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Registry No. $W_2Br_2(NEt_2)_4$, 60803-45-4; $W_2(NEt_2)_4I_2$, 60803-46-5; $W_2(NEt_2)_4(CH_2SiMe_3)_2$, 60828-76-4; $W_2(NEt_2)_4Cl_2$, 57088-63-8; ^{13}C, 14762-74-4.

Supplementary Material Available: Listings of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of New Perovskite Type Oxides Containing Divalent Europium

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New mixed europium(II) oxides of the type $EuM_2M'O_{5.5}$ and $Eu_2MM'O_{5.5}$ (M = Ca, Sr, Ba; M' = Nb, Ta) were prepared by the reaction of europium sesquioxide, alkaline earth oxide, tantalum (or niobium) metal, and tantalum (or niobium) pentoxide at 1250–1350 °C under vacuum. The oxides obtained have an ordered cubic perovskite structure with oxygen deficiency. Divalent europium ions in the oxides occupy both 12-fold A sites and 6-fold B sites. The emission spectra of the divalent europium ions confirm the distribution of the divalent europium ions in these oxides.

Introduction

There are many perovskite type oxides of the divalent europium ion. McCarthy and Greedan[1] have proposed guidelines for the prediction of new perovskite type oxides $Eu(M,M')O_3$. One of them is a well-known Sr^{2+} analogue. An analogue of Sr_3WO_6, "Eu_3WO_6", is not a stable phase.[2] Brixner[3] reported the first defect perovskites $Ba_3TaO_{5.5}$ and $Sr_3TaO_{5.5}$. An analogue of $Sr_3TaO_{5.5}$, "$Eu_3TaO_{5.5}$", is not a stable phase as well as "Eu_3WO_6".[4] If the hypothetical oxide did exist, it would have the ordered perovskite $(NH_4)_3FeF_6$ structure type and one Eu^{2+} would have to occupy the 6-fold B sites. In previously known phases, Eu^{2+} occupies a site with a coordination number higher than 6 and this suggests that Eu^{2+} prefers a higher than 6-fold coordination number site in mixed oxides. Consequently, it seemed that Eu^{2+} would not be able to occupy the 6-fold B sites in the perovskite type oxides and would occupy only the 12-fold A sites.

In this study, we have discussed with the aid of crystal data and emission spectra whether Eu^{2+} would occupy the 6-fold B sites in some new prepared perovskite type oxides.

Experimental Section

Reagents. Europium sesquioxide was obtained from Shin-etsu Chemical Corp., in minimum purity of 99.9%. Niobium metal, niobium pentoxide, tantalum metal, tantalum pentoxide, and strontium oxide were purchased from Wako Chemical Industries, Ltd., in purity of 99.7%, 99.9%, 99.9%, 99.8%, and 99.0%, respectively. Calcium oxide (99.0%) and barium oxide (97.0%) were available from Kanto Chemical Corp. and Merck Corp., respectively. Alkaline earth oxides were calcined at 1200 °C for several hours under vacuum ($\sim 10^{-2}$ mmHg) before used in the preparation.

Preparation of $EuM_2M'O_{5.5}$. Starting mixtures were ground together in an agate mortar and pressed into pellets at 2400 kg/cm^2 and fired on a molybdenum plate at 1250–1350 °C under vacuum ($\sim 10^{-4}$ mmHg). Several conditions of starting mixture ratios and heating time were used in the preparation. The sample obtained from the starting mixture having the stoichiometric ratio always indicated lower Eu^{II} content than that expected regardless of heating time. The mixtures were heated for 24 h to improve homogenization, but the samples obtained also had lower Eu^{II} content. These phenomena are probably caused both by the volatilization of europium from Eu^{II} mixed oxides and by the effect of oxygen leakage into the furnace during the heating period.[5] Consequently, the most appropriate starting mixture ratio and heating time are Eu_2O_3:MO:M':M'_2O_5 = 1:4:0.6:0.7 (M=Ca, Sr, Ba; M' = Nb, Ta) and 3 h. The surface of each pellet heated was removed, and the residue was used as a sample for subsequent experiments.

Preparation of $Eu_2MM'O_{5.5}$. Starting mixtures (Eu_2O_3:MO:M':M'_2O_5 = 1:1:0.6:0.2) were treated as described in the preparation of $EuM_2M'O_{5.5}$.

