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Preparation and Oxidation of Europium(II) Niobium Bronze Eu_xNbO_{3-y}

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Mixed oxides containing bivalent europium, Eu_xNbO_{3-y} ($0.5<x<1.0$), were synthesized by the solid state reaction of Eu_2O_3, Nb_2O_5, and Nb powder. The structural change of Eu_xNbO_{3-y} from a tetragonal to cubic form takes place at $x=0.65$. The mechanism of oxidation for the bronzes was studied. Each bronze shows different behavior in oxidation, the cubic bronze giving an amorphous phase and the tetragonal bronze complex crystalline products. $EuNbO_4$ was crystallized from both the amorphous and crystalline phases at 950 K and 1070 K, respectively. TG-DTA and magnetic studies indicated that the oxidized phases play an important role in the rate-determining step of oxidation for the bronzes.

Europium (II) niobium bronzes are nonstoichiometric compounds. Fayolle *et al.*[1] reported the preparation of the bronzes. They found a cubic form for a high Eu^{2+} content region and a tetragonal form for a low Eu^{2+} content region. Oxidation of the bronzes has attracted our attention because each phase undergoes changes in different ways. Krylov *et al.*[2] reported on the oxidation of the bronze whose composition is $EuNbO_3$ and concluded that $EuNbO_4$ is an oxidized product of $EuNbO_3$. So far stoichiometry of oxygen of the bronzes has not been considered seriously. However, oxygen content is a very influential factor for understanding the physical and chemical properties of the bronzes, since the valence state of niobium is controlled by the amount of oxygen. We have determined the oxygen content thermogravimetrically, and found that the bronze is described by a general formula, Eu_xNbO_{3-y}. Discussion is given on the oxidation process of the bronze.

Experimental

Reagents. Europium sesquioxide (Shin-etsu Chemical Corp., minimum purity 99.99%), diniobium pentaoxide and niobium metal (Wako Chemical Industries, Ltd., purity 99.99%, and 99.9%, respectively). Europium sesquioxide and diniobium pentaoxide were calcinated at 1000 K for half an hour in the air before being weighed.

Preparative. Mixtures of Eu_2O_3, Nb_2O_5, and Nb with various compositions were ground together in an agate mortar, pressed into pellets and heated in a vacuum (10^{-2} Pa) at 1173 K for 2 h. After cooling, the pellets were grounded and pressed into pellets again. They were packed into a Mo box, sealed in a vacuum (10^{-3} Pa) in a silica capsule and heated at 1473 K for 48 h. The reaction was assumed to occur according to the reaction

$$5xEu_2O_3 + a(6x-2)Nb + (5+a-3ax)Nb_2O_5 \longrightarrow 10Eu_xNbO_{3-y}. \quad (1)$$

Niobium metal was taken a times the amount needed to prepared Eu_xNbO_3 in order to compensate slight oxidation loss of the bronzes during the course of synthesis. Reaction conditions and analytical values of the bronzes are summarized in Table 1.

Analytical Method. The atomic ratios (Eu:Nb) in the compounds obtained were determined with a Rigaku Denki energy dispersion type X-ray fluorescent spectrograph unit, "Ultra trace system," having a tungsten target X-ray tube, a stannum second target, and a Si(Li) semiconductor detector. The oxygen content was determined by oxidation of the bronzes in the air. Assuming that the reaction is

$$Eu_xNbO_{3-y} + zO_2 \longrightarrow \frac{x}{2}Eu_2O_3 + \frac{1}{2}Nb_2O_5, \quad (2)$$

y can be determined by means of Eu content (x) and the increase in mass due to oxidation (z). The phase purity and structure type of materials were characterized by X-ray powder data, using a Rigaku Denki "Rotor-flex" diffractometer (Table 2).

Magnetic Measurements. The magnetic susceptibility data of the resulting materials were obtained with a Shimadzu "MB-11" magnetic balance (Table 2).

Thermal Measurements. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in the air at a heating rate of 10 K/min in the tempera-

Table 1. Reaction conditions and analysis of Eu_xNbO_{3-y}

Exp. No.	Reaction mix		Condition		Analytical composition	
	x	a[a]	Temp/K	Time/h	x	y
24	0.50	1.05	1473	48	0.51	+0.02
30	0.55	1.05	1473	48	0.56	−0.01
25	0.60	1.05	1473	48	0.59	−0.01
31	0.65	1.05	1473	48	0.65	0.00
26	0.70	1.05	1473	48	0.70	−0.10
32	0.75	1.05	1473	48	0.72	−0.06
27	0.80	1.05	1473	48	0.79	+0.05
33	0.85	1.05	1473	48	0.85	+0.01
28	0.90	1.05	1473	48	0.89	−0.02
34	0.95	1.05	1473	48	0.91	−0.05
29	1.00	1.05	1473	48	0.97	−0.13

a) Niobium metal was taken a times the amount needed to prepare Eu_xNbO_3.

