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Luminescence in Some Tantalate Host Lattices

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The luminescence of the following systems are reported: $ScTa_{1-x}Nb_xO_4$, $Li_3Ta_{1-x}Nb_xO_4$, $CaTa_{2-2x}Nb_{2x}O_6$ and $Mg_4Ta_{2-2x}Nb_{2x}O_9$. The dependence of the luminescence properties on x becomes more pronounced if the distance between the pentavalent ions becomes shorter. In these systems the NbO_6 group gives an efficient blue emission at 300°K. The compound $Mg_4Ta_2O_9$ gives an efficient ultraviolet emission at 300°K. At 77°K both $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ show in addition a weaker emission peaking at wavelengths longer than the wavelength of the room temperature emission. This low-temperature emission can be excited by radiation with wavelengths longer than that of the absorption edge. The Mn^{2+} ion in $Mg_4Ta_2O_9$–Mn acts as an efficient activator with a deep-red emission.

Introduction

In a recent paper we have described the luminescence of yttrium and the lanthanide tantalates and of several centres in these compounds (*1*). The tantalate emission in these lattice is situated in the ultraviolet. Efficient luminescence centres in $YTaO_4$ are the niobate group on the tantalate sites and some of the trivalent rare earth ions on the Y^{3+} sites. In the structure of $YTaO_4$ the tantalate group is a TaO_4 tetrahedron. Usually, however, the Ta^{5+} ion in oxides occupies octahedral holes, forming TaO_6 groups. We have shown before that this group can also give rise to efficient luminescence (*2*). In the present paper we will describe briefly the luminescence of some compounds with TaO_6 octahedra and the luminescence of some activators in these tantalate compounds, especially the luminescence of the niobate group.

Experimental

The experimental procedures have been described in a previous paper (*1*).

Results and discussion

We have investigated the following compositions:

$ScTa_{1-x}Nb_xO_4$. The compounds $ScNbO_4$ and $ScTaO_4$ have wolframite structure in contradistinction to the lanthanide tantalates (*3*). The two Sc compounds are completely miscible. In this solid solution series the Ta^{5+} ions occupy octahedral holes, whereas in the lanthanide tantalates with fergusonite structure they occupy tetrahedral holes. These tetrahedra share corners; the octahedra, however, share edges. In the latter case a stronger interaction between the tantalate groups is expected. Eu^{3+} and Tb^{3+} were used as activators.

$Li_3Ta_{1-x}Nb_xO_4$. The Li_3TaO_4 phase exists up to $x = 0.2$ (*4*). Here again there is edge-sharing between TaO_6 octahedra.

$CaTa_{2-2x}Nb_{2x}O_6$. The compounds $CaTa_2O_6$ and $CaNb_2O_6$ have different crystal structure both with $Me^{5+}O_6$ octahedra (*5, 6*).

$Mg_4Ta_{2-2x}Nb_{2x}O_9$. The compounds $Mg_4Ta_2O_9$ and $Mg_4Nb_2O_9$ are isomorphous. They have an ordered corundum structure in which the pentavalent cations form pairs by face sharing of their octahedra (*7*). This means that the interaction between these octahedral groups will now again be expected to be stronger compared to the cases with edge-sharing octahedra and corner-sharing tetrahedra. The distance between the pentavalent cations in the compounds $Mg_4(Ta, Nb)_2O_9$ is only 3.1 Å (*7*). In the case of edge-sharing octahedra this distance is longer, e.g., 3.34 Å in Li_3NbO_4 (*8*). In the compounds $Mg_4Ta_2O_9$ manganese was incorporated to investigate the luminescence of the Mn^{2+} ion.

Table I presents a survey of the materials that show efficient luminescence at room temperature.

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TABLE I

Luminescence at Room Temperature of some of the Compositions Studied

Composition	Emission region	Maximum quantum efficiency in uv (%)	Position maximum excitation band (nm)
$Mg_4Ta_2O_9$	uv	40	220
$Mg_4Ta_{1.9}Nb_{0.1}O_9$	Blue	60	230
$Mg_4Nb_2O_9$	Blue	30	248
$Mg_{3.96}Mn_{0.04}Ta_2O_9$	Red	60	270
$ScTa_{0.95}Nb_{0.05}O_4$	Blue	50	240
$Sc_{0.97}Eu_{0.03}TaO_4$	Red	25	250
$Sc_{0.97}Tb_{0.03}TaO_4$	Green	35	275
$Li_3Ta_{0.95}Nb_{0.05}O_4$	Blue	50	240
$CaNb_{1.9}Ta_{0.1}O_4$	Blue-green	50	260