Analytical Methods. The sample obtained was treated with hot concentrated hydrochloric acid. Europium ion dissolved as trivalent ion in the solution, and the alkaline earth ion also dissolved. The residue corresponded to M'_2O_5, from which the content of tantalum

Table I. Analytical Data for Samples Obtained

Compd	% calcd		% found		Color
	M'^a	Eu	M'^a	Eu	
$EuCa_2NbO_{5.5}$	22.5	36.8	23.5	36.4	Dark brown
$Eu_2CaNbO_{5.5}$	17.7	57.9	16.9	56.9	Dark brown
$EuSr_2NbO_{5.5}$	18.3	29.9	18.9	29.4	Brown
$Eu_2SrNbO_{5.5}$	16.2	16.5	16.5	52.2	Dark brown
$EuBa_2NbO_{5.5}$	15.3	25.0	15.7	24.3	Dark brown
$Eu_2BaNbO_{5.5}$	14.9	48.8	15.4	48.2	Brown
$EuCa_2TaO_{5.5}$	36.1	30.3	36.4	30.0	Reddish brown
$Eu_2CaTaO_{5.5}$	29.5	49.6	30.2	48.8	Brown
$EuSr_2TaO_{5.5}$	30.4	25.5	30.9	25.1	Yellow brown
$Eu_2SrTaO_{5.5}$	27.4	46.0	27.7	45.3	Dark brown
$EuBa_2TaO_{5.5}$	26.0	21.8	26.2	21.4	Dark purple
$Eu_2BaTaO_{5.5}$	25.5	42.8	26.2	42.1	Dark brown

[a] M′ = Nb for the oxides containing niobium ion; M′ = Ta for the oxides containing tantalum ion.

metal and niobium metal in the sample was calculated. Europium in the solution was determined by polarography. The analytical results are summarized in Table I with the color of the sample obtained.

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 Kα radiation (λ 1.5418 Å). Silicon of 99.999% purity (a = 5.4301 Å) was employed as an internal standard. Precision cell 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 DTA "Thermoflex", and the heating rate used was 10 °C/min.

Spectral Measurements. The emission spectra for 254-nm excitation were measured on a Shimadzu recording spectrofluorophotometer equipped with a double monochromator. The excitation source was a 500-W xenon lamp. The excitation slit and emission slit were routinely set at 19 and 7.5 nm, respectively. For measurements at 77 K the sample was placed in a quartz tube of 4-mm i.d. and immersed in a Dewar flask which had a quartz tail and was filled with liquid nitrogen. For measurements at room temperature, the same system was used except for the absence of the liquid nitrogen, and a system where the sample was exposed directly to the excitation light was also employed.

Results and Discussion

X-Ray Data. Table II summarizes the x-ray diffraction data for $EuBa_2NbO_{5.5}$ and $Eu_2BaTaO_{5.5}$. Their x-ray data could be indexed on a cube with lattice constants of 8.490 and 8.394 Å, respectively. X-ray diffraction patterns for the other oxides contained are very similar to those for $EuBa_2NbO_{5.5}$ and $Eu_2BaTaO_{5.5}$. Both $EuM_2M'O_{5.5}$ and $Eu_2MM'O_{5.5}$ crystallize in space group O_h^5-$Fm3m$, which may be expected in analogy to Sr^{2+}.

The lattice constants and the densities of the samples obtained are listed in Table III as well as the lattice constants of Sr^{2+} compounds for comparison. The density measurements confirmed the presence of four formula units of $EuM_2M'O_{5.5}$ or $Eu_2MM'O_{5.5}$ in a unit cell.

An intensity calculation was made assuming that the oxides obtained have the perovskite type structure with oxygen deficiency arranged at random (Figure 1). Three values of the oxygen parameters, u = 0.20, u = 0.225, and u = 0.25, were used in the calculation for all cases. The agreement index

