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Some Studies on the Solid Solutions in the Systems $Sr_2Nb_2O_7$–$Eu_2Nb_2O_7$ and $Sr_2Ta_2O_7$–$Eu_2Ta_2O_7$

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Preparation of new solid solutions containing divalent europium have been tried in the systems $Eu_2Nb_2O_7$–$Sr_2Nb_2O_7$ and $Eu_2Ta_2O_7$–$Sr_2Ta_2O_7$. These solid solutions described as $Eu_{2x}Sr_{2(1-x)}M_2O_7$ (M = Nb and Ta) exist in a pure orthorhombic phase in a limited region of x from 0 to about 0.5. The compounds with compositions close to $Eu_2M_2O_7$ exist but techniques have not been found to prepare them in pure form.

Introduction

Several mixed oxides in the systems Eu–Ta–O and Eu–Nb–O have been prepared by the use of a Sr analog (*1–5*). However, an analog of $Sr_3TaO_{5.5}$, "$Eu_3TaO_{5.5}$," is not a stable phase (*6*, *7*). The existence of the hypothetical oxide would require the presence of Eu^{2+} on the 6-fold site. In previously known phases, most of Eu^{2+} occupies a site with a coordination number higher than 6 and this suggests that Eu^{2+} prefers a higher-than-6 coordination number site in mixed oxides. Therefore, it seems that originally Eu^{2+} would not be able to occupy the 6-fold site, and then "$Eu_3TaO_{5.5}$" would not exist.

It is interesting to study other analogs of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$, "$Eu_2Nb_2O_7$," and "$Eu_2Ta_2O_7$," respectively, because the existence of these analogs would require the presence of Eu^{2+} on a site with a coordination number of lower than 12. In $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$, one Sr^{2+} is surrounded by 12 oxygen ions and another Sr^{2+} is surrounded by 7 and 8 oxygen ions, respectively (*8*, *9*).

In this study, the preparation of "$Eu_2Nb_2O_7$" and "$Eu_2Ta_2O_7$" has been tried and the solid solutions in the systems Eu_2NbO_7–$Sr_2Nb_2O_7$ and $Eu_2Ta_2O_7$–$Sr_2Ta_2O_7$ have been also studied.

Experimental

Reagents. The purity and source of the reagents used (europium sesquioxide, niobium metal, and so on) have already been reported (*10*).

Preparative methods. Solid-state reactions were carried out using two distinct environments, a sealed tube system, and a dynamic vacuum furnace. For the sealed tube preparations, starting mixture ratio is Eu_2O_3:M:M_2O_5:SrO = $5x:2x:(5-x):10(1-x)$ ($0 \leqq x \leqq 1$, M = Nb and Ta). Starting mixtures were ground together in an agate mortar and pressed into pellets at 2400 kg/cm^2 and the pellets were given a preliminary firing to 900°C for 2 hr under vacuum. After further grinding, the resulting materials were pressed and loaded into a welded Ta crucible or a quartz tube. The Ta crucible was made from

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Ta tubing by means of electron beam welding techniques under vacuum ($\sim 10^{-4}$ mm Hg) and was used at temperatures above 1200°C. The quartz tube was fitted with a liner of Mo foil to prevent a reaction between the samples and the silica wall. The quartz tube and contents were outgassed on a vacuum line and then the tube was sealed. The quartz tube was heated at temperatures below 1200°C. For the dynamic vacuum furnace, starting mixtures ($Eu_2O_3 : M : M_2O_5 : SrO = 10x : 6x : (10 - 3x) : 20(1 - x)$) were treated as described in Ref. (*10*).

X-ray diffraction technique. The phase purity and structure type of the resulting materials were characterized by X-ray powder data, using a Rigaku–Denki "Rota-flex" diffractometer with a scintillation detector and Cu*Ka* radiation ($\lambda = 1.5418$ Å). Silicon of 99.999% purity ($a = 5.4301$ Å) was employed as an internal standard. Precision lattice constants were determined by a least-squares computer refinement of unambiguously indexed reflections.

Magnetic susceptibility measurements. The magnetic susceptibility data of the resulting materials were obtained with a Shimadzu MB-11 magnetic balance in the temperature range of 77–300°K.

