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Influence of Crystal Structure on the Luminescence of Ions with s^2 Configuration

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It is shown that the Stokes shift and thermal quenching temperature of the luminescence of Pb^{2+} and Bi^{3+} depend strongly on the stiffness of the host lattice, as is to be expected from the configurational coordinate diagram.

Introduction

The luminescence of the Pb^{2+} ion in $CaZrO_3$ has been investigated by two groups (*1*, *2*). One of these reports yellow emission (*1*), the other ultraviolet emission (*2*). Recently, we have solved this contradiction and shown that the Pb^{2+} ion in $CaZrO_3$ absorbs and emits in the ultraviolet (*3*). The efficiency of the luminescence is high even at room temperature (*2*). The Stokes shift is small. In (*2*) the luminescence of Pb^{2+} in CaO-modified ZrO_2 with fluorite structure also has been reported. It differs significantly from that of $CaZrO_3$–Pb^{2+}. In particular, the Stokes shift is larger and the thermal quenching temperature (T_q) is lower. This prompted us to investigate the Pb^{2+} luminescence in compounds which are in some way related to $CaZrO_3$ and to try to explain the results in a simple way.

Experimental

Samples were prepared by the usual techniques. Activator concentrations were 1 at% or less. Samples were checked by X-ray analysis. The performance of the optical measurements is the same as in (*3*). The measurements on $LaAlO_3$–Bi^{3+} were slightly perturbed by the presence of a small amount of a luminescent second phase, viz., La_2O_3–Bi^{3+}.

The following compositions were studied: $CaZrO_3$–Pb^{2+}, $SrZrO_3$–Pb^{2+}, $BaZrO_3$–Pb^{2+}, Sr_2ZrO_4–Pb^{2+}, Ba_2ZrO_4–Pb^{2+}, and $LaAlO_3$–Bi^{3+}. Data for other materials were taken from the literature, viz., CaO-modified ZrO_2–Pb^{2+} and Bi^{3+} (*2*, *4*), $CaZrO_3$–Bi^{3+} (*4*), and $LaGaO_3$–Bi^{3+} (*5*).

Results

All samples show broad emission and excitation bands at all temperatures. The relevant data are compiled in Tables I and II. The thermal quenching temperature is given according to Kröger's definition (*6*). The data for $LaAlO_3$–Bi^{3+} are very much like those reported for $LaGaO_3$–Bi^{3+} (*5*) and are, therefore, not given here. The same holds for Sr_2ZrO_4–Pb^{2+} and Ba_2ZrO_4–Pb^{2+}.

Discussion

The difference between the luminescence of Pb^{2+} and Bi^{3+} in perovskite-phase $CaZrO_3$ and fluorite phase CaO–ZrO_2, reported but not discussed in (*2*, *4*), is impressive. The perovskite-phase has a smaller Stokes shift and a higher T_q. There seems to be a simple explanation for this fact. From the configurational coordinate model it follows immediately that a small Stokes shift should imply a high value of T_q (*8*). In fact, a small

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TABLE I

SOME LUMINESCENCE PROPERTIES OF THE COMPOSITIONS INVESTIGATED

Composition	Maximum excitation band (at 77°K) (nm)	Maximum emission band (at 77°K) (nm)	T_q (°K)
$CaZrO_3$–Pb	285	365	450
$SrZrO_3$–Pb	275	360	400
$BaZrO_3$–Pb	260	495	260
Ba_2ZrO_4–Pb	290	530	250

TABLE II

THERMAL QUENCHING TEMPERATURE (T_q) AND STOKES SHIFT OF THE LUMINESCENCE OF SOME Pb^{2+}- AND Bi^{3+}-ACTIVATED OXIDES

Composition	Stokes shift (eV)	T_q (°K)	Reference
$LaGaO_3$–Bi^{3+}	0.8	400	*6*
$CaZrO_3$–Bi^{3+}	0.9	460	*5*
$CaZrO_3$–Pb^{2+}	1.0	450	Present work, *2*
$SrZrO_3$–Pb^{2+}	1.1	400	Present work
La_2O_3–Bi^{3+}	1.4	350	*6, 8*
CaO–mod. ZrO_2–Bi^{3+}	1.4	$\simeq 320$	*5*
CaO–mod. ZrO_2–Pb^{2+}	1.5	$\simeq 320$	*2*
Ba_2ZrO_4–Pb^{2+}	2.0	250	Present work
$BaZrO_3$–Pb^{2+}	2.2	260	Present work

Stokes shift means that Δr, the difference between the equilibrium distances of the ground and emitting states, is small. We may expect that in a close-packed crystal structure (as perovskite), Δr will be smaller than in a structure with a high concentration of vacancies (as the fluorite lattice of CaO-modified ZrO_2). The difference between the luminescence properties of the isoelectronic Pb^{2+} and Bi^{3+} ions in these lattices can, therefore, be related to a difference between the host lattices. The nature of the luminescent ion is not involved. In fact, analogous differences have been observed for Ti^{4+} (*9*) and indirectly for Pr^{3+} (*10*).

This idea was used as a guide line for further study. It predicts that:

(a) Replacement of Ca^{2+} in $CaZrO_3$–Pb^{2+} by the larger Sr^{2+} and Ba^{2+} ions (i.e., decreasing the stiffness of the perovskite lattice) will result in an increase of Δr and the Stokes shift and a decrease of T_q, as observed experimentally. Note that the ${}^1S_0 \rightarrow {}^3P_1$ absorption band (excitation band) shifts to higher energy from Ca to Ba. It seems reasonable to assume that the degree of covalency of the Pb–O bond decreases in this sequence, since the size of the available site increases, It is well known that the position of the ${}^1S_0 \rightarrow {}^3P_1$ transition and the degree of covalency are related (*11*, *12*).

(b) Introduction of relatively soft *M*O layers in the three-dimensional perovskite structure of $MZrO_3$ (i.e., formation of M_2ZrO_4 with K_2NiF_4 structure) will have an effect similar to that in (a), as observed experimentally. Note that the similar values of the Stokes shift of $BaZrO_3$–Pb^{2+} and Ba_2ZrO_4–Pb^{2+} seem to indicate that there is a certain limit to the value of the Stokes shift, as argued earlier by Dexter *et al.* (*13*). From a simple configurational-coordinate model these authors derived the condition $E_{em} \geqslant \frac{1}{2} E_{abs}$. Our results for the barium compounds are very near this limit.

(c) The s^2 ions in perovskites with not too large cations should luminesce efficiently. This is demonstrated by the fact that the luminescence properties of chemically different, but electronically comparable compositions with about the same lattice dimensions, like $CaZrO_3$–Pb^{2+} and $LaGaO_3$–Bi^{3+}, are similar. In La_2O_3–Bi^{3+} (with large cations only), the value of T_q is again lower than in the perovskites.

The present results demonstrate that a consideration of the crystal structure of a phosphor host lattice is of great help in predicting luminescent materials with high T_q.

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