Table II. Powder Diffraction Data for $EuBa_2NbO_{5.5}$ and $Eu_2BaTaO_{5.5}$

$EuBa_2NbO_{5.5}{}^e$ [a = 8.490 Å, $u(O^{2-})$ = 0.225]						$Eu_2BaTaO_{5.5}{}^f$ [a = 8.394 Å, $u(O^{2-})$ = 0.225]					
hkl	d_{obsd}	d_{calcd}	I_{obsd}	$I_A{}^a$	$I_B{}^b$	hkl	d_{obsd}	d_{calcd}	I_{obsd}	$I_A{}^c$	$I_B{}^d$
220	3.003	3.002	100	100	100	111	4.853	4.846	1.1	1.4	0.7
311	2.560	2.560	2	2	3	200	4.206	4.197	2.1	0.6	2.0
400	2.123	2.123	35	26	26	220	2.969	2.968	100	100	100
331	1.948	1.948	1	1	1	311	2.533	2.531	0.7	0.5	
422	1.733	1.733	44	49	49	400	2.100	2.099	26.7	26.0	26.0
440	1.500	1.501	19	15	15	420	1.874	1.877	0.7		0.8
620	1.3422	1.3424	20	19	19	422	1.714	1.713	40.5	52.6	52.6
444	1.2255	1.2254	7	5	5	440	1.4839	1.4839	13.3	16.0	16.0
642	1.1338	1.1345	21	24	24	531	1.4194	1.4188	0.9	1.3	0.9
800	1.0610	1.0613	4	3	3	600 442	1.3986	1.3990	0.5		0.6
						620	1.3272	1.3272	14.7	18.1	18.1
						444	1.2117	1.2116	4.1	5.1	5.1
						642	1.1218	1.1217	15.9	24.7	24.7
						800	1.0493	1.0493	2.0	2.7	2.7

[a] Calculated relative intensity assuming that Eu^{2+} occupies the 12-fold A sites. [b] Calculated relative intensity assuming that Eu^{2+} occupies the 6-fold B sites. [c] Calculated relative intensity assuming that two Eu^{2+} occupy the 12-fold A sites. [d] Calculated relative intensity assuming that one Eu^{2+} occupies the B sites. [e] Agreement factors: $R_A = 0.075; R_B = 0.079$. [f] Agreement factors: $R_A = 0.152; R_B = 0.140$.

Table III. Lattice Constants, μ_{eff}, and Densities for Perovskite Oxides

Europium oxide	a_0, Å	μ_{eff}(obsd),[a] μ_B	Density, g/cm³		Strontium oxide	a_0, Å
			Found	Calcd[b]		
$EuCa_2NbO_{5.5}$	8.131	7.94	5.07	5.11		
$Eu_2CaNbO_{5.5}$	8.200	7.55	6.17	6.32	$Sr_2CaNbO_{5.5}{}^c$	8.20
$EuSr_2NbO_{5.5}$	8.292	6.67	5.87	5.92	$Sr_3NbO_{5.5}{}^c$	8.34
$Eu_2SrNbO_{5.5}$	8.290	7.30	6.63	6.68		
$EuBa_2NbO_{5.5}$	8.490	5.28	6.25	6.60	$SrBa_2NbO_{5.5}{}^d$	8.54
$Eu_2BaNbO_{5.5}$	8.396	6.80	6.93	6.98		
$EuCa_2TaO_{5.5}$	8.133	8.01	6.14	6.19		
$Eu_2CaTaO_{5.5}$	8.205	7.62	7.31	7.37		
$EuSr_2TaO_{5.5}$	8.308	6.87	6.94	6.95	$Sr_3TaO_{5.5}{}^c$	8.34
$Eu_2SrTaO_{5.5}$	8.299	7.21	7.57	7.68		
$EuBa_2TaO_{5.5}$	8.483	6.68	7.37	7.57		
$Eu_2BaTaO_{5.5}$	8.394	6.88	7.98	7.98		

[a] μ_{eff}(calcd) = 7.94 μ_B. [b] Four formula units in a unit cell (Z = 4). [c] Reference 9. [d] Reference 10.

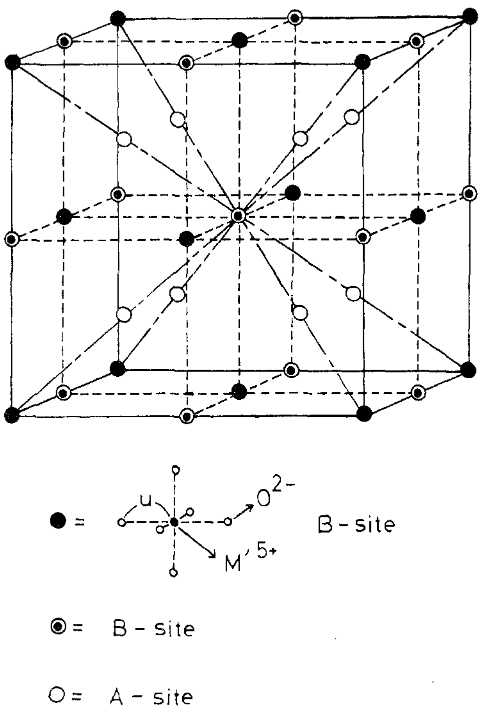

Figure 1. Atomic arrangement in a perovskite type oxide containing divalent europium. One of 12 oxygen ions is missing in this oxide.

