

SEARCH FOR LUMINESCENCE IN SOME LEAD PHOSPHATES

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ABSTRACT

Below 200 K $\text{Pb}_3(\text{PO}_4)_2$ shows a weak bluish luminescence. The apatite $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ and the eulytite $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$ do not luminescence (LHeT). The reasons for the absence of luminescence are discussed.

INTRODUCTION

There is considerable interest in efficient luminescence from heavy element compounds for use as X-ray phosphors and scintillators. An example of the former is the lanthanide tantalates [1], of the latter $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ [2]. Recently also some Pb^{2+} compounds have been reported to emit efficiently at room temperature, viz. PbAl_2O_4 and PbGa_2O_4 [3]. With this in mind we investigated the luminescence of some lead phosphates, viz. $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ and $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$. The results are reported in this paper.

EXPERIMENTAL

Sample preparation was performed as described before [4-6]. The optical instrumentation is the same as in ref. [7].

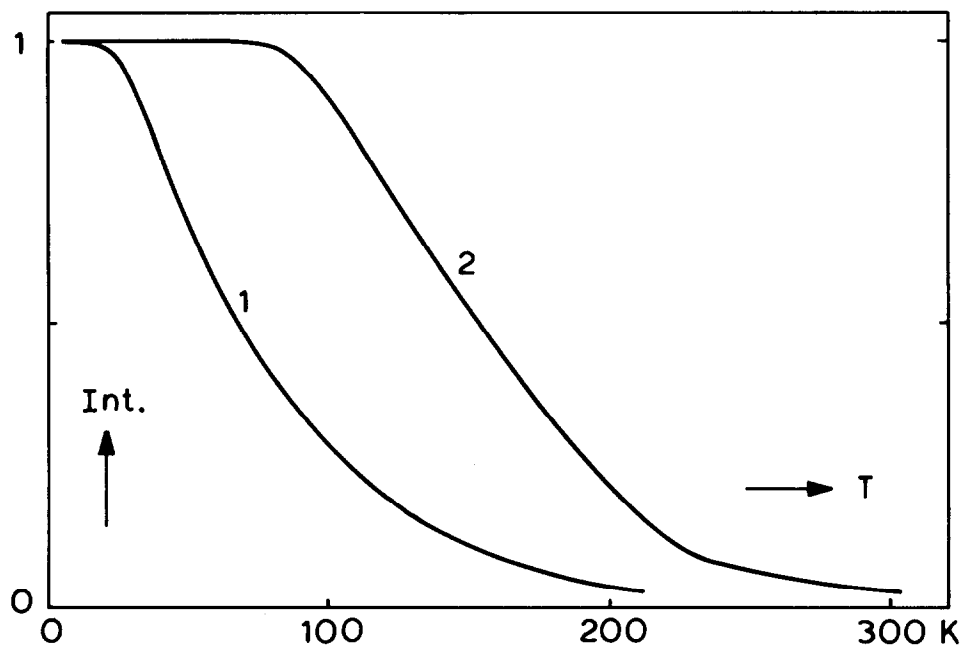


Fig. 1. Temperature dependence of the luminescence intensity of $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$ (2) and $\text{Pb}_3(\text{PO}_4)_2$ (1).

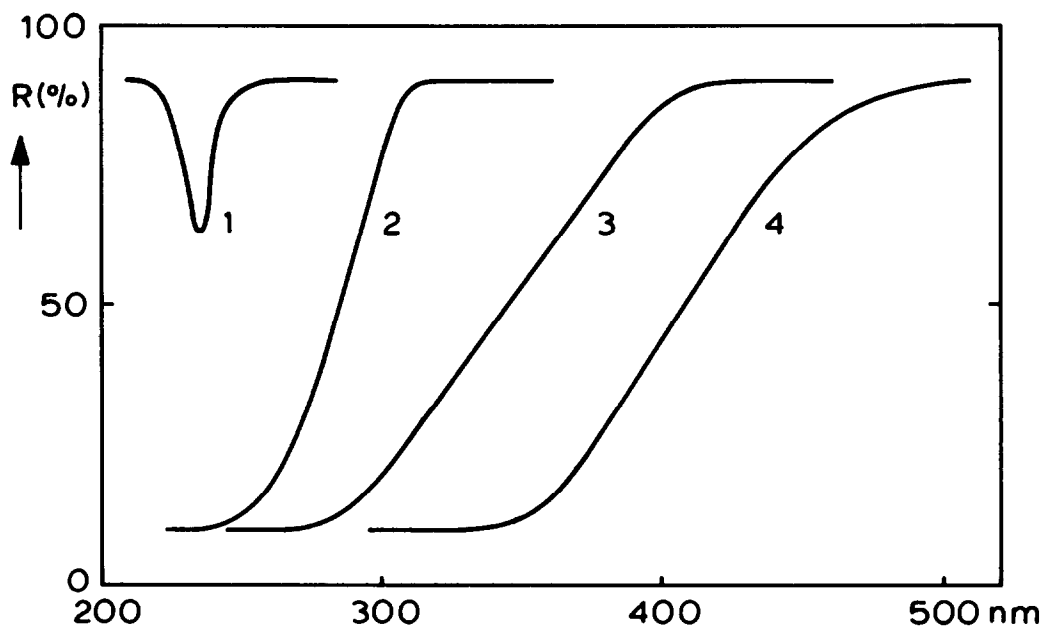


Fig. 2. Diffuse reflection spectrum of $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$ (1), $\text{Pb}_3(\text{PO}_4)_2$ (2), $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ (3) and $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$ (4) at 300 K.

