

On the Luminescence of Titanium-Doped Lithium Zirconate (Li_2ZrO_3)

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The luminescence of Li_2ZrO_3 -Ti is described. The emission and excitation spectra are reported. The temperature dependence of the decay time is discussed and points to a complicated energy-level scheme. Further, the decay time of the luminescence of ZrO_2 -Ti has been measured. It appears to be very long (~ 1 msec).

1. Introduction

The luminescence of titanate groups is a well-known phenomenon (1-5). Here a titanate group is defined as a group consisting of a central Ti^{4+} ion surrounded by several oxygen ions (usually 4, 5, or 6). The optical transitions involved are of the charge-transfer type. Usually broadband spectra result (6).

In the course of a study on the solid-electrolyte properties of Li_2ZrO_3 , Hellstrom found that this compound luminesces at room temperature (7). In this paper we report on this luminescence which is due to titanium impurities in the zirconate. Also some additional measurements on ZrO_2 -Ti have been performed. The long decay time of the low-temperature luminescence is the most striking property of these systems.

2. Experimental

Titanium-free ZrO_2 was prepared by repeated crystallization of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as described by Sarver (8). Samples

$\text{Li}_2\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ ($0 \leq x \leq 0.1$) were prepared by firing mixtures of ZrO_2 , TiO_2 and Li_2CO_3 in the appropriate ratio at 700°C and subsequently at 1000°C in oxygen. Samples $\text{Zr}_{1-x}\text{Ti}_x\text{O}_2$ ($0 \leq x \leq 0.01$) were prepared by firing intimate mixtures of ZrO_2 and TiO_2 up to 1300°C . All samples were checked by X-ray diffraction analysis using $\text{CuK}\alpha$ radiation (Philips diffractometer).

The optical measurements were performed using Perkin-Elmer spectrofluorimeters, as described before (9). Temperatures below liquid helium temperature could be obtained.

3. Results

a. Li_2ZrO_3 -Ti

At room temperature, but especially at lower temperatures, the samples Li_2ZrO_3 -Ti show a bluish luminescence. Figure 1 presents the emission and the excitation spectra of this luminescence at liquid helium temperature. The emission maximum is at 450 nm at LHeT and shifts a few

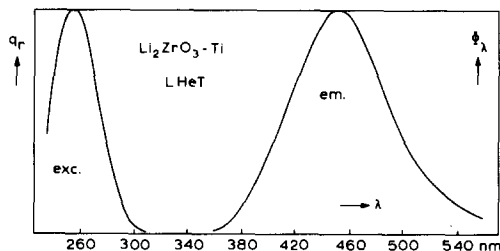


FIG. 1. Emission and excitation spectra of the luminescence of $\text{Li}_2\text{ZrO}_3\text{-Ti}$ at liquid helium temperature. q_r gives the relative quantum output and Φ_λ the radiant power per constant wavelength interval, both in arbitrary units.

nanometers to shorter wavelengths at room temperature. The excitation maximum is at 225 nm at LHeT and shifts to 260 nm at 300 K. The luminescence properties do not depend markedly on the titanium concentration in the region studied ($0 \leq x \leq 0.1$). Even small amounts of titanium (e.g., $x < 0.001$) yield an efficient luminescence. This explains why Li_2ZrO_3 prepared from unpurified ZrO_2 (which usually contains some titanium) shows this luminescence too.

The reflection spectra of these samples at room temperature show that the optical absorption edge of Li_2ZrO_3 is situated at roughly 210 nm. Introduction of titanium yields an extra absorption band extending from 300 to 210 nm and coinciding with the excitation spectrum. The

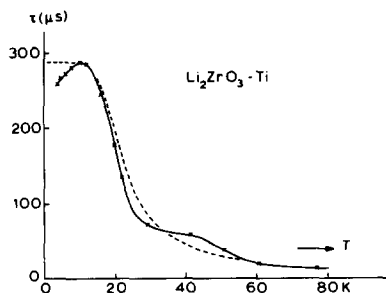


FIG. 2. Temperature dependence of the decay time of the emission of $\text{Li}_2\text{ZrO}_3\text{-Ti}$. The broken line is a fitted curve using a three-level scheme (see text).

excitation is, therefore, in the titanate group. The quenching temperature of the luminescence is situated around room temperature.

