CHEMISTRY LETTERS, pp. 623-626, 1982.

PREPARATION AND ELECTRICAL PROPERTIES OF $Eu(II)_xNb(II)_{1-x}O$

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Two new compounds, $Eu_{0.33}Nb_{0.67}O$ and $Eu_{0.5}Nb_{0.5}O$, have been found in the ternary system $Eu(II)_xNb(II)_{1-x}O$. Electrical resistivity measurements have shown that $Eu_{0.33}Nb_{0.67}O$ is a metallic conductor while $Eu_{0.5}Nb_{0.5}O$ is a semiconductor. Strontium analogs of these compounds, $Sr_{0.33}Nb_{0.67}O$ and $Sr_{0.5}Nb_{0.5}O$, have also been attempted to prepare. The former was obtained as a single phase.

Presence of a mixed oxide containing bivalent europium and niobium ions, $Eu_{0.5}Nb_{0.5}O$, has been reported in the previous paper[1]. The objects of this study are to search new compounds in the system $Eu_xNb_{1-x}O$ and clarify some chemical and physical properties of these products. The Sr^{2+} compounds have the same crystal structure as the corresponding Eu^{2+} compounds have, because ionic radii of Sr^{2+} and Eu^{2+} are almost identical[2)-5)]. Thus, strontium analogs of the system, $Sr_xNb_{1-x}O$, have been prepared in order to confirm the electrical properties of $Eu_xNb_{1-x}O$.

Europium sesquioxide (purity 99.9 %; Shin-etsu Chemical Co.,), strontium carbonate (L.G., Nichia Kagaku Industries, Ltd.,), and diniobium pentaoxide (purity 99.9 %; Wako Chemical Industries. Ltd.,) were heated at 1000 K, 700 K, and 1000 K respectively for half an hour in air before being weighed. Niobium metal (purity 99.9 %; Wako Chemical Industries. Ltd.,) was weighed without any treatment.

Europium niobium oxides, $Eu_xNb_{1-x}O$, were prepared by the solid state reaction of europium sesquioxide, diniobium pentaoxide, and niobium. Mixtures of the starting materials with stoichiometric compositions were pelletized, packed into evacuated quartz tubes, and heated at 1423 K for 6 h. The heated samples were regrounded, pelletized, sealed into evacuated quartz tubes again, and sintered at 1423 K for 6 h. The reaction is assumed to proceed as follows:

$$0.5xEu_2O_3 + (0.2-0.3x)Nb_2O_5 + (0.6-0.4x)Nb \longrightarrow Eu_xNb_{1-x}O. \quad (1)$$

Strontium niobium oxides, $Sr_xNb_{1-x}O$, were prepared by the manner described above from strontium carbonate and niobium monoxide, which was obtained from the reaction of diniobium pentaoxide and niobium. Mixtures of strontium carbonate and niobium monoxide with the same composition as the single phase $Eu_xNb_{1-x}O$ were pelletized, and reacted at 1423 K under continuously pumped vacuum (10^{-3} Pa) for 4 h. The reaction is as follows:

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Table 1. Analytical data for $Eu_xNb_{1-x}O$

$Eu_xNb_{1-x}O_y$ (Nominal) x	y	$Eu_xNb_{1-x}O_y$ (Analytical) x	y	Phase	a / Å	ρ/g·cm^{-3}
0.13	1.00	0.14	0.97	(1) + NbO	-	-
0.25	1.00	0.26	1.01	(1) + NbO	-	-
0.33	1.00	0.33	1.08	(1)	4.019	7.51
0.40	1.00	0.38	1.00	(1) + (2)	-	-
0.50	1.00	0.49	1.08	(2)	4.135	7.65
0.75	1.00	0.72	1.20	(2) + EuO	-	-

(1) $Eu_{0.33}Nb_{0.67}O$; (2) $Eu_{0.5}Nb_{0.5}O$

Table 2. Electrical and magnetic data for $Eu_xNb_{1-x}O$ and $Sr_xNb_{1-x}O$

Compound	Electrical Property	Ea/eV[a]	Magnetism	μ_{eff}/μ_B (Found)	μ_{eff}/μ_B[b] (Calcd)	χ_g(300K) / emu·g^{-1}
$Eu_{0.33}Nb_{0.67}O$	metallic	-	para	4.70	4.56	7.4×10^{-5}
$Eu_{0.5}Nb_{0.5}O$	semiconductive	0.32	para	5.30	5.61	8.8×10^{-5}
$Sr_{0.33}Nb_{0.67}O$	metallic	-	Pauli-para	-	-	8×10^{-10}
$Sr_{0.6}Nb_{0.4}O$	semiconductive	-	dia	-	-	$< 10^{-10}$

a) Ea is activation energy in a equation; $\rho = \rho_o \exp(Ea/kT)$.

