

LUMINESCENCE OF LEAD-CONTAINING TUNGSTATES WITH PEROVSKITE STRUCTURE

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The luminescence of perovskites with formula $\text{Sr}_{1-x}\text{Pb}_x\text{LaLiWO}_6$ and $\text{Ba}_{2-x}\text{Pb}_x\text{MgWO}_6$ is reported. The lower-energy emission in the lead-containing compounds is ascribed to a transition within a centre consisting of a tungstate octahedron with lead-ion neighbours. The presence of Bi^{3+} in SrLaLiWO_6 causes a similar emission.

1. Introduction

Kröger [1] has described the influence of Pb^{2+} on the luminescence of alkaline-earth tungstates. Later these investigations have been extended by Blasse and Brill [2]. They examined the system $\text{M}_{1-x}\text{Pb}_x\text{S}_{1-y}\text{W}_y\text{O}_4$ ($\text{M} = \text{Ca}, \text{Ba}$). In this system the sulfate serves as a host lattice for the tetrahedral tungstate centre. These authors concluded that in this system emission can occur from three different centres, viz.

- (a) from the “isolated” WO_4^{2-} -centre (i.e. transition within the tungstate group);
- (b) from the “isolated” Pb^{2+} -ion (i.e. transition on the Pb^{2+} -ion);
- (c) from a centre consisting of a tungstate group with lead-ion neighbours.

The relevant transitions were assumed to be lead-tungsten charge-transfer transitions. Its emission wavelength depends on the lead content of the centre, but is always longer than that of the isolated centres.

The measurements showed that the absorption and the emission band of the $\text{Pb}^{2+}-\text{WO}_4^{2-}$ centre shift to longer wavelength with increasing number of Pb^{2+} neighbours. This result is in accordance with the properties that have been found for charge-transfer bands [3], since their maxima shift to longer wavelength as the number of donating ligands increases. Van Loo described the $\text{Pb}^{2+}-\text{WO}_4^{2-}$ centre in PbWO_4 in greater detail [4].

In the course of investigations on optical properties of tungstates with ordered perovskite structure it seemed interesting to study the influence of Pb^{2+} and of the isoelectronic Bi^{3+} on the tungstate luminescence. We have found that the compounds Ba_2MgWO_6 and SrLaLiWO_6 can be doped with Pb^{2+} and SrLaLiWO_6 with Bi^{3+} . The Pb^{2+} -ions are situated at Ba^{2+} -sites or at Sr^{2+} -sites, the Bi^{3+} at La^{3+} sites. In compound with perovskite structure the W^{6+} ion is octahedrally surrounded by oxygen ions, so that the present systems are suitable for our purpose. The lumin-

escence of undoped Ba_2MgWO_6 has been described previously [5,6]. The compound SrLaLiWO_6 has been reported recently in the literature to be an ordered perovskite [7].

2. Experimental

All samples were prepared by mixing the starting materials in stoichiometric proportions and firing them in an oxygen atmosphere for about four hours at temperatures of 850–1200°C. Starting materials were high-purity SrCO_3 , BaCO_3 , PbCO_3 , Li_2CO_3 , basic magnesium carbonate (all p.a. Merck), Bi_2O_3 , La_2O_3 and WO_3 (all 99.9% quality Koch Light). The compounds were checked on a Philips X-ray diffractometer using $\text{CuK}\alpha$ -radiation. All samples show the ordered perovskite structure. The performance of the optical measurements has been described previously [8].

3. Results and discussion

3.1. The system $\text{Sr}_{1-x}\text{Pb}_x\text{LaLiWO}_6$

In this system the luminescence of compositions with $x = 0.00, 0.05, 0.70$ and 1.00 has been studied at 5 K. SrLaLiWO_6 shows a blue-green emission peaking at 2.55 eV (fig. 1). The excitation band of this emission peaks at 4.20 eV. The quenching temperature of the emission is about 200 K in accordance with a relation given before [9]. The occupation of the larger cation lattice by Sr^{2+} and La^{3+} ions shows

