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INFLUENCE OF CHARGE COMPENSATION ON UV-EXCITATION OF RARE-EARTH FLUORESCENSE

by

W. Viehmann

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U.S. ARMY MATERIEL COMMAND
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ABSTRACT

Excitation spectra for the fluorescence transitions of Tb^{3+}, Eu^{3+}, and Dy^{3+} were obtained at room temperature on single crystals of the tungstates and molydates of Ca, Sr, Pb, and Cu, having the Scheelite structure, and on terbium-doped crystals of CaF_2 and SrF_2. Rare-earth concentrations were nominally one atomic percent and charge compensation was provided by vacancy formation or interstitials, by substitution in cation-sites or by anionic substitutions. Strong UV-excitation bands were found for Tb- and Eu-doped crystals and weaker bands for Dy-doped matrices. The bands generally occur near the host-lattice absorption-edge but their intensities and energy positions are strongly influenced by the charge-compensating defects near the active ion. The long wavelength peaks of the bands occur at energies coinciding with 4f-level positions of the rare-earth ions, suggesting a strong perturbation of 4f-levels by charge transfer states. The short-wavelength regions of the excitation bands are ascribed to exchange transfer from UV-absorbing groups.

1. INTRODUCTION

Following the work of Botden and Kroeger on energy transfer and energy transport in samarium-activated calcium tungstate (ref 1, 2), host sensitization of rare-earth fluorescence has been studied extensively in a number of oxide matrices (ref 3-13).* Many of these investigations have been stimulated by the importance of these processes for solid-state laser materials. In Y_2O_3: Eu^{3+}, for example, the broad UV-excitation band for Eu^{3+} fluorescence just below the lattice absorption edge of Y_2O_3 enabled laser action to be induced in this material (ref 4). However, from a theoretical point of view, investigations of luminescence sensitization by lattice processes are also of considerable interest, since, at least in principle, such experiments yield information on excited states of the lattice. The present investigation was undertaken to elucidate some of the mechanisms and processes responsible for energy transfer and energy transport in rare-earth doped crystals. Specifically, the influence of the defect structure of the host lattice on these processes is of interest here.

The incorporation of trivalent rare-earth ions into host lattices having divalent cations, such as alkaline earth fluorides, tungstates and molybdates, creates specific electronic defects in the lattice, depending on the mechanism of charge compensation employed (ref 14).

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*For a review of recent work on luminescence in rare-earth doped matrices see: L. G. Van Uitert-"Luminescence of Insulating Solids for Optical Masers" in "Luminescence of Inorganic Solids." Ed. by Paul Goldberg, Acad. Press. 1966.

If no charge-compensating ions are intentionally incorporated, charge compensation is accomplished by the creation of cation vacancies, as in the case of the tungstates and molybdates, according to the scheme: $2RE^{3+}$ + (Ca) vacancy replace 3 Ca^{2+}.

In the fluorides, the extra positive charge of rare-earth ions is thought to be compensated by the incorporation of interstitial fluorine ions (ref 15, 16). Another mechanism of charge compensation in fluorides as well as tungstates and molybdates is provided by the substitutional incorporation of monovalent cations, such as Na, according to: RE^{3+} + Na^+ replace 2 Ca^{2+} (ref 14, 17).

Proper substitutions in the anionic site can also be employed. For instance, RE^{3+} + Nb^{5+} replace Ca^{2+} + W^{6+} in the case of tungstates and RE^{3+} + S^{2-} replace Ca^{2+} + F^- for the fluorides.

The latter type of substitutional charge compensation has been employed in Eu^{3+}-doped CdF_2 by Kingsley and Prener (ref 18) who found an intense excitation band for the Eu^{3+} fluorescence in this material below the absorption edge of pure CdF_2 and ascribed it to exciton processes in europium-sulfide ion pairs and subsequent transfer of excitation to Eu^{3+}. In the present work, single crystals of CaF_2, SrF_2, $CaWO_4$, $SrWO_4$, $PbWO_4$, $CaMoO_4$, $SrMoO_4$, $PbMoO_4$, and $CdMoO_4$ activated by Tb, Eu, and Dy and with the various charge compensation ions as outlined above were prepared and their excitation spectra measured.

Table I. Materials Investigated

Active Ion	Charge Comp	Matrix
Tb^{3+}	Na	CaF_2, SrF_2
	F_{i-}	CaF_2, SrF_2
	Vac(=θ)	$CaWO_4$, $SrWO_4$, $SrMoO_4$, $PbMoO_4$
	Na	$CaWO_4$, $SrWO_4$, $SrMoO_4$, $CaMoO_4$, $CdMoO_4$
	Nb	$CaWO_4$, $SrWO_4$, $SrMoO_4$, $CaMoO_4$, $PbWO_4$, $PbMoO_4$, $CdMoO_4$
	Ta	$CaWO_4$
Dy^{3+}	Vac	$CaWO_4$, $SrWO_4$, $CaMoO_4$, $SrMoO_4$
	Na	$CaWO_4$, $SrWO_4$, $CaMoO_4$, $SrMoO_4$
	Nb	$CaWO_4$, $SrWO_4$, $CaMoO_4$, $SrMoO_4$, $CdMoO_4$, $PbMoO_4$
Eu^{3+}	Na	$CaWO_4$
	Nb	$CaWO_4$, $CdMoO_4$, $PbWO_4$, $CaMoO_4$
	Ta	$CaWO_4$, $SrWO_4$, $CaMoO_4$

2. CRYSTAL GROWTH

Rare-earth doped crystals of the tungstates and molybdates listed in table I were grown by the Czochralski method in an apparatus similar to that described by Nassau and Broyer (ref 19). Optical-grade commercial powders were used as starting materials except for $PbMoO_4$ and $PbWO_4$, which were prepared from reagent-grade constituent oxides. The rare earths were added to the melt in the form of their trivalent oxides of 99.9 percent purity, sodium was added in the form of reagent grade $Na_2(WO_4)_3$ and $Na_2(MoO_4)_3$, and niobium and tantalum as optical-grade Nb_2O_5 and Ta_2O_5. For uncompensated and sodium-compensated crystals, melt compositions were computed on the basis of the various distribution coefficients as published by Nassau and Loiacono (ref 14) to yield crystals having rare-earth concentrations of one atomic percent. Rare-earths and niobium were added to the melts in molar ratios of 1:1 and distribution coefficients as given by Brixner (ref 20, 21) were used. Since no exact distribution coefficients for the cadmium and lead compounds are known, the crystal compositions given in these cases represent only approximate values.

Vacancy-compensated molybdates showed pronounced formation of color centers, which could generally be annealed out by heating the crystals in oxygen for about 24 hr at 1300°C. Europium, which enters the Scheelite structure in the divalent form, could be converted to Eu^{3+} by heating in oxygen in $CaWO_4$: Eu; Nb, $CaWO_4$: Eu; Ta, $CaMoO_4$: Eu; Nb, $CaMoO_4$: Eu; Ta, $PbWO_4$: Eu; Nb and $CdMoO_4$: Eu; Nb. In $CaWO_4$: Eu; Na and $SrWO_4$: Eu; Ta the conversion was only partial, even after 60 hr in O_2 at 1300°C.

