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Emission Spectra of Cs_2KTbCl_6 and Cs_2KEuCl_6, and $Tb^{3+} \rightarrow Eu^{3+}$ Non-Radiative Energy Transfer in $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$

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A spectral assignment of the first excited states of Tb^{3+} in Cs_2KTbCl_6 and Eu^{3+} in Cs_2KEuCl_6 obtained from excitation and emission spectra is presented. A non-radiative energy transfer process from Tb^{3+} to Eu^{3+} ions was found to occur in $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$. This process is strongly temperature dependent, such that it becomes quenched at low temperature. The most probable mechanisms responsible for such energy transfer are suggested for the case in which the Tb^{3+} $^5D_4$ state is excited.

Keywords: Elpasolites; solid solutions; luminescence; energy transfer

I. INTRODUCTION

The elpasolites form an interesting family of cubic symmetry compounds. The spectroscopic, electric and magnetic properties of these compounds have been the subject of a considerable amount of work during the last two decades [1]. In particular, the A_2BLnCl_6

cubic hexachloroelpasolites have resulted to be of interest, since the trivalent lanthanide (Ln^{+3}) ions occupy a cubic site surrounded by six chloride ions with perfect octahedral symmetry [2,3]. This facilitates to study the spectroscopic properties of such ions associated with their f→f transitions under conditions of high-symmetry, well-defined coordination and without charge-compensation problems. Moreover, excited state Ln^{3+} ions in centrosymmetric sites should have much longer relaxation times than those localized in non-centrosymmetric sites. This promises interesting possibilities for optical pumping and for energy storage and transfer [4].

In this paper we present excitation and emission results of Tb^{3+} and Eu^{3+} in the Cs_2KTbCl_6 and Cs_2KEuCl_6 hexachloroelpasolites, which allowed us to make a spectral assignment of their first excited states. It has been found previously [5] that such compounds are cubic and isoestructural to $Rb_2NaTmCl_6$. Europium and terbium are well known as easily excitable ions. Thus, it would expect an intrinsic fluorescence response in the visible region, because they occupy high octahedral symmetry sites in the elpasolite. The interesting of this possibility is to use these compounds as light absorbing-emitting devices.

Taking into account that codoping the hexachloroelpasolites with other lanthanide ion improves their quantum yield and modifies the wavelength of their produced radiation [4], the $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$ system was also studied. The optical information obtained with Cs_2KTbCl_6 and Cs_2KEuCl_6 was useful to study the $Tb^{3+}\rightarrow Eu^{3+}$ non-radiative energy transfer process taking place in $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$, and thus, to establish the most probable mechanisms of transfer.

II. EXPERIMENTAL

$Cs_2KTb_{1-x}Eu_xCl_6$ powder samples, with x = 0, 0.1 and 1, were prepared by slowly evaporating to dryness a hot aqueous HCl solution of the appropiate chlorides. The used reagents were CsCl (99.99 %), KCl (99.99 %), $TbCl_3o6H_2O$ (99.99 %) and $EuCl_3$ (99.99 %) from

Aldrich. Products were analysed by X-ray powder diffraction using a Siemens D5000 diffractometer with Cuk_α radiation, a secondary graphite monochromator and a nickel filter. Optical spectroscopic measurements were performed on powder samples having the shape of disk (~ 6 mm in diameter and ~ 1 mm in thickness).

Continuous fluorescence spectra were obtained with a Perkin-Elmer 650-10S spectrofluorimeter equipped with a 150 W Xenon lamp and a red sensitive Hamamatsu R928 photomultiplier tube. Samples were cooled to 11 K in a He-closed-cycle cryostat Air Products.

