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EVIDENCE FOR ENERGY MIGRATION AND TRANSFER IN $TbTa_3O_9$, $EuTa_3O_9$ AND $Tb_{0.9}Eu_{0.1}Ta_3O_9$ POWDER SAMPLES.

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Abstract. In this paper the optical properties (emission and excitation spectra) of powder samples of the double oxides of $RETa_3O_9$ (RE=Tb, Eu) were analyzed. The results of lifetime measurements and time resolved experiments performed at 11 and 300 K are discussed. Within the range of the continuous solid solution $Tb_{1-x}Eu_xTa_3O_9$, the optical characterization of our powder sample $Tb_{0.9}Eu_{0.1}Ta_3O_9$ is presented and combined with the previous results obtained by X-ray diffraction techniques to develop a better understanding on the effect of the RE ions on the crystalline structure of our samples.

INTRODUCTION.

Recently, the synthesis of the $RETa_3O_9$ (RE=Tb, Eu) compounds by solid state reaction was reported along with their characterization by X-ray powder diffraction techniques[1]. The compounds have a perovskite related structure with the europium and terbium in dodecahedral sites and the tantalum ions in octahedral sites. The continuous solid solution $Tb_{1-x}Eu_xTa_3O_9$, were obtained, characterized, and a solid solution mechanism Eu → Tb was identified[1]. It was found that the solid solution has an orthorhombic structure for $x \geq 0.5$ and tetragonal structure for $x < 0.5$.

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Nevertheless, the results of a systematic study of the optical properties of these powder samples have not been reported. As has been shown before, it is important to perform chemical and spectroscopic measurements in parallel, in order to get a reasonable characterization of the sites occupied by the RE ions in powder ceramics[2].

Therefore, the aim of this work is to present a detailed study on the optical properties of $TbTa_3O_9$, $EuTa_3O_9$ and $Tb_{1-x}Eu_xTa_3O_9$ in order to get a better insight on the effects of the RE ions on the crystalline structure of our powder samples.

EXPERIMENTAL.

All measurements performed in this work were taken on powder samples which were synthesized by solid state reactions according to the technique described by Ibarra-Palos et.al.[1] The optical spectroscopic measurements were carried out in samples having the shape of disk of 5mm in diameter and 0.5 mm in thickness.

Continuos fluorescence spectra were obtained with a Perkin-Elmer model 650-10S spectrofluorometer equipped with a 150 W xenon lamp. The photoluminescence measurements were also carried out using a Perkin-Elmer LS-5 fluorescence spectrophotometer fitted with a R-928 photomultiplier tube. This spectrophotometer provides corrected emission and excitation spectra. The light source was a 10 W pulsed xenon lamp with a pulse width at half peak intensity of 0.01 ms.

Lifetime and laser time resolved spectroscopy data were obtained using an EGG 2100 tunable DYE laser as the excitation source. The sample fluorescence was monitored by a 0.45 m Czerni-Turner monochromator, detected by a cooled Hamamatsu R-943-03 photomultiplier tube, and processed by an EGG/PAR 162 boxcar averager. For the low-temperature measurements the sample was mounted in the cold finger of an Air-Products model CS-202 cryogenic refrigerator with a temperature controller capable of temperature variation between 11 and 300 K.

RESULTS.

a) $TbTa_3O_9$.

Figure 1 portrays the RT emission spectrum of a $TbTa_3O_9$ powder sample under continuos excitation at 484 nm ($^7F_6 \rightarrow {}^5D_4$). In the range of 500 - 750 nm the strongest bands correspond to radiative transitions from the $^5D_4$ to the $^7F_5$, $^7F_4$ and $^7F_3$ levels of the Tb^{3+} ions. They are superimposed on an emission tail whose origin will be discussed below.

The results of time resolved experiments performed at RT with 0.01 ms width pulses at 484 nm are shown in Figure 1 (inset). Differences were observed in the emission spectrum of our sample as a function of the time delay (t_d) after the pulse excitation. As it is shown, the background emission tail which is observed in the samples under continuos excitation is not detected, within the limits of resolution of our experimental setup, when $t_d \geq 0.07$ ms.

The excitation spectrum corresponding to the Tb-emission light peaking at 545 nm ($^5D_4 \rightarrow {}^7F_5$) is shown in Figure 2, as a function of t_d. It consists of a number of sharp lines which are due to transitions within the terbium 4f shell.