The doped fluorides of calcium and strontium were grown in a graphite crucible by the Stockbarger method. The starting materials were optical-grade commercial powders to which lead fluoride was added as a scavenger. Sodium was added as reagent grade NaF and the rare earth as trifluoride of 99.9 percent purity. Growth proceeded in an atmosphere of dry argon. Tb concentrations in the melt were one atomic percent and the sodium-to-terbium ratio was 5:1 to insure complete compensation.

3. MEASUREMENTS

Absorption spectra were measured on optically ground and polished crystals of 6 mm thickness using a Carey 14 spectrophotometer. Excitation and emission spectra were obtained on the same samples at room temperature with the aid of a commercial instrument having two monochromators, which could be programmed independently to yield either excitation or emission spectra. The excitation source was a xenon arc lamp and the detection system consisted of a 1P21 phototube and an

Aminco photomultiplier microphotometer. The resolution of the instrument is about 25 Å. The excitation spectra were not corrected for constant excitation energy nor for the wavelengths dependence of the detector sensitivity, since we were interested in relative results only.

4. RESULTS

4.1 Absorption Spectra Near the Band Edge

Figure 1 depicts the UV-absorption spectra of Tb-doped CaF_2, SrF_2, and $CaWO_4$, measured at 77°K, with the various charge-compensating ions as indicated in the legend. The doping level is nominally one atomic percent in all samples.

The line spectra associated with 4f-4f transitions within the Tb^{3+} ion are weak compared with those for other rare-earth ions, even in $CaWO_4$, where the forbiddenness is lifted by interconfigurational mixing in the crystal field of S_4 symmetry. They are considerably weaker still in the fluorides, since interconfigurational mixing is absent and 4f-4f transitions are forbidden in crystal fields of cubic symmetry. In the fluoride crystals containing no intentional charge-compensating ion and in which charge compensation is believed to take place by the incorporation of interstitial fluorine, 4f-absorption transitions of Tb^{3+} are barely discernible and they are practically absent in the sodium-compensated samples.

A surprising result is the appearance of a rather broad (100 Å) band with a superimposed line spectrum in the CaF_2: Tb; Na samples about 350 Å below the absorption edge.

In SrF_2: Tb; Na, the band is somewhat weaker and is shifted to higher energy. Absorption measurements at room temperature showed that the bands broaden but do not shift with temperature. No such bands are found in the crystals without sodium added for charge compensation.

In $CaWO_4$, in which charge compensation takes place in substitutional sites only, the bands appearing below the intrinsic absorption edge of the pure base lattice are much stronger and are not resolved as such within the absorption range obtainable with our equipment.

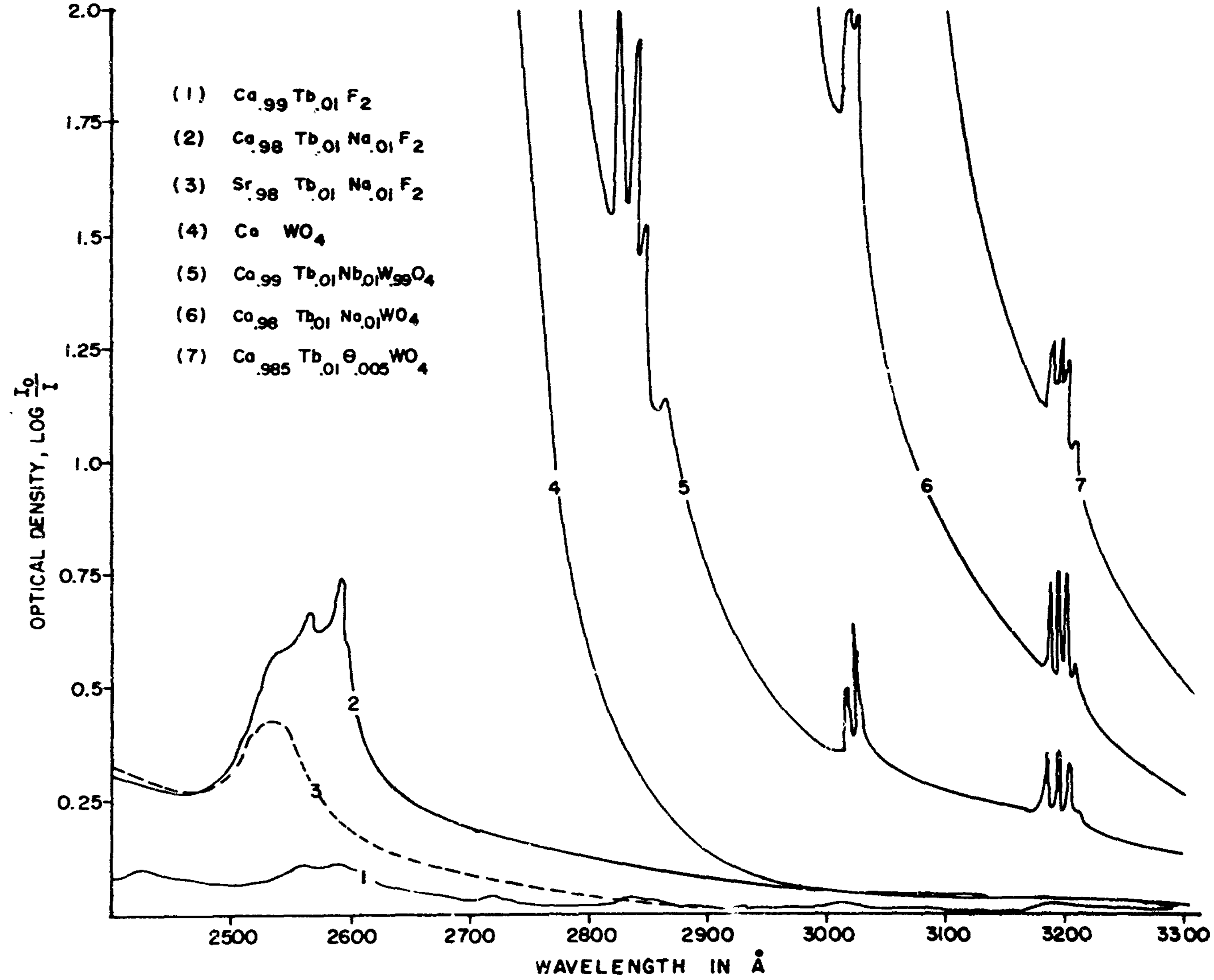

Figure 1. UV-absorption spectra of Tb^{3+}-doped $CaWO_4$, CaF_2, and SrF_2 with various charge compensating defects, measured at 77°K.

4.2 Tb^{3+} Excitation

The strong interaction between these absorption bands and 4f-levels of Tb^{3+} becomes apparent in the excitation spectra. Figure 2 shows the intensity of the $^5D_4$-$^7F_5$ transition of Tb^{3+} as a function of the exciting wavelength in CaF_2: Tb; Na and CaF_2: Tb. In the sodium-compensated crystal, a rather pronounced excitation band centered at 2600 Å coinciding with the absorption band of figure 1 is found, in contrast to the interstitially compensated sample, where only direct excitation of Tb^{3+} in its 4f-levels is observed. It should be noted here that in this sample pumping into the lower-lying 4f-levels of Tb^{3+} leads to stronger excitation than in the Na-compensated crystal in accordance with the stronger absorption lines observed in CaF_2: Tb.