III. RESULTS AND DISCUSSION.

1. Cs_2KTbCl_6.

The average energies of the manifold levels of the Tb^{3+} ion in Cs_2KTbCl_6 are given in Table 1. These data were determined from room-temperature (RT) emission and excitation spectra displayed in Figure 1. The emission spectrum was obtained under excitation into the $^7F_6(A_{1g}, T_{1g}, T_{2ga})\rightarrow{}^5D_3$ absorption band at 380 nm. The peaks appearing in this spectrum are associated with transitions from the levels $^5D_4$ and $^5D_3$. Excitation into the $^7F_6(A_{1g}, T_{1g}, T_{2ga})\rightarrow{}^5D_4$ absorption band at 489 nm produces emissions only from the $^5D_4$ level. The excitation spectrum was taken at 545 nm, which corresponds to the $^5D_4\rightarrow{}^7F_5(T_{1ga})$ emission.

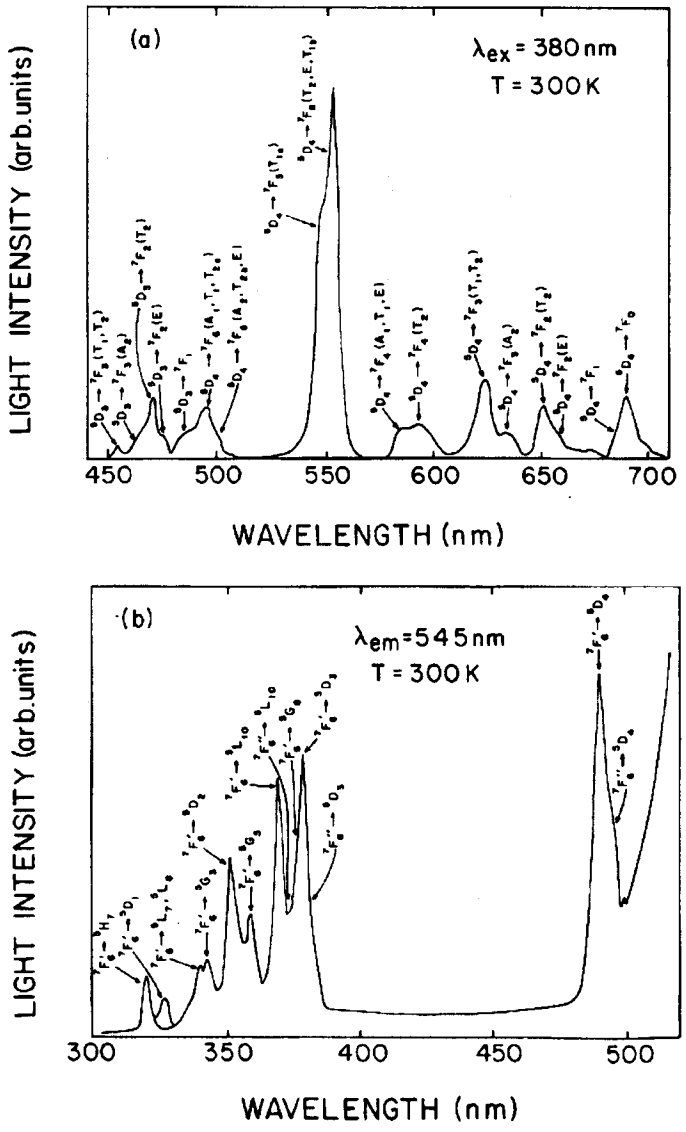

FIGURE 1. RT spectra of (a) emission and (b) excitation of Tb^{3+} ions in Cs_2KTbCl_6. The absorptions from the sublevels A_{1g}, T_{1g} and T_{2ga} or A_{2g}, T_{2gb} and E_g of the $^7F_6$ state are marked by $^7F_6'$ and $^7F_6''$, respectively.

