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BRIEF COMMUNICATIONS

The Luminescence of Trigonal Bipyramidal NbO_5^{5-} and TaO_5^{5-} and a Comparison with Other Niobates and Tantalates

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The luminescence of $La_3NbO_4Cl_6$ with trigonal bipyramidal NbO_5^{5-} groups is reported. The Nb^{5+} coordination does not seem to influence the niobate emission. The luminescence and Raman spectrum of $La_3TaO_4Cl_6$ are also reported. Finally, differences in luminescence of the *M* and *M'* modifications of $YTaO_4$ are discussed.

Introduction

Recently, Brixner *et al.* (*1*) described the crystal structure of $Pr_3NbO_4Cl_6$. This structure contains highly unusual NbO_5^{5-} trigonal bipyramidal groups. It seemed interesting to study the luminescence of this group and to compare the results with those of niobate groups in nearly octahedral and closely tetrahedral coordination. For this reason, $La_3NbO_4Cl_6$ as well as the isostructural $La_3TaO_4Cl_6$ were prepared. The results are described in this paper.

Experimental

Synthesis

$La_3NbO_4Cl_6$ and $La_3TaO_4Cl_6$ were prepared by Reaction 2 described in (*1*):

$$3LaOCl + 3LaCl_3 + Nb_2O_5 \rightarrow 2La_3NbO_4Cl_6.$$

The samples are isomorphous and their lattice constants are reported below. The performance of the optical measurements has been described before (*2*).

X-Ray Powder Diffraction

A Guinier–Hägg focusing camera (r = 40 mm) was used to obtain X-ray powder diffraction data. The radiation was monochromatic $CuK_{\alpha 1}$ (λ = 1.5405 Å). Silicon powder (a = 5.4305 Å) was used as an internal standard. Line positions on the film were determined to ±5 μm with a David Mann film reader (a precision screw, split-image comparator). Lattice parameters for $La_3NbO_4Cl_6$ and $La_3TaO_4Cl_6$ were calculated by a least-squares refinement of the Guinier

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TABLE I

LATTICE PARAMETERS AND THEIR STANDARD DEVIATIONS FOR THE $La_3MeO_4Cl_6$ COMPOUNDS (SPACE GROUP: $P\bar{6}_3/m$)

Me	*a* (Å)	*c* (Å)	*V* (Å³)
Nb	12.811(1)	4.0382(8)	573.96
Ta	12.859(1)	4.0029(9)	573.27

data. The refined cell constants are summarized in Table I.

Results

$La_3NbO_4Cl_6$ shows a bluish emission below 200 K. The maximum of the emission band is at 460 nm, that of the corresponding excitation band at 275 nm (4.2 K values). Figure 1 shows the spectra. The decay time of the emission at 4.2 K is about 80 μsec. All decay curves were exponential. The decay time is temperature-independent up to the temperature where quenching of the luminescence becomes observable.

The luminescence of $La_3TaO_4Cl_6$ is difficult to excite with our instrument. Diffuse reflection spectra show that the optical band edge at 300 K is at about 230 nm. Excitation with this wavelength (the spectral limit of the instrument) yields a UV emission band with a maximum of 335 nm at 4.2 K. We were not able to measure the excitation spectrum. The quenching temperature of the luminescence is at about 300 K.