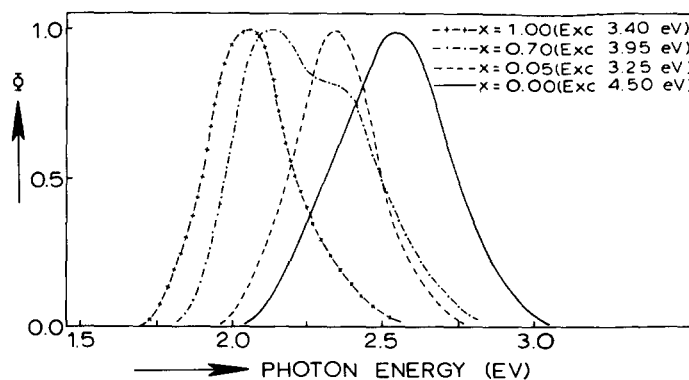


Fig. 1. Spectral energy distribution of the emission at 5 K of several compositions in the system $\text{Sr}_{1-x}\text{Pb}_x\text{LaLiWO}_6$. Φ gives the radiant power per energy interval in arbitrary units.

a fair degree of disorder. This follows from vibrational spectroscopy [10] and from the emission spectrum of Eu^{3+} in SrLaLiWO_6 (broad lines [11]).

When the lead-containing compounds are excited in the 4.2 eV excitation band, a blue-green emission is observed that seems to be the same as the emission of undoped SrLaLiWO_6 . Obviously this is the emission of the isolated tungstate octahedron. Under lower-energy excitation the lead-containing compounds show an additional longer wavelength emission (fig. 1). Like in the system $(\text{Ca,Pb})(\text{S,W})\text{O}_4$ this emission band shifts to longer wavelength with increasing lead-concentration.

The concentration of isolated and Pb^{2+} -tungstate groups can be estimated as follows. We assume that in SrLaLiWO_6 each WO_6^{6-} group is surrounded by four Sr^{2+} -neighbours, i.e. there is a reasonable amount of short-range order in the larger-cation lattice (see also [12]). If we further assume a statistical distribution of Pb^{2+} ions among the Sr^{2+} -sites we estimate that in $\text{Sr}_{0.95}\text{Pb}_{0.05}\text{LaLiWO}_6$ 81% of the WO_6^{6-} -groups has no Pb^{2+} -neighbours. A fraction of 17% has one Pb^{2+} -neighbour and less than 2% of the WO_6^{6-} -octahedra has two or more Pb^{2+} -neighbours.

In $\text{Sr}_{0.3}\text{Pb}_{0.7}\text{LaLiWO}_6$ 24% of the tungstate octahedra has four Pb^{2+} neighbours, 41% three, 26.5% two, 7.5% one and about 1% none. These data together with fig. 1 suggest the following rough assignment: the tungstate octahedra with three or four Pb^{2+} neighbours emit in the region around 2.1 eV and those with one or two neighbours in the region around 2.35 eV.

In the diffuse reflection spectra we also find a similarity with the results that have been found for the system $(\text{Ca,Pb})\text{WO}_4$ [1]: for a higher lead concentration the absorption edge shifts to a longer wavelength (table 1). We ascribe the lead-induced emission and excitation (absorption) bands to lead-tungsten charge-transfer transitions. We note a striking agreement between the luminescence of the system $(\text{Sr,Pb})\text{LaLiWO}_6$ and Kröger's $(\text{M,Pb})\text{WO}_4$. This holds even for PbWO_4 and PbLaLiWO_6 which both show a blue (pure) tungstate emission and a yellow Pb^{2+} -tungstate emission at low temperatures.

3.2. The system $\text{Ba}_{2-x}\text{Pb}_x\text{MgWO}_6$

In this system the following compositions have been investigated: $x = 0.0$, $x = 0.1$ and $x = 2.0$. Fig. 2 shows the spectral energy distribution of the emission of these

Table 1
Position of the optical absorption edge in the system $\text{Sr}_{1-x}\text{Pb}_x\text{LaLiWO}_6$ at 300 K.