TGA and DTA measurements. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were made in air at 25–700°C. The heating curve was recorded on a Rigaku–Denki "Thermoflex" and the heating rate used was 10°C/min.

Spectral measurements. The emission spectra for 254-nm excitation were measured at room temperature and 77°K (liquid N_2) on a Shimadzu recording spectrofluorophotometer equipped with a double monochromator. The excitation source was a 500-W xenon lamp. The excitation and emission slits were routinely set at 19 and 7.5 nm, respectively.

Results and Discussion

Attempts to Prepare $Eu_2Nb_2O_7$ and $Eu_2Ta_2O_7$ in a Sealed Tube System

The appropriate mixtures were fired in an evacuated and sealed tube. Results and details of the heat treatment including actual temperature and duration for each preparation are given in Tables I and II. Heating temperatures were 1200°C for $Eu_2Nb_2O_7$ and 1350°C or above for $Eu_2Ta_2O_7$, respectively, because of the difference in activity between niobium and tantalum systems. Two phases in the product were found, consisting of an orthorhombic phase as a major component and a hexagonal phase identified as $Eu_5Nb_4O_{15}$ or $Eu_5Ta_4O_{15}$ (*2*). Phase identification was done by the X-ray diffraction technique. This orthorhombic phase seems to be a $Sr_2Nb_2O_7$- or $Sr_2Ta_2O_7$-like compound whose basic structure is $Ca_2Nb_2O_7$ (*11*). The orthorhombic phase would be slightly cation-deficient because $Eu_5M_4O_{15}$ is richer in europium than the initial mixture. The amount of the hexagonal phase could not be reduced by the following intermediate regrinding and refiring steps. If $Eu_2Nb_2O_7$ and $Eu_2Ta_2O_7$ did exist, they would have a $Sr_2Nb_2O_7$- or $Sr_2Ta_2O_7$-like structure and one Eu^{2+} would occupy a 12-fold site and another Eu^{2+} would occupy a 7- or 8-fold site, respectively. However, $Eu_2Nb_2O_7$ and $Eu_2Ta_2O_7$ could not be obtained in pure form. This may be related with the site preference of Eu^{2+} and suggests that Eu^{2+} could easily occupy a 12-fold site than that with a coordination number of lower than 12.

To test whether Eu^{2+} behaves in this manner or not, solid solutions $Eu_{2x}Sr_{2(1-x)}$-M_2O_7 (M = Nb and Ta) were prepared. The phases obtained for specimens $Eu_{0.5}$-$Sr_{1.5}M_2O_7$ and $EuSrM_2O_7$ whose Eu^{2+} would occupy a 12-fold site could be prepared free of a hexagonal phase as shown in Tables I and II. On the other hand, $Eu_{1.5}Sr_{0.5}M_2O_7$ whose Eu^{2+} may occupy a site with a coordination number of lower than 12 as well as a 12-fold site, contained a hexagonal phase.

TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS FOR $Eu_{2x}Sr_{2(1-x)}Nb_2O_7$

Specimen expected	Firing schedule (°C)	Firing schedule (hr)	Phases detected in product
$Eu_2Nb_2O_7$	1200	12[a]	orthorhombic + hexagonal
	1200	3[b]	orthorhombic + hexagonal + cubic
$Eu_{1.5}Sr_{0.5}Nb_2O_7$	1200	20[a]	orthorhombic + hexagonal
	1200	3[b]	orthorhombic + hexagonal + cubic
$EuSrNb_2O_7$	1200	20[a]	orthorhombic
	1200	3[b]	orthorhombic
$Eu_{0.5}Sr_{1.5}Nb_2O_7$	1200	20[a]	orthorhombic
	1200	3[b]	orthorhombic
$Sr_2Nb_2O_7$	1200	20[c]	orthorhombic

[a] Prepared in the sealed tube system (silica tube).

[b] Prepared in the dynamic vacuum furnace.

[c] Prepared in air.

