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The luminescence of $K_2(NbO)_2Si_4O_{12}$

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Abstract

The luminescence of $K_2(NbO)_2Si_4O_{12}$ is described and discussed. It consists of a greenish emission below room temperature. The results are discussed in connection with the recently described crystal structure and the non-linear optical properties of this compound.

1. Introduction

The structural dependence of the luminescence of niobate compounds has been studied for some time in our laboratories [1–4]. Especially interesting is the efficient luminescence of compounds in which niobate groups with one short Nb–O distance (sometimes called a niobyl group) occur. This has also been observed for other d^0 oxo complexes [5] and recently confirmed by the example of $K_2NbOF_5 \cdot H_2O$ [6]. Molecular orbital calculations are able to describe and explain this observation [7].

Recently the crystal structure of $K_2(NbO)_2Si_4O_{12}$ has been reported [8]. This structure consists of corner-sharing NbO_6 octahedra running parallel to the 4-fold tetragonal axis. The chains are coupled together by four-membered Si_4O_{12} rings. The NbO_6 octahedra are almost regular, but the central niobium atoms are displaced from the centre by about 0.28 Å for Nb(1) and 0.25 Å for Nb(1′), leading to alternating short and long Nb–O distances along the 4-fold axis (Nb(1)–O(2), 1.76 Å; Nb(1)–O(3), 2.31 Å; Nb(1′)–O(3), 1.78 Å; Nb(1′)–O(2), 2.28 Å).

There are several reasons to investigate the luminescence of this compound. The presence of the short Nb–O bonds may result in efficient luminescence. Also, $K_2(NbO)_2Si_4O_{12}$ is a promising non-linear optical material [9] with a structural analogy to the well-known non-linear optical compound $KTiOPO_4$ [10] for which a very unusual luminescence has been described [11, 12]. Therefore we investigated the luminescence of $K_2(NbO)_2Si_4O_{12}$ and discuss it in relation to its crystal structure and non-linear optical properties.

2. Experimental details

The compound $K_2(NbO)_2Si_4O_{12}$ was prepared as a powder according to procedures described before [8, 9]. X-ray powder diffraction showed the samples to be single phase. The optical measurements were performed on a Perkin–Elmer Lambda 7 spectrometer equipped with a reflection unit and a Perkin–Elmer MPF-44B spectrofluorometer equipped with a liquid helium cryostat [2–6].

Results

The diffuse reflection spectrum of $K_2(NbO)_2Si_4O_{12}$ exhibits at room temperature strong optical absorption for $\lambda < 300$ nm with an optical absorption edge at $\lambda \approx 280$ nm. On excitation into this absorption band the compound displays a greenish emission below 250 K. At 4.2 K the emission consists of a broad band with a maximum at about 500 nm (Fig. 1). The corresponding excitation maximum at that temperature is at 270 nm. This is considered to be in good agreement with the results of the diffuse reflection spectrum if the temperature dependence is taken into account. The quenching temperature of this luminescence is at about 250 K.

In addition to this main luminescence there is an additional and much weaker luminescence with an

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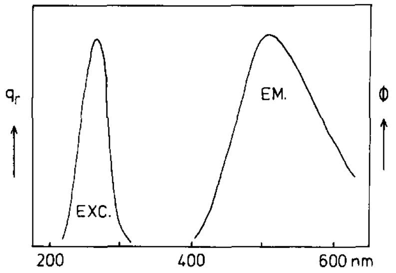

Fig. 1. Emission (EM) and excitation (EXC) spectra of the luminescence of $K_2(NbO)_2Si_4O_{12}$ at 4.2 K. The exciting wavelength is 270 nm, and the monitored emission wavelength is 500 nm. The relative quantum output is denoted by q_r, whereas ϕ is the relative spectral radiant power per unit of wavelength interval.