Table 2. Lattice constants and magnetic properties for Eu_xNbO_{3-y}

Exp. No.	Eu_xNbO_{3-y}		Lattice constants			Magnetic moments	
	x	y	(Cubic) a/Å	(Tetragonal) a/Å	(Tetragonal) c/Å	Obsd/μ_B	Calcd/μ_B[a]
24	0.51	+0.02		12.355	3.901	5.47	5.69
30	0.56	−0.01		12.363	3.892	5.89	5.97
25	0.59	−0.01		12.361	3.885	5.75	6.14
31	0.65	0.00	3.978			6.24	6.47
26	0.70	−0.10	3.980			6.13	6.69
32	0.72	−0.06	3.985			6.46	6.81
27	0.79	+0.05	4.002			6.77	7.20
33	0.85	+0.01	4.009			7.10	7.47
28	0.89	−0.02	4.012			7.26	7.64
34	0.91	−0.05	4.013			7.43	7.72
29	0.97	−0.13	4.016			7.64	7.95

a) Magnetic moment (calcd) $= \sqrt{x\mu^2(Eu^{2+})+(Nb^{4+}/Nb)\mu^2(Nb^{4+})}$, $\mu(Eu^{2+})=7.94\mu_B$, $\mu(Nb^{4+})=1.73\mu_B$.

ture range 300—1173 K. All thermal measurements were performed on a Rigaku Denki DTA "Thermoflex." Powder samples (30—60 mg) were used, alumina powder (99.9%) being employed as a reference. The heat of oxidation for the bronzes was measured with a differential scanning calorimeter (DSC). Measurements were carried out in the air at a heating rate of 10 K/min in the temperature range 300—1173 K. The heat of oxidation was determined from the area beneath a DSC peak. The heat of oxidation of NbO_2 to Nb_2O_5 was used as a standard.[8]

Results and Discussion

X-Ray Data. X-Ray analysis revealed that the samples having europium concentration x=0.5—0.65 are of tetragonal symmetry, and those with x=0.65—1.0 cubic symmetry (Table 2). A small amount of Eu_3NbO_6 confirmed by the X-ray technique was assigned to a second phase for the slightly oxidized bronzes of high europium concentration (x>0.9). Oxidation tendency of the bronzes seemed to increase with x, 1.2 times excess of reducing agent being required for the preparation of single phase bronzes. The niobate Eu_3NbO_6 seems to be formed by the solid state reaction in the bronze of high x. A plot

$$Eu_xNbO_{3-y} \longrightarrow aEu_3NbO_6 + (1-a)Eu_{\frac{x-3a}{1-a}}NbO_{3-\frac{y-6a}{1-a}} \qquad (3)$$

of the lattice constant *vs.* the europium concentration of the cubic phase for x=0.65 to 1.0 is given in Fig. 1. Ridgley and Ward[9] reported that the lattice constant for an analogous bronze, Sr_xNbO_3, of cubic symmetry is proportional to x. However, our observation (Fig. 1) does not agree with theirs. The result of X-ray analysis supports the assumption that the solid state reaction (Eq. 3) takes place at high x.

Magnetic Susceptibilities. The magnetic susceptibilities χ_m of the bronzes obey the Curie-Weiss law in the range 77—300 K. The observed and calculated values of effective magnetic moments for the bronzes are summarized in Table 2. The observed moments are close to the calculated values, small lowering of the observed magnetic moments exceeding experimental errors being observed. Europium ions in the starting material are considered to be substantially reduced to the Eu (II) state. However, the reduction power of niobium is not strong enough to reduce all of Eu^{3+} to Eu^{2+},[4] a small amount of Eu^{3+} remaining with Eu^{2+}. The lowering observed in our products would also be interpreted in terms of the reduction power of niobium.

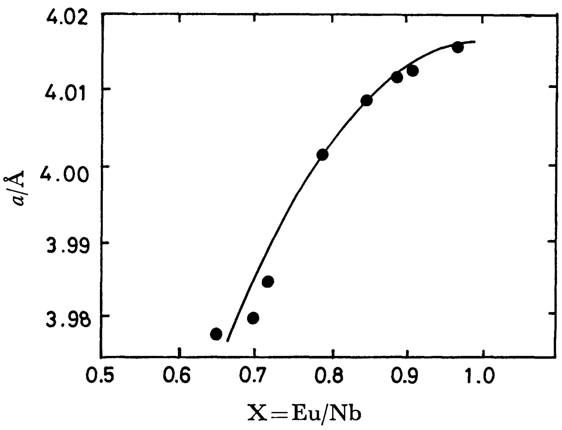

Fig. 1. The variation of lattice constant with europium content in the cubic phase Eu_xNbO_{3-y}.

