

ON THE LUMINESCENCE OF  $Ti^{4+}$  IN  $Mg_5SnB_2O_{10}$  AND  $Mg_3ZrB_2O_8$ 

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## ABSTRACT

The following new compounds are reported:  $Mg_5TiB_2O_{10}$  (ludwigite structure),  $Mg_5SnB_2O_{10}$  (orthopinakiolite structure) and  $Mg_3ZrB_2O_8$  (warwickite structure). The luminescences of the systems  $Mg_5(Sn,Ti)B_2O_{10}$  and  $Mg_3(Zr,Ti)B_2O_8$  were measured. The results are discussed in terms of delocalization in clusters of titanate octahedra. A general scheme for the luminescence of  $Ti^{4+}$ -activated compositions is given. The composition  $Mg_5SnB_2O_{10}$ : Ti is a very efficient luminescent material for titanium concentrations below some 20 mole percent.

## INTRODUCTION

Luminescence of titanium-activated stannates and zirconates is well known [1-4]. The transitions involved are of the charge-transfer type. In this paper we wish to report on borates of this type. Luminescence has been reported for a material consisting of  $SnO_2$  and  $TiO_2$  containing magnesium borate, the precise composition of which has not been given [5]. Benderskaya *et al.* [6] have suggested that the corresponding composition was 6.5 MgO - 1  $SnO_2$  - 1.5  $B_2O_3$ . We found the relevant composition is  $Mg_5SnB_2O_{10}$ . In this paper we describe the compounds  $Mg_5SnB_2O_{10}$  and  $Mg_5TiB_2O_{10}$  and the luminescence of their solid solutions. We were able to prepare  $Mg_3ZrB_2O_8$ . The luminescence of the system  $Mg_3(Zr,Ti)B_2O_8$  appears to be rather complicated.

## EXPERIMENTAL

For the preparation of the samples, Reagent grade MgO,  $TiO_2$ ,  $SnO_2$ ,  $ZrO_2$  and  $H_3BO_3$  were mixed together and fired twice for 2 h at 1300 °C in an alundum crucible inside an electric furnace under atmospheric conditions. Samples were checked by X-ray diffraction. Optical measurements were performed with equipment described elsewhere [7].

## RESULTS

Crystallographic data

The crystal structures of  $Mg_5SnB_2O_{10}$ ,  $Mg_5TiB_2O_{10}$  and  $Mg_3ZrB_2O_8$  were found by comparison with the powder patterns of certain borate minerals. The results are as follows:

$Mg_5SnB_2O_{10}$ : orthopinakiolite ( $Mg_3Mn^{2+}Mn_2^{3+}B_2O_{10}$ ) [8],  
 $a = 19.12 \text{ \AA}$ ,  $b = 12.37 \text{ \AA}$ ,  $c = 11.44 \text{ \AA}$ .

$Mg_5TiB_2O_{10}$ : ludwigite ( $Mg_4Fe_2^{3+}B_2O_{10}$ ) [9],  
 $a = 9.29 \text{ \AA}$ ,  $b = 12.33 \text{ \AA}$ ,  $c = 3.02 \text{ \AA}$ .

$Mg_3ZrB_2O_8$ : warwickite ( $Mg_3TiB_2O_8$ ) [9],  
 $a = 9.49 \text{ \AA}$ ,  $b = 9.37 \text{ \AA}$ ,  $c = 3.21 \text{ \AA}$ .

These crystal structures are closely related [8,9]. The  $B^{3+}$  ions are in triangular coordination, all other ions are in octahedral coordination.

We were not able to prepare  $Mg_5ZrB_2O_{10}$  and  $Mg_3SnB_2O_8$ . These compounds seem to be non-existent.

The compounds  $Mg_5SnB_2O_{10}$  and  $Mg_5TiB_2O_{10}$  form a solid solution series. The extra diffraction lines of the orthopinakiolite structure are observable up to the composition with equal amounts of tin and titanium. The compounds  $Mg_3ZrB_2O_8$  and  $Mg_3TiB_2O_8$  form a solid solution series with warwickite structure.

