Luminescence of Li$_2$ZrTeO$_6$

T. J. M. DE BRUIN, M. WIEGEL, G. J. DIRKSEN, AND G. BLASSE*

Debye Research Institute, Utrecht University, Postbox 80.000, 3508 TA Utrecht, The Netherlands

The compound Li$_2$ZrTeO$_6$ with ordered LiNbO$_3$ structure shows a yellow emission of moderate intensity below room temperature. This emission is ascribed to a charge-transfer transition within the tellurate octahedron. © 1993 Academic Press, Inc.

1. Introduction

A new type of superstructure was reported some years ago for Li$_2$ZrTeO$_6$ and Li$_2$HfTeO$_6$(*1*). These compounds are ordered variants of LiNbO$_3$, which itself is an ordered variant of corundum (α-Al$_2$O$_3$). In Li$_2$ZrTeO$_6$, for example, the Zr(IV) and Te(VI) ions are distributed among the niobium sites of LiNbO$_3$ in such a way that Li/Zr and Li/Hf layers alternate and that the alternating layers are connected by pairs of face-sharing Li–Zr or Li–Te octahedra (*1*).

The composition LiNbO$_3$ is a well-known optoelectronic material. Its defect chemistry has been studied extensively (*2*). Luminescence appeared also to be a technique to contribute to this problem (*3*). Therefore we investigated the luminescence properties of Li$_2$ZrTeO$_6$. Activation by Eu(III) also played a role in this study. The most interesting result is that the emission of Li$_2$Zr TeO$_6$ can be ascribed to a charge-transfer transition in the tellurate group.

2. Experimental

Powder samples were prepared as described previously (*1*). They were checked

* To whom correspondence should be addressed.

by X-ray powder diffraction, and appeared to be single phase. Next to Li$_2$ZrTeO$_6$ we prepared also Li$_2$ZrTeO$_6$: Eu (0.5 at%).

The optical measurements were performed as described elsewhere (*4*) using a Spex Fluorolog spectrofluorometer equipped with a liquid helium cryostat and a Perkin–Elmer Lambda 7 spectrometer.

3. Results

Upon being cooled below room temperature Li$_2$ZrTeO$_6$ shows a luminescence of moderate intensity. Figure 1 shows the emission and excitation spectra of this luminescence at 4.2 K. The broad emission band has a maximum at about 610 nm; the corresponding excitation band is at 305 nm. The Stokes shift is estimated to be some 17,000 cm^{-1}. The absorption edge in the diffuse reflection spectrum is at about 300 nm.

The Eu-doped samples show an intense Eu(III) emission upon 395 nm excitation, i.e., into the $^7F_0$–$^5L_6$ transition of Eu(III) itself. This emission consists of $^5D_3$ and $^5D_2$ emission (<0.1%), $^5D_1$ emission (~1%) and $^5D_0$ emission. There is one $^5D_0$–$^7F_0$ line and there are three $^5D_0$–$^7F_1$ lines, whereas the other transitions could not be well resolved. This points to inhomogeneous broadening.

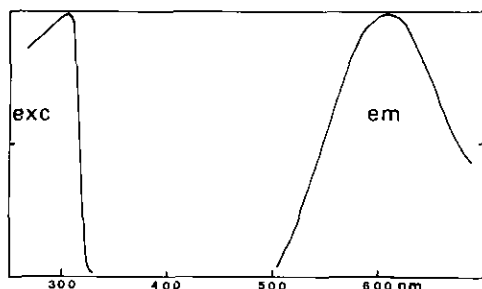Upon host lattice excitation (300 nm) the emission consists of Eu(III) emission and

FIG. 1. Emission and excitation spectra of the luminescence of Li_2ZrTeO_6 at 4.2 K. Excitation is by radiation at 305 nm; the monitored emission wavelength is 600 nm. Spectra are corrected for photomultiplyer sensitivity and lamp intensity.

broad-band emission (610 maximum) with an integrated intensity ratio 1 : 5. This points to a certain amount of energy transfer from the host lattice to the activator. Figure 2 shows the excitation spectrum of the Eu(III) emission. It consists of the intraconfigurational $4f^6$ lines of the Eu(III) ion and the host lattice excitation band. Since both emissions coincide, the presence of the latter does not necessarily point to energy transfer. The $^7F_0$–$^5D_0$ and $^5D_2$ transitions are accompanied by two vibronic lines as indicated in Fig. 2. The vibrational frequencies involved are 710 and 370 cm^{-1} (with an estimated inaccuracy of some 25 cm^{-1}).

4. Discussion

a. Host Lattice Luminescence

First we consider the optical data in which the Eu(III) ion is not involved and consider the possibilities for assigning the spectra. The most obvious possibility is to assign the luminescence to the zirconate octahedra. Complexes with "d^0 metal ions" are well known for their luminescence. Examples are vanadates, niobates, and tungstates (5). Also, for zirconates, luminescence has been reported (5). However, their lowest absorption band is always at much higher energy than reported here (>10,000 cm^{-1}), and the emission is in the ultraviolet (see also Ref.