$ScTa_{1-x}Nb_xO_4$

Results. The luminescence of $ScNbO_4$ has been described previously by us (*9*). This compound shows at room temperature a weak niobate emission consisting of a broad band peaking at 430 nm. At lower temperatures the efficiency remains low. In the system $ScTa_{1-x}Nb_xO_4$ the position of the emission band depends slightly on x. For $x = 0.02$, e.g. it is situated at 410 nm. For decreasing values of x the position of the niobate excitation (and absorption) band shifts to higher energies and the quenching temperature of the niobate luminescence increases, see Fig. 1. The relation between the position of the excitation band and the quenching temperature is linear. The decay time of the niobate emission in $ScTa_{0.95}Nb_{0.05}O_4$ is 12×10^{-6} sec.

The compound $ScTaO_4$ does not luminescence at room temperature. At liquid N_2 temperature it gives a blue-green emission under 254 nm excitation. The spectral energy distribution of the emission consists of a broad band peaking at about 490 nm. This is remarkable because usually the tantalate emission is situated at shorter wavelengths than the niobate emission in the same host lattice [Ref. (*1*) and this paper].

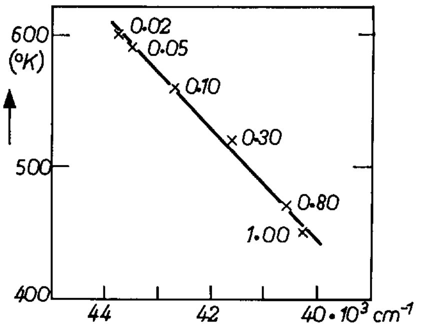

FIG. 1. Quenching temperature (T_q) of the niobate emission versus the maximum of the excitation band of this emission for the system $ScTa_{1-x}Nb_xO_4$. Values of x are indicated in the figure.

The rare-earth ions Eu^{3+} and Tb^{3+} in $ScTaO_4$ are activators with moderate efficiency, see Table I.

Discussion. The linear relation between the quenching temperature of the niobate emission and the position of its excitation band is in good agreement with our earlier work on the NbO_6 group where such a relation was found to exist in independence of the host lattice in which the NbO_6 group was introduced (*10*). The slope of the straight line reported in Ref. (*10*) was about 25 deg/1000 cm^{-1}. This value is also found for the system $ScTa_{1-x}Nb_xO_4$.

Note that the excitation band or, in other words, the charge-transfer band, of the niobate group shifts to higher energies with decreasing value of x. This has also been observed in the series $YP_{1-x}V_xO_4$ (*11*). The influence of this shift on the NbO_6 luminescence efficiency of the system $ScTa_{1-x}Nb_xO_4$ is considerable. This can be related to our earlier work on the niobates where we found that NbO_6 groups with an excitation band peaking at or below 37,000 cm^{-1} do not give efficient luminescence. The compound $ScNbO_4$ (with 38,000 cm^{-1}) is very near to this limit. If the excitation band moves to higher frequencies, however, efficient luminescence from the NbO_6 group can occur. The consequence of this is that $ScNbO_4$ shows a low efficiency, whereas the NbO_6 group in the isomorphous $ScTaO_4$ shows a high efficiency (see Table I). At first sight this sounds like concentration quenching, but we prefer the description given above, because none of the niobates investigated by us (*10*) shows concentration quenching and $ScNbO_4$–Eu has also a low efficiency (*9. 11*).

If we compare the luminescence of the system $ScTa_{1-x}Nb_xO_4$ with that of the system $YTa_{1-x}Nb_xO_4$ (*1*) we find that the luminescence properties of the NbO_4 group in the Y-system are independent of x, whereas in the Sc-system there is a certain dependence on x. This may probably be related to the fact that in the Y-system corner-sharing of NbO_4 tetrahedra occurs, whereas in the Sc-system edge-sharing of NbO_6 octahedra is found.

$Li_3Ta_{1-x}Nb_xO_4$

This system has the Li_3TaO_4 structure (*12*) in the region $0 \leqslant x \leqslant 0.2$. The spectral energy distribution of the niobate group in this system consists of a broad band peaking at about 400 nm and does not depend on the value of x. Also, the position of the excitation band (240 nm) and the quenching temperature (500°K) do not depend on x within the experimental error.

The luminescence of Li_3TaO_4 has been reported previously (*2*).