In SrF_2: Tb; Na, the strong excitation band is centered at 2550 Å. It is only about 1/3 as strong in the interstitially compensated sample in excitation as well as absorption (latter not shown in figure 2). Direct excitation of 4f transitions, however, leads to stronger fluorescence of Tb^{3+} in this material, an observation in accordance with the effect previously observed in CaF_2: Tb and CaF_2: Tb; Na. In both matrices, rather weak host sensitization bands centered at 2200 and 2300 Å can be discerned, which correspond to bands also seen in absorption.

Tb^{3+} when present in low concentrations shows fluorescence from a second, higher metastable state, $^5D_3$, to the ground-state manifold in various matrices.

With increasing concentration, however, fluorescence from this level quenches strongly due to a Varsanyi-Dieke type interaction between coupled Tb-ion pairs, which is made possible by the circumstance that the width of the ^7F multiplet is almost exactly equal to the separation between the $^5D_3$ and $^5D_4$ manifolds (ref 22, 23, 24). In the fluorides studied here, $^5D_3$-$^7F_4$ fluorescence is only very weakly excited by pumping into the exciton band and practically absent under direct absorption into the 4f-levels of Tb^{3+}.

Similar results are obtained on $CaWO_4$ and $SrWO_4$. As shown in figures 3 and 4, strong excitation bands for the $^5D_4$ fluorescence are observed below the intrinsic absorption edge of the base lattice.

Weaker excitation bands are present for the $^5D_3$-^7F fluorescence transitions. They do not, however, generally coincide in energy with those for the $^5D_4$-^7F transitions and they are weaker in $SrWO_4$ than in $CaWO_4$. Below these bands, the usual line spectra for $^5D_3$-^7F as well as $^5D_4$-^7F transitions are found.

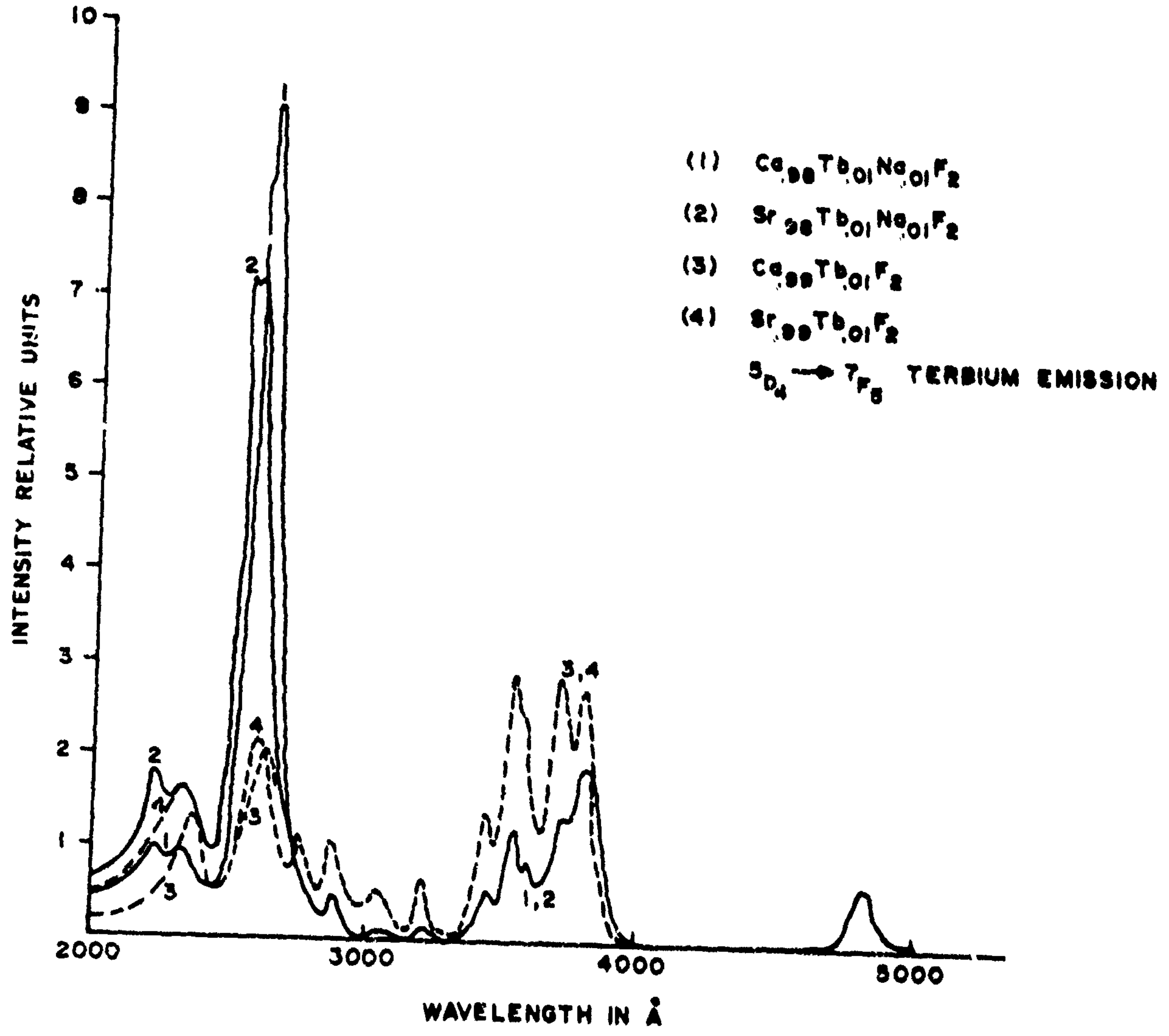

Figure 2. Excitation spectra for the $^5D_4$-$^7F_5$ fluorescence transition of Tb^{3+} in CaF_2 and SrF_2 at room temperature.