6). Therefore, it is unlikely that the emission of Li_2ZrTeO_6 is due to the zirconate groups.

A second possibility is the presence of titanium in the zirconium starting material. This yields often strong luminescence. Examples are ZrO_2 : Ti (7) and Li_2ZrO_3 : Ti (8). The low amount of titanium induces a weak additional absorption band at energies below the optical band gap of the host lattice. Further, the titanate emission in zirconates is in the blue. Since the emission of Li_2Zr TeO_6 is clearly excited in the optical band gap of the host lattice, this second possible explanation is highly unlikely.

The third possibility is to assign the luminescence to the tellurate octahedron in Li_2ZrTeO_6. This does not seem to be very obvious, because complexes of d^{10} metal ions are not generally known as luminescent centers. One of us has recently shown that there is ample evidence that complexes of d^{10} ions show luminescence (9). Examples are Zn(II) and Ga(III). The proposal is supported by a theoretical calculation for Zn(II) (10). It has also been shown that the antimonate group can show luminescence (11). The optical transition involved is of the charge-transfer type and is expected to shift to lower energies if the formal charge of the central ion increases. This is observed. Further, a large Stokes shift of the emission is
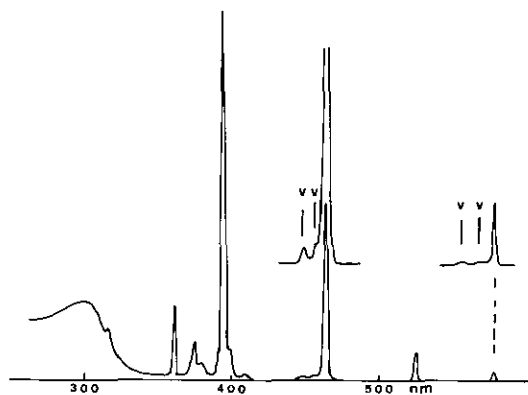

FIG. 2. Excitation spectrum of the 614 nm emission of Li_2ZrTeO_6 : Eu(III) (0.5%) at 4.2 K. The inset shows the vibronic transitions on the high-energy side. See also text.

TABLE I

Some Data on the Luminescence of Complexes with Central d^{10}
Metal Ions

Compound (Ref.)	Complex	Emission maximum	Excitation maximum	Stokes shift
Zn$_4$B$_6$O$_{13}$ (12)	Zn(II)O$_4$	22.000	40.000	18.000
LiGaO$_2$ (13)	Ga(III)O$_4$	27.000	45.000	18.000
KSbSiO$_5$ (11)	Sb(V)O$_6$	21.000	41.500	20.500
Li$_2$ZrTeO$_6$	Te(VI)O$_6$	16.000	33.000	17.000

Note. All values are at 4.2 K and in cm^{-1}.

expected in view of the considerable relaxation in the excited state after optical absorption. This is also observed. The present data on the luminescence of Li$_2$ZrTeO$_6$ fit smoothly into the spectral data available for this type of luminescence, as is shown in Table I. This confirms the proposal to assign the luminescence of Li$_2$ZrTeO$_6$ to the tellurate group.

The relatively low quantum efficiency and thermal quenching temperature of this emission are readily understood from a single configurational coordinate diagram (14). Energy migration to quenchers is unlikely in view not only of the large Stokes shift, but also of the large Te–Te distance in the lattice (>5 Å, Ref.(1)). This excludes also the possibility to ascribe the emission to impurity centres. This would further not be consistent with a certain amount of energy transfer to a low concentration of Eu(III) ions as observed in our experiments.

b. The Eu-Doped Composition

First we consider the intraconfigurational spectra of the Eu(III) ion. The presence of one $^5D_0$–$^7F_0$ emission line points to the presence of one type of Eu(III) ions. The threefold splitting of the $^5D_0$–$^7F_1$ emission transition points to a symmetry lower than the C_{3v} site symmetry of the metal ions of Li$_2$Zr TeO$_6$. The broadening of the emission lines points to a crystal field which varies from site to site.