Table 1. Energy levels of Tb^{3+} in Cs_2KTbCl_6

Manifold	Positions at 300 K (cm^{-1})	
	Excitation	Emission
$^5H_7$	31 250	
$^5D_1$	31 095	
$^5L_7$, $^5L_8$	29 343	
$^5G_3$	29 112	
$^5D_2$	28 249	
$^5G_5$	27 778	
$^5L_{10}$	27 027	
$^5G_6$	26 567	
$^5D_3(T_{1g}, T_{2g}, A_{2g})$	26 357	26 146
$^5D_4(T_{2g}, E_g, T_{1g}, A_{1g})$	20 442	20 289
$^7F_0(A_{1g})$		5 779
$^7F_1(T_{1g})$		5 561
$^7F_2(E_g)$		5 052
$^7F_2(T_{2g})$		4 892
$^7F_3(A_{2g})$		4 496
$^7F_3(T_{2g}, T_{1g})$		4 227
$^7F_4(T_{2g})$		3 448
$^7F_4(E_g, T_{1g}, A_{1g})$		3 172
$^7F_5(T_{1gb}, E_g, T_{2g})$		2 081
$^7F_5(T_{1ga})$		1 927
$^7F_6(E_g, T_{2gb}, A_{2g})$	289	289
$^7F_6(T_{2ga}, T_{1g}, A_{1g})$	0	0

2. Cs_2KEuCl_6.

Figure 2 portrays the 11 K emission spectrum of Eu^{+3} ions in Cs_2KEuCl_6 under excitation into the $^7F_0 \rightarrow {}^5D_2(E_g)$ absorption band at 465 nm. The peaks appearing in this spectrum correspond to the emission transitions either from the $^5D_1$ or $^5D_0$ level to the ^7F_j manifold (j = 0, 1, 2, 3, 4). The most intense emission corresponds, like ferroelectric materials, to the transition $^5D_0 \rightarrow {}^7F_1$. From this band has been possible to infer the two possible Eu^{3+} ion centers occupying non-centrosymmetric sites in $LiNbO_3$:Eu^{3+} [6] and $LiTaO_3$:Eu^{3+} [7]

since, due to its high intensity, it has been easy to distinguish two superimposed bands.

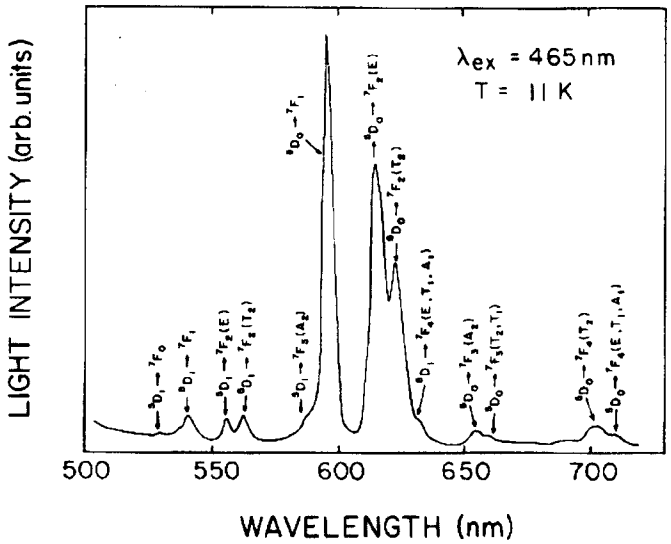

FIGURE 2. 11 K emission spectrum of Eu^{3+} ions in Cs_2KEuCl_6 under excitation at 465 nm.

The RT and 11 K excitation spectra taken at 622 nm (transition $^5D_0 \rightarrow {}^7F_2(T_{2g})$) for the Cs_2KEuCl_6 sample are shown in Figure 3. At 11 K the absorptions only occur from the $^7F_0$ ground state, and the $^7F_0 \rightarrow {}^5D_0$ strictly forbidden transition appears with a vibronic structure, arising, therefore, from a phonon-assisted electric-dipole process. The intensity of the known hypersensitive transition $^7F_0 \rightarrow {}^5D_2$ [8] is rather vibronic, since it decreases at 11 K.