Under pulsed excitation at 230 nm a broad emission band centered at about 455 nm was observed at RT (Figure 2, inset). It corresponds to the tail emission shown in Figure 1, and seems to be similar to that previously reported in powder samples of $LiTaO_3$ and $NaTaO_3$, which has been associated with intrinsic tantalate groups [2].

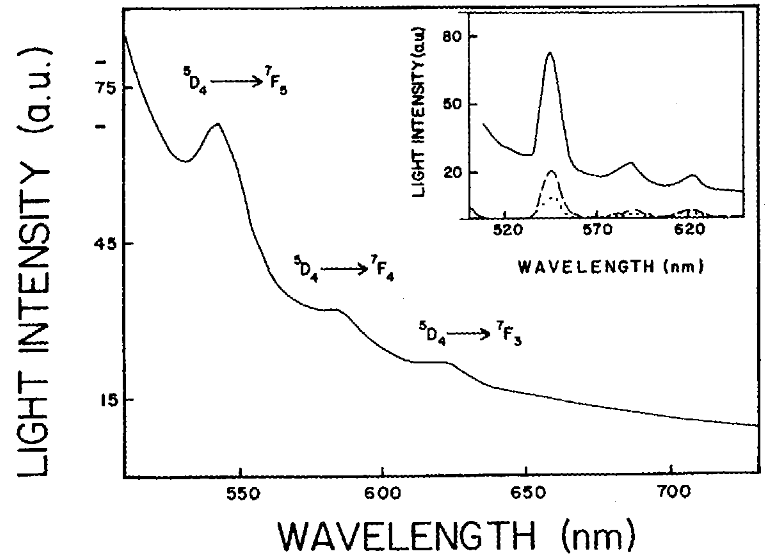

FIGURE 1. Room temperature (RT) emission spectrum of a $TbTa_3O_9$ powder sample under continuos excitation at 484 nm. The inset shows the RT time-resolved luminescence spectrum of the samples as a function of the time delay t_d = 0.03 ms (——), t_d = 0.07 ms (-----) and t_d = 0.12 ms (• • •).

Despite of the fact that the intrinsic emission overlaps the Tb absorption spectrum, the results of the time resolved experiments performed in our sample showed no evidence of energy transfer between the Ta groups and the Tb ions. The characteristic lifetime constant of the intrinsic emission band was estimated to be ~ 4 µs.

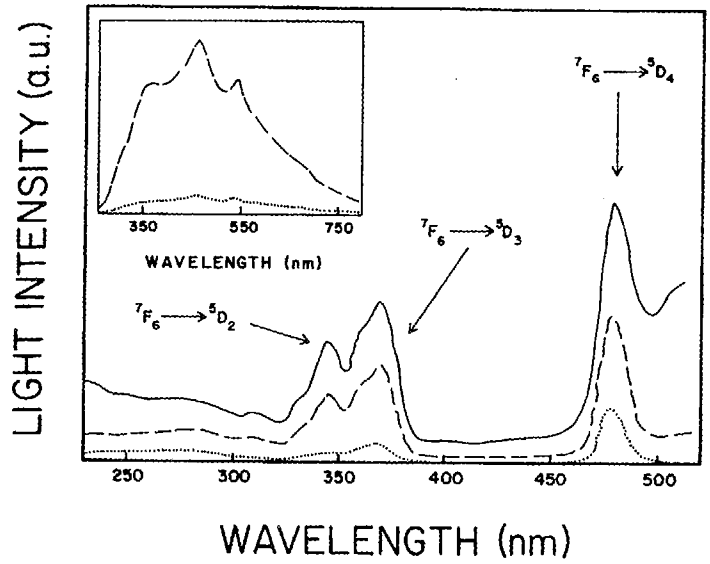

FIGURE 2. Excitation spectrum of the $^5D_4 \to {}^7F_5$ emission transition of the Tb ions in the $TbTa_3O_9$ sample as a function of t_d, for t_d = 0.03 ms (——), t_d = 0.04 ms (-----) and t_d = 0.1 ms (• • •). The inset shows the RT time-resolved intrinsic luminescence spectrum of the sample under pulsed excitation at 230 nm for t_d = 0.01 ms (-----) and t_d = 0.02 ms (• • •).

Lifetime measurements of the Tb-emission band peaking at 545 nm were performed under pulsed laser excitation at 484 nm, in the range of 10 - 300 K. The decay curves of the Tb luminescence, I(t), from the $^5D_4$ excited state were found to be non-exponential, with a characteristic τ constant- has been defined such that $I(t=\tau)=e^{-1}I_0$, with $I(t=0)=I_0$.

