

Luminescence of the Isolated Niobate Octahedron in $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$

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Recently Averbuch-Pouchot and Durif [1] have described two new phosphates, *viz.* $\text{MNB}_2(\text{P}_2\text{O}_7)_3$ ($\text{M} = \text{Mg}$ and Co). They also reported the crystal structure of these isomorphous compounds. The structure is essentially a superstructure of the ZrP_2O_7 structure, but the magnesium compound shows a certain amount of disorder (a few atomic percent). The crystal structure consists of P_2O_7 groups bound together by the metal ions. The latter are in octahedral coordination. The niobate octahedra do not share oxygen ions, so that they are isolated from each other.

There are several reasons which prompted us to investigate the luminescence of $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$. In the first place, ZrP_2O_7 is an efficient luminescent material [2, 3]. Since Zr^{4+} and Nb^{5+} are isoelectronic, one might expect a similar result for $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$. In the second place, host lattices with isolated niobate groups are rather rare. The other examples are the ordered perovskites. However, compounds like $\text{La}_2\text{LiNbO}_6$, SrLaMgNbO_6 and Ba_2YNbO_6 [4] do not show any noticeable luminescence at all [5]. In the third place, many niobates show efficient luminescence [6, 7]. They all have crystal structures with condensed niobate octahedra. Finally, disorder between Mg^{2+} and Nb^{5+} ions had been studied before by us, using the niobate luminescence [8, 9].

Experimental

Crystalline powders were prepared from solutions in H_3PO_4 (85%) as described in ref. 1. They were checked by X-ray powder diffraction. The luminescence measurements were performed using a Perkin-Elmer Model MPF-3 spectrofluorometer equipped with an Oxford liquid helium cryostat. Diffuse reflection spectra were measured at room temperature on a Perkin-Elmer Lambda-7 spectrometer.

Results

The diffuse reflection spectrum of $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$ shows an optical absorption edge at 310 nm. At 4.2 K, excitation with this and shorter wavelengths

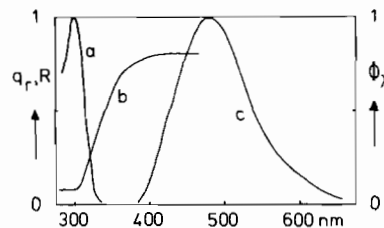


Fig. 1. Spectra of $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$: (a) excitation spectrum of the emission at 4.2 K; (b) diffuse reflection spectrum at 300 K; (c) emission spectrum for 295 nm excitation at 4.2 K. ϕ_λ gives the radiant power per constant wavelength interval and q_r the relative quantum output, both in arbitrary units; R gives the reflection.

results in a greenish emission of low intensity. The emission spectrum consists of a broad band with a maximum at 480 nm. The corresponding excitation spectrum has its maximum at 300 nm. This is in good agreement with the diffuse reflection spectrum, taking the temperature dependence into account. The spectra are presented in Fig. 1.

From these data the Stokes shift of the emission is found to be $13\,000\text{ cm}^{-1}$. Upon increasing the temperature, the spectra do not change considerably but thermal quenching occurs. At 150 K the emission intensity is about 50% of its value at 4.2 K, and at 250 K only a few percent is left. There is no indication of any other emission from the sample than the one described.

Discussion

It is clear that the disorder between Mg and Nb reported in ref. 1 has no consequences for the spectra, as was the case for MgNb_2O_6 [8, 9]. However, in $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$ the niobate octahedra are isolated, so that the disorder does not have such a pronounced influence on the energy levels of the disordered niobate groups as in the case of condensed niobate octahedra (MgNb_2O_6). It is nevertheless interesting to note that MgNb_2O_6 with a superstructure of $\alpha\text{-PbO}_2$ [7] frequently shows disorder, as $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$ with a superstructure of ZrP_2O_7 also seems to do.

It also becomes clear that the structurally isolated niobate group is not an efficient luminescent centre. In the ordered perovskites there is no luminescence at all [5], and in $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$ the luminescence efficiency is only low, even at 4.2 K.

Many years ago we argued that a necessary requirement for efficient niobate luminescence is a high energy position of the first absorption band [10]. Only edge and face sharing of the niobate octahedra

TABLE 1. Position of the Lowest Absorption Maximum of some Isolated Octahedral Complexes in Connection with their Luminescence Efficiency

Complex	Maximum absorption band (10^3 cm^{-1})	Luminescence efficiency	Reference
TiO_6^{8-} in $\text{BaTi}(\text{PO}_4)_2$	30	low	13
ZrO_6^{8-} in ZrP_2O_7	43	high	2, 3
NbO_6^{7-} in $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$	32	low	this work
MoO_6^{6-} in $\text{K}_2\text{MoO}_3(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$	31	low	15
WO_6^{6-} in $\text{Ba}_2\text{CaTeO}_6$	37	high	14

shift this absorption band to such high energies that efficient luminescence occurs [11]; examples are Li_3NbO_4 and $\text{Mg}_4\text{Nb}_2\text{O}_9$. The driving force for this edge and face sharing has also been discussed [12].

From the position of the absorption band of the niobate octahedron in $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$, we do not expect efficient luminescence at all [10].

It is tempting to compare the luminescence of $\text{MgNb}_2(\text{P}_2\text{O}_7)_3$ with that of $\text{BaTi}(\text{PO}_4)_2$ [13], which presents a case of isolated titanate octahedra. These may be considered as isoelectronic to the niobate octahedron. Also here the absorption band of the titanate group is at relatively long wavelength, viz. 330 nm, and the quenching temperature is low (100 K).

The conclusion seems justified that not only the niobate but also the titanate octahedra do not emit luminescence efficiently if isolated. This does not mean that octahedra of this type cannot emit efficiently if isolated. Examples are the zirconate octahedron in ZrP_2O_7 [2,3] and the tungstate octahedron in $\text{Ba}_2\text{CaTeO}_6$ [14]. However, the molybdate octahedron has low efficiency again [15]. Comparison of all these data suggests strongly that it is the position of the absorption band which determines whether efficient luminescence occurs or not (see Table 1). Actually this is in very good agreement with the simple configurational coordinate model [16]. This conclusion runs parallel with that for the isoelectronic tetrahedral complexes [6], where MnO_4^- and CrO_4^{2-} (which are coloured) show no efficient luminescence, whereas colourless VO_4^{3-} , MoO_4^{2-} ,

NbO_4^{3-} , WO_4^{2-} and TaO_4^{3-} do. However, the limiting absorption energy is higher for the octahedral than for the tetrahedral complexes.

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