An important factor in the interpretation

of these data is the vibronic lines in the $^7F_0$–$^5D_0$ and $^5D_2$ excitation transitions. The nature and intensity of such vibronic lines have been discussed elsewhere (15). Coupling occurs with vibrational modes with wavenumbers 710 and 370 cm^{-1}. The vibrational spectra of Li$_2$ZrTeO$_6$ are given in Ref. (1). It is clear that the 710 cm^{-1} mode is the ν_3 mode of the tellurate octahedron; i.e., the Eu(III) ion occupies a site next to the tellurate octahedron. The 370 cm^{-1} mode is a translational mode of the Li(I) ions (1). The infrared spectrum of Li$_2$ZrTeO$_6$ shows intense absorptions for these modes at 700 cm^{-1}, and at 390 (^{7}Li) and 406 (^{6}Li) cm^{-1}, respectively. Therefore, the nearest metal–ion neighbors of Eu(III) are Li(I) and Te(VI); i.e., the Eu(III) ion occupies a zirconium site. In a study on Li$_2$ZrO$_3$: Eu(III) it has been found that Eu$'_{Zr}$ is compensated by Eu$''_{Li}$ or Li$'_i$ (6). The former is obviously not present here. Actually the latter is highly probable, since the corundum structure (and its superstructures) leaves $\frac{1}{3}$ of the octahedral sites in the hexagonal close packing of anions empty. The inhomogeneous line broadening is explained by a variety of Eu$'_{Zr}$–Li$'_i$ couples with varying distances. At least part of these Li$'_i$ ions are not on the trigonal axis through the Eu(III) ion, so that the trigonal site symmetry is lost as required by the threefold splitting of the $^5D_0$–$^7F_1$ emission transition.

In view of the low Eu(III) concentration the low intensity of the higher-level emis-

sions is ascribed to the presence of high-frequency accepting modes, viz. the tellurate stretching vibrations (14).

The site of the Eu(III) ion now having been characterized, we return to the host lattice and consider the energy transfer from the host to the activator. As argued above, energy transfer from tellurate to tellurate can be neglected, so that we need only to consider single-step energy transfer from tellurate to Eu(III). This type of transfer is usually restricted to nearest neighbors (16). This is certainly the case here, since the spectral overlap between tellurate emission and Eu(III) absorption is small and practically restricted to the strongly forbidden $^7F_0-^5D_0$ transition. This points to transfer by exchange, which is restricted to short distances.

Assuming a statistical distribution of Eu(III) over the zirconium sites, the probability that a tellurate group has no Eu(III) neighbors is $(0.995)^6 = 97\%$, since the Eu(III) concentration is 0.5% and every Te(VI) ion has six nearest Zr(IV) neighbors. Therefore the ratio of Eu(III) to tellurate emission will be 3 : 97 or less. This contradicts the experimental ratio of 1 : 5. Since energy transfer over larger distances than the nearest neighbors is very unlikely, this contradiction is ascribed to nonradiative transitions in the tellurate group. In this way we are able to estimate the quantum effi-

ciency of the tellurate emission, viz. about 15%. This agrees with remarks made above.

In conclusion, Li_2ZrTeO_6 shows a broad-band emission due to the tellurate group; at 4.2 K the quantum efficiency is already low.

References

1. J. CHOISNET, A. RULMONT, AND P. TARTE, *J. Solid State Chem.* **75**, 124 (1988).
2. See, for example, O. F. SCHIRMER, Abstract K-B10 Int. Conf. Defects Insulating Materials, Aug. 1992, Nordkirchen, and to be published.
3. D. M. KROL, G. BLASSE, AND R. C. POWELL, *J. Chem. Phys.* **73**, 163 (1980).
4. D. VAN DER VOORT AND G. BLASSE, *J. Solid State Chem.* **87**, 350 (1990).
5. G. BLASSE, *Struct. Bonding* **42**, 1 (1980).
6. D. VAN DER VOORT AND G. BLASSE, *Chem. Mater.* **3**, 1041 (1991).
7. J. F. SARVER, *J. Electrochem. Soc.* **113**, 124 (1966).
8. G. A. M. DALHOEVEN AND G. BLASSE, *J. Solid State Chem.* **39**, 35 (1981).
9. G. BLASSE, *Chem. Phys. Lett.* **175**, 237 (1990).
10. R. BERTONCELLO, M. BETTINELLI, M. CASARIN, A. GULINO, E. TONDELLO, AND A. VITTADINI, *Inorg. Chem.* **31**, 1558 (1992).
11. M. HAMOUMI, M. WIEGEL, G. BLASSE, J. F. FAVARD, AND Y. PIFFARD, *Mater. Res. Bull.* **27**, 699 (1992).
12. A. MEIJERINK, G. BLASSE, AND M. GLASBEEK, *J. Phys. Condens. Matter* **2**, 6303 (1990).
13. G. J. DIRKSEN, A. N. J. M. HOFFMAN, T. P. VAN DE BOUT, M. P. G. LAUDY, AND G. BLASSE, *J. Mater. Chem.* **1**, 1001 (1991).
14. G. BLASSE, *Prog. Solid State Chem.* **18**, 79 (1988).
15. G. BLASSE, *Int. Rev. Phys. Chem.* **11**, 71 (1992).
16. R. C. POWELL AND G. BLASSE, *Struct. Bonding* **42**, 43 (1980).