The hexagonal phase contained in the resulting materials is considered to be an $Eu_5M_4O_{15}$-like oxide whose Eu^{2+} occupies the 12-fold site. A large portion of $Eu_{1.5}Sr_{0.5}Ta_2O_7$ was the orthorhombic phase, as shown in Table II. It appears that $Eu_{1.5}Sr_{0.5}Ta_2O_7$ could be obtained in a pure orthorhombic phase. Attempts to prepare the pure orthorhombic $Eu_{1.5}Sr_{0.5}Ta_2O_7$ as well as $Eu_2M_2O_7$ were unsuccessful, however. These results seem to be consistent with the hypothesis for the site preference of Eu^{2+}.

The lattice constants for the orthorhombic $Eu_{2x}Sr_{2(1-x)}M_2O_7$ are listed in Table III. Since the X-ray spectrum of $Eu_{2x}Sr_{2(1-x)}M_2O_7$ obtained was identical to that of $Sr_2Nb_2O_7$, those

TABLE II

EXPERIMENTAL CONDITIONS AND RESULTS FOR $Eu_{2x}Sr_{2(1-x)}Ta_2O_7$

Specimen expected	Firing schedule (°C)	Firing schedule (hr)	Phases detected in product
$Eu_2Ta_2O_7$	1350	3[a]	orthorhombic + hexagonal
	1350	20[a]	orthorhombic + hexagonal
	1350	3[b]	orthorhombic + hexagonal
	1350	20[b]	orthorhombic + hexagonal
	1450	3[a]	orthorhombic + hexagonal
$Eu_{1.5}Sr_{0.5}Ta_2O_7$	1350	20[a]	orthorhombic + hexagonal (trace)
	1350	3[b]	orthorhombic + hexagonal
	1350	20[b]	orthorhombic + hexagonal (trace)
$EuSrTa_2O_7$	1350	20[a]	orthorhombic
	1350	3[b]	orthorhombic
$Eu_{0.5}Sr_{1.5}Ta_2O_7$	1350	20[a]	orthorhombic
	1350	3[b]	orthorhombic
$Sr_2Ta_2O_7$	1350	20[c]	orthorhombic

[a] Prepared in the sealed system (Ta tube).

[b] Prepared in the dynamic vacuum furnace.

[c] Prepared in air.

TABLE III

LATTICE CONSTANTS AND μ_{eff} FOR SAMPLES OBTAINED

	Lattice constant (Å)			$\mu_{eff}(\mu_B)$		Weight gain (%)	
Sample obtained	a	b	c	obs	calc	ΔW_o	ΔW_c
$Eu_2Nb_2O_7$	3.952	26.80	5.685	10.78	11.23	2.51	2.66
$Eu_{1.5}Sr_{0.5}Nb_2O_7$	3.973	26.81	5.682	9.61	9.72	2.04	2.11
$EuSrNb_2O_7$	3.966	26.78	5.680	7.54	7.94	1.43	1.49
$Eu_{0.5}Sr_{1.5}Nb_2O_7$	3.953	26.83	5.680	5.51	5.61	0.68	0.79
$Sr_2Nb_2O_7$	3.954	26.83	5.686	—	—	—	—
$Eu_2Ta_2O_7$	3.946	27.15	5.694	11.23	11.23	2.02	2.06
$Eu_{1.5}Sr_{0.5}Ta_2O_7$	3.978	27.37	5.726	9.63	9.72	1.60	1.61
$EuSrTa_2O_7$	3.953	27.22	5.686	8.00	7.94	1.12	1.12
$Eu_{0.5}Sr_{1.5}Ta_2O_7$	3.938	27.22	5.682	5.47	5.61	0.62	0.59
$Sr_2Ta_2O_7$	3.946	27.18	5.695	—	—	—	—