The non-exponential decay observed for I(t) in our samples might be attributed to an energy migration process taking place between the Tb^{3+} ions, as expected owing to the high concentration of these ions in our samples. The $Tb^{3+} \to Tb^{3+}$

energy migration could involve transitions connecting the lowest crystal - field components of the $^5D_4$ and $^7F_6$ states. These transitions are electric quadrupole allowed and, therefore, the fact that energy migration is present even at 11 K agrees with an electric quadrupole - quadrupole mechanism for the Tb → Tb interaction, which is temperature independent[3].

b) $EuTa_3O_9$.

Figure 3 displays the 11 K excitation spectrum of a $EuTa_3O_9$ powder sample. The spectrum was taken for the $^5D_0 \rightarrow {}^7F_4$ Eu-emission peaking at 689 nm, and consists of several sharp lines associated with transitions from the ground state $^7F_0$ to the excited state Stark components of the $4f^6$ configuration of the Eu^{3+} ion. In addition to the absorption lines, a broad band is observed in the region of 250 - 350 nm. This band might be associated with the Eu-O charge transfer transition[4].

As it is shown in Figure 3 (inset), differences are observed in the RT emission spectrum of the $EuTa_3O_9$ sample under pulsed excitation into the $^7F_0 \rightarrow {}^5L_6$ absorption band peaking at 389 nm, as a function of t_d. As in the case of $TbTa_3O_9$, the time resolved experiments carried out in our $EuTa_3O_9$ sample did not give any evidence of energy transfer between the intrinsic Ta groups and the Eu ions.

For $t_d > 0.07$ ms all the emission lines observed in the emission spectrum exhibit identical excitation spectra, associated with transitions involving $^5D_0$ as the emitting level. The quite intense emissions correspond to the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions. The other transitions are lower in intensity.

The luminescence decay of the Eu^{3+} emitting level consists of a pure exponential time function, with lifetime values (τ) of 18 and 1026 μs at RT and 11 K, respectively. These values were obtained from the $^5D_0 \rightarrow {}^7F_4$ emission at 689 nm under excitation into the $^7F_0 \rightarrow {}^5D_2$ absorption band. The decay constant determined at RT is quite shorter than that previously reported for different kinds of solids doped with low concentrations of Eu^{3+} ions [5]. However, it is similar to those found for the Eu emission in heavily doped systems. Such results have been interpreted in terms of resonant cross relaxation between the Eu ions, and reveal the presence of a fast energy diffusion mechanism [6].

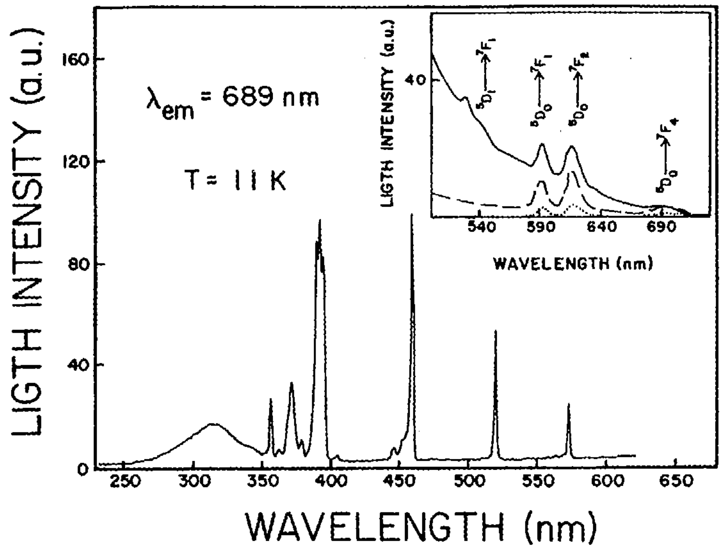

FIGURE 3. Excitation spectrum of the $^5D_0 \rightarrow {}^7F_4$ emission transition of the Eu ions in the $EuTa_3O_9$ sample. The inset shows the RT time-resolved luminescence spectrum of the sample as a function of the time delay for t_d = 0.01 ms (——), t_d = 0.02 ms (-----) and t_d = 0.03 ms (• • •), λ_{ex} = 389 nm.