$CaTa_{2-2x}Nb_{2x}O_6$

The compound $CaNb_2O_6$ shows an efficient blue-green luminescence under 254 nm excitation (*13*). It seemed interesting to study $CaTa_2O_6$ and the system $CaTa_{2-2x}Nb_{2x}O_6$ as well.

The structure of $CaNb_2O_6$ and $CaTa_2O_6$ are different and the system shows a large miscibility gap. The columbite structure of $CaNb_2O_6$ was found for values $x \gtrsim 0.85$ and the $CaTa_2O_6$ structure for values $x \lesssim 0.3$. The limiting single-phased compositions were selected for luminescence studies ($CaTa_{1.4}Nb_{0.6}O_6$ and $CaTa_{0.3}Nb_{1.7}O_6$).

These two phases once again demonstrate the considerable influence of crystal structure on luminescence. Both phases show luminescence in the blue-green part of the spectrum. The emission band of the $CaNb_2O_6$ phase peaks at 475 nm (300°K) and 430 nm (77°K); the $CaTa_2O_6$ phase at 475 nm (77°K). The quenching temperatures are very different, viz., 400°K for $CaTa_{0.3}Nb_{1.7}O_6$ and 180°K for $CaTa_{1.4}Nb_{0.6}O_6$. The position of the maximum of the absorption band of the NbO_6 group in these two compositions is 260 and 285 nm, respectively. From our relation between the quenching temperature and the position of the absorption band of the niobate group (*10*) we find for these wavelengths quenching temperatures of 420 and 200°K, respectively. This is in good agreement with the values observed experimentally.

The compound $CaTa_2O_6$ was not observed to luminescence at temperature down to 77°K.

$Mg_4Ta_{2-2x}Nb_{2x}O_9$

Results. At room temperature the compound $Mg_4Ta_2O_9$ shows an efficient uv emission under cathode-ray or very short wavelength uv excitation (e.g. the 229 nm line of a Cd discharge). The broad emission band peaks at about 365 nm, the excitation band at about 220 nm, see Fig. 2. At 77°K, however, $Mg_4Ta_2O_9$ also shows a blue emission under 254 nm excitation. The emission band peaks at 450 nm (Fig. 2). Note that the absorption for 254 nm is negligible in the diffuse reflection spectrum. A similar phenomenon was also observed for $YTaO_4$ (*1*). The spectral energy distribution of $Mg_4Ta_2O_9$ given by us before (*2*) contains only the 450 nm band because the excitation was by 254 nm radiation.

The compound $Mg_4Nb_2O_9$ shows a similar phenomenon, see Fig. 3. At room temperature a deep-blue emission is excited by 254 nm radiation, as reported for the first time by Wachtel (*13*). Our spectral energy distribution agrees well with the literature data. At 77°K, however, the emission of $Mg_4Nb_2O_9$ under 254 nm excitation consists of two bands (Fig. 3). One of these is obviously the same as the band observed at room temperature, but the other at about 475 nm is a new one. This band can also be obtained separately by excitation with wavelengths in the 300–315 nm region, i.e., wavelengths longer than those corresponding to the absorption edge (Fig. 3).

The luminescence properties of $Mg_4Ta_{2-2x}Nb_{2x}O_9$

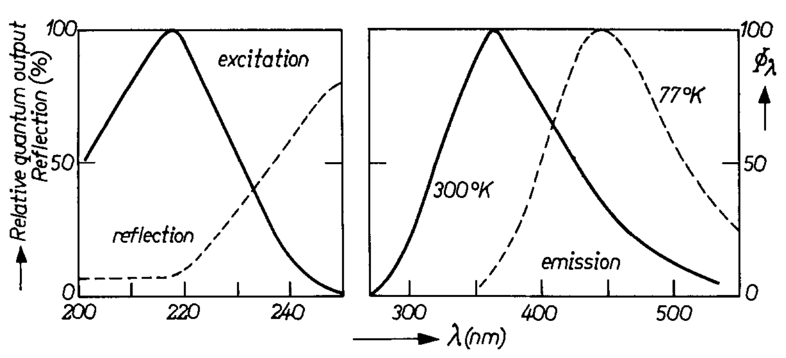

FIG. 2. Left: relative excitation spectrum of the emission of $Mg_4Ta_2O_9$ at 300°K (full line) and diffuse reflection spectrum of $Mg_4Ta_2O_9$ (broken line). Right: spectral energy distribution of the emission of $Mg_4Ta_2O_9$. Full line, at 300°K under cathode-ray excitation; broken line, at 77°K under 254 nm excitation. Φ: gives the radiant power per constant wavelength interval in arbitrary units.