Luminescence properties

$Mg_5Sn_{1-x}Ti_xB_2O_{10}$  Unactivated  $Mg_5SnB_2O_{10}$  absorbs hardly 254 nm radiation and shows no luminescence. The introduction of titanium induces a strong absorption in the short wavelength uv region. Excitation into this absorption region results in an efficient blue emission.

Figure 1 shows the emission spectrum of  $Mg_5Sn_{0.9}Ti_{0.1}B_2O_{10}$  together with that of  $CaWO_4$ . The emission maximum is practically independent of the  $Ti^{4+}$  concentration up to  $x = 1$ . Figure 2 shows the excitation spectra as a function of  $x$ . It is clear that the excitation region shifts to lower energies for increasing values of  $x$ . Figure 3 shows the temperature dependence of the luminescence intensity. The quenching temperature decreases with increasing values of  $x$ . Table I lists the quantum efficiencies at room temperature. There is a gradual, and not a pronounced, decrease for higher  $Ti^{4+}$  concentrations.

$Mg_3Zr_{1-x}Ti_xB_2O_8$  The luminescence properties of this system are rather complicated and the light outputs for 254 nm excitation are lower than in the system described above. No luminescence is observed for  $Mg_3ZrB_2O_8$ , because no

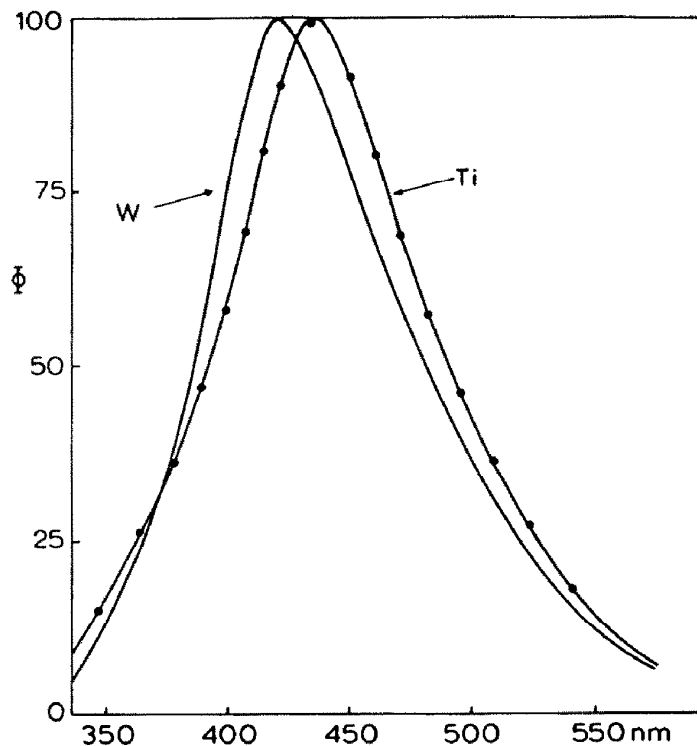


Fig. 1. Spectral energy distribution of the emission of  $\text{Mg}_5\text{Sn}_{0.9}\text{Ti}_{0.1}\text{B}_2\text{O}_{10}$  (Ti) in comparison with that of  $\text{CaWO}_4$  (W) at 300 K. Excitation is by 254 nm radiation.  $\Phi$  denotes the spectral radiant power in arbitrary units.