must have the same structure. There appears to be an interesting variation in lattice constants and cell volume for the orthorhombic phase as the Eu content is decreased. A maximum in cell volume occurs for $x = 0.75$ both in the niobium and tantalum systems. Table IV summarizes the lattice constants for the hexagonal phase in $Eu_{1.5}Sr_{0.5}M_2O_7$ and $Eu_2M_2O_7$. Cell volume for $x = 0.75$ is also larger than the other for the hexagonal phase. The shape of divalent europium ion having d orbital character (d^1) deviates from spherical symmetry, while Sr^{2+} has spherical symmetry. In a solid solution containing both Eu^{2+} and Sr^{2+}, nonspherical Eu^{2+} and spherical Sr^{2+} distribute at random, and the effective ionic radius of Eu^{2+} would appear to be a little bit larger than that expected in a pure compound. In other words, a random distribution of Eu^{2+} and Sr^{2+} in the oxygen packing would cause formation of some dead space in these solid solutions. This may result in a maximum in cell volume for a series of the systems $Eu_2M_2O_7$–$Sr_2M_2O_7$. It seems that this effect appears pronouncedly for the specimens with $x = 0.75$. The cell volume for $Eu_2M_2O_7$ is smaller than that for $Eu_{1.5}Sr_{0.5}M_2O_7$, which may be related with the following two points: First, non-spherical Eu^{2+} in $Eu_2M_2O_7$ mingles with no Sr^{2+}, and is closely packed together, and the lattice constants for $Eu_2M_2O_7$ are the same as those for $Sr_2M_2O_7$ because the ionic size of Eu^{2+} is approximately equal to that of Sr^{2+}; second, cation-deficiency arising from contamination by the hexagonal phase decreases the lattice constants for $Eu_2M_2O_7$.

TABLE IV

LATTICE CONSTANTS FOR HEXAGONAL PHASE IN $Eu_2M_2O_7$ AND $Eu_{1.5}Sr_{0.5}M_2O_7$

	Lattice constant (Å)	
Specimen obtained	a	c
$Eu_2Nb_2O_7$	5.630	11.42
$Eu_{1.5}Sr_{0.5}Nb_2O_7$	5.635	11.46
$Eu_2Ta_2O_7$	5.654	11.47
$Eu_{1.5}Sr_{0.5}Ta_2O_7$	5.660	11.51

The magnetic susceptibility for all of the samples was measured in the range of 77–300°K. The susceptibilities obeyed the Curie–Weiss law in this range. Analysis of the linear portion of the $1/\chi_{Eu}$ vs T curve yields the values of μ_{eff} in Table III. The value of the Weiss constant lies between 0 and −5°K. The effective magnetic moments obtained for $Eu_{2x}Sr_{2(1-x)}Ta_2O_7$ are very close to the theoretical ones, while μ_{eff} for $Eu_{2x}Sr_{2(1-x)}$-Nb_2O_7, where $x \geqq 0.5$, are relatively smaller than those calculated. This may be associated with the existence of Nb^{4+} in the niobium system.

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out in air from 25 to 700°C to determine the europium(II) ion content in the resulting materials. Total weight gain of the samples is shown in Table III. The weight gain ΔW_c is calculated assuming that Eu^{2+} in the samples obtained is completely oxidized by oxygen, and ΔW_0 is the weight gain observed. The weight gain of $Eu_{2x}Sr_{2(1-x)}M_2O_7$ where $x = 0.25$ and $x = 0.5$ occurs in one step and a corresponding exothermic DTA peak with maximum at 330°C is observed. Two exothermic DTA peaks (maxima, 320 and 410°C) are observed for $Eu_{2x}Sr_{2(1-x)}M_2O_7$ where $x = 0.75$ and $x = 1.0$, whereas the weight gain of these samples are found to occur in one step.

The oxidation with two exothermic DTA peaks for the specimens with $x = 0.75$ and 1.0 may be a result of the existence of two phases which are oxidized at different temperatures. However, this is not clearly mentioned because the shape and position of exothermic DTA peaks due to oxidation processes may be strongly influenced by the particle size and particle size distribution in the samples.

The emission spectra for the resulting materials were measured at room temperature and 77°K. The shape for the emission spectra did not change between room temperature and 77°K. The results are illustrated in Fig. 1. The emission spectra observed divided into three groups: (a) spectra for the specimens with $x = 0.25$ and 0.5, which consist of one broad peak at about 395 nm (peak A); (b) spectra for the specimens containing tantalum ions with $x = 0.75$ and 1.0, which consist of a large peak A and a shoulder at about 500 nm (shoulder B); (c) spectra for the specimens containing niobium ions with $x = 0.75$ and 1.0, which shows two sharp peaks at about 590 and 620 nm additional to the large peak A and the shoulder B.

