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Luminescence of Tellurite Anti-glass Phases

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The luminescence of two series of anti-glass tellurites of La, Gd, and Y, one Te-rich and the other lanthanide-rich, are reported. It is the first example of an oxidic system with high Te^{4+} concentration which shows luminescence. The thermal quenching temperature is low (~100 K). As far as possible the results are discussed in terms of the strongly disordered nature of these compositions.

Introduction

Trömel *et al.* (*1, 2*) have reported on several anti-glass phases which can be considered as metal–oxide-modified TeO_2 with the fluorite structure. Examples are $SrTe_5O_{11}$ (*1*) and $Ln_2Te_6O_{15}$ (Ln = lanthanide) (*2*). An anti-glass is here defined as a solid with a clear long-range order, but without short-range order (*1*). In a glass the situation is the reversed one. In the tellurite anti-glasses the metal ions and the Te^{4+} ions occupy the metal positions in the CaF_2 structure in a disordered way, whereas the anion positions are incompletely populated. Such a structure does not meet the geometrical requirements of the Te^{4+} coordination in oxides (*3*), resulting in large irregular displacements of all ions. These become apparent from the large Debye-Waller factors (*1, 2*).

The Te^{4+} ion has $5s^2$ outer electron configuration. Metal ions with this configuration are well known for their luminescence (*4*) and have been studied in detail (*5*). However, the luminescence of s^2 ions with charge higher than three has only been reported a few years ago (*6, 7*). These observations were made for halides, for example Rb_2TeBr_6. In the course of the investigations on the luminescence of diluted and concentrated s^2 ions in the Utrecht group (*8*), it seemed interesting to investigate the tellurite anti-glass systems. The results are reported in this paper.

Experimental

Samples were prepared as described in Ref. (*2*). Optical measurements were performed with the instrumentation described in Refs. (*8*) and (*9*).

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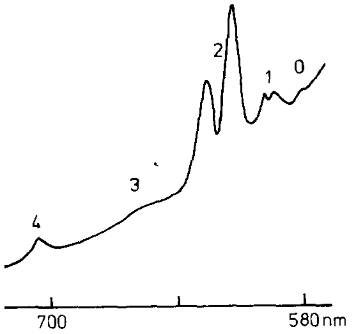

FIG. 1. Emission spectrum of the Eu^{3+} luminescence of $Gd_7Te_5O_{20.5}$ at 4.2 K. Excitation by 466 nm (in $^7F_0 \rightarrow {}^5D_2$ Eu^{3+}). The emission lines are indicated by the value of J in $^5D_0 \rightarrow {}^7F_J$. The background is due to the use of broad slits in the excitation beam.

Results and Discussion

General

The following compositions were investigated: $La_2Te_6O_{15}$, $Gd_2Te_6O_{15}$, $Y_2Te_6O_{15}$; $La_8Te_5O_{22}$, $Gd_7Te_5O_{20.5}$, $Y_5Te_4O_{15.5}$. The Te-rich samples do not contain Te^{6+} and the oxygen content given cannot be far off from the real one. The Ln-rich samples contain about 1.5 wt% Te^{6+} (*2*), so that the oxygen content given (calculated for Te^{4+}) is an underestimate, which is used here for simplicity. The lattice parameters are 569.5, 561.1, 558.6, 573.9, 550.8, and 546.4 pm, respectively (*2*).

The luminescence properties of the two series are different. The Te-rich series yields a weak red luminescence. At about 75 K the luminescence intensity has decreased to 50% of that at 4.2 K (which was weak anyhow). The excitation spectra do not coincide with the diffuse reflection spectra. The Ln-rich samples yield a much stronger, yellow-green luminescence. Its intensity has decreased to 50% of the 4.2 K value at about 125 K. The excitation spectra correlate well with the reflection spectra. The sample $Gd_7Te_5O_{20.5}$ showed also Eu^{3+} luminescence. The starting Gd_2O_3 (99.9%) will contain Eu^{3+} as an impurity. We will now deal with the several emissions separately.

The Eu^{3+} Emission of $Gd_7Te_5O_{20.5}$

In addition to the Te^{4+} emission (next section) this composition shows red Eu^{3+} emission consisting of the well-known $^5D_0$–^7F_J transitions (see Fig. 1). What is of interest here is the following:

(i) If the Eu^{3+} ion would occupy an undistorted metal site in the CaF_2 structure, the emission would be dominated by the $^5D_0$–$^7F_1$ transition (*10*). This is not the case. The $^5D_0$–$^7F_2$ transition is dominating, indicating a deviation from inversion symmetry. The splitting of the $^5D_0$–$^7F_{1,2}$ transitions also indicates a deviation from cubic symmetry.

(ii) The line width of the $^5D_0$–$^7F_2$ emission lines is 7–8 nm. Since this value does not decrease for smaller slit widths, it can be considered as an inhomogeneous line broadening due to a varying crystal field at the Eu^{3+} ions. For well-crystallized powders of Eu^{3+}-activated materials linewidths of 1 nm or less are easily measured on the present instrumentation.