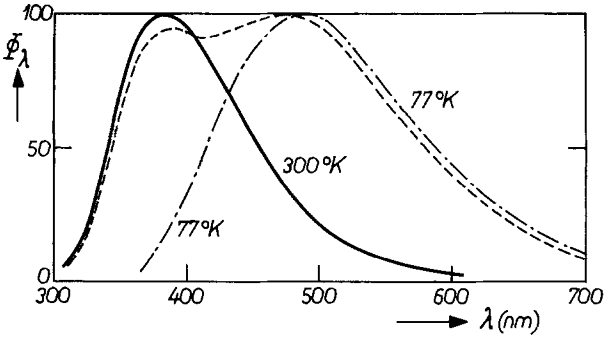

FIG. 3. Spectral energy distribution of the emission of $Mg_4Nb_2O_9$. Full line, mainly 250–270 nm excitation at 300°K. Broken line, mainly 250–270 nm excitation at 77°K. Broken line with dots, mainly 300–315 nm excitation at 77°K.

are interesting, because they deviate from the behaviour shown by other tantalate–niobate systems. Figure 5 shows the spectral energy distribution of the niobate emission in this system. The shape and position of the emission band depends on x. For clarity we have given the emission spectra for two diverging cases only, viz., for $x = 0.02$ and $x = 0.8$. The curve for high x values (e.g. $x = 0.8$) resembles that for $Mg_4Nb_2O_9$ itself. It consists of a broad band peaking at 385 nm. Such an emission band is by no means exceptional for niobate emission. For decreasing values of x there is a small shift of the emission band to shorter wavelengths. For low values of x we even observed an indication of splitting of the emission band, as shown in Fig. 5 for $x = 0.02$.

The dependence of the position of the excitation band and the quenching temperature of the niobate emission on x is more pronounced. This is shown in Fig. 6. The relation between both quantities is linear as usual, but the slope exceeds the usual value (25 deg/1000 cm^{-1}) considerably. It amounts to nearly 45 deg/1000 cm^{-1}.

At room temperature the decay time of the emission of $Mg_4Ta_2O_9$ is 6×10^{-6} sec, and that of the niobate emission of $Mg_4Ta_{1.9}Nb_{0.1}O_9$ is 25×10^{-6} sec.

The Mn^{2+} ion acts as an efficient activator in $Mg_4Ta_2O_9$ (but not in $Mg_4Nb_2O_9$). The phosphor $(Mg, Mn)_4Ta_2O_9$ shows a deep-red emission band peaking at about 670 nm, see Fig. 4. The excitation band of this emission peaks at 270 nm. The quantum efficiency for this exciting wavelength amounts to about 60%. This phosphor shows a marked temperature-persistance, as observed for a number of other Mn-activated phosphors too. The quenching temperature is as high as 680°K. The luminescence properties were independent of the firing atmosphere (air, N_2, or N_2–H_2 mixtures). This, together with the broad-band emission, shows that we are not dealing with Mn^{4+}.

Discussion

The emission and absorption process in the niobate and tantalate group is due to a charge

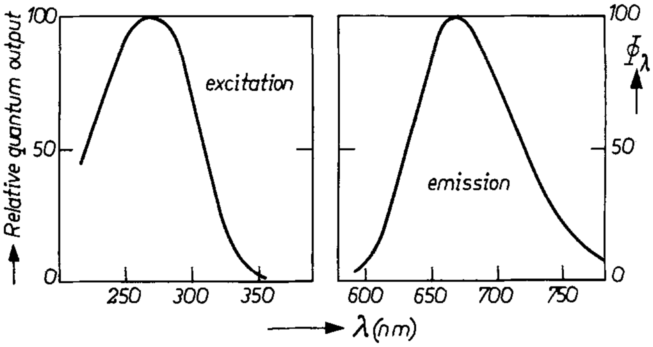

FIG. 4. Left: relative excitation spectrum of the emission of $Mg_{3.96}Mn_{0.04}Ta_2O_9$. Right: spectral energy distribution of this emission (254 nm excitation).

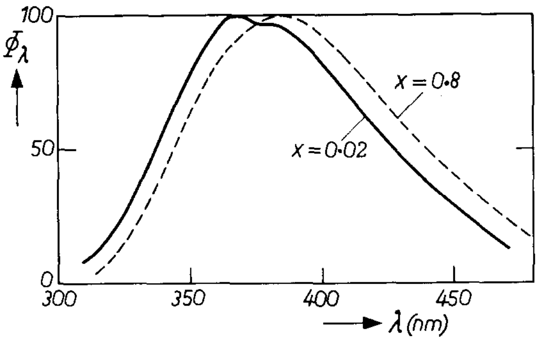

FIG. 5. Spectral energy distribution of the emission of $Mg_4Ta_{1.96}Nb_{0.04}O_9$ (full line) and of $Mg_4Ta_{0.4}Nb_{1.6}O_9$ (broken line). 254 nm excitation.