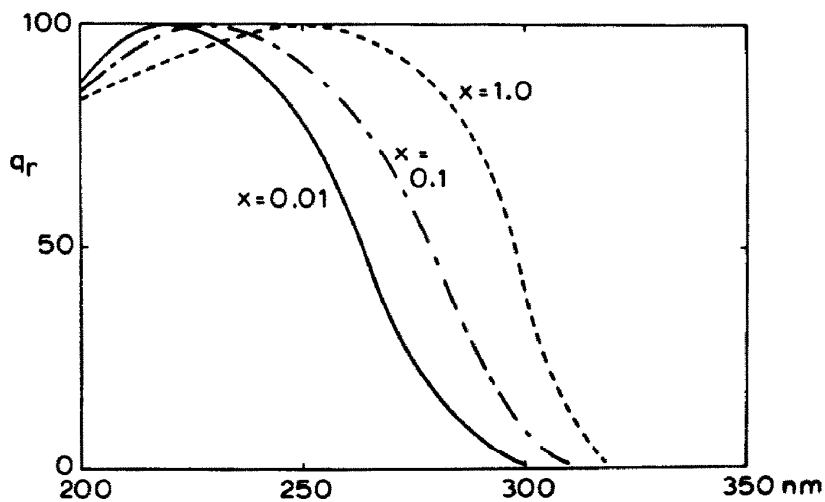


Fig. 2. Excitation spectra of the emission of  $\text{Mg}_5\text{Sn}_{1-x}\text{Ti}_x\text{B}_2\text{O}_{10}$  at 300 K for several values of  $x$ . The quantity  $q_r$  denotes the relative quantum output.

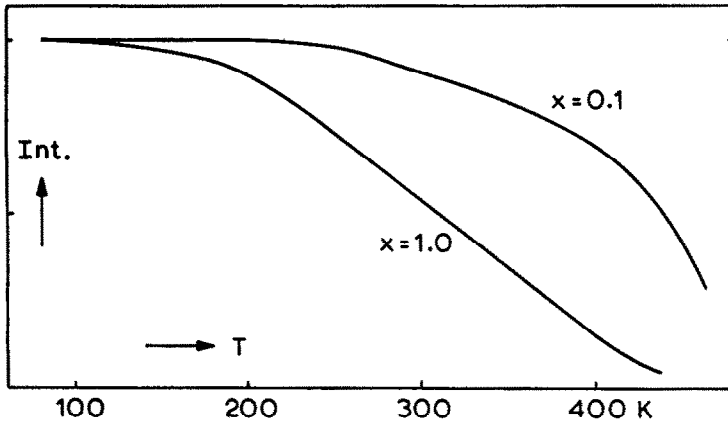


Fig. 3. Temperature dependence of the emission of  $\text{Mg}_5\text{Sn}_{1-x}\text{Ti}_x\text{B}_2\text{O}_{10}$  ( $x = 0.1$  and  $x = 1.0$ ).

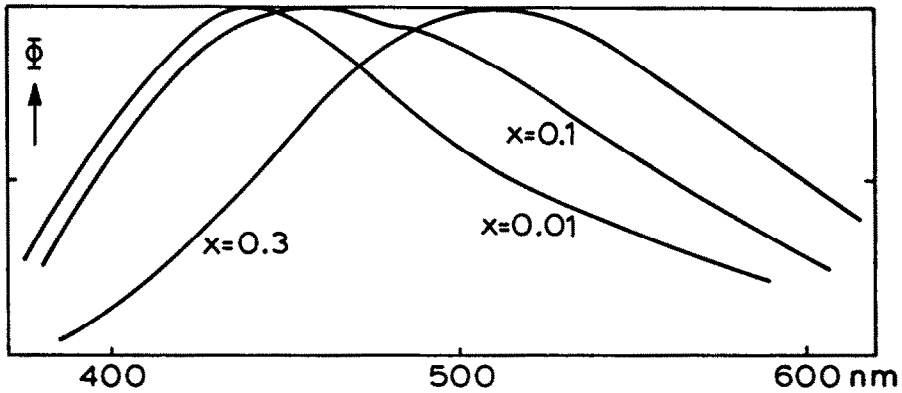


Fig. 4. Spectral energy distribution of the emission of  $\text{Mg}_3\text{Zr}_{1-x}\text{Ti}_x\text{B}_2\text{O}_8$  at 300 K for several values of  $x$ . Excitation is by 254 nm radiation.