Due to the increase of the τ constant value at low temperature, the phonon-assisted $^7F_1 \rightarrow {}^5D_0$ magnetic dipole transition must be involved in the mechanism for the Eu → Eu energy migration observed at RT. It requires the excitation of phonons in the sample to be operative and, therefore, it is inactive at 11 K.

c) $Tb_{0.9}Eu_{0.1}Ta_3O_9$.

Figure 4 displays the 11 K emission spectrum of a $Tb_{0.9}Eu_{0.1}Ta_3O_9$ powder sample at t_d = 0.05 ms, under pulsed laser excitation into the terbium $^7F_6 \rightarrow {}^5D_4$ absorption transition peaking at 484 nm. At this wavelength the Eu^{3+} ions are not excited; however, emissions from the $^5D_0$ (Eu) state are observed.

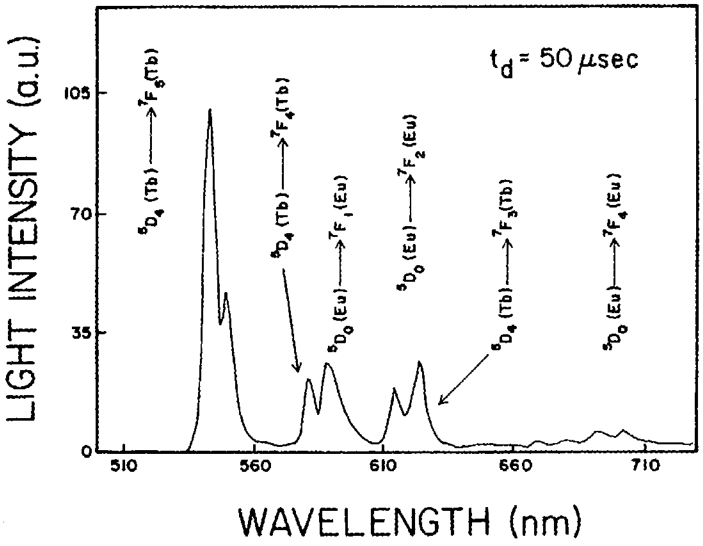

FIGURE 4. Liquid helium temperature (LHT) time-resolved luminescence spectrum of the $Tb_{0.9}Eu_{0.1}Ta_3O_9$ sample recorded at 50 μs after the pulse excitation at 484 nm.

The 11 K excitation spectrum for the $^5D_0 \rightarrow {}^7F_4$ Eu-emission at 689 nm is shown in Figure 5. As can be appreciated, it contains not only absorption transitions of this ion, but also of the Tb^{3+} ion. This fact indicates that energy transfer from Tb^{3+} to Eu^{3+} ions takes place in the sample. This process is expected to occur since the Tb emission ($^5D_4 \rightarrow {}^7F_4$) overlaps the Eu absorption ($^7F_0 \rightarrow {}^5D_0$). Taking into account that the $^5D_4 \rightarrow {}^7F_4$ transition is, in the intermediate-coupling scheme, magnetic dipole or electric quadrupole allowed and the $^7F_0 \rightarrow {}^5D_0$ transition is allowed by vibronic effects, then the process of $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer must involve the coupling of an electric quadrupole transition on the Tb^{3+} ion to an electric dipole vibronic transition on the Eu^{3+}. The magnetic dipole contribution of Tb3+ ion has been neglected, since it is well know that couplings involving magnetic dipole transitions give rise to negligible energy transfer probabilities [7].

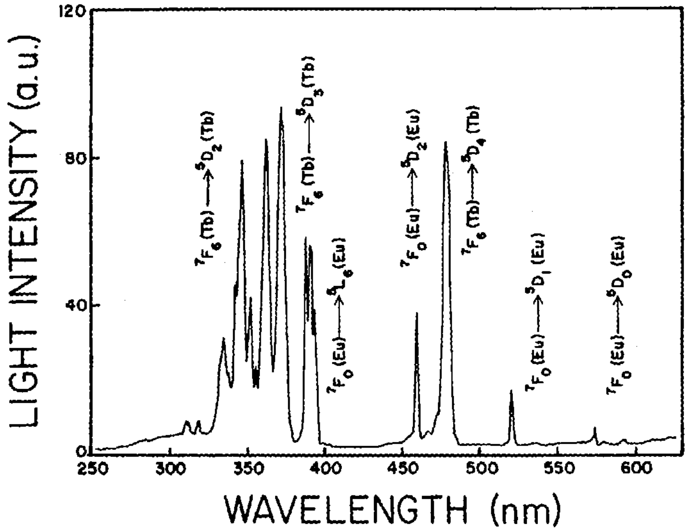

FIGURE 5. LHT excitation spectrum of the $^5D_0 \rightarrow {}^7F_4$ Eu^{3+} emission transition.