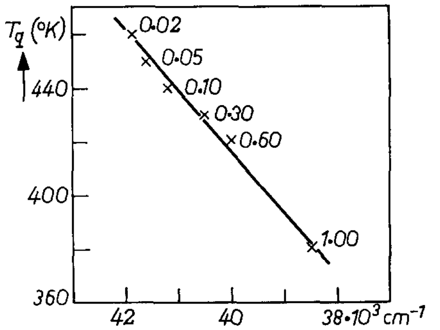

FIG. 6. Quenching temperature of the niobate emission versus the position of the maximum of the excitation band of this emission for the system $Mg_4Ta_{2-2x}Nb_{2x}O_9$. Values of x are indicated in the figure.

transfer transition. In Ref. (*1*) we have shown that the number of excited states of the tetrahedral niobate or tantalate group is so large that a complicated energy level diagram results. Not only singlet but also triplet levels are present. The tetrahedral groups show two emissions, one of which was ascribed to a singlet–singlet transition, the other—which had a much lower quenching temperature—to a triplet–singlet transition.

The number of energy levels of the octahedral niobate and tantalate group is even larger (*2*). Their relative positions are unknown. Therefore we will not discuss the decay times of the tantalate and niobate emission in the system $Mg_4Ta_{2-2x}Nb_{2x}O_9$. They are of the same order of magnitude as the decay time of the emission of the isoelectronic WO_6 group in, e.g., $MgWO_4$ (40×10^{-6} sec according to Ref. *14*).

The fact that $Mg_4Nb_2O_9$ as well as $Mg_4Ta_2O_9$ show different types of emission depending on the excitation wavelength resembles closely the results observed for the fergusonite niobates and tantalates (*1*). In view of the energy level diagram this is not surprising. It may be that the shorter wavelength emission with high quenching temperature is due to a singlet–singlet transition and the longer wavelength emission with low quenching temperature to a triplet–singlet transition, for reasons given in Ref. (*1*).

A comparison of the luminescence of the systems $YTa_{1-x}Nb_xO_4$, $ScTa_{1-x}Nb_xO_4$, and $Mg_4Ta_{2-2x}Nb_{2x}O_9$ reveals that the luminescence properties in the Y-system do not depend on x, that in the Sc-system they depend slightly on x and that in the Mg-system the dependence on x is more pronounced. This observation runs parallel with the fact that the distance between the pentavalent cations decreases in the sequence Y-, Sc-, Mg-system. It is obvious to assume that the shorter distance will cause a stronger interaction and therefore a more pronounced dependence on x. Here we will not consider the nature of this interaction any further.

The splitting of the emission band of, e.g., $Mg_4Ta_{1.96}Nb_{0.04}O_9$ (see Fig. 5) can be explained as follows. In $Mg_4Ta_2O_9$ the Ta^{5+} ions occur in isolated pairs; if part of the Ta^{5+} ions are replaced by Nb^{5+} ions the structure contains Ta^{5+}–Ta^{5+}, Ta^{5+}–Nb^{5+}, and Nb^{5+}–Nb^{5+} pairs. Under 254 nm excitation the tantalate groups are not excited, so that only the isolated niobate group and the face-sharing niobate groups are excited. The isolated niobate group probably shows the shorter wavelength emission (at about 365 nm), the paired niobate groups the longer wavelength emission (at about 385 nm).

The efficient red luminescence of $(Mg, Mn)_4Ta_2O_9$ is undoubtedly due to octahedrally surrounded Mn^{2+} ions. Ample evidence for this comes from the shape and position of the emission band and from the fact that the luminescence properties are not influenced by the firing conditions.

Conclusions

Tantalates containing TaO_6 groups may give efficient tantalate emission in the ultraviolet or blue region of the spectrum. The NbO_6 group in these lattices is usually an efficient activator. The luminescence of the tantalate–niobate systems with $(Ta, Nb)O_6$ octahedra is different from and more complicated than the luminescence of the tantalate–niobate systems with $(Ta, Nb)O_4$ tetrahedra. $(Mg, Mn)_4Ta_2O_9$ is an efficient phosphor with red emission.

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