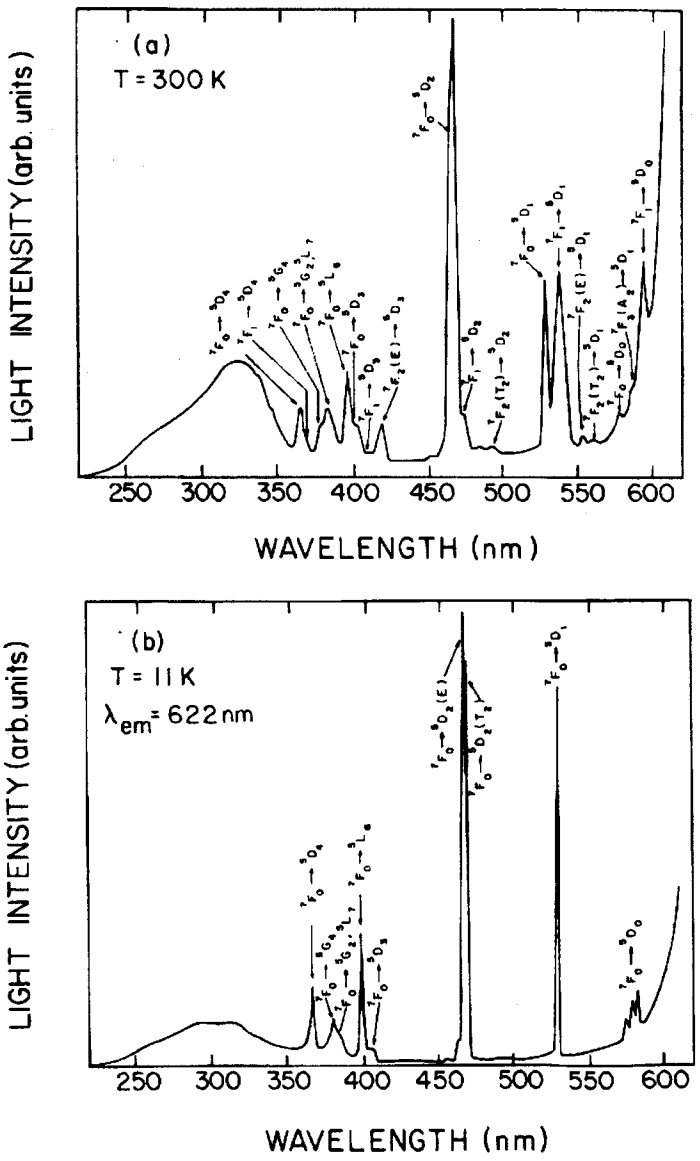

FIGURE 3. Excitation spectra at (a) RT and (b) 11 K of Eu^{3+} ions in Cs_2KEuCl_6 (λ = 622 nm).

The energies of the observed transitions in the Eu^{3+} emission and excitation spectra are given in Table 2.

TABLE 2. Energy levels of Eu^{3+} in Cs_2KEuCl_6

Manifold	Possitions at 300K (cm^{-1})	
	Excitation	Emission
$^5D_4(A_{1g}, T_{1g}, E_g, T_{2g})$	27 473	
$^5G_4$	26 462	
$^5G_2$, $^5L_7$	26 171	
$^5L_6$	25 278	
$^5D_3(A_{2g}, T_{2g}, T_{1g})$	24 814	
$^5D_2(E_g, T_{2g})$	21 427	
$^5D_1(T_{1g})$	18 937	18 900
$^5D_0(A_{1g})$	17 241	17 160
$^5F_4(A_{1g}, T_{1g}, E_g)$		3 076
$^5F_4(T_{2g})$		2 895
$^7F_3(T_{1g}, T_{2g})$		2 020
$^7F_3(A_{2g})$	1 907	1 886
$^7F_2(T_{2g})$	1 113	1 086
$^7F_2(E_g)$	880	868
$^7F_1(T_{1g})$	350	350
$^7F_0(A_{1g})$	0	0

3. Non-Radiative Energy Transfer $Tb^{3+} \rightarrow Eu^{3+}$ in $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$