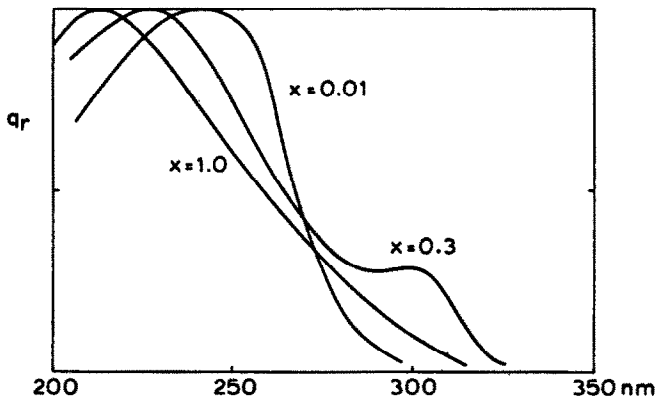


Fig. 5. Excitation spectra of the emission of  $\text{Mg}_3\text{Zr}_{1-x}\text{Ti}_x\text{B}_2\text{O}_8$  at 300 K for several values of  $x$ . Blue emission monitored.

Table I. Quantum efficiency of  $Ti^{4+}$  luminescence in  $Mg_5Sn_{1-x}Ti_xB_2O_{10}$  under excitation with 254 nm radiation at room temperature

x	Quantum efficiency (%)
0.01	75
0.05	80
0.10	80
0.20	80
0.40	75
0.70	55
1.00	45

optical absorption is observed for the accessible spectral region. The presence of titanium introduces a broad excitation region. Depending on the  $Ti^{4+}$  concentration, several emission maxima can be observed. In Fig. 4 some examples are given. Figure 5 presents some examples of excitation spectra. For  $x = 0.01$  the emission maximum is around 440 nm. This maximum shifts gradually to longer wavelengths. For  $x = 0.3$  it is situated at about 510 nm. For higher  $x$  values there is practically no further change. For low values of  $x$  there is an excitation maximum at about 240 nm. For higher  $x$  values this maximum shifts to higher energies, whereas another maximum around 310 nm evolves. All these spectra are slightly dependent on the applied excitation wavelength or the monitored emission wavelength, indicating the presence of several, different luminescent centres. Due to the broad band character of the transitions involved, it is not possible to separate these different transitions any further.

#### DISCUSSION

In order to interpret the observed luminescence properties, it is necessary to consider the two crystal structures involved, *viz.* warwickite ( $Mg_3(Zr,Ti)B_2O_8$ ) and ludwigite/orthopinakiolite ( $Mg_5(Sn,Ti)B_2O_{10}$ ). In warwickite the octahedrally coordinated cations occupy two different crystallographic sites. From X-ray investigations, no indications could be observed for any order between  $Mg^{2+}$  and  $Ti^{4+}$  in  $Mg_3TiB_2O_8$  [9], so that we have to assume that the tetravalent ions are statistically distributed among all the octahedral sites. These sites are connected to seven other octahedral sites by shared oxygen ions. For  $Mg_3Zr_{1-x}Ti_xB_2O_8$  this means that for  $x = 0.01$  98% of the  $Ti^{4+}$  ions are isolated from other ions. For  $x = 0.1$  this decreases to 84%. The fraction of  $Ti^{4+}$  ions with one  $Ti^{4+}$  neighbour amounts to 15%. For

$x = 1$  these values are 13% and 31%, respectively. The fraction of  $Ti^{4+}$  ions with two  $Ti^{4+}$  neighbours is 31%, with three or more neighbours, 25%. Due to short-range order the figures for clustered  $Ti^{4+}$  ions may be overestimated. Note that a given group of  $Ti^{4+}$  clusters consists of subgroups, since the connection with the seven nearest neighbours is not the same in all cases.