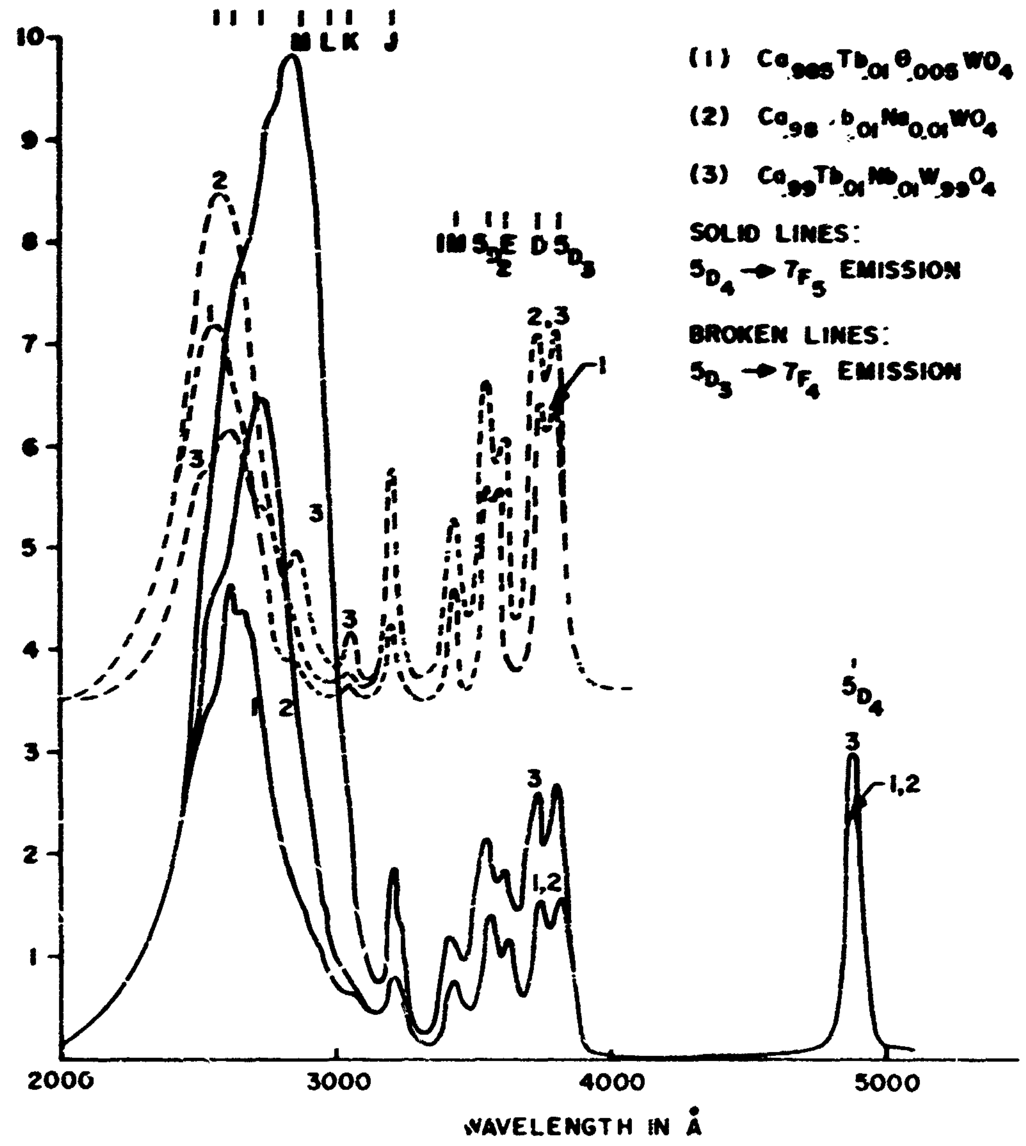

Figure 3. Excitation spectra for the $^5D_4$-$^7F_5$ and $^5D_3$-$^7F_4$ fluorescence transitions of Tb^{3+} in $CaWO_4$ at room temperature. The base line for the latter has been shifted for clarity. Spectra for Ta-compensated crystals are identical to those with Nb-compensation. Known 4f-levels of Tb^{3+} are indicated in the figure.

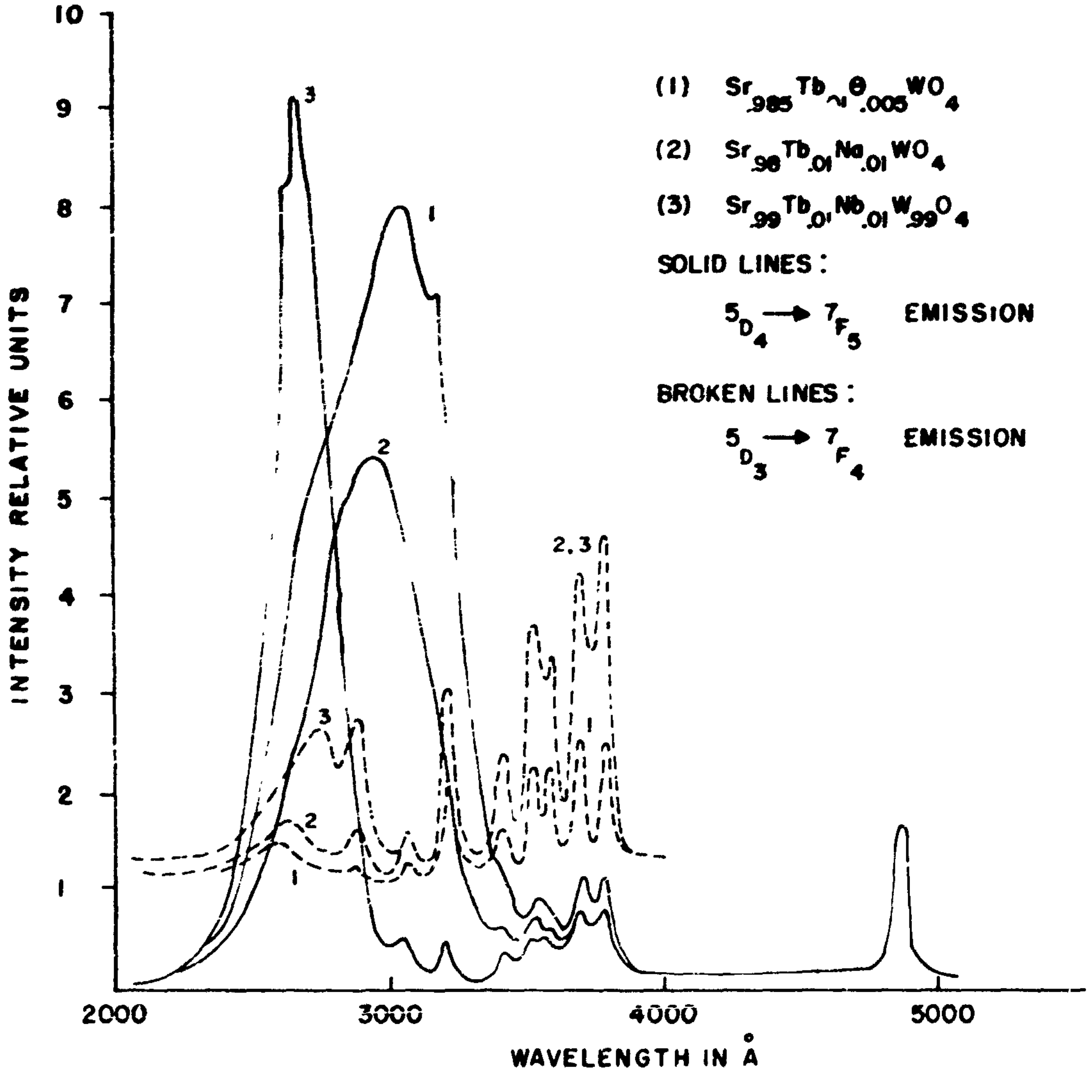

Figure 4. Room-temperature excitation spectra for the fluorescence transitions of Tb^{3+} in $SrWO_4$ with various charge compensations. Base lines have been shifted for clarity.