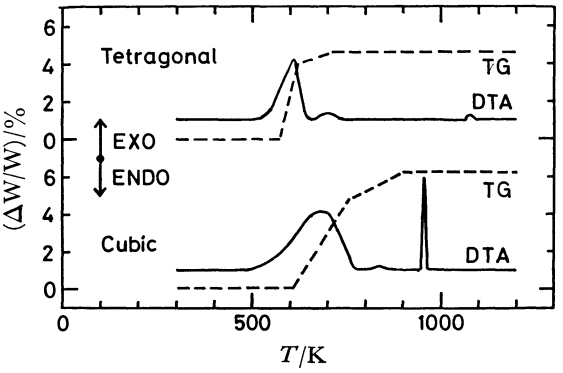

Fig. 2. TGA and DTA curves of $Eu_{0.51}NbO_{2.98}$ (tetragonal) and $Eu_{0.74}MbO_{2.81}$ (cubic).

Thermal Analysis. Typical TGA and DTA

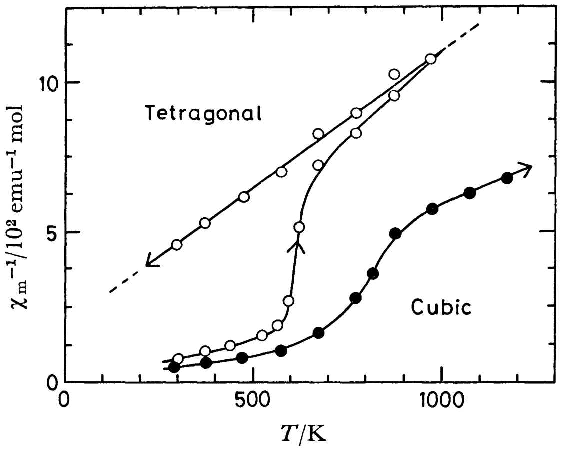

Fig. 3. Inverse magnetic susceptibility *vs.* temperature for $Eu_{0.51}NbO_{2.98}$ (tetragonal) and $Eu_{0.74}NbO_{2.81}$ (cubic).

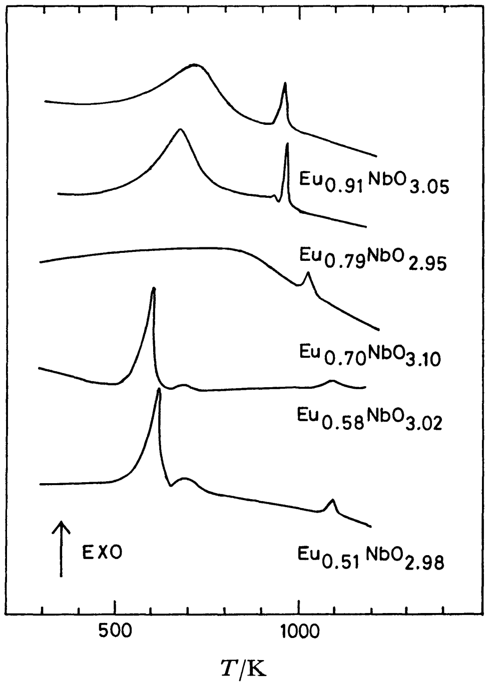

Fig. 4. DTA curves for Eu_xNbO_{3-y}.

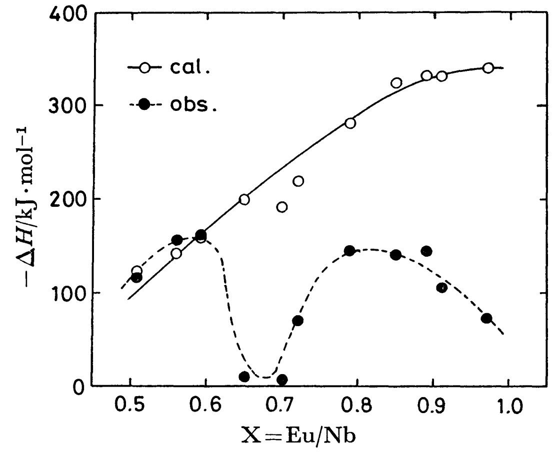

Fig. 5. Heat of oxidation for Eu_xNbO_{3-y}.

