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On the Luminescence of Titanium-Activated Stannates

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The luminescence of the following systems is reported: $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ and $Zn_2Sn_{1-x}Ti_xO_4$. The luminescence properties are independent of x and cannot be due to the titanium ions. The emission transitions are ascribed to centers with energy levels within the forbidden energy gap.

1. Introduction

It is well known that the Ti^{4+} ion can act as an efficient luminescent center in stannates. Some examples are the following: $Mg_2Sn_{1-x}Ti_xO_4$, $Sr_2Sn_{1-x}Ti_xO_4$, and $CaSn_{1-x}Ti_xO_3$ (*1–3*). Mainly, stannates of the alkaline earth metals have been investigated. In these, the energy levels of the undoped host lattice are at higher energies than those of the activator, the Ti^{4+} ion. In this way it is possible to excite the Ti^{4+} ion selectively. In a number of cases efficient titanate luminescence results upon excitation into the titanate group. The highest efficiency and thermal quenching temperature has been reported for the spinel system $Mg_2Sn_{1-x}Ti_xO_4$.

Recently a new type of mixed metal oxide with a four-layer (ABAC) hexagonal close packing of oxygen ions has been described (*4*). The crystal structure is closely related to the spinel structure. The general formula is $Li_{1.6}M_{1.6}Sn_{2.8}O_8$ (M = Zn, Mg) with one-third of the cations in tetrahedral sites and two-thirds in octahedral sites. In the zinc compound it is possible to replace tin by titanium. It turns out that $x = 0.25$ is the limiting composition in the solid solution series $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ (*4*).

In view of the structural and chemical analogy with the spinel system $Mg_2Sn_{1-x}Ti_xO_4$, it seemed interesting to investigate the luminescence properties of the system $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$. These, however, appeared to be strikingly different from those of the titanium-activated stannates reported until now (*1–3*). In order to investigate a possible explana-

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tion for this difference we investigated also the luminescence of a simple system, viz., the spinel system $Zn_2Sn_{1-x}Ti_xO_4$.

2. Experimental

Samples of $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ were prepared as described in Ref. (*4*). Samples of $Zn_2Sn_{1-x}Ti_xO_4$ were prepared as described by Macke (*3*) for the corresponding magnesium system. They were checked by X-ray diffraction. The performance of the optical measurements has been described before (*5*).

3. Results

Samples of $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ show efficient luminescence below 250 K. The spectra are quite complicated. Excitation with wavelengths shorter than 280 nm yields an emission band peaking at 465 nm; excitation with wavelengths longer than 280 nm yields emission bands with maxima at longer wavelengths, viz., in the region 490–540 nm. The longer the excitation wavelength, the longer the emission wavelength (see Fig. 1).

Samples of $Zn_2Sn_{1-x}Ti_xO_4$ ($x \leq 0.1$) show efficient luminescence below 300 K. The emission spectra show broad bands with maxima around 600 nm, depending slightly on x (Fig. 2). The excitation spectra start around 370 nm and reach a maximum around 310 nm, in good agreement with the diffuse reflection spectra. These samples show pronounced thermoluminescence phenomena.

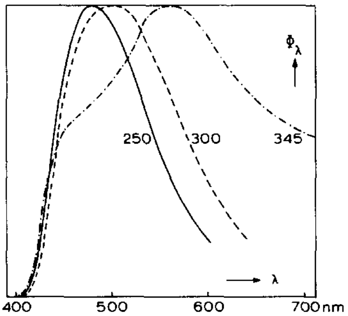

FIG. 1. Emission spectra at 4 K of $Li_{1.6}Zn_{1.6}Sn_{2.45}Ti_{0.35}O_8$. The figures indicate the excitation wavelength in nanometers.

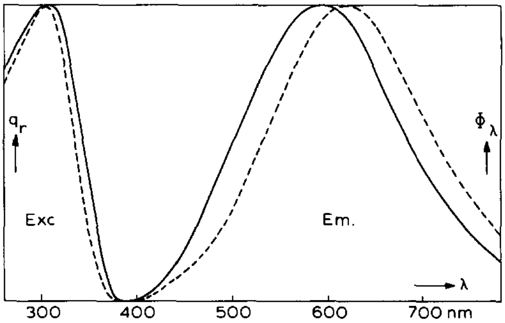

FIG. 2. Emission and excitation spectra at 77 K of the luminescence of Zn_2SnO_4 (full line) and $Zn_2Sn_{1-x}Ti_xO_4$ (broken line). (Excitation wavelength-320 nm. Emission wavelength-600 nm.)