Peak A and shoulder B of the emission spectra are ascribed to $4f$–$5d$ transitions within the Eu^{2+} ions. Peak A is attributed to the Eu^{2+} emission in the 12-fold sites and shoulder B is attributed to the Eu^{2+} emission in the lower-fold sites as mentioned in the previous paper (*10*). The fact that shoulder B appears in the emission spectra for the specimens with $x = 0.75$ and 1.0 suggests that Eu^{2+} could occupy the lower-fold sites. If Eu^{2+} may occupy the lower-fold sites, the specimens with $x = 0.75$ and 1.0 could form an orthorhombic $Sr_2M_2O_7$-like phase. However, a detailed study for the behavior of Eu^{2+} in these solid solutions must be made by means of other techniques such as an X-ray technique with a single crystal or Mössbauer spectroscopy.

Two additional sharp peaks for the specimens with $x = 0.75$ and $x = 1.0$ in the niobium system are ascribed to $4f$–$4f$ transitions within Eu^{3+} ions, and peaks at about 590 and 620 nm are attributed to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively. The lower magnetic moments for these samples could be interpreted by the existence of Eu^{3+}.

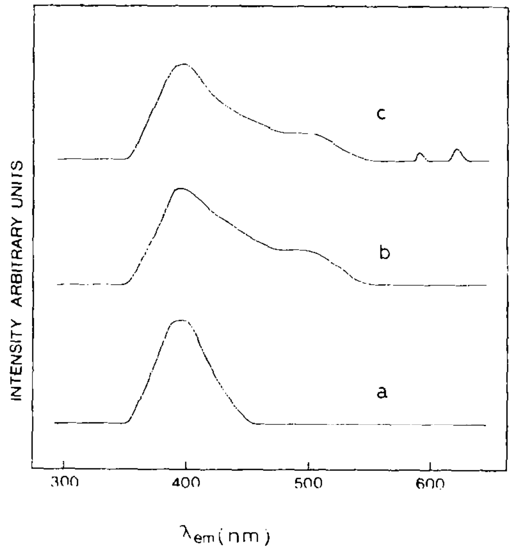

FIG. 1. Emission spectra of the resulting materials. (a) Specimens with $x = 0.25$ and 0.5; (b) specimens containing tantalum ion with $x = 0.75$ and 1.0; (c) specimens containing niobium ion with $x = 0.75$ and 1.0.

Preparation in a Dynamic Vacuum Furnace

Preparation was carried out in a furnace connected to a vacuum line in order to compare with preparation in a sealed tube. Results and experimental conditions are shown in Tables I and II. All of the phases obtained except for $Eu_{1.5}Sr_{0.5}Ta_2O_7$, $Eu_2Nb_2O_7$, and $Eu_{1.5}Sr_{0.5}Nb_2O_7$ were the same as those obtained in a sealed tube. The amount of time of the hexagonal phase in $Eu_{1.5}Sr_{0.5}Ta_2O_7$ decreased as heating time was increased. This specimen, as well as $Eu_{1.5}Sr_{0.5}Ta_2O_7$ in a sealed tube, was not completely free from the hexagonal phase, however. The phases in both $Eu_2Nb_2O_7$ and $Eu_{1.5}Sr_{0.5}Nb_2O_7$ consisted of a cubic phase (a = 4.01 Å) in addition to orthorhombic and hexagonal phases. This cubic phase is considered to be Eu_xNbO_3 with x = about 0.95 using the values of the lattice constants in the Ref. (*12*). During the heating period, Eu volatilized from the specimens and the Eu/Nb ratio became smaller than the nominal value. Moreover, excess niobium metal was used in part for reduction from Nb^{5+} to Nb^{4+}, and then Eu_xNbO_3 would have been formed.

Conclusion

The compounds with compositions close to $Eu_2Nb_2O_7$ and $Eu_2Ta_2O_7$ exist but techniques have not been found yet to prepare them in pure form. The solid solutions $Eu_{2x}Sr_{2(1-x)}M_2O_7$ exist in a pure orthorhombic phase in the region of x from 0 to about 0.5. This suggests that Eu^{2+} could easily occupy a 12-fold site than a lower-fold site in these systems.

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