Lifetime measurements performed in our $Tb_{0.9}Eu_{0.1}Ta_3O_9$ powder sample revealed that the Eu^{3+} luminescence decay was purely exponential without any excitation built-up observed, within the limits of resolution of our experimental setup. The results obtained are listed in Table I. From the data presented in this table is observed that larger values for the characteristic decay time constant τ associated with the Eu-emission were measured whenever the sample was excited into the $^5D_4 \rightarrow {}^7F_6$ terbium absorption transition, at 484 nm. On the other hand, the Tb emission decay scheme was found to be quite similar to the one observed in the $TbTa_3O_9$ sample.

TABLE I. Lifetime measurements

SAMPLE	λ_{ex} (nm)	λ_{em} (nm)	Luminescence Decay Scheme (exp.)	(non exp.)	Decay Constant (μs)	R
$EuTa_3O_9$	459	689	x	—	18 (RT) 1026 (11 K)	1.4
$TbTa_3O_9$	484	545	—	x	650 (RT) 847 (11 K)	—
$Tb_{0.9}Eu_{0.1}Ta_3O_9$	484	545	—	x	580 (RT) 840 (11 K)	—
$Tb_{0.9}Eu_{0.1}Ta_3O_9$	459	689	x	—	908 (RT) 1025 (11 K)	1.4
$Tb_{0.9}Eu_{0.1}Ta_3O_9$	484	689	x	—	1020 (RT) 1080 (11 K)	1.2

The above results may be explained considering that, whenever the Eu ions occupy sites with low symmetry, their emission spectrum may include dipole-electric lines such as the $^5D_0 \rightarrow {}^7F_{0,2,4,6}$.The fluorescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is determined only the $\Omega_2 < | | U^{(2)} | | >$ term in the expression for the strength of transition in Jud-Ofelt theory[12]. Were Ω_2 in one phenomenological parameters and $< | | U^{(2)} | | >$ is one of reducer tensor operators in Judd-Ofelt theory[13,14] and the $^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to the variation of environment of Eu^{3+} ions[9,10]. Their relative intensities give the degree of asymmetry of the Eu ion environment [8-11]. Also, the $^5D_0 \rightarrow {}^7F_1$ transition, which is of the magnetic-dipole type, is always observed and its intensity is independent of the site symmetry. Therefore, it is generally admitted that the fluorescence intensity ratio R= ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) indicates the degree of asymmetry in the vicinity of europium ions. However it must be underlined that the degree of covalence of the Eu-O bond brings its own contribution to the $^5D_0 \rightarrow {}^7F_2$ transition intensity by modulating the admixture of the $4f^65d$ states into the $4f^6$ states [8-11]. Values for R in our $EuTa_3O_9$ and $Tb_{0.9}Eu_{0.1}Ta_3O_9$ powder samples are also presented in Table I.

The fluorescence intensity ratio give information on the relation of the powder sample structure to fluorescence, and its variation is related to the structural changes in the vicinity of the Eu ions. Then, our spectroscopic data seems to reveal that the Eu^{3+} ions occupy two crystallographic sites in the $Tb_{0.9}Eu_{0.1}Ta_3O_9$ sample: The europium ions are located in sites where (i) the R value are quite similar to those observed in our $EuTa_3O_9$ sample and (ii) in sites characterized by higher R values, where there are Tb donor ions located in the vicinity of the Eu acceptor ions.

On the basis of our experimental observations it may also be concluded that the Tb ions also occupy two crystallographic sites in the $Tb_{0.9}Eu_{0.1}Ta_3O_9$ compound such that: (i) some of them are not interacting with Eu^{3+} and, therefore, their decay scheme is not affected by the presence of the europium ions in the sample and, (ii) there are some other terbium ions which are forming Tb-Eu complexes. In such kind of complexes the terbium emission is completely quenched by Tb → Eu energy transfer.

In view of all the results presented in this paper the previous work in which the mechanism for europium substitution Eu→Tb in the $TbTa_3O_9$ - Eu_2O_3 solid solution has been identified. It could be possible that small amounts of Eu_2O_3 not detectable by x-ray powder diffraction were present in the samples
This makes also apparent the significance to be able to perform chemical and spectroscopic measurements in parallel, in order to get a reasonable characterization of the sites occupied by the RE ions in powder ceramic materials.

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