Superimposed on figure 3 are the energy levels of Tb^{3+} and their labels (where known) as published by Dieke (ref 25). It is apparent from figures 3 and 4 that the excitation bands for both transition groups peak at energies coinciding with 4f-levels of the Tb^{3+} ion. This evidence strongly suggests that interactions between exciton bands and 4f-levels lead to these pronounced excitation bands. Which 4f-levels are involved depends on the base lattice as well as on the charge-compensating ion or local defect structure, in an apparently complicated manner. These findings are supported by the results obtained on Tb-Nb-doped $PbWO_4$, shown in figure 5. Only a line spectrum is found for the $^5D_3$-$^7F_4$ fluorescence excitation; i.e., this transition is only excited by direct pumping of the Tb^{3+}-4f levels, whereas in addition to a line spectrum, a pronounced band is found for the $^5D_4$-$^7F_5$ fluorescence excitation, which peaks over Tb-4f levels. This band is centered at about the absorption edge of $PbWO_4$ (3400 Å).

In the molybdates of Ca and Sr, the energy position of the broad excitation bands is essentially independent of the charge-compensating ion, as shown in figure 6. In both hosts the bands peak at approximately 3100 Å, a wavelength that falls between two 4f-multiplets of Tb^{3+}, (J, K).

It may be noted here that the intensity of the excitation depends quite strongly on the charge compensator, with Nb giving the highest, vacancy compensation the lowest, and Na an intermediate intensity in $SrMoO_4$. In $CaMoO_4$, this order is reversed, with sodium giving noticeably higher intensity than Nb. (A satisfactory vacancy-compensated $CaMoO_4$: Tb crystal could not be grown due to excessive color center formation.)

In $PbMoO_4$ the excitation bands are very weak (fig. 5), with niobium compensation giving the stronger band, and in $CdMoO_4$ no Tb^{3+} fluorescence could be observed, regardless of charge compensation employed.

In $SrMoO_4$ the $^5D_3$-$^7F_4$ fluorescence transition could be excited by direct pumping into Tb^{3+} -4f levels below the absorption edge; whereas in $CaMoO_4$ and $PbMoO_4$ this transition was about 2 to 3 orders of magnitude weaker than the $^5D_4$-$^7F_5$ fluorescence transition.

4.3 Eu^{3+} Excitation

Our data on the excitation of Eu^{3+} fluorescence are limited to a few host crystal-charge compensator systems, in which Eu could be obtained in trivalent form (sect 2). Trivalent Eu in Scheelite structures shows fluorescence transitions from four metastable levels, $^5D_3$, $^5D_2$, $^5D_1$, and $^5D_0$, to various levels of the ^7F ground-state manifold, with those originating from the $^5D_0$ level being the more intense (ref 26).

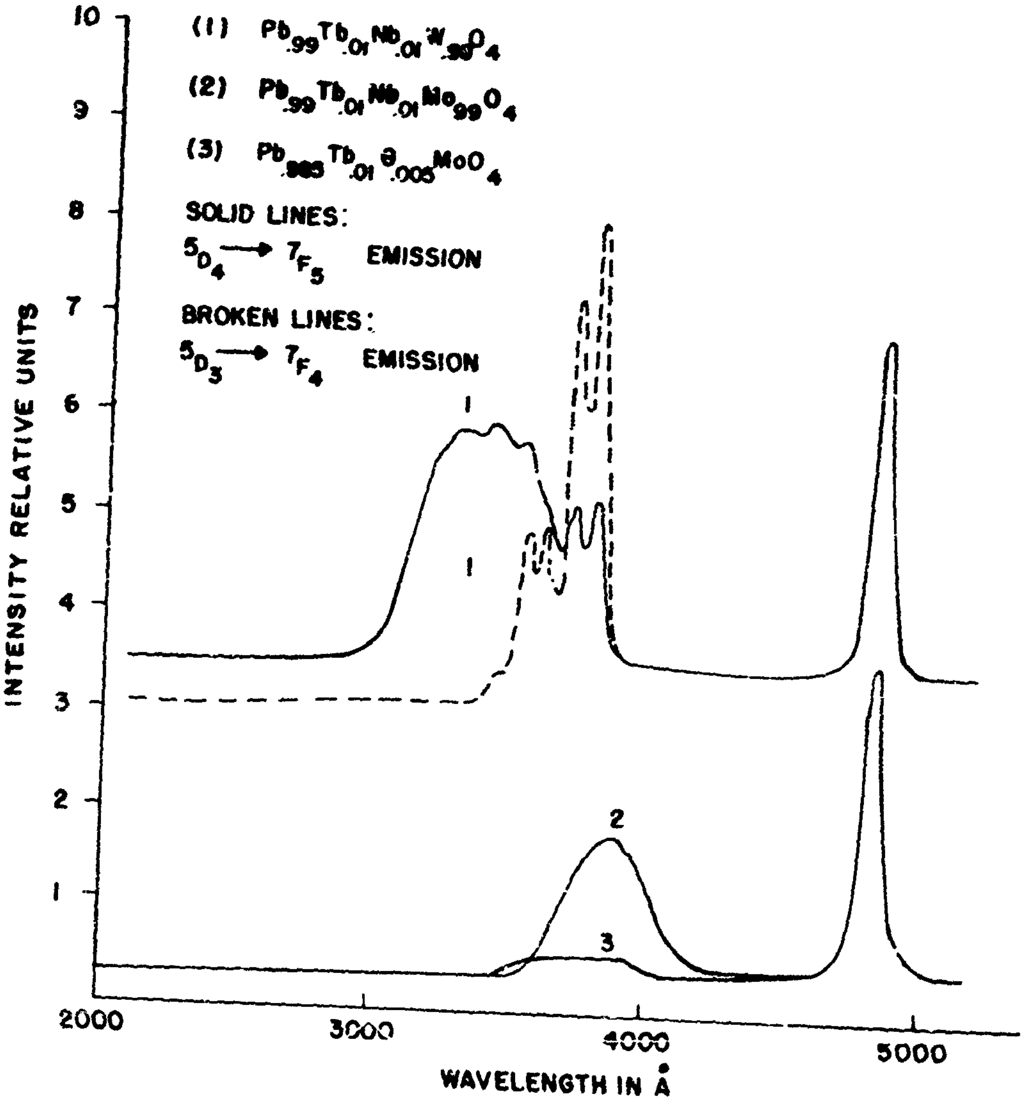

Figure 5. Room-temperature excitation spectra for the fluorescence-transitions of Tb^{3+} in $PbWO_4$ and $PbMoO_4$. Base lines have been shifted for clarity.