Combining (i) and (ii), we conclude that the crystal field at the Eu^{3+} (and therefore at the Gd^{3+}) sites varies strongly from site to site, as is to be expected from the X-ray diffraction studies (*2*). However, the observed crystal-field splittings in Fig. 1 indicate that this variation is not at random. Obviously a certain site symmetry is preferred.

The excitation spectrum of this luminescence consists of several features:

(i) (Broad) lines due to transitions within the $4f^6$ configuration of Eu^{3+}, i.e., direct excitation of the Eu^{3+} ions. These lines are also strongly inhomogeneously broadened.

(ii) A broad band due to Te^{4+} excitation (see next section) which indicates $Te^{4+} \rightarrow Eu^{3+}$ energy transfer. In fact excitation into this band yields 1–2% Eu^{3+} emission (the

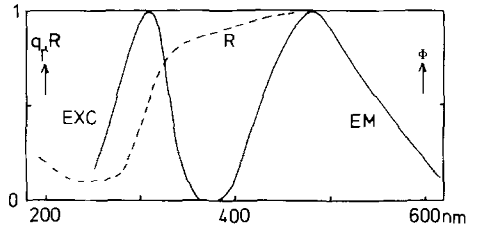

FIG. 2. Spectra of $La_8Te_5O_{22}$. Broken line (R): diffuse reflection spectrum at 300 K. Drawn line (Em): Emission spectrum at 4.2 K for 310-nm excitation. Drawn line (Exc): Excitation spectrum at 4.2 K of the 480-nm emission. Φ gives the radiant power per constant wavelength interval, q_r the relative quantum output, and R the reflection.

rest being Te^{4+} emission). Using the formula $R_c^6 = 0.6 \times 10^{28} \cdot Q_{Eu} \cdot E^{-4} \cdot SO$ (*11*), the critical distance (R_c) for this transfer can be calculated. The energy for maximum spectral overlap (E) and the spectral overlap (SO) are derived from the spectra and the absorption cross section (Q_{Eu}) from the literature (*12*). This yields $R_c = 5.3$ Å which enables transfer from Te^{4+} to nearest and, possibly, next-nearest Eu^{3+} neighbors. Using the crystallographic data and assuming that the 0.1% impurity in Gd_2O_3 exists of Eu_2O_3 only, this yields 2% Eu^{3+} emission upon Te^{4+} excitation. In spite of the approximations made, the agreement with experiment is excellent.

(iii) On the higher-energy side of the Te^{4+} excitation band, a band at about 280 nm. Excitation into this band yields more Eu^{3+} emission than excitation into the Te^{4+} band. Therefore we assign the 280-nm band to a Eu^{3+} charge-transfer transition.

Luminescence of the Ln-rich Series

At 4.2 K this series shows a strong luminescence. All data presented here refer to this temperature, except for the diffuse reflection spectra which were taken at 300 K. Figure 2 contains the several spectra for $La_8Te_5O_{22}$ as a representative example. The figure shows the main emission band with a maximum at 480 nm. The excitation band peaks at 310 nm. However, these bands consist of several components which we cannot resolve optically because of a large spectral overlap. If the excitation spectrum is taken for the 420- or 540-nm emission (i.e., on the high-energy or low-energy side of the emission maximum), the excitation band shifts to 300 or 320 nm, respectively. In a similar way the emission maximum varies slightly (some 10 nm) if the excitation is varied from 310 nm to 300 or 320 nm. This is typical for all the tellurite luminescence spectra reported here. The disorder in the lattice results in a varying surroundings of the Te^{4+} ions and, as a consequence, the emission and excitation spectra vary from site to site. We feel that this spectral variation is even less than what should be expected for such a disordered arrangement.

The La-rich sample is exceptional in that there is also an excitation band at about 280 nm which results in longer wavelength emission, viz., a broad band with a maximum at 530 nm. This luminescence is much weaker than the luminescence mentioned above. The Stokes shift of this additional emission is about 17,000 cm^{-1}, whereas that of the main emission is about 10,000 cm^{-1}.

Table I shows a summary of band maxima observed. These maxima relate to bands which can be resolved in the spectra. The individual bands are inhomogeneously broadened as mentioned above.

Figure 3 shows for $Y_5Te_4O_{15.5}$ the decay time of the luminescence as a function of temperature. The decay curves were not completely exponential. Analysis with a three-level scheme yields $\Delta E = 25$ cm^{-1}, $\tau_1 = 250$ μs and $\tau_2 = 2$ μs, where ΔE is the energy difference between the emitting levels 1 and 2 and τ_i the radiative decay time of level i (*7*).