Composition	Absorption edge (eV)
$x = 0.00$ SrLaLiWO_6	4.1
$x = 0.05$ $\text{Sr}_{0.95}\text{Pb}_{0.05}\text{LaLiWO}_6$	4.0
$x = 0.70$ $\text{Sr}_{0.3}\text{Pb}_{0.7}\text{LaLiWO}_6$	3.6
$x = 1.00$ PbLaLiWO_6	3.4

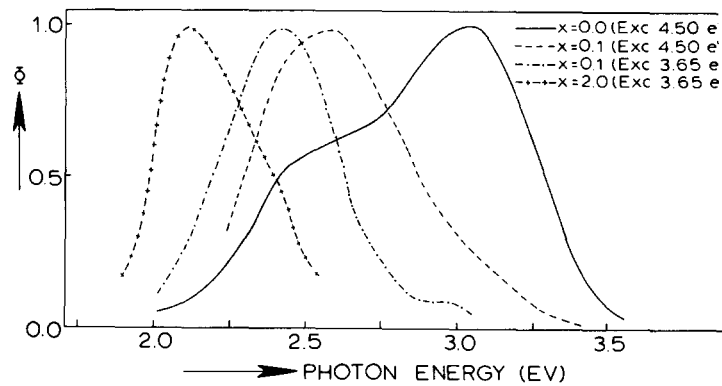


Fig. 2. Spectral energy distribution of the emission at 5 K of several compositions in the system $\text{Ba}_{2-x}\text{Pb}_x\text{MgWO}_6$. Φ gives the radiant power per energy interval in arbitrary units.

compositions at 5 K. The emission of Ba_2MgWO_6 excited with 4.50 eV radiation consists of two bands with maxima at 3.0 and 2.5 eV [5,6]. Under 4.50 eV excitation $\text{Ba}_{1.9}\text{Pb}_{0.1}\text{MgWO}_6$ also shows these two emission bands, but in this case the 2.5 eV emission has the higher intensity. Under 3.65 eV excitation emission bands are found with maxima at 2.40 eV in $\text{Ba}_{1.9}\text{Pb}_{0.1}\text{MgWO}_6$ and at 2.10 eV in Pb_2MgWO_6 (see figs. 2 and 3). It is obvious to ascribe the 3.0 eV emission to the isolated WO_6^{6-} -centre and the longer-wavelength emissions to centres consisting of a WO_6^{6-} -group with nearest Pb^{2+} -neighbours. The 2.5 eV band of undoped Ba_2MgWO_6 has been discussed elsewhere [6] and is not considered here. Assuming a statistical distribution of Pb^{2+} among Ba^{2+} sites it is found that in $\text{Ba}_{1.9}\text{Pb}_{0.1}\text{MgWO}_6$ 66% of the WO_6^{6-} octahedra has no Pb^{2+} -neighbours. The fraction with one Pb^{2+} -neighbour

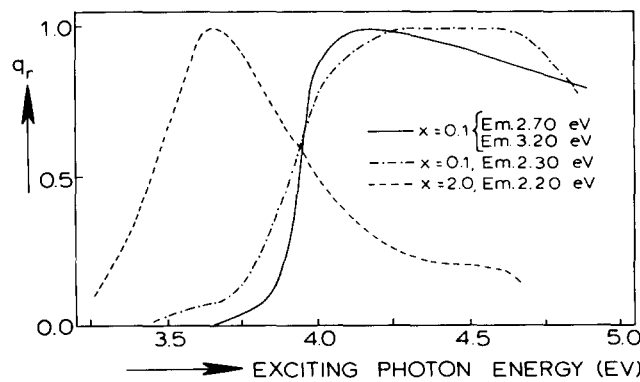


Fig. 3. Excitation spectra at 5 K of the emission in the system $\text{Ba}_{2-x}\text{Pb}_x\text{MgWO}_6$. q_r gives the relative quantum output in arbitrary units.

is 28%, 5% has two Pb^{2+} -ions on the nearest Ba^{2+} -site, and less than 1% of the WO_6^{6-} -groups has three or more Pb^{2+} -neighbours.

