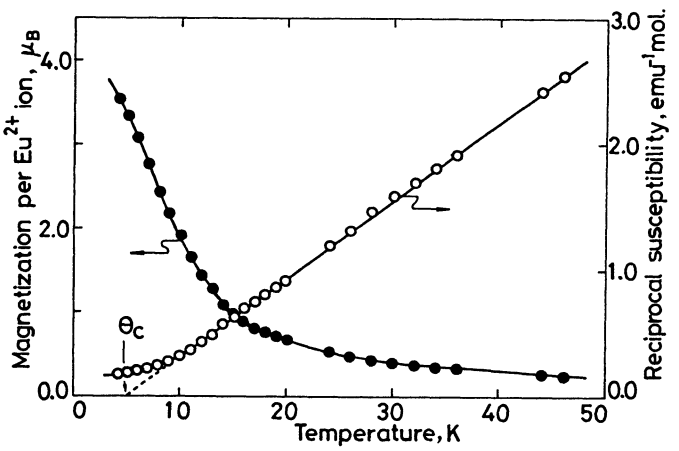

Fig. 1. Temperature dependences for the magnetization and reciprocal susceptibility of Eu_2BO_3Br. The applied magnetic field is 3.5 kOe.

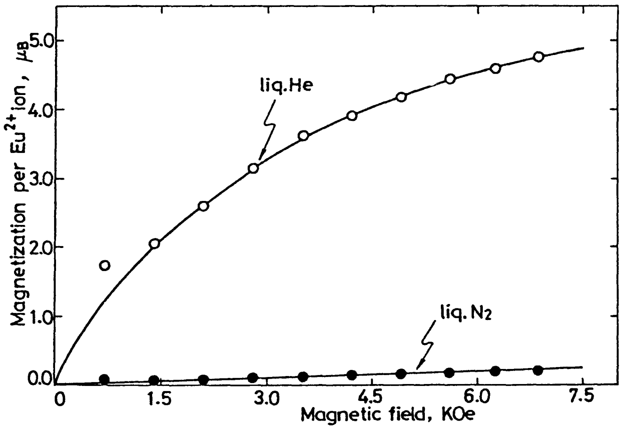

Fig. 2. Magnetic field dependences for the magnetizations of Eu_2BO_3Br at liq.He (4.2 K) and liq.N_2 (77.4 K) temperatures.

magnetic field dependences for the magnetization and reciprocal susceptibility of Eu_2BO_3Br. From Fig. 1, the reciprocal susceptibility can be seen to be proportional to the temperature above 10 K, but at the temperature below 10 K the reciprocal susceptibility deviates from the Curie-Weiss law. The paramagnetic Curie temperature is about 5 K. For the magnetic field dependence of the magnetization at liq. He temperature (see Fig. 2), one can observe that the magnetization curve is asymptotic to the value at which the spins of the 4f electrons of Eu^{2+} ion are ferromagnetically arranged. It is, therefore, concluded that Eu_2BO_3Br is a ferromagnet with $4.2<T_c<5$ K.

In Table 3, we summarize the magnetic and structural properties for some europium(II compounds. The magnetisms of these compounds are interpreted by considering the exchange and superexchange interactions between the neighboring Eu^{2+} ions, which are sensitive to the Eu^{2+}-Eu^{2+} spacing. The Eu^{2+} ions in Eu_2BO_3X are located at two kinds of sites, Eu(1) and Eu(2). From the model of Eu_2BO_3Br structure with R=0.10 for observed, non-equivalent 566 reflections, mean distances between the neighboring Eu^{2+} ions are estimated to be 3.60 or 3.63 Å for the nearest neighbors and 5.27 or 5.14 Å

Table 3. Magnetic and structural properties for some europium(II) compounds

Compound	Magnetism	$\mu_{eff}(\mu_B)^a$	T_c(K)	$\theta_c(K)^b$	Atom	Mean Eu-Eu dist.(Å)^c nn	nnn	Ref.
$Eu_3(BO_3)_2$	Ferromagnetic	7.74	7.5	8	Eu	3.688(×6)	5.450(×4)	3
$EuBr_2$	Paramagnetic	7.87	—	0	Eu(1) Eu(2)	4.98(×9) 4.86(×8)	6.19(×5) 5.99(×4)	7
Eu_2BO_3Br	Ferromagnetic	7.85	$4.2\sim5$	5	Eu(1) Eu(2)	3.60(×6) 3.63(×4)	5.27(×6) 5.14(×4)	This work
$Eu_2B_5O_9Br$	Paramagnetic	7.73	—	≃0	Eu(1) Eu(2)	4.432(×4)	5.589(×4) 5.796(×4)	7

[a] μ_{eff}= magnetic moment per Eu^{2+} ion. The theoretical value is 7.94 μ_B.

[b] θ_c= paramagnetic Curie temperature.

[c] nn and nnn represent the nearest and second-nearest Eu neighbors, respectively.

for the second-nearest neighbors, respectively. These distances are comparable to that of $Eu_3(BO_3)_2$ with T_c=7.5 K, and hence the magnetic interactions in Eu_2BO_3Br are effective for the ferromagnetic interactions at low temperature. Since the superexchange interaction via X^- ion is less contributable than that interaction via O^{2-} ion, however, the T_c value of Eu_2BO_3Br would be low compared with that of $Eu_3(BO_3)_2$.

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