Figure 4(a) shows the RT emission spectrum of $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$ obtained with excitation into the Tb^{3+} $^7F_6(A_{1g}, T_{1g}, T_{2ga}) \rightarrow {}^5D_4$ absorption band at 488 nm. At this wavelength, no emission of Eu^{3+} ions in Cs_2KEuCl_6 is achieved; however, emissions from the Eu^{3+} $^5D_1$ and $^5D_0$ levels are observed in $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$. On the other hand, the RT excitation spectrum for the $^5D_0 \rightarrow {}^7F_2(E_g)$ Eu-emission, taken at 610 nm, not only contains absorption transitions from the $^7F_0$, $^7F_1$ and $^7F_2$ levels of the Eu^{3+} ion but also Tb^{3+} transitions from the $^7F_6$ level as can be appreciated in Figure 4(b). The fact that Eu^{3+} emission is produced via excitation of Tb^{3+} ions clearly demonstrates that energy

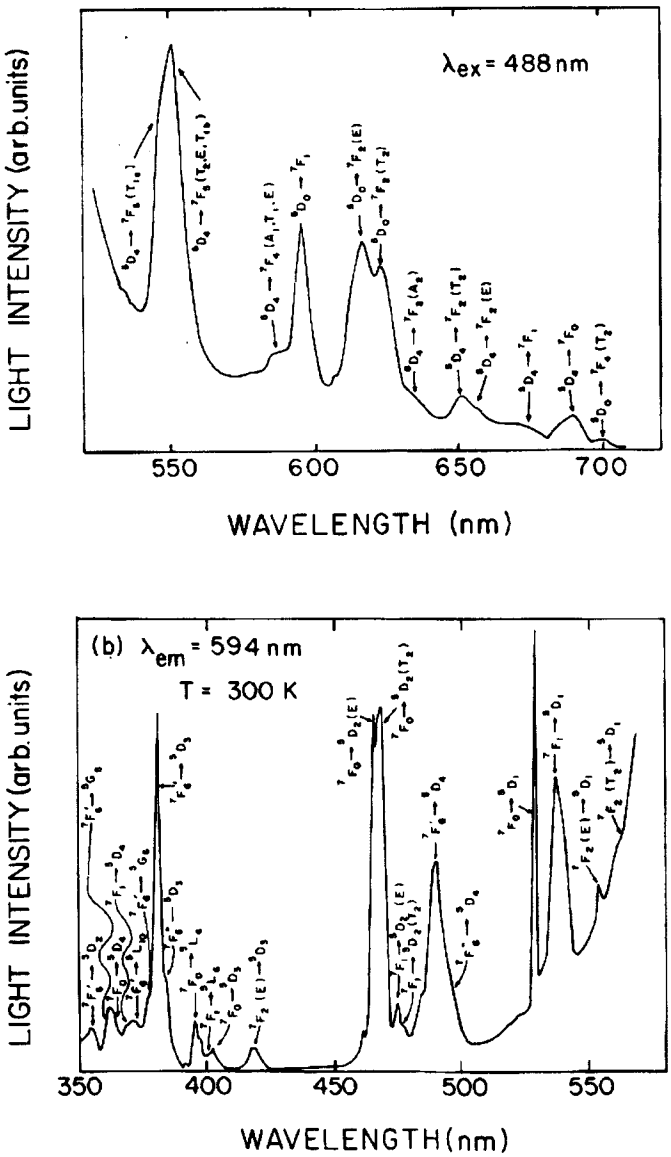

FIGURE 4. RT spectra of (a) emission and (b) excitation of $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$. The absorptions from the sublevels A_{1g}, T_{1g} and T_{2g} or A_{2g},T_{2gb} and E_g of the Tb $^7F_6$ state are marked by $^7F_6$' and $^7F_6$", respectively.