b) $\mu_{eff}(Calcd) = \sqrt{x}\,\mu(Eu^{2+})$; $\mu(Eu^{2+}) = 7.94\ \mu_B$

$$xSrCO_3 + (1-x)NbO \longrightarrow Sr_xNb_{1-x}O + xCO_2. \quad (2)$$

The Eu/(Eu+Nb) ratios, namely x in $Eu_xNb_{1-x}O$, were determined by means of fluorescence X-ray analysis with a Rigaku-Denki "Ultra Trace Unit". Oxygen compositional ratios O/(Eu+Nb) were determined by weighing the samples before and after complete oxidation. The oxygen content is given, assuming that the oxidation reaction proceeds as follows:

$$Eu_xNb_{1-x}O + ZO_2 \longrightarrow 0.5x\ Eu_2O_3 + (0.5-0.5x)Nb_2O_5. \quad (3)$$

Magnetic susceptibility measurements were done from 77.4 to 300 K with a Shimadzu magnetic balance "MB-11".

Electrical resistivity measurements were done for the polycrystalline samples in a helium atmosphere from 4.2 to 300 K, and from 300 to 1073 K the measurements were done under vauum lest the samples should be oxidized. A simple four probe method was employed for metallic samples, while a two probe method was employed for semiconductiove samples.

The phase and analytical data for $Eu_xNb_{1-x}O$ obtained are shown in Table 1. Single phases are obrained at x = 0.33 and 0.5. One of the single phases,

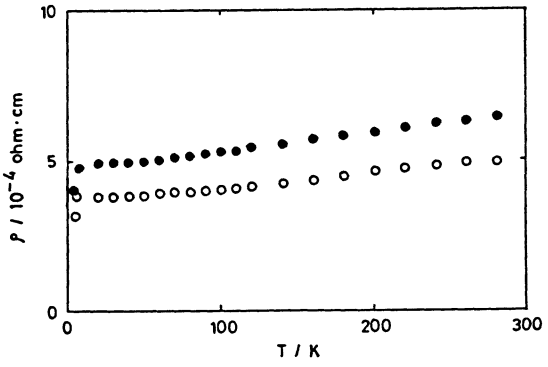

Fig. 1. Electrical resistivity vs. temperature for $Eu_{0.33}Nb_{0.67}O$ (●) and $Sr_{0.33}Nb_{0.67}O$ (○).

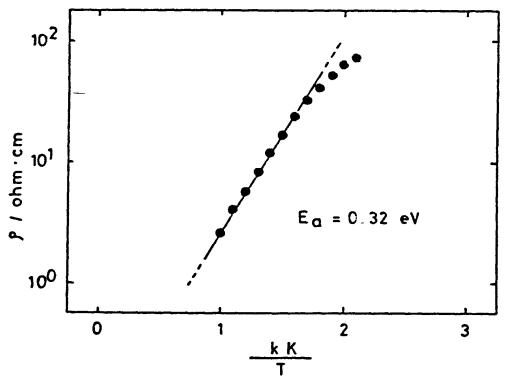

Fig. 2. Electrical resistivity vs. inverse temperature for $Eu_{0.5}Nb_{0.5}O$.

$Eu_{0.33}Nb_{0.67}O$, is a purple tinged dull blue polycrystal, and has a cubic lattice with a = 4.019 Å. On the other hand, $Eu_{0.5}Nb_{0.5}O$ has a grayish blue color and a cubic lattice with a = 4.135 Å.