RESULTS AND DISCUSSION

 $\text{Pb}_3(\text{PO}_4)_2$

The compound $\text{Pb}_3(\text{PO}_4)_2$ shows luminescence only below 200 K, but even at LHeT (liquid helium temperature) the luminescence intensity is relatively weak. Figure 1 shows the temperature dependence curve. The emission band shows a maximum at 460 nm. The corresponding excitation spectrum peaks at about 290 nm. The Stokes shift is some $12,000 \text{ cm}^{-1}$. The diffuse reflection spectrum is given in Fig. 2.

Since the crystal structure of the low-temperature modification of $\text{Pb}_3(\text{PO}_4)_2$ is closely related to that of the high-temperature modification [8], we studied also $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}(\sim 1\text{a/o})$. This composition is isostructural with the high-temperature modification of $\text{Pb}_3(\text{PO}_4)_2$ and contains isolated Pb^{2+} ions. The luminescence has been mentioned superficially by Butler [9]. Here we report further details. There is an emission band with a broad maximum at about 430 nm. The excitation band peaks at 235 nm. The Stokes shift is $20,000 \text{ cm}^{-1}$, which is a very high value. The temperature dependence curve is given in Fig. 1, the diffuse reflection spectrum in Fig. 2. The spectral changes between the luminescences of $\text{Pb}_3(\text{PO}_4)_2$ and $\text{Sr}_3(\text{PO}_4)_2$ are not very large. It is clear that in $\text{Sr}_3(\text{PO}_4)_2$ the efficiency of the Pb^{2+} emission at room temperature is also very low.

The low quenching temperature of the luminescence of $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$ is obviously related to the large Stokes shift. Such a large Stokes shift has also been reported for PbAl_2O_4 and PbGa_2O_4 [3]. However, from a structural point of view the situations are not comparable. In the lead compounds the Pb^{2+} ions are asymmetrically coordinated by O^{2-} ions. There are theoretical reasons to assume that the asymmetry is less in the excited state. The corresponding reorganization of the lead-oxygen complex is responsible for the large Stokes shift. In $\text{Sr}_3(\text{PO}_4)_2$ the Sr^{2+} sites are rather symmetrical with high coordination number. An asymmetrical coordination for Pb^{2+} in the ground state seems not too likely, especially since the Pb^{2+} ion is somewhat larger than the Sr^{2+} ion [10]. In the $\text{Sr}_3(\text{PO}_4)_2$ structure, three Sr^{2+} polyhedra are situated along the c-axis sharing triangular faces. The lowest empty orbital of Pb^{2+} is 6p. Due to the coupling of the three Sr^{2+} polyhedra along the c-axis, the $6p_z$ orbital is directed along the c-axis and will have the lower energy of the 6p orbitals. The excited Pb^{2+} ion in $\text{Sr}_3(\text{PO}_4)_2$ will, therefore, have a more or less ellipsoidal shape, so that the relaxation after excitation must be considerable. This results in a large Stokes shift and, in turn, in a low quenching temperature of the luminescence.

With this model we now turn to $\text{Pb}_3(\text{PO}_4)_2$. Here we have the same linear row, which now consists of three Pb^{2+} ions. All $6p_z$ orbitals are directed along the axis of the row, which will result in a certain electron delocalization in the excited state. The interaction between the three Pb^{2+} ions will lower the absorption transition in comparison with the $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$ system, as observed experimentally.

We note that in PbGe_3O_7 linear Pb^{2+} chains are present [3]. This leads to a semiconducting behaviour. In fact we assume that the situation in $\text{Pb}_3(\text{PO}_4)_2$ is in between $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$ and PbGe_3O_7 . In PbGe_3O_7 the absorption has even shifted to much lower energies [3].

The emission spectra of $\text{Pb}_3(\text{PO}_4)_2$ and $\text{Sr}(\text{PO}_4)_2\text{-Pb}$ are not essentially different (460 and 430 nm, respectively). We therefore assume that after excitation of the linear row of three Pb^{2+} ions, relaxation occurs on one of the Pb^{2+} ions from which emission arises.