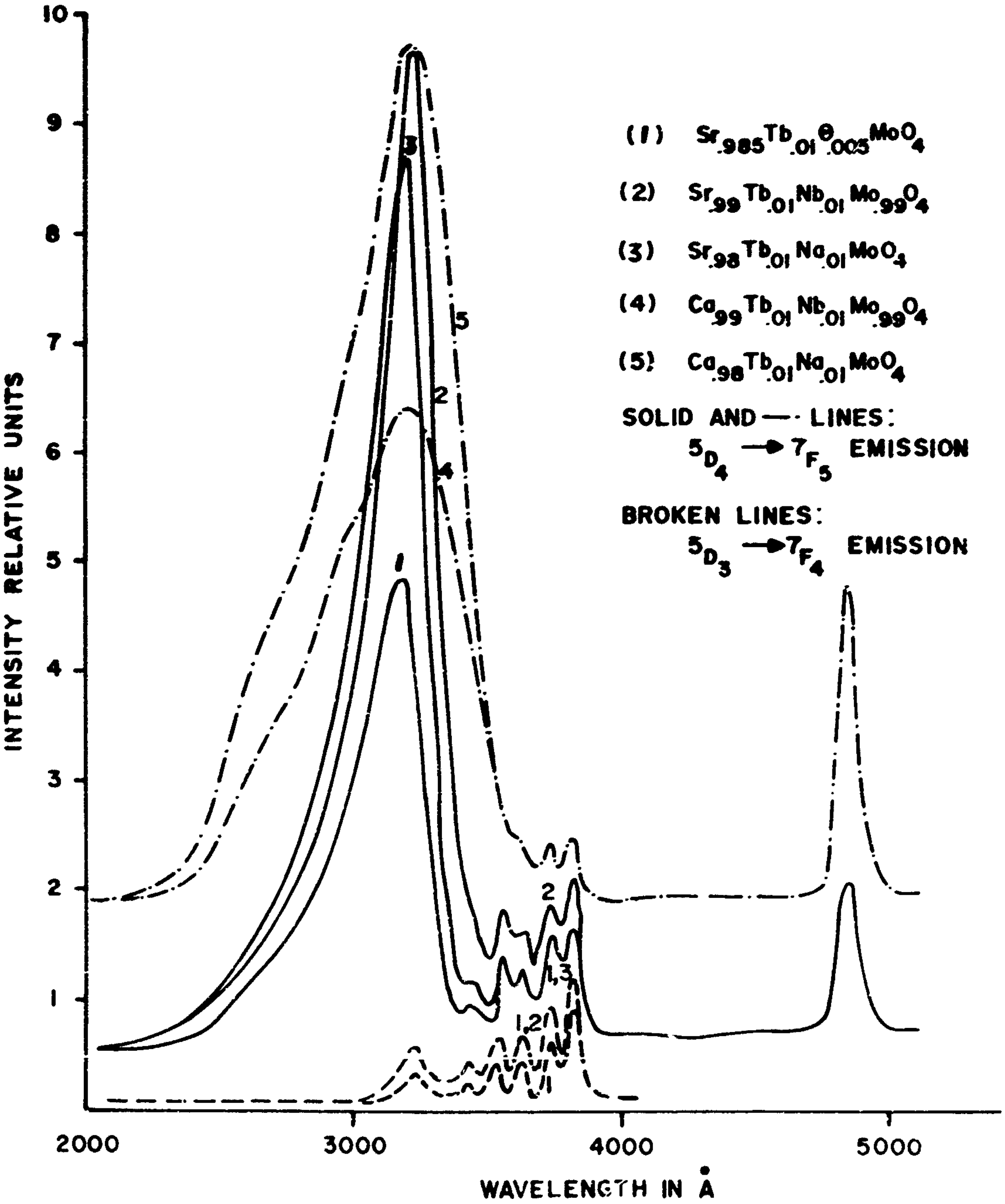

Figure 6. Room-temperature excitation spectra for the fluorescence transitions of Tb^{3+} in $CaMoO_4$ and $SrMoO_4$ with various charge compensations. Base lines have been shifted for clarity.

Excitation spectra of the $^5D_0$-$^7F_2$ transition of Eu^{3+} are shown in figure 7 for Eu^{3+} concentration of nominally one atomic percent. Incomplete conversion of Eu^{2+} to Eu^{3+} in $CaWO_4$: Eu; Na and $SrWO_4$: Eu; Ta causes a tail on the absorption edge of these crystals, extending to about 4500 Å. This band accounts for the observed reduction of excitation below this wavelength. Whereas Tb^{3+} did not fluoresce in $CdMoO_4$, a very intense excitation band is observed for Eu^{3+} in this material with a peak at 3600 Å.

In $CaWO_4$ and $CaMoO_4$, Nb compensation and Ta compensation yield identical excitation spectra. The excitation band for $CaMoO_4$: Eu; Nb and $CaWO_4$: Eu; Nb peaks at the same wavelength, 3200 Å but is quite weak in $CaWO_4$, as it is in $SrWO_4$: Eu; Ta, where the peak position is at approximately 2850 Å. If Na is used as charge compensation in $CaWO_4$, a rather intense band is observed at 2750 Å with a shoulder at 2500 Å.

No excitation band could be found in $PbWO_4$: Eu; Nb. $^5D_0$-$^7F_2$ fluorescence in this host could be excited only by pumping into the $^5D_2$ and $^5D_1$ levels directly. Fluorescence from the higher metastable levels of Eu^{3+} could be excited only by direct excitation of 4f-levels; i.e., no excitation bands were observed for these transitions in any of the hosts examined here.

Some of the lower-lying 4f-levels of Eu^{3+} are identified and indicated in figure 7, using the assignments by Dieke and Crosswhite (ref 25). Above the $^5D_3$ levels, experimentally verified assignments are not available. Calculations by Ofelt (ref 27) on the basis of free-ion wave functions indicate a very dense group of levels consisting of the ^5G and ^5L multiplets, as well as the $^5D_4$ level to occur above the $^5D_3$ level. Following this group, there is the ^5H multiplet, followed by a complex grouping of the ^5F, ^5I, and ^5K multiplets and the ^3P levels.

It is apparent from figure 7, that as previously observed in Tb-doped crystals, the excitation bands for the $^5D_0$-$^7F_2$ fluorescence transition of Eu^{3+} peak at energies coinciding with 4f-levels of the Eu^{3+} ion. The intensity and position of these peaks depend on the base lattice, as well as the charge-compensating ion, i.e., the local defect structure associated with the incorporation of the rare-earth ions.

4.4 Dy^{3+} Excitation

Excitation spectra for the $^4F_{9/2}$-$^6H_{13/2}$ fluorescence transition of Dy^{3+} in various Scheelite matrices are presented in figure 8. Apart from direct excitation of Dy-4f levels, only comparatively weak excitation bands are observed for this ion in the tungstates as well

