

THE LUMINESCENCE OF TITANITE (CaTiSiO_5)

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ABSTRACT

The luminescence of CaTiSiO_5 crystals is reported. The emission band has its maximum at 520 nm. The results are discussed in connection with titanium compounds containing comparable titanate polyhedra.
MATERIALS INDEX: titanites

Introduction

The luminescence of titanate polyhedra is well known and has a long history (1,2). The optical transitions involved are of the charge-transfer type and the Stokes shifts involved are therefore large.

We have been interested in the luminescence of titanates which contain titanate polyhedra with one short Ti-O distance and have shown that the charge-transfer transition involved is strongly localized in this short Ti-O bond. Examples are the compounds NaLnTiO_4 (Ln=La,Gd,Y,Lu) (3,4) and $\text{Ba}_2\text{TiOSi}_2\text{O}_7$ (fresnoite) (5). In these compounds the vibrational spectra show evidence for such a short Ti-O bond (4,6), which in a number of cases has been directly demonstrated by X-ray diffraction studies (7,8).

Such a short Ti-O distance has also been reported for titanite, CaTiSiO_5 (9), viz. 1.766 Å. However, here the titanate polyhedra form linear chains by sharing one oxygen ion, viz. O(1). This ion does not belong to the silicate tetrahedra, so that the formula can be written CaTiOSiO_5 . The Ti-O(1) distances along the chain alternate in distance: short (1.766 Å) and long (1.974 Å). This chain is very similar to the one observed in $\alpha\text{-NbPO}_5$ for the niobate polyhedra (10) for which we also investigated the luminescence (11).

In KTiOPO_4 there are zig-zag chains of titanate polyhedra, also with short and long Ti-O distances (12). The luminescence of this compound is very remarkable because of the small Stokes shift which indicates electron charge delocalization (13).

All these facts prompted us to investigate the luminescence of CaTiSiO_5 , to find out whether its luminescence would be related to one or more of the structurally related titanates.

Experimental

Single crystals of CaTiSiO_5 were grown by the floating - zone method as described before (14). The luminescence measurements were performed on a Perkin-Elmer spectrofluorometer MPF-3 equipped with a helium flow cryostat. The details have been described elsewhere (15).

Results

The CaTiSiO_5 crystals show a greenish luminescence under ultraviolet excitation. The spectra consist of broad bands as has been reported many times before (1,2,4,5). The emission maximum is at about 520 nm, the corresponding excitation maximum at 290 nm. The Stokes shift is, therefore, $15,000 \text{ cm}^{-1}$. At room temperature this emission is partly quenched, but the real quenching temperature is considerably higher than 300 K. The temperature at which the emission intensity has dropped to 50 % of its 4.2 K value is about 250 K.

There is a weak additional luminescence with an emission maximum at about 600 nm and a corresponding excitation maximum at about 305 nm. A similar observation was made for fersnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$, ref. 5). There it has been assigned to a centre due to the presence of a small amount of Ti on Si sites. We follow the same interpretation here. Only the 520 nm emission will be discussed below.

In table I we have compiled the present results together with those for a number of structurally related compounds.

TABLE I

Luminescence Data of CaTiSiO_5 and some Structurally Related Compounds. All Values at 4.2⁵K. Spectral Data in Units 10^3 cm^{-1} .

compound	maximum excitation band	maximum emission band	Stokes shift	T _q [*]	ref.
CaTiSiO_5	34	19	15	>300 K	this work
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	36	19	17	>300 K	5
NaYTiO_4	35	21	14	275 K	3
$\alpha\text{-NbPO}_5$	38.5	20	18	150 K	11
KTiPO_5	30	25.5	4.5	100 K	13

* temperature above which the luminescence is quenched.

Discussion

From table I it is seen that the luminescence characteristics of CaTiSiO_5 are very similar to those of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and NaYTiO_4 . Also those for $\alpha\text{-NbPO}_5$ are not strikingly different. This shows that in these compounds we are dealing with localized luminescence transitions, which occur mainly in the short Ti-O (Nb-O) band. The Stokes shift is due to the larger relaxation after excitation (16,17).

The case of KTiPO_5 is completely different as follows from the small Stokes shift, the low energy of the excitation maximum, and the low quenching temperature. Actually quenching starts already at 25 K (13). This has been interpreted as due to electron charge delocalization (13,16). In NaYTiO_4 and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ the short Ti-O distance is not in a chain of titanate polyhedra, so that delocalization is not possible. However, in CaTiSiO_5 , $\alpha\text{-NbPO}_5$, and KTiPO_5 the short Ti-O distance is in the polyhedra chain. It is not clear why only in case of KTiPO_5 this leads to delocalization. The structural details of these chains are rather complicated. Also, Van der Waals et al. (18) have shown that the processes in the excited state of polyhedra like titanates can be very complicated, so that we have to assume that our knowledge today is not sufficient to explain the different behaviour of CaTiSiO_5 and KTiPO_5 .

In conclusion, the luminescence properties of CaTiSiO_5 are very similar to those of $\text{Ba}_2\text{TiSi}_2\text{O}_8$.

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