curves for the tetragonal and the cubic phases are shown in Fig. 2. An abrupt weight gain is observed in the TGA curve for the tetragonal sample at 550—700 K, and a moderate weight gain at 550—900 K for the cubic one. We see that the oxidation proceeds in two steps for both the tetragonal and cubic phases. Magnetic susceptibility measurements were carried out for the same sample in the air in the temperature range 300—1173 K, at a heating rate of 10 K/min (Fig. 3). The magnetic moments of Eu^{2+}, Eu^{3+}, Nb^{4+}, and Nb^{5+} are 7.94, 3.4, 1.73, and 0 μ_B, respectively. The decrease in the magnetic moment is much larger in the oxidation of Eu^{2+} to Eu^{3+} than in the oxidation of Nb^{4+} to Nb^{5+}. From a comparison of the TG-DTA curves (Fig. 2) with the χ_m^{-1} *vs.* *T* curves (Fig. 3), we see that the initial stage of the oxidation would be due to the oxidation of Eu^{2+}, the second to the oxidation of Nb^{4+}. Figure 3 also shows that the initiating temperature of the oxidation of Eu^{2+} is 550 K for both the tetragonal and cubic phases, the rate of oxidation of Eu^{2+} being larger for the tetragonal phase than for the cubic phase.

The stability of the bronze against oxidation mainly depends on that of Eu^{2+}. The temperature at which oxidation of Eu^{2+} starts is the same for both the tetragonal and cubic phases. The stability of Eu^{2+} to oxidation seems to be of the same order for both bronzes. The rate of oxidation of Eu^{2+} is considered to determine the rate of oxidation of the bronzes. The thermal analyses (TGA and DTA) were carried out for EuO under the same conditions as those for the bronzes. EuO oxidized at 520—580 K, showing that the rate of oxidation of Eu^{2+} in EuO is much greater than that in the bronzes. The oxidation of Eu^{2+} proceeds from the surface to the bulk of the bronze grain. The rate of oxidation of Eu^{2+} in the bulk should be determined by the probability of Eu^{2+} encounter with oxygen. Thus the rate of diffusion of oxygen in the oxidized product layer should control the rate of oxidation of Eu^{2+}.

X-Ray analysis was carried out for the bronzes oxidized at various temperatures. Oxidation of the cubic bronze gave an amorphous phase crystallizing at 950 K. On the other hand, the tetragonal phase underwent oxidation giving complex crystalline products which recrystallized at 1070 K. The difference in the rate of oxidation between the tetragonal and cubic phases can be attributed to the difference in the rate of diffusion of oxygen in the layer of the oxidized product. The diffusion coefficient of oxygen for the product obtained by the oxidation of the tetragonal phase should be much larger than that for the amorphous phase resulting from the cubic phase.

On heating the bronzes in the air, $EuNbO_4$ appeared at 1070 K for the tetragonal bronze and at 950 K for the cubic bronze. Exothermic peaks, 950 and 1070 K, due to crystallization are seen in the DTA curves with no weight change (Figs. 2 and 4), suggesting that the amorphous phases are less stable than the crystalline phases. The difference in the stability of the intermediate states affects the heats of oxidation for the bronzes. Figure 5 shows the observed and calculated heats of oxidation for the bronzes of various Eu^{2+} contents. Both the observed and calculated values show a minimum at $x=0.65$. For the evaluation of the heat of oxidation, the bronze is assumed to be a mixture of EuO, NbO_2, and Nb_2O_5,

$$Eu_xNbO_{3-y} = x\mathrm{EuO} + [2(x+1)-1]NbO_2 + (1-x-y)Nb_2O_5. \quad (4)$$

The oxidation reaction is assumed to proceed as follows:

$$Eu_xNbO_{3-y} + \left(\frac{3}{4}x+\frac{y}{2}-\frac{1}{4}\right)O_2 \longrightarrow \frac{x}{2}Eu_2O_3 + \frac{1}{2}Nb_2O_5. \quad (5)$$

The minimum of the heat of oxidation at $x=0.65$ corresponds to the phase transition.

The heats of oxidation for the tetragonal phases are almost equal to the calculated values. The result indicates that the heat of formation for the crystalline phase is close to that for the mixture of Eu_2O_3, and Nb_2O_5 represented by Eq. 4. The heat of transformation from an unknown crystalline phase to the final products, mainly $EuNbO_4$, as well as $EuNb_3O_9$ and $EuNb_5O_{14}$, might be very small. Thermal analysis (TGA-DTA) supports the assumption.

The heat of oxidation for the cubic phases is much lower than that for the calculated ones, a maximum being obtained at $x=0.85$. The result indicates that the heat of formation for the amorphous phase obtained from oxidation of the cubic bronzes is considerably larger than that for the mixture of Eu_2O_3 and Nb_2O_5 shown by Eq. 4. A second cubic phase, Eu_3NbO_6, appears at $x>0.9$. The heat of formation for the existing cubic bronzes, $Eu_xNbO_{3-y}+Eu_3NbO_6$, seems to be smaller as compared with that for single-phased Eu_xNbO_{3-y}, the apparent heat of oxidation decreasing for $x>0.9$. The minimum of the heat of oxidation at $x=0.65$ is due to the difference in stability of these two intermediate phases.

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