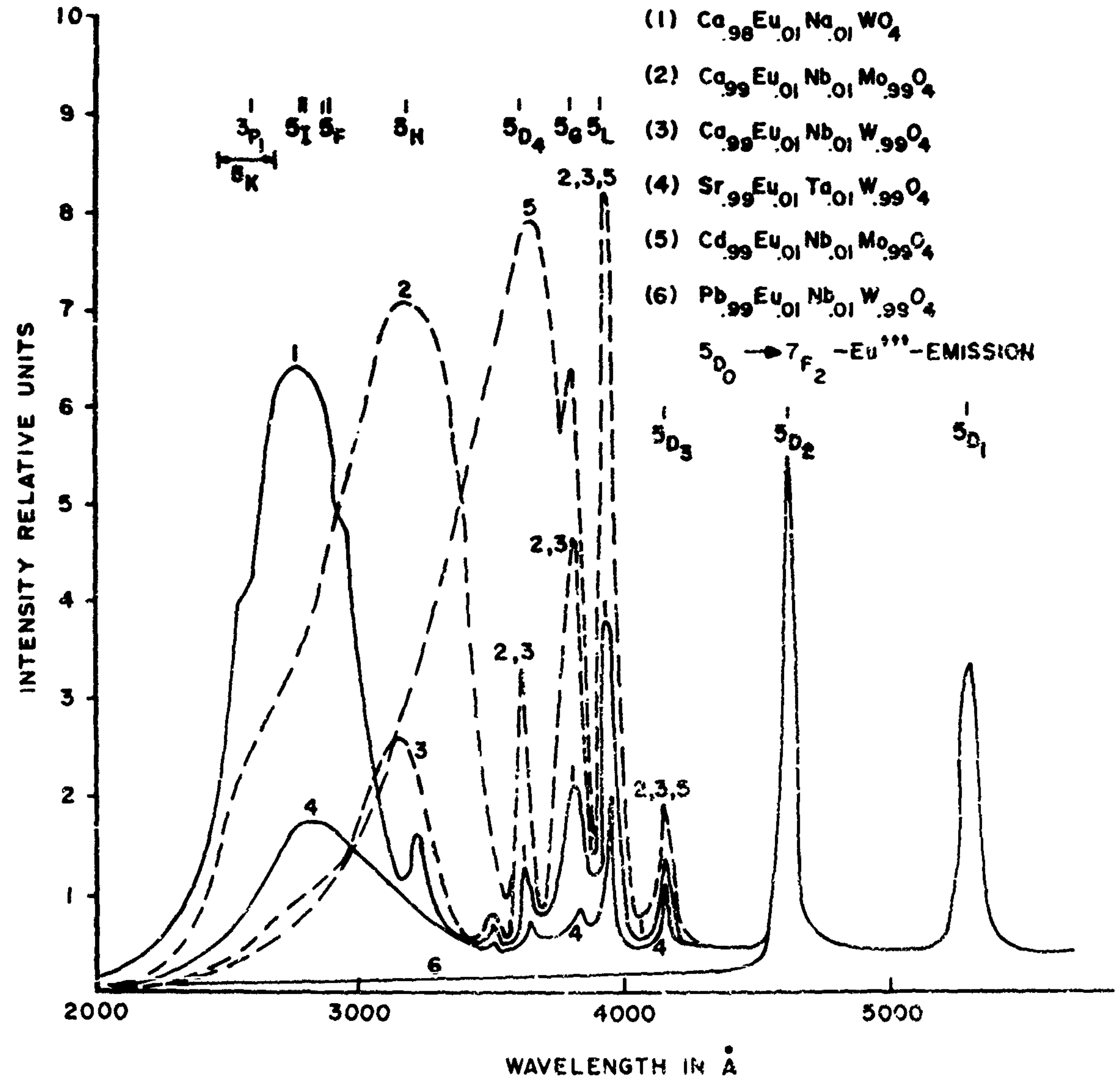

Figure 7. Excitation spectra for the $^5D_0$-$^7F_2$ fluorescence transition of Eu^{3+} at room temperature in various Scheelites as indicated in the legend. Known 4f-levels of Eu^{3+} are shown.

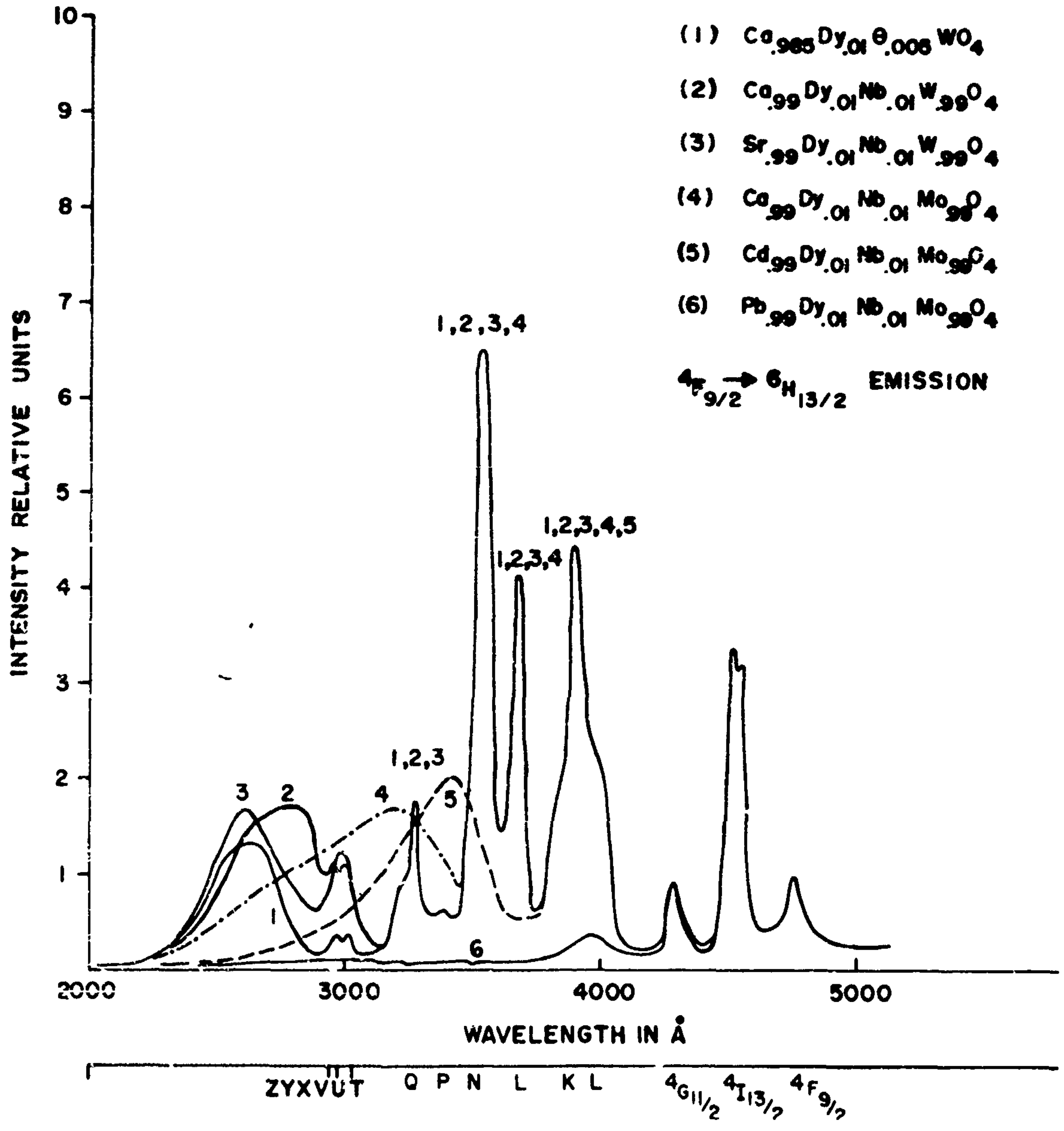

Figure 8. Excitation spectra for the ${}^4F_{9/2}-{}^6H_{13/2}$ fluorescence transition of Dy^{3+} in various Scheelites as indicated in the legend. Known 4f-levels of Dy^{3+} are marked.

as in the molybdates. In $CaMoO_4$ and $SrMoO_4$, the charge-compensating ion has no influence on the position and very little effect on the intensity of the excitation bands. In all cases, however, the band maxima occur at energies coinciding with those of various Dy^{3+} -4f levels. A particularly interesting behavior is presented by $CdMoO_4$: Dy; Nb. In this case the band peaks at Dy^{3+} levels centered at 3400 Å (PQ), a wavelength well inside the host absorption of $CdMoO_4$. The Dy-levels that lie directly below in the band edge of the base lattice and yield strong fluorescence in the other materials, are strongly quenched (L,N). The Dy-level at 3400 Å on the other hand yields only weak fluorescence in the other matrices.