TABLE 1. Luminescence properties of $K_2(NbO)_2Si_4O_{12}$ and α-$NbOPO_4$ [13]

	$K_2(NbO)_2Si_4O_{12}$	α-$NbOPO_4$
Emission maximum (4.2 K) (nm)	500	490
Excitation maximum (4.2 K) (nm)	270	260
Quenching temperature (K)	250	150

emission at longer wavelength. The emission maximum is at about 540 nm and the excitation maximum at about 290 nm. This additional luminescence is, as usual [1, 4], ascribed to the presence of a niobate-containing second phase or to niobate groups in the main phase which are close to defects. This weak emission is not considered any further.

4. Discussion

At first sight it seems disappointing that the presence of short Nb–O distances in $K_2(NbO)_2Si_4O_{12}$ does not result in efficient luminescence at room temperature. The experimental evidence for such a relation [3–7] is so overwhelming that there is no reason to assume that $K_2(NbO)_2Si_4O_{12}$ is an exception to this rule. As we will show now, the relative orientation of the niobyl groups in $K_2(NbO)_2Si_4O_{12}$ is responsible for the relatively low quenching temperature of the luminescence.

First, however, we would like to draw attention to the analogy between the luminescences of $K_2(NbO)_2Si_4O_{12}$ and α-$NbOPO_4$ [13]. Some data are given in Table 1. This is the more interesting because the niobate sublattices of $K_2(NbO)_2Si_4O_{12}$ and α-$NbOPO_4$ [14] are also similar. In both cases there are linear chains of niobate octahedra and the niobium atom is displaced along the chain direction in such a way that short and long Nb–O distances alternate.

Ab initio calculations [7] show, as was predicted qualitatively long ago [15], that the lowest absorption transition of d^0 oxo complexes with a short metal–oxygen bond is localized in this short bond. Because this short bond is weakened in the excited state, the niobium atom will lose at least part of its off-centre character after excitation. However, linear chains with niobium atoms in a more or less central position are expected to have a highly delocalized character.

The large shift of the niobium atom implies a large relaxation in the excited state, and this, in turn, a low quenching temperature of the luminescence. Simultaneously, delocalization of the excited state will result in a decrease in the expected high quenching temperature [16].

Finally two observations are in order because they confirm the model proposed.

(a) In β-$NbOPO_4$ the niobate octahedra have equal Nb–O distances and share corners in three directions; the absorption band shifts to 360 nm, indicating extended delocalization, and the luminescence is weak, even at 4.2 K [16].

(b) In $KTiOPO_4$ the titanate octahedra form linear zigzag chains and each has one short Ti–O bond. Although the structural build up of these chains is different from that in $K_2(NbO)_2Si_4O_{12}$, there is also a clear analogy with the structure of $K_2(NbO)_2Si_4O_{12}$, *i.e.* the short $M(d^0)$–O bonds belong to octahedra which are connected by corner sharing. The luminescence of $KTiOPO_4$ quenches at much lower temperatures than expected [11, 12]. This has been ascribed to delocalization of the excited state, which in $KTiOPO_4$ has an even more drastic influence on the luminescence than in $K_2(NbO)_2Si_4O_{12}$: the quenching temperature of the luminescence of the titanate is 100 K, whereas that of the niobate is 250 K. On the contrary, compounds with isolated titanate groups with one short Ti–O distance emit efficiently at room temperature (for example $CaTiOSiO_4$ and $Ba_2TiOSi_2O_7$ [5]).

Phillips *et al.* [17] have recently shown that the non-linear optical properties of $KTiOPO_4$ are determined by delocalization of the excited state. The charge transfer state of the titanate octahedra is delocalized along the chain, representing a conduction band. In this way a high degree of polarization with unusually large excited state dipole moment contributions results.

This is exactly the same model as proposed before in order to explain the luminescence properties of $KTiOPO_4$ [11, 12]. It is interesting to note that $K_2(NbO)_2Si_4O_{12}$ is a promising non-linear optical material [9, 18]. The analogy between the optical properties of $KTiOPO_4$ and $K_2(NbO)_2Si_4O_{12}$ seems, therefore, to be larger than the difference in the chemical formulae suggests.

5. Conclusions

The luminescence of $K_2(NbO)_2Si_4O_{12}$ with short Nb–O bonds is quenched below room temperature. This is ascribed to delocalization of the excited state. The non-linear optical properties of this compound may also be related to this effect.

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