R ($=\sum|I_o - I_c|/\sum I_o$) was minimized for all cases at $u = 0.225$ which seemed reasonable considering ionic radii and cell dimensions.

Three divalent ions exist in one formula unit cell of these oxides. One of these divalent ions would have to share the 6-fold B sites with M'^{5+}. The x-ray diffraction intensity was calculated in order to determine the site of Eu^{2+} in the perovskite, A or B (in $EuM_2M'O_{5.5}$), and A and B or only A (in $Eu_2MM'O_{5.5}$). For example, the results for $EuBa_2NbO_{5.5}$ and $Eu_2BaTaO_{5.5}$ are listed in Table II. The resulting agreement indexes of $EuBa_2NbO_{5.5}$ were $R_A = 0.075$ and $R_B = 0.079$, and those of $Eu_2BaTaO_{5.5}$ were $R_A = 0.152$ and $R_B = 0.140$. The tolerance factor of these oxides in which Eu^{2+} occupies the B sites is closer to 1.0 than that of these oxides in which Eu^{2+} occupies the A sites. This suggests that only the results for $Eu_2BaTaO_{5.5}$ are reasonable. However, the structures of $EuBa_2NbO_{5.5}$ and $Eu_2BaTaO_{5.5}$ are not clearly determined because of small differences in the agreement indexes. The agreement indexes in the calculation for other oxides are also less than 0.2. Consequently, the site of Eu^{2+} in the oxides obtained could not be determined from the x-ray diffraction intensities alone.

TGA and DTA. The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out in air from room temperature to 700 °C to determine the europium(II) ion content in the oxides obtained. The results are illustrated in Figure 2. The weight gain ΔW_c is calculated assuming that Eu^{2+} in the oxides obtained is completely oxidized by the oxygen, and ΔW_o is the weight gain observed. The weight gain of each sample occurs in two steps and corresponding exothermic DTA peaks are observed. The ratio of total weight gain $\Delta W_o/\Delta W_c$ represents the europium(II) ion content.

The two-step oxidation for these oxides is relatively unknown. This phenomenon suggests that europium(II) ions occupy two different sites; that is, europium(II) ions distribute among the A sites and B sites. Because cations having a smaller ionic radius easily occupy the B sites[6] ($Ca^{2+} < Eu^{2+} \approx Sr^{2+} < Ba^{2+}$), europium(II) ions probably occupy the B sites in the oxides containing barium ions. The europium(II) ions that occupy the A sites in $EuZrO_3$[7] are oxidized in one step corresponding to the peak at lower temperature. Therefore, it seems that the peaks at lower temperature and at higher temperature correspond to the oxidation of Eu^{2+} in the A sites and B sites, respectively. However, the two-step oxidation may be a result of the dissociation on heating in air of the perovskite into two phases which oxidize at different temperatures. This can be answered by more detailed investigation for the oxidation products.