This is analogous to the case of the CrO_4^{2-} ion. Upon condensation to the complex $\text{Cr}_2\text{O}_7^{2-}$ ion, the lowest absorption band shifts to lower energy (and the colour from yellow to orange), but the emission of $\text{Cr}_2\text{O}_7^{2-}$ occurs from one chromate tetrahedron, since the excitation is localized there after relaxation [11]. A similar situation was recently observed for the titanate luminescence in $\text{Mg}_5\text{SnB}_2\text{O}_{10}$ where we are also dealing with linear rows [12].

The quenching of the $\text{Pb}_3(\text{PO}_4)_2$ luminescence is not easy to compare with that of $\text{Sr}_3(\text{PO}_4)_2\text{-Pb}$. This is because the Stokes shifts are not comparable in view of the difference in the excited state (more vs less delocalization, respectively).

In the system $\text{Pb}_3(\text{P}_{1-x}\text{V}_x\text{O}_4)_2$ the absorption shifts rapidly to lower energy with increasing value of x , so that $\text{Pb}_3(\text{VO}_4)_2$ is reddish brown [1]. Since Pb^{2+} and V^{5+} in $\text{Sr}_3(\text{PO}_4)_2$ yield only ultraviolet absorption (see above and ref. [13]), the additional absorption due to the combined presence of Pb^{2+} and V^{5+} is ascribed to a charge-transfer transition from the $6s$ orbital of Pb^{2+} to the empty $3d$ orbital of V^{5+} . A similar transition has been observed for PbMoO_4 and PbWO_4 [14]. No luminescence was observed for compositions $\text{Pb}_3(\text{P}_{1-x}\text{V}_x\text{O}_4)_2$ at LHeT. We assume that nonradiative transitions dominate due to the low-energy position of the transition involved. This is a well-known phenomenon [15].

$\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$

This composition has an apatite structure. Figure 2 shows the diffuse reflection spectrum which extends into the visible. Down to LHeT we did not observe luminescence of any importance.

In the apatite structure there are two crystallographic sites for the Pb^{2+} ions, viz. (6h) and (4f). The latter form infinite linear chains by face sharing in a way which is reminiscent of the row of three cations in the $\text{Sr}_3(\text{PO}_4)_2$ structure. The (6h) sites are asymmetrically coordinated due to the absence of an anion between the three (6h) sites (this is the F^- ion site in fluoroapatite). In fact it has been observed that Pb^{2+} favours the (6h) sites, so that Na^+ occupies the (4f) sites [16], where it will interrupt the Pb^{2+} chains along the c-axis.

Even on an energy scale, the slope of the diffuse reflection spectrum of $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ is less steep than that of $\text{Pb}_3(\text{PO}_4)_2$, indicating a more or less disordered arrangement. The absorption edge has shifted to considerably lower energy in comparison with that of $\text{Pb}_3(\text{PO}_4)_2$. This implies a strong coupling between the Pb^{2+} ions (the (6h) and (4f) sites are also connected). This coupling between $6s^2$ ions in the apatite structure is also clear from the yellow to ochre colour of bismuth apatites [17]. Therefore $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ cannot be compared with $\text{Pb}_3(\text{PO}_4)_2$ where delocalization seems to be restricted to three Pb^{2+} ions. The absence of luminescence can be ascribed to energy transfer to killer sites by charge carriers, comparable to the situation in PbGe_3O_7 [3]. The nature of the killer centres remains unclear. Photoconductivity measurements would be helpful to solve the problem.

$\text{Pb}_7\text{Ti}(\text{PO}_4)_6$

Figure 2 shows the diffuse reflection spectrum of $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$. Down to LHeT no luminescence has been observed. The crystal structure of $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$ is that of eulytite [18-19] with a disordered arrangement of Pb^{2+} and Ti^{4+} ions among the Bi^{3+} sites of eulytite $\text{Bi}_4(\text{SiO}_4)_3$. Since $\text{Sr}_7\text{Ti}(\text{PO}_4)_6$ and $\text{Pb}_7\text{Sn}(\text{PO}_4)_6$, both with eulytite structure, are colourless [19], the yellow colour of $\text{Pb}_7\text{Ti}(\text{PO}_4)_6$ is ascribed to a Pb^{2+} - Ti^{4+} charge-transfer transition, comparable to that in PbMoO_4 . Obviously this transition is at too low an energy to yield luminescence (compare $\text{Pb}_3(\text{VO}_4)_2$, see above). That the low absorption would be due to coupling of Pb^{2+} polyhedra seems to be unlikely in view of the fact that $\text{Bi}_4\text{Si}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ with the isoelectronic Bi^{3+} ions show absorption at high energy [3].

CONCLUSION

We conclude that lead phosphates are not suitable as efficient luminescent materials. This is related to structural details. Up till now only lead compounds which contain asymmetrically coordinated Pb^{2+} ions that are isolated in the crystal structure show efficient luminescence (e.g. PbAl_2O_4).

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