Decay curves of the luminescence were measured in the low-temperature region. All decay curves were pure exponential. Figure 2 presents the temperature dependence of the decay time of $\text{Li}_2\text{Zr}_{0.99}\text{Ti}_{0.01}\text{O}_3$. At LHeT the decay time amounts to 300 μsec , but at somewhat higher temperatures a rapid decrease occurs.

b. $\text{ZrO}_2\text{-Ti}$

The greater part of our results on $\text{ZrO}_2\text{-Ti}$ agree with those reported by Sarver (8). The luminescence of our samples has a somewhat lower quenching temperature, viz., 300–350 K, than reported by Sarver. The reason for this is not clear. We found the same, rather pronounced, temperature dependence of the emission maximum (510 nm at liquid nitrogen temperature and 475 nm at room temperature); the excitation maximum shifts only a few nanometers in the opposite direction. Also we observed the pronounced concentration quenching, but this phenomenon has not been investigated further.

In addition to Sarver's data (8) we present in Fig. 3 the temperature depen-

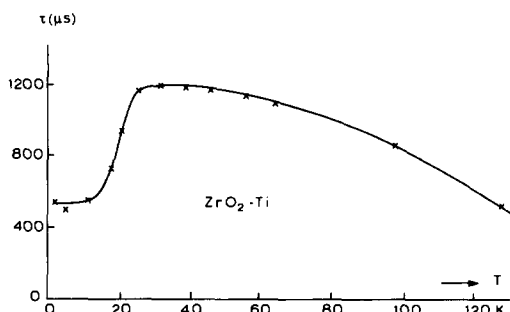


FIG. 3. Temperature dependence of the decay time of the emission of $\text{ZrO}_2\text{-Ti}$.

dence of the luminescence decay time. All decay curves appeared to be exponential. Note the rather long values (above 1 msec around 40 K).

4. Discussion

a. $\text{Li}_2\text{ZrO}_3\text{-Ti}$

The broadband emission and excitation spectra (Fig. 1) are usually observed for titanate group luminescence. The Stokes shift of some 16000 cm^{-1} is also in line with values observed for isoelectronic groups (6). Compared with other titanium-activated systems (1-3) these data are fairly simple, because in many cases more than one emission and excitation spectrum have been observed. In these cases the longer-wavelength set of bands was ascribed to titanate groups near defects in the structure (often a slight amount of disorder in ordered compounds). Also Li_2ZrO_3 has an ordered crystal structure, because it can be derived from the rocksalt structure by a superstructure between the Li^+ and Zr^{4+} ions (10). Obviously the amount of disorder in the crystal structure is very low in agreement with the crystallographic results. The fact that it is possible to find titanate phosphors with a single emission and excitation band supports the explanation for the double-band phosphors, viz., the presence of two different centers. If the two emissions were due to one and the same ion, there is no reason why they should not be observed in the case of Li_2ZrO_3 .

The temperature dependence of the decay time (Fig. 2) is very complicated and points to the presence of several excited levels just above the lowest. For simplicity we have fitted the data to a simple three-level system. If the ground state is numbered 1 and the two excited states 2 and 3, we have (11)

$$p = \frac{1}{\tau_F} = p_{21} \frac{e^{\epsilon/kT}}{1 + e^{\epsilon/kT}} + p_{31} \frac{1}{1 + e^{\epsilon/kT}}$$

Here τ_F is the measured decay time, ϵ the energy difference between levels 2 and 3, p_{21} and p_{31} the transition probability between the levels 2 and 1 on one hand and 3 and 1 on the other hand. Further we assume a Boltzmann distribution of populations of levels 2 and 3. The fitted curve is shown as a broken line in Fig. 2. The parameters used for this curve are $\epsilon = 70\text{ cm}^{-1}$, $p_{21} = 3.5 \times 10^3\text{ sec}^{-1}$ and $p_{31} = 3.1 \times 10^5\text{ sec}^{-1}$.