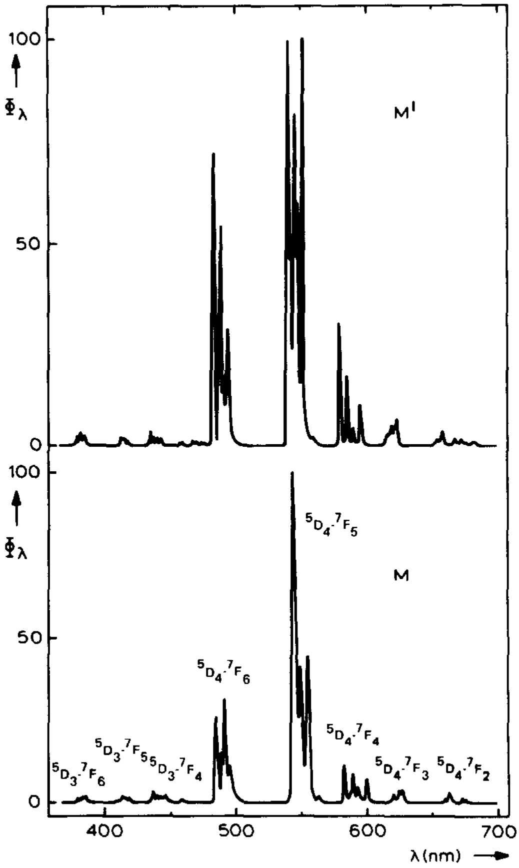

FIG. 2. Emission spectra of Tb^{3+}-activated *M*- and *M'*-$GdTaO_4$ at LHeT for excitation into the Tb^{3+} (4*f*–5*d*) band.

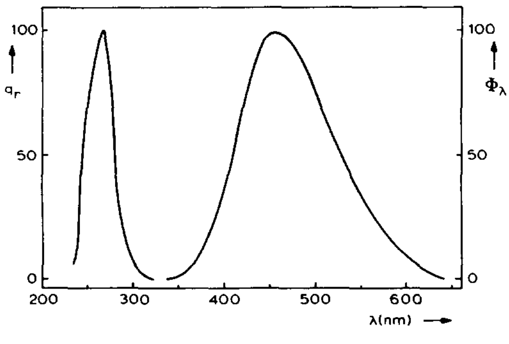

FIG. 1. Emission and excitation spectra of the luminescence of $La_3NbO_4Cl_6$ at LHeT. q_r denotes the relative quantum output and Φ_λ the spectral radiant power per constant wavelength interval.

In addition, Fig. 2 shows the emission spectra of *M*- and *M'*-$GdTaO_4$: Tb and Fig. 3 gives the Raman spectrum of $La_3TaO_4Cl_6$, which is similar to that of $La_3NbO_4Cl_6$

Discussion

Recently, we have reported on the luminescence of the trigonal bipyramidal tungstate group (WO_5^{4-}) in $LaWO_4Cl$ (*3*). It was

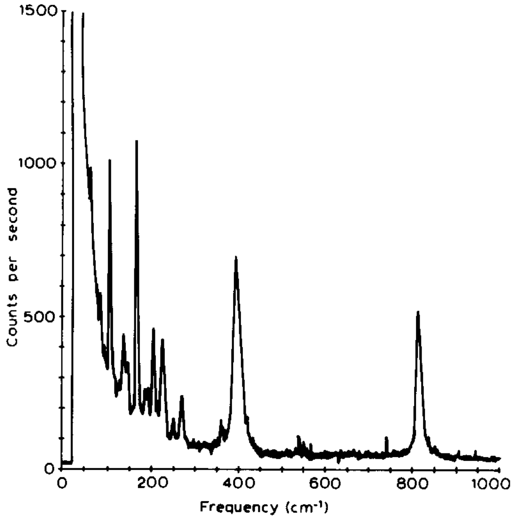

FIG. 3. Raman spectrum of $La_3TaO_4Cl_6$ at room temperature.

found that the luminescence showed a strong similarity to that of the octahedral tungstate group but differed from the luminescence of the tetrahedral tungstate group. Especially the Stokes shift of the tetrahedral tungstate group is much larger (16,000 cm^{-1}) than that of the octahedral or trigonal bipyramidal tungstate groups (11,000–12,000 cm^{-1}) (*4*).

The present data for $La_3NbO_4Cl_6$ reveal a Stokes shift of 15,000 cm^{-1}. This is the same value characteristically observed for the octahedral niobate group (*4*). For $YNbO_4$, the only case of nearly tetrahedral Nb^{5+}, this value is also observed (*5, 6*). This suggests that the Stokes shift of the niobate luminescence does not depend on the niobium coordination.