It seems obvious, therefore, that the emission around 2.5 eV will be mainly due to a $\text{Pb}^{2+}-\text{WO}_6^{6-}$ -centre with one or two Pb^{2+} -neighbours, while the emission band at about 2.1 eV will be caused by a centre consisting of a WO_6^{6-} -group with exclusively Pb^{2+} -ions on the nearest Ba^{2+} -sites.

Note in fig. 2 that for $\text{Ba}_{1.9}\text{Pb}_{0.1}\text{MgWO}_6$ under 4.5 eV (i.e. isolated tungstate) excitation the emission consists mainly of $\text{Pb}^{2+}-\text{WO}_6^{6-}$ emission although the isolated tungstate fraction is 66%. This indicates that energy transfer from isolated tungstate groups to $\text{Pb}^{2+}-\text{WO}_6^{6-}$ centres occurs. On the other hand this transfer cannot explain completely why the excitation spectra of the 2.7 and 3.2 eV emission of this composition are identical (see fig. 3). Probably the absorption band of the tungstate group with one Pb^{2+} neighbour lies at the same or even higher energy than the absorption band of the isolated tungstate group, although the former emission is at lower energy than that of the latter. This indicates that the influence of the Pb^{2+} ion on the tungstate group is not always equally pronounced.

"Pure" WO_6^{6-} -emission has not been observed in Pb_2MgWO_6 . Apparently relaxation to the emitting $\text{Pb}^{2+}-\text{WO}_6^{6-}$ -level is fast. As we would expect from the results in the systems $(\text{Ca},\text{Pb})(\text{S},\text{W})\text{O}_4$ and $(\text{Sr},\text{Pb})\text{LaLiWO}_6$ the excitation band of the lower-energy emission shifts to lower energy as the Pb^{2+} -concentration increases (fig. 3).

4. The luminescence of $\text{SrLa}_{0.95}\text{Bi}_{0.05}\text{LiWO}_6$

We have also investigated the luminescence of the compound $\text{SrLa}_{0.95}\text{Bi}_{0.05}\text{LiWO}_6$. When this phosphor is excited in the 4.2 eV excitation band of SrLaLiWO_6 , an

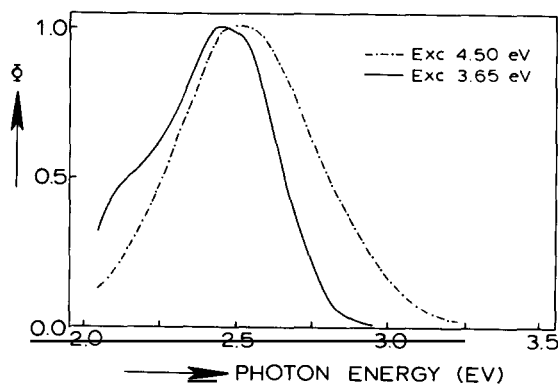


Fig. 4. Spectral energy distribution of the emission at 5 K of $\text{SrLa}_{0.95}\text{Bi}_{0.05}\text{LiWO}_6$. Φ gives the radiant power per energy interval in arbitrary units.

emission band at 2.50 eV occurs. Under longer-wavelength excitation (e.g. 3.65 eV) an additional emission band is observed at approximately 2.20 eV (fig. 4). The first band will originate from the isolated WO_6^{6-} centre, the latter emission will be due to a $\text{Bi}^{3+}-\text{WO}_6^{6-}$ centre. Unfortunately it was impossible to introduce more than a few percent of bismuth in SrLaLiWO_6 .

In CaWO_4 the quenching temperature of the luminescence increases upon addition of a small amount of Pb^{2+} [1]. An analogous increase of the quenching temperature has been found in $\text{SrLa}_{0.95}\text{Bi}_{0.05}\text{LiWO}_6$. The blue-green emission of SrLaLiWO_6 is thermally quenched at about 200 K, while the 2.20 eV emission is still present up till about 250 K. The influence of Pb^{2+} on the quenching temperature of SrLaLiWO_6 , however, is very small. In our opinion these phenomena are not understood at the moment.

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