From a comparison between the experimental results and the curve calculated for this three-level scheme (see Fig. 2) we see that the lower level 2 consists of two levels in view of the decrease of the decay time for very low, decreasing temperature. The lower of the two levels has a higher transition probability to the ground state than the higher one. But also the assumption of one level 3 is too simple, as is clear from the deviation of the experimental curve from the calculated one in the temperature range 30-60 K. From this we conclude that at least four components of the excited state play a role in the emission process in the case of $\text{Li}_2\text{ZrO}_3\text{-Ti}$. Because it is not clear how to correlate all these levels with a theoretical energy level scheme, we abandoned a further quantitative evaluation of the experimental curve of Fig. 2.

For a tetrahedral titanate group these energy levels are nowadays known (6), but for the octahedral case they are not. In view of the crystal structure of Li_2ZrO_3 the Ti^{4+} ion coordination in our samples will be octahedral with different Ti-O distances. It has been shown recently that the temperature dependence and the value of the decay time of complexes of this type is extremely sensitive to the exact position of the surrounding oxygen ions (12). This is now confirmed

for the octahedral titanate group: for $\text{La}_2\text{MgSnO}_6\text{-Ti}$ (2) and $\text{Mg}_2\text{SnO}_4\text{-Ti}$ (3) a different behavior for the temperature dependence of the decay time has been reported. Finally we note that the long value of the decay time of the luminescence of $\text{Li}_2\text{ZrO}_3\text{-Ti}$ at low temperature is at least partly due to a spin-selection rule, since the levels which emit at low temperatures have a triplet character (6).

b. $\text{ZrO}_2\text{-Ti}$

The crystal structure of monoclinic ZrO_2 is quite complicated; the Zr^{4+} ions occur in a seven coordination. The Zr-O distances vary from 2.04 to 2.26 Å. Since the Ti^{4+} ion is smaller than the Zr^{4+} ion, we can only speculate on the exact coordination of the Ti^{4+} ion in ZrO_2 . In view of the sensitivity of the decay time of the luminescence on the position of the oxygen ions (see above), it seems impossible to give any explanation for the experimental results given in Fig. 3. Nevertheless the following is noteworthy:

—The decay time is very long for a titanate group. In fact the decay time of $\text{Li}_2\text{ZrO}_3\text{-Ti}$ is already long for octahedral titanate. Only the decay time of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (with pyramidal TiO_5 groups) is still longer (4) than that of $\text{ZrO}_2\text{-Ti}$.

—The energy level scheme of the lowest excited state must be rather complicated. For the temperature dependence given in Fig. 3 at least a four-level scheme is necessary. If the levels are numbered: 1 (ground state), 2, 3, 4, we find the following from Fig. 3. The energy difference between levels 2 and 3 is rather small (some 20 cm^{-1}). Transitions from levels 2 or 3 to the ground state are strongly forbidden (from 3 even more than from 2). There must be an energy gap of several hundreds of wavenumbers between level 4 and level 3. The transi-

tion $4 \rightarrow 1$ is considerably less forbidden. Sarver, who had higher quenching temperatures than we, found for the decay time at room temperature $15\ \mu\text{sec}$. The pronounced shift of the emission maximum to higher energies if the temperature is increased, may be due to the fact that at higher temperatures the $4 \rightarrow 1$ transition is also observed. Probably, however, level 4 is not a single level, but stands for a number of energy levels at different energies, so that quantitative calculations are impossible.

Note also, that the Stokes shift of the emission of $\text{ZrO}_2\text{-Ti}$ at room temperature has become relatively small ($11,000\text{ cm}^{-1}$), so that energy transfer to other titanate groups becomes rather probable. Nevertheless the concentration quenching below $x = 0.01$ in $\text{Zr}_{1-x}\text{Ti}_x\text{O}_2$ seems not to be due to this effect, in view of earlier calculations (13).

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