Syntheses of analogs, $Sr_{0.33}Nb_{0.67}O$ and $Sr_{0.5}Nb_{0.5}O$, were attempted. The mixtures of $SrCO_3$ and Nb_2O_5 were subjected to the solid state reaction in a flow of H_2 at 1623 K for 20 h. The reducing power of H_2 was not strong enough to convert Nb_2O_5 to NbO, and a great amount of NbO_2 was found in the product. Therefore, $Sr_xNb_{1-x}O$ could not be obtained in this manner. Syntheses of mixed oxides, $Sr_xNb_{1-x}O$, were hence tried by the reaction of $SrCO_3$ and NbO under continuously pumped vacuum (10^{-3} Pa). A purple single phased $Sr_{0.33}Nb_{0.67}O$, was obtained. However, a single phased $Sr_{0.5}Nb_{0.5}O$ was not given and a mixture of $Sr_{0.5}Nb_{0.5}O$ and $Sr_{0.33}Nb_{0.67}O$ was obtained. An excess of $SrCO_3$ was required to prepare the Sr analog of $Eu_{0.5}Nb_{0.5}O$. At the nominal composition of $Sr_{0.6}Nb_{0.4}O$, the Sr analog of $Eu_{0.33}Nb_{0.67}O$ disappeared and a compound which resembled $Eu_{0.5}Nb_{0.5}O$ was detected in the powder X-ray pattern. However, $Sr_{0.6}Nb_{0.4}O$ may be the mixed phase of the Sr analog of $Eu_{0.5}Nb_{0.5}O$ and amorphous SrO, since $Sr_{0.6}Nb_{0.4}O$ is hygroscopic. The single phase of the Sr analog of $Eu_{0.5}Nb_{0.5}O$ was not prepared even in the reaction of $SrCO_3$ and NbO.

Electrical resistivity measuements were done for $Eu_{0.33}Nb_{0.67}O$, $Eu_{0.5}Nb_{0.5}O$, and $Sr_{0.33}Nb_{0.67}O$ (Figs. 1 and 2). Resistvities of $Eu_{0.33}Nb_{0.67}O$ and $Sr_{0.33}Nb_{0.67}O$ are very low at room temperature and the thermal coefficients of resistivity for these compounds are positive, indicating that these are metallic conductors (Fig. 1). On the other hand, $Eu_{0.5}Nb_{0.5}O$ is a typical semiconductor (Fig. 2), and its temperature dependence of resistivity is expressed by the well-known relationship:

$$\rho = \rho_o \exp(Ea/kT). \quad (4)$$

The activation energy (Ea) for $Eu_{0.5}Nb_{0.5}O$ was 0.32 eV. These resistivity data indicate that 4d electrons of niobium are collective for $Eu_{0.33}Nb_{0.67}O$ and $Sr_{0.33}Nb_{0.67}O$, and localized for $Eu_{0.5}Nb_{0.5}O$.

Magnetic susceptibility measurements were done for $Eu_{0.33}Nb_{0.67}O$, $Eu_{0.5}Nb_{0.5}O$, $Sr_{0.33}Nb_{0.67}O$, and $Sr_{0.6}Nb_{0.4}O$ (Table 2). The magnetic data show that

$Eu_{0.33}Nb_{0.67}O$ and $Eu_{0.5}Nb_{0.5}O$ are paramagnetic substances, and $Sr_{0.33}Nb_{0.67}O$ and $Sr_{0.6}Nb_{0.4}O$ are a Pauli paramagnetic and a diamagnetic substances respectively. The magnetic data for $Sr_{0.33}Nb_{0.67}O$ and $Sr_{0.6}Nb_{0.4}O$ indicate that there is no unpaired Nb4d spin. Paramagnetic properties of $Eu_{0.33}Nb_{0.67}O$ and $Eu_{0.5}Nb_{0.5}O$ are arised from paramagnetic Eu^{2+} ions. The observed magnetic moments of $Eu_{0.33}Nb_{0.67}O$ and $Eu_{0.5}Nb_{0.5}O$ agree closely with the calculated values, which are derived on the assumption that all the 4d spins are paired. The good agreements between the observed and the calculated values indicate that all the europium ions are in a bivalent state and that there is no unpaired Nb4d spin. The diamagnetic properties of the Sr analogs also support the assumption that all the 4d spins are paired in the Eu compounds. The metallic conduction and Pauli paramagnetism of $Sr_{0.33}Nb_{0.67}O$ ($Eu_{0.33}Nb_{0.67}O$ analog) suggest that the Nb4d electrons exist as conduction electrons in $Eu_{0.33}Nb_{0.67}O$. Similarly, the semiconduction and diamagnetic properties suggest that the Nb4d electrons are paired in $Eu_{0.5}Nb_{0.5}O$.

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(Received February 5, 1982)