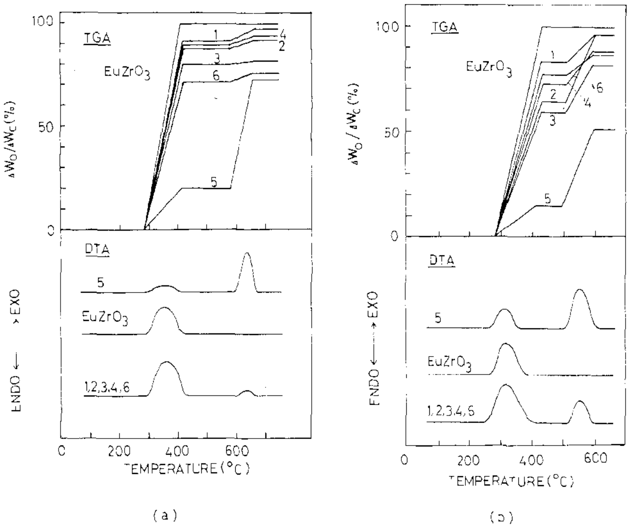

Figure 2. TGA and DTA curves for the oxides obtained and $EuZrO_3$. (a) Oxides containing tantalum ion: 1, $EuCa_2TaO_{5.5}$; 2, $Eu_2CaTaO_{5.5}$; 3, $EuSr_2TaO_{5.5}$; 4, $Eu_2SrTaO_{5.5}$; 5, $EuBa_2TaO_{5.5}$; 6, $Eu_2BaTaO_{5.5}$. (b) Oxides containing niobium ion: 1, $EuCa_2NbO_{5.5}$; 2, $Eu_2CaNbO_{5.5}$; 3, $EuSr_2NbO_{5.5}$; 4, $Eu_2SrNbO_{5.5}$; 5, $EuBa_2NbO_{5.5}$; 6, $Eu_2BaNbO_{5.5}$. The weight gain ΔW_c is calculated according to the following reactions: $EuM_2M'O_{5.5} + 0.25O_2 \rightarrow EuM_2M'O_6$; $Eu_2MM'O_{5.5} + 0.5O_2 \rightarrow Eu_2MM'O_{6.5}$.

The weight gains at higher temperature of $EuBa_2NbO_{5.5}$ and $EuBa_2TaO_{5.5}$ are large in comparison with those of the other oxides. The total weight gains of these two oxides are smaller than those of the other oxides. This suggests that europium(II) ions in $EuBa_2NbO_{5.5}$ and $EuBa_2TaO_{5.5}$ can easily occupy the B sites rather than the A sites, and that europium(II) ion content of $EuBa_2NbO_{5.5}$ and $EuBa_2TaO_{5.5}$ is less than that of the other oxides.

Magnetic Susceptibility. The magnetic susceptibility for all of the samples was measured in the temperature range of 77–300 K. The susceptibilities obeyed the Curie law in this range. Paramagnetic susceptibility data were collected up to 300 K. Analysis of the linear portion of the $1/\chi_{Eu}$ vs. T curve yields the values of μ_{eff} in Table III. The effective magnetic moments calculated for $EuCa_2NbO_{5.5}$ and $EuCa_2TaO_{5.5}$ are very close to the theoretical ones, and the effective magnetic moments for $EuBa_2NbO_{5.5}$ and $EuBa_2TaO_{5.5}$ are relatively smaller than those calculated. In $EuCa_2NbO_{5.5}$ and $EuCa_2TaO_{5.5}$, Eu^{2+} favors the A sites rather than the B sites because Eu^{2+} is the largest cation in these oxides. Therefore, Eu^{2+} easily occupies the A sites, and the effective magnetic moments for these oxides are close to the theoretical ones. On the other hand, Eu^{2+} in $EuBa_2NbO_{5.5}$ and $EuBa_2TaO_{5.5}$ occupies the B sites rather than the A sites. However, it has been known that it is difficult for Eu^{2+} to share the B sites in perovskite type oxides. The europium ion occupies the B sites more easily in the trivalent state than in the divalent state. For example, the trivalent compound $EuBa_2TaO_6$ in which the europium ion occupies the B sites in a trivalent state is structurally more stable than the divalent compound $EuBa_2TaO_{5.5}$. Therefore, $EuBa_2TaO_{5.5}$ is contaminated by small amounts of $EuBa_2TaO_6$, and μ_{eff} for $EuBa_2TaO_{5.5}$ is smaller

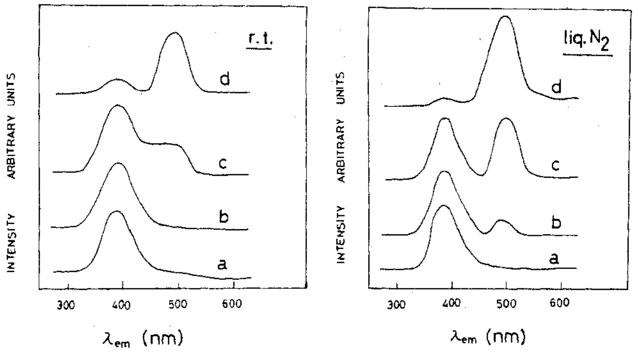

Figure 3. Emission spectra of the oxides obtained and $EuZrO_3$ at room temperature and at 77 K. A, $EuZrO_3$; b, oxides other than $EuBa_2M'O_{5.5}$ and $Eu_2BaM'O_{5.5}$; c, $Eu_2BaM'O_{5.5}$; d, $EuBa_2M'O_{5.5}$.

than the theoretical one. From the value of μ_{eff} for $EuBa_2TaO_{5.5}$, this oxide obtained is represented by the formula $Eu^{II}_{0.8}Eu^{III}_{0.2}Ba_2TaO_{5.6}$. This is expected from the results of TGA and DTA experiments. As is shown in Table III, the lattice constants for the other oxides than $EuCa_2M'O_{5.5}$ and $Eu_2CaM'O_{5.5}$ are smaller than those for the corresponding Sr^{2+} compounds. This also suggests that oxides other than $EuCa_2M'O_{5.5}$ and $Eu_2CaM'O_{5.5}$ are contaminated by small amounts of Eu(III) phases.