From this it can be immediately concluded that the 440 nm emission band in the system  $Mg_3Zr_{1-x}Ti_xB_2O_8$  is due to isolated titanate groups. The corresponding excitation maximum is at 235 nm, so that the Stokes shift amounts to  $19.000\text{ cm}^{-1}$ . For octahedral titanate this is a high value [2]. For higher values of  $x$ , the concentration of connected titanate groups increases rapidly. The longer wavelength emission is ascribed to the connected groups. Note the large change between the isolated centres on one hand and the connected centres on the other. It seems that the number and the type of connections is of minor importance. All the connected centres emit around 500 nm. The lowest excitation band seems to be situated at about 300 nm, so that the Stokes shift ( $\sim 13.000\text{ cm}^{-1}$ ) is considerably smaller than for the isolated luminescent centres. Due to its complicated nature, the system  $Mg_3(Zr,Ti)B_2O_8$  is hard to analyse in more detail. This is different, however, in the system  $Mg_5(Sn,Ti)B_2O_{10}$ , which will be discussed now.

We will neglect the difference between ludwigite and orthopinakiolite in view of the work by Randmets [8]. In the case of  $Mg_5SnB_2O_{10}$  and  $Mg_5TiB_2O_{10}$  this may well be due to the presence or absence of a superstructure, since it is known that  $Sn^{4+}$  and  $Mg^{2+}$  order more easily than  $Ti^{4+}$  and  $Mg^{2+}$  [3,10]. In ludwigite ( $Mg_4Fe_2^3B_2O_{10}$ ) there are four crystallographic sites for the octahedral ions. Three of these are occupied by  $Mg^{2+}$  and one by (exclusively)  $Fe^{3+}$ . The  $Fe^{3+}$  octahedra share edges along the  $c$  axis, forming linear chains. These chains do not have contact with each other, because they are separated by borate groups and  $Mg^{2+}$  octahedra. Every  $Fe^{3+}$  octahedron is connected, therefore, with two other  $Fe^{3+}$  octahedra. We assume now that the tetravalent ions in  $Mg_5(Sn,Ti)B_2O_{10}$  occupy the  $Fe^{3+}$  sites, *i.e.*  $2 Fe^{3+} \rightarrow (Sn,Ti)^{4+} + Mg^{2+}$ . This assumption can only be justified by a careful X-ray diffraction study which is outside the scope of this work. However, it seems reasonable to put the tetravalent cations on the sites which in ludwigite are occupied by the higher-charged cations ( $Fe^{3+}$ ). If the tetravalent cations also occupy the  $Mg^{2+}$  sites, the luminescence properties of our ludwigite series should be similar to those of our warwickite series, in view of the structural analogy. Since this is not the case, our structural assumption seems to be acceptable. Let us now see what this means for the luminescent properties.

For  $Mg_5Sn_{1-x}Ti_xB_2O_{10}$  we find that for  $x = 0.01$  all  $Ti^{4+}$  are essentially isolated, since the  $Ti^{4+}$  concentration on the  $Fe^{3+}$  sublattice is  $\frac{1}{2}$  and the

number of possible nearest sites only 2. Ordering would decrease this number to zero. For  $x = 0.1$ , still 90% of the  $Ti^{4+}$  ions are isolated and 10% has one  $Ti^{4+}$  neighbour (probably less, due to order on the  $Fe^{3+}$  sublattice). For  $x = 1$ , 25% is isolated, 50% has one neighbour and 25% two neighbours. Qualitatively summarized, the concentration of connected centres increases with  $x$ . The two-neighbour concentration is probably overestimated due to neglecting short-range order effects. This makes the system very simple, since we are dealing exclusively with isolated titanate groups, pairs of titanate groups (of only one type) and a low concentration of trimers (of one type).