Neither in the series $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ nor in the series $Zn_2Sn_{1-x}Ti_xO_4$ ($x \leq 0.1$) do the luminescence properties depend clearly on x. This is different from the luminescence properties of the alkaline earth stannates activated with Ti^{4+} ions, where the luminescence intensity increases with x and no titanate luminescence is observed for the composition with $x = 0$. We checked our samples with $x = 0$ carefully for Ti impurities by using high-purity SnO_2. Although titanium is absent, the luminescence properties of our samples with $x = 0$ are equal to those of the samples with $x > 0$. Our results for Zn_2SnO_4 agree with those reported earlier (*6*).

4. Discussion

The luminescence of the samples $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ must be due to the host lattice and not to the titanium ions, because the luminescence is the same for the titanium-free and the titanium-containing compositions. For the moment we use the general term "host lattice emission" without further specification. The energy levels of the titanate group in this solid solution series are obviously situated above the energy levels of the host lattice. This is in contradiction with the situation in systems like $Mg_2Sn_{1-x}Ti_xO_4$, where the titanate energy levels lie below those of the stannate host lattice, so that they determine the luminescence properties.

In the titanate-activated stannates studied until now (*1–3*), the other cations in the stannate host lattice have noble-gas configuration. This is different in $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$, where a considerable amount of Zn^{2+} ions with $3d^{10}$ configuration are present. They must be responsible for the fact that the host lattice absorption is at such low energy in this system that those of the titanate group lie above those of the host lattice. Electrostatic potentials have been calculated on the different crystallographic sites of the hexagonal structure in a way previously described (*7*). Direct comparison with atomic orbitals energy and taking into account the polarization energy on octahedral sites occupied by Sn^{4+}, Ti^{4+}, Zn^{2+}, and Li^+ simultaneously, give a good idea of the energy levels in the structure. It confirms the place of $Ti^{3+}(3d^1)$ and $Sn^{3+}(5s^1)$ far above (≈ 10 eV) the $O^{2-}(2p^6)$ valence band. In that case, the conduction band should be built up from the 4*s* orbitals of Zn^{2+} in octahedral sites which lie in the vicinity of the valence band.

To investigate the correctness of this hypothesis, we investigated the system $Zn_2Sn_{1-x}Ti_xO_4$, where the only cations next to the tetravalent ones are Zn^{2+} ions. The absorption edge is in fact at still lower energy and, once again, practically no influence of x upon the luminescence properties was observed. So we conclude that in this system the luminescence is also due to host lattice emission, independent of the value of x.

A further discussion of the nature of the luminescence transitions is rather difficult. First it should be remembered that luminescence of mixed metal oxides containing cations with d^{10} configuration is a general phenomenon (*6*). The luminescence is not due to transitions on a specific d^{10} ion (as in the case of titanate), but to radiative transitions across the band gap (electron–hole pair recombination). A compound for which these phenomena have been investigated in detail is β-Ga_2O_3, which shows an intrinsic ultraviolet emission due to recombination of an electron (hole) with a self-trapped hole (electron) (*8*) and a blue and a green extrinsic emission (*9*).

The luminescences observed for the systems under study seem to be of the same type. The strong thermoluminescence of Zn_2SnO_4 is an indication in this direction (*6, 8, 9*). It is impossible, however, to assign the orange luminescence of Zn_2SnO_4 any further on the basis of the present results. The slight dependence of the position of the emission band on the titanium concentration may be due to the influence of this concentration on the width of the forbidden zone, which is connected with the lattice contraction.

The emissions of the system $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ are even more difficult to understand. It cannot be excluded, however, that the longer wavelength emission and excitation band are due to a small amount of SnO_2–Ti. A similar observation has been made for the system $Mg_2Sn_{1-x}Ti_xO_4$ (*3*). The influence of disorder, however, cannot be excluded completely. The longer wavelength emission and excitation band coincide with those observed for SnO_2–Ti (*3, 9*).

In the earlier papers (*3, 10*) the luminescence of SnO_2–Ti has been tacitly ascribed to titanate groups. In light of the present observations this seems to be doubtful. In fact, undoped SnO_2 shows the same emission as SnO_2–Ti and the same excitation spectrum (*11*), so that the system $Sn_{1-x}Ti_xO_2$ belongs to the same type as $Zn_2Sn_{1-x}Ti_xO_4$ and $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$.

Returning now to the system $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$, we assume that the longer wavelength emission and excitation bands are due to a second phase, probably a small amount of SnO_2 which contains some titanium. In that case, the 465-nm emission band and the 280-nm excitation band belong to the system $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$. The latter corresponds to band gap excitation, the nature of the former cannot even be speculated on in view of the complicated composition of these samples.

In conclusion we note that there exist two types of titanium-activated stannates, viz., those of the type $Mg_2Sn_{1-x}Ti_xO_4$, where the titanate group really acts as an activator with its own characteristic luminescence, and those of the type $Zn_2Sn_{1-x}Ti_xO_4$, where the luminescence properties are determined by the host lattice and the emission transition occurs across the band gap.

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