5. DISCUSSION

Sensitization of rare-earth fluorescence in hosts containing UV-absorbing groups, such as WO_4^{2-}, MoO_4^{2-}, NbO_4^{3-}, and VO_4^{3-}, is thought to be due to absorption in these groups and subsequent transfer of energy to the rare-earth ions via other absorbing groups. The conditions necessary for efficient sensitization have recently been discussed by Blasse (ref 12), on the basis of a model in which transport from absorbing group to absorbing group as well as transfer to the rare-earth ion are regulated by exchange. The probability of energy transfer by exchange is equal to the product of wave function overlap and energy overlap (ref 28). Blasse and Bril (ref 11) conclude from studies of the system $Y_2W_{1-x}Mo_xO_6$ that transfer from tungstate to tungstate or molybdate group takes place, whereas there is no transfer from molybdate to molybdate or tungstate group due to lack of energy overlap. Similar results had been obtained earlier by Kroeger (ref 2) for the system $CaW_{1-x}Mo_xO_4$.

Exchange-regulated energy transfer from the absorbing groups to the rare-earth ions is also determined by the wave function overlap of the respective orbitals, and the energy overlap of the group emission and the rare-earth absorption levels.

Scheelites emit broad bands centered around 23,000 cm^{-1} for the tungstates and around 18,000 cm^{-1} for the molybdates (ref 2). The requirement of energy overlap with emitting levels of Tb, Eu and Dy is therefore satisfied and energy transfer to these ions is determined mainly by orbital overlap (ref 12). For the tungstates of Ca and Sr, the energy overlap with the Tb-$^5D_3$ level is actually better than with the $^5D_4$-level. Judging from figures 3 and 4, the excitation of the former appears to be derived mainly from the WO_4 group, since the excitation bands for the $^5D_3$-$^7F_4$ emission of terbium coincide with those for the host-lattice emission (not shown) and are influenced in intensity but not in position by the various charge compensations.

In the molybdates, energy overlap with the Tb-$^5D_3$ level is quite poor, but very good for the $^5D_4$-level. Excitation spectra for this level are little influenced in their position by the various charge compensators as previously noticed in the tungstates for the excitation of the $^5D_3$-level. NbO_4^{3-} substitution shows opposite effects on transfer probability to the $^5D_4$-level in $CaMoO_4$ and $SrMoO_4$ and on transfer to the $^5D_3$-level in the calcium and strontium tungstates. Niobium substitution reduces transfer in the Ca compounds and enhances transfer in the Sr compounds. A possible explanation would be that good energy overlap between WO_4^{2-} or MoO_4^{2-} emission with the NbO_4^{3-} emission is present in $SrWO_4$ and $SrMoO_4$, and poor overlap exists in the Ca compounds. Due to lack of this overlap, NbO_4^{3-} groups will inhibit energy transport from remote WO_4^{2-} groups to the groups next to the rare-earth ions.

The excitation bands for the $^5D_4$-$^7F_5$ fluorescence transition of Tb^{3+} in $CaWO_4$ and $SrWO_4$ consist of two or more overlapping bands. Of these, the high-energy portion coincides with the excitation band for the host-lattice emission and is therefore ascribed to energy transfer from WO_4^{2-} groups.

A different excitation mechanism must be responsible for the low-energy portions of the bands. Broad excitation bands below the intrinsic absorption edge of rare-earth-doped oxide matrices have been investigated by Ropp (ref 5) and by Blasse and Bril (ref 13). Ropp ascribed these bands to allowed transitions in highly perturbed 4f-levels and Blasse and Bril have presented evidence that a charge-transfer process from O^{2-} to Eu^{3+}, resulting in orbital mixing between the two ions, is responsible for these bands. It appears that our findings on Tb-doped fluorides lend support to these arguments. From the absorption measurements presented in figure 1, it is evident that Tb^{3+} is directly excited in the 2500 to 2600 Å region. The fluoride hosts do not absorb in this region. The band appearing in the sodium-compensated crystal below the matrix absorption edge is thought to be due to a charge-transfer process from F^- to Tb^{3+} ions, the energy for such a transfer being lowered by the replacement of divalent cations by monovalent ions.

Similarly, a shift of the charge transfer bands to lower energy is observed in Tb-doped $SrWO_4$ upon substitution of monovalent sodium for Sr^{2+} and to still lower energy in the vacancy-compensated crystals.

These charge transfer states apparently couple quite strongly into certain 4f-states of the rare-earth ions, inducing strong transitions within this configuration. In Eu-Nb or Eu-Ta-doped $CaWO_4$ and $SrWO_4$, the excitation bands clearly occur below the host-absorption edge with their peak positions closely coinciding with 4f-level positions of Eu^{3+}. In the molybdates, the situation is not so clear.

Bands due to transfer from MoO_4^{2-} groups and those due to charge transfer apparently overlap quite closely. In the Dy-doped matrices, transfer from WO_4^{2-} and MoO_4^{2-} groups as well as charge transfer leads to weak excitation. The quenching of the host matrix emission of $CaWO_4$ and $SrWO_4$ under short wave UV-excitation is smaller in Dy-doped crystals than in Tb- or Eu-doped crystals, suggesting that the low efficiency of Dy excitation is not due to greater losses to the phonon spectrum or radiationless transitions but to weak transfer efficiency. Since the energy overlap of the Dy-$^4F_{9/2}$ level and WO_4^{2-} emission is only slightly less favorable than for the Tb-$^5D_4$ level, the low transfer probability must be due to lack of wave function overlap.

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13. ABSTRACT

Excitation spectra for the fluorescence transitions of Tb^{3+}, Eu^{3+}, and Dy^{3+} were obtained at room temperature on single crystals of the tungstates and molybdates of Ca, Sr, Pb, and Cd, having the Scheelite structure, and on terbium-doped crystals of CaF_2 and SrF_2. Rare-earth concentrations were nominally one atomic percent and charge compensation was provided by vacancy formation or interstitials, by substitution in cation-sites or by anionic substitutions. Strong UV-excitation bands were found for Tb- and Eu-doped crystals and weaker bands for Dy-doped matrices. The bands generally occur near the host-lattice absorption-edge but their intensities and energy positions are strongly influenced by the charge-compensating defects near the active ion. The long wavelength peaks of the bands occur at energies coinciding with 4f-level positions of the rare-earth ions, suggesting a strong perturbation of 4f-levels by charge transfer states. The short-wavelength regions of the excitation bands are ascribed to exchange transfer from UV-absorbing groups.

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