Although there does not seem to be an obvious reason for this observation, it explains why it was possible to relate the quenching temperature of the niobate luminescence to the position of the absorption (or excitation) band maximum (*7*). Such a relation is only expected to hold if the offset between the parabolae of the excited and ground states in the configurational coordinate model is the same for all niobate groups. Since it is the offset which determines the Stokes shift, equal Stokes shifts imply equal offsets in good approximation.

It is, furthermore, interesting that the tantalate luminescences of *M*- and *M'*-$YTaO_4$ are identical, although the coordinations of tantalum are definitely not (*6*). The identical luminescences fit in the general observation stated above. The fact that the crystal structures of *M*- and *M'*-$YTaO_4$ are different can be observed by a study of the luminescence of rare-earth activators in the two modifications.

The crystal structures of the *M*-type compounds $GdTaO_4$ and $GdNbO_4$ are identical, while the *M'* modification only exists for $GdTaO_4$ (*6*). Two of us reported on the luminescence properties of Tb^{3+}-activated *M*-type $GdTaO_4$ (*8*). Recently, we also measured the luminescence of Tb^{3+}-activated *M'*-$GdTaO_4$. The emission spectra of both modifications for excitation into the $Tb^{3+}(4f\text{–}5d)$ band at LHeT are shown in Fig. 2. The different splittings of the several $^5D_4$–^7F_J emissions point to different crystal fields on the $Tb^{3+}(Gd^{3+})$ sites in the *M*- and *M'* modifications, respectively. This confirms the fact that there is a difference between the crystal structures of these modifications as was also shown by the different Raman spectra (*6*).

Returning to $La_3NbO_4Cl_6$ we conclude that the low quenching temperature of the luminescence is directly related to the relatively low energy of the first absorption (excitation) transition. This is due to the fact that the equatorial oxygen ions of the NbO_5^{5-} group are surrounded by one 5-coordinated Nb^{5+} and two 9-coordinated La^{3+} ions, so that they are not completely saturated (*9*). Consequently the Nb–O distance involved is short [1.86 Å, (*1*)] and the absorption transition is at relatively low energy (*9*).

The only luminescent property which will relate to the Nb coordination is the temperature dependence of the decay time which depends critically on the crystal field at the Nb^{5+} site and the value of the spin-orbit coupling (*4*). The temperature-independent decay time of $La_3NbO_4Cl_6$ is unusual, because generally the decay time increases at very low temperatures due to the presence of optical traps (*9*). However, the situation without such a trap is not in conflict with the models presented. The relatively large value (80 μs) of the decay time is due to the spin-selection rule.

The case of $La_3TaO_4Cl_6$ is difficult to discuss in the present context, because the position of the excitation band is not known with large enough accuracy. If we consider the data available in the literature (*4–6*) and those for $La_3TaO_4Cl_6$, there is at least no reason to suppose that the tantalate luminescence is influenced by the Ta^{5+} coordination.

Finally, Fig. 3 presents the Raman spectrum of $La_3TaO_4Cl_6$. The higher energy part is dominated by two peaks (at about 400 cm^{-1} and 830 cm^{-1}). Since the TaO_5 groups form a linear chain by sharing the oxygen ions on top of the trigonal bipyramid, the linear chain $(Ta–O)_n$ is in first approximation Raman-inactive as far as Ta–O stretching vibrations are concerned. The 830-cm^{-1} line has, therefore, to be ascribed to the symmetric valence stretching mode of the TaO_3 group perpendicular to the $(Ta–O)_n$ chain. The 830-cm^{-1} value for the TaO_3 group has to be compared with 815 cm^{-1} for the TaO_4 group (10) and ~800 cm^{-1} for the TaO_6 group (*11*). The 400 cm^{-1} peak in Fig. 3 must be due to a Ta–O deformation mode.

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