It is now easy to conclude what is the effect of clustering on the titanate luminescence. The isolated titanate group shows emission with a maximum at 435 nm. The corresponding excitation band peaks at about 230 nm, indicating again a very large Stokes shift. Clustering shifts the lowest absorption band to lower energy, but does not seem to influence the emission properties. The Stokes shift becomes smaller, but, nevertheless, the quenching temperature decreases.

These results can find an obvious interpretation by comparison with  $K_2CrO_4$  (isolated chromate groups) and  $K_2Cr_2O_7$  (two chromate groups sharing an  $O^{2-}$  ion). It is well known that the chromate-group condensation shifts the absorption to lower energy (the colour changes from yellow to orange). Since the energy levels in the pair will split in comparison with those of the isolated centre, the lowest absorption transition will move to lower energy. The stronger the interaction, the larger will be the shift. This is what is usually observed, also in the systems under study. Note that this effect implies delocalization of the excited state over the cluster.

The question is now what the relaxed excited state in the pair will be. According to calculations by Baerends [11] the relaxed excited state of the  $Cr_2O_7^{2-}$  ion is not symmetrical, since the excitation energy appears to be localized on one of the two constituting chromate tetrahedra. This may be compared to the situation in  $SrTiO_3$ , a compound with a sublattice of corner-sharing titanate octahedra. Excitation into the band gap of this semiconductor results at low temperatures in an excited state which is localized on one of the constituting titanate octahedra (self-trapped exciton) [12].

This implies that absorption is a pair property, but that emission is, to a first approximation, a single octahedron property. The shift in the absorption (excitation) spectra, does not necessarily correspond to a possible shift in the emission spectra. This is exactly what is observed in the present systems, especially in  $Mg_5(Sn,Ti)B_2O_{10}$ , where the emission is independent of the  $Ti^{4+}$  concentration, whereas the absorption band shift is to lower energy with increasing  $Ti^{4+}$  concentration. In  $Mg_3(Zr,Ti)B_2O_8$ , the effect is less

clear, but on clustering the lowest absorption band shifts stronger than the emission band. It would be interesting to have available the results of calculations on titanate groups similar to those made for the bichromate case [11].

Thermal quenching is now becoming a different process for different values of  $x$ . For isolated ions we have the simple Mott-Seitz picture (configurational coordinate model). For the pairs, the relation between Stokes shift and quenching temperature [13] is no longer valid, since absorption and emission occur in different configurational coordinate space. Probably the first step here is the thermal derelaxation, which obviously opens the route to non-radiative return to the ground state. The lower quenching temperatures for higher  $Ti^{4+}$  concentrations are, therefore, ascribed to thermal quenching in the clustered centres. Note that the temperature for which no luminescence is left is practically independent of the  $Ti^{4+}$  concentration. The reason for this is that all compositions still contain a certain concentration of isolated titanate octahedra. Their quenching temperature does not depend strongly on the composition of the sample.

Finally we note that the luminescence of titanates is a very complicated subject because of the many situations possible. The situation in the pairs (clusters) as described in this paper is in between two extreme cases; viz. compounds with completely isolated titanate groups and compounds in which the interaction between the titanate groups is so strong that a semiconductor results. An example of the first case is  $BaTi(PO_4)_2$  [2]. All titanate octahedra are isolated from each other and behave as isolated titanate groups. The latter case is exemplified by  $TiO_2$  and  $SrTiO_3$ . For  $TiO_2$ , the self-trapped exciton has never been observed and probably does not exist, whereas for  $SrTiO_3$  it has been observed at very low temperatures only ( $T < 35$  K) [12].

In many cases the situation is made very complicated by the presence of 'defect' titanate groups [2].  $La_2MgTiO_6$ , for example, belongs to the class of isolated titanate groups, but due to disorder there are defect titanate groups which trap the intrinsic titanate emission [3]. This is a rather general phenomenon [3]. Another situation occurs in those  $Ti^{4+}$ -activated stannates in which the titanate levels lie above the stannate levels (e.g.  $SnO_2$ ,  $Zn_2SnO_4$ ) [14].

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