The effective magnetic moment for $EuBa_2NbO_{5.5}$ is smaller than that for $EuBa_2TaO_{5.5}$. This may be associated with the existence of Nb^{4+}.

For oxides other than $EuCa_2M'O_{5.5}$ and $EuBa_2M'O_{5.5}$, the values of μ_{eff} are intermediate between those for $EuCa_2M'O_{5.5}$ and $EuBa_2M'O_{5.5}$, which would be consistent with the description above.

Emission Spectra. The results are illustrated in Figure 3. The emission spectra observed divide into three groups: (a) spectra for the oxides other than $EuBa_2M'O_{5.5}$ and $Eu_2BaM'O_{5.5}$, which consist of one broad band peaking at about 395 nm (peak A) at room temperature and show two band peaks at about 395 and 495 nm (peak B) at 77 K; (b) spectra for $Eu_2BaM'O_{5.5}$, which consist of a large peak A and a small peak B at room temperature and a peak A as large as peak B at 77 K; (c) spectra for $EuBa_2M'O_{5.5}$, which show a small peak A and a large peak B at room temperature and 77 K. In all cases, peak A and peak B were not shifted. Peak A did not grow large at 77 K, but peak B increased. Consequently, thermal quenching occurred only for peak B between room temperature and 77 K.

Peak A and peak B of the emission spectra are ascribed to 4f–5d transitions within the Eu^{2+} ions. As mentioned in the foregoing section these ions in the oxides obtained are assumed to occupy the A sites and B sites, which are surrounded by 12 oxygen ions with cubic symmetry and by 6 oxygen ions octahedrally, respectively. In comparison with the emission spectrum for a perovskite type compound, $EuZrO_3$, where Eu^{2+} occupies the A sites, peak A is attributed to the Eu^{2+} emission in the A sites and peak B to the B site emission. For cubic symmetry the 5d level of Eu^{2+} splits into a t_{2g} level and an e_g level, the former having the higher energy. For an octahedral symmetry the t_{2g} level is expected to be the lower one. These band peaks are attributed to the Eu^{2+} emission concerning the lower level splitting in each symmetry. Consequently, peak A and peak B are ascribed to $4f^65d_{e_g} \rightarrow 4f^7$ transitions and $4f^65d_{t_{2g}} \rightarrow 4f^7$ transitions, respectively, within the Eu^{2+} ions. The wavelength of peak B is longer than that of peak A because the splitting of the 5d level in the octahedral field is wider than that in the cubic field and the Stokes shift of the Eu^{2+} emission in the B sites is longer than that in the A sites.[8] Thermal quenching occurs for peak B, which also indicates that peak B is the Eu^{2+} emission peak ascribed to the $4f^65d_{t_{2g}} \rightarrow 4f^7$ transitions in the octahedral field (B sites).

Conclusion

From this investigation on new divalent europium oxides with the perovskite type structure it appears that europium(II) ions can occupy the B sites in the perovskite type oxides. This was supported by TGA and DTA experiments and the emission spectra measurements.

Registry No. $EuCa_2NbO_{5.5}$, 60920-49-2; $Eu_2CaNbO_{5.5}$, 60920-47-0; $EuSr_2NbO_{5.5}$, 60920-51-6; $Eu_2SrNbO_{5.5}$, 60920-53-8; $EuBa_2NbO_{5.5}$, 60920-45-8; $Eu_2BaNbO_{5.5}$, 60920-43-6; $EuCa_2TaO_{5.5}$, 60920-50-5; $Eu_2CaTaO_{5.5}$, 60920-48-1; $EuSr_2TaO_{5.5}$, 60920-52-7; $Eu_2SrTaO_{5.5}$, 60920-54-9; $EuBa_2TaO_{5.5}$, 60920-46-9; $Eu_2BaTaO_{5.5}$, 60920-44-7.

References and Notes

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