transfer from Tb^{3+} to Eu^{3+} ions takes place in the hexachloroelpasolite lattice. This process is expected to occur at RT since the Tb^{3+} $^5D_4 \rightarrow {}^7F_4$ emission overlaps the Eu^{3+} $^7F_1 \rightarrow {}^5D_0$ and $^7F_3(A_{2g}) \rightarrow {}^5D_1$ absorptions, and the Tb^{3+} $^5D_4 \rightarrow {}^7F_5(T_{2g}, E_g, T_{1gb})$ emission overlaps the Eu^{3+} $^7F_2(E_g) \rightarrow {}^5D_1$ absorption. Considering that these Eu^{3+} transitions disappear at low temperature (see Fig. 3(b)), the transfer process results, then, strongly temperature dependent. In fact, the $Tb^{3+} \rightarrow Eu^{3+}$ transfer is quenched at low temperature, such that the intense $^5D_0 \rightarrow {}^7F_2(E_g)$ transition of Eu^{3+} is hardly manifested in the 11 K 488-nm-excited emission spectrum (Figure 5).

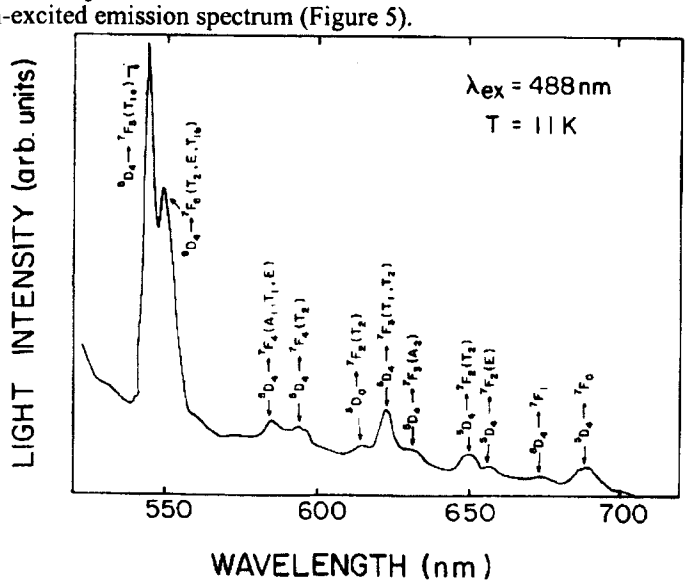

FIGURE 5. 11 K emission spectrum of $Cs_2KTb_{0.9}Eu_{0.1}Cl_6$ obtained with 488 nm excitation.

Thus, the most probable mechanisms responsible for the energy transfer from the Tb^{3+} $^5D_4$ state to the Eu^{3+} $^5D_1$ and $^5D_0$ states at RT are:

$$^5D_4[Tb] + {}^7F_1[Eu] \rightarrow {}^7F_4(T_{2g})[Tb] + {}^5D_0[Eu], \quad (1)$$

$$^5D_4[Tb] + {}^7F_2(E_g)[Eu] \rightarrow {}^7F_5(T_{2g}, E_g, T_{1gb})[Tb] + {}^5D_1[Eu] \quad (2)$$

and $$^5D_4[Tb] + {}^7F_3(A_{2g})[Eu] \rightarrow {}^7F_4[Tb] + {}^5D_1[Eu]. \quad (3)$$

However, the contribution of the transfer mechanisms (1) and (2) is likely to be almost negligible, since these processes involve the Eu^{3+} electronic absorption transitions $^7F_1 \rightarrow {}^5D_0$ and $^7F_2(E_g) \rightarrow {}^5D_1$, which are purely magnetic dipole allowed, and it is well known that couplings involving this type of transitions give rise to negligible energy transfer probabilities [9]. On the other hand, the process (3) involves the $^7F_3(A_{2g}) \rightarrow {}^5D_1$ Eu^{3+} absorption and the $^5D_4 \rightarrow {}^7F_4$ Tb^{3+} emission, and therefore, it must involve the coupling of an electric dipole vibronic transition on the Eu^{3+} ion to an electric quadrupole or electric dipole vibronic transition on the Tb^{3+} ion. We can, therefore, assign the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer mechanism as a combination of these three processes, but with a contribution of (1) and (2) likely almost negligible.

Further information about the mechanisms responsible for this transfer can be achieved by studying the kinetics of the Tb^{3+} and Eu^{3+} luminescence as a function of the fractional concentration x.

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