The emission and excitation bands observed can all be ascribed to transitions between the $5s^2$ ground state and the $5s5p$ ex-

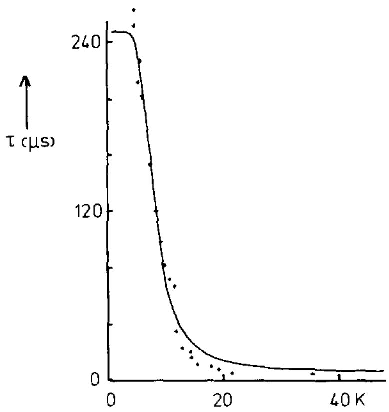

FIG. 3. Decay times of the luminescence of $Y_5Te_4O_{15.5}$ as a function of temperature. Crosses are experimental points; the solid curve presents the best possible fit using a one-ion three-level scheme.

cited state of the Te^{4+} ion. The decay times are also typical for this (*5, 7–9*). The present results are, as far as we know, the first example of Te^{4+} luminescence in oxides. Unfortunately, the s^2 ion luminescence is not characteristic of the surroundings. There is no doubt that the surroundings influences the luminescence characteristics, but the way in which this happens is only poorly understood and cannot help us much to elucidate the surroundings of the Te^{4+} ions in the anti-glasses any further. Nevertheless, the following can be remarked.

TABLE I

MAXIMA OF EMISSION AND EXCITATION BANDS OF TELLURITE ANTI-GLASSES[a]

Composition (approximate)	Emission	Excitation
$La_8Te_5O_{22}$	480 530[b]	310 280[b]
$Gd_7Te_5O_{20.5}$	530	340
$Y_5Te_4O_{15.5}$	530	340
$La_2Te_6O_{15}$	~590	~330
$Gd_2Te_6O_{15}$	~590	~330
$Y_2Te_6O_{15}$	~590	~330

[a] All values in nm and at 4.2 K; see also text.
[b] Additional, weak emission.

Concentration quenching of the Te^{4+} luminescence is obviously of no importance in the present systems. This can be understood from the considerable Stokes shift of the emission (about 10,000 cm^{-1}). As a consequence the emission and excitation (absorption) bands do not show spectral overlap, so that energy transfer between Te^{4+} ions mutually becomes rather improbable (*13*).

The spectra of the sample $La_8Te_5O_{22}$ are at shorter wavelength than those of the corresponding Gd and Y samples in the Ln-rich series. Since this phenomenon is not observed in the Te-rich series (see Table I), we ascribe it to the different composition. The Ln/Te ratio is 1.6, 1.4, and 1.25 for Ln = La, Gd, and Y, respectively.

For yttria-stabilized zirconia (similar to metal-oxide stabilized TeO_2) doped with Bi^{3+} ($6s^2$) (similar to Te^{4+} ($5s^2$)) a Bi^{3+} emission was observed with a Stokes shift of 9100 cm^{-1} (emission 460 nm, excitation 325 nm) (*14*). This emission is more or less comparable to the one under discussion. It was ascribed to a BiO_7V_O center, V_O presenting an oxygen vacancy. Then it might be suggested that the present luminescence is due to a TeO_7V_O center (without specifying the exact bonding conditions). Only the La sample contains a substantial amount of another center. In view of the higher V_O concentration in this sample, the additional emission might well be due to $TeO_6(V_O)_2$. The larger Stokes shift agrees with this proposal (*14*). In the Gd and Y samples the concentration of this centre must be lower which is not unreasonable. We stress that this assignment is rough and tentative. However, there is no doubt that the La sample contains a certain amount of a Te^{4+} polyhedron which is different from the dominating one. As discussed above, the spectra show also, that there is a certain spread in these centres due to the disorder in the lattice.

We note that the excitation spectra and diffuse reflection spectra coincide apart from a small shift which must be due to a thermal shift, since these spectra were recorded at 4.2 and 300 K, respectively. This is not the case in the high absorption range (a usual phenomenon), nor in the long-wavelength tail (cf. Fig. 2). This tail is less pronounced in the cases of the Gd- and Y-rich samples. It seems hard to explain this extra absorption in terms of Te^{4+} ions. Since these samples contain some Te^{6+}, it cannot be excluded that we are dealing with a tellurium intervalence charge-transfer absorption.

Finally the decay measurements yield the following, additional information. The slight deviation from purely exponential decay can be ascribed to the fact that we are dealing with slightly different Te^{4+} ions, each with its own and slightly different decay characteristics. This might also explain why it is not possible to obtain a better fit to a one-ion, three-level scheme than presented in Fig. 3. The value of ΔE is relatively low. This is in agreement with low ΔE values observed for $Bi^{3+}(6s^2)$ and $Sb^{3+}(5s^2)$ in asymmetrical coordination (*8*, *15*). The value of τ_1 is for a $5s^2$ ion relatively short since values of 1 to 2 ms have been observed. However, we have to assume that nonradiative losses will be important down to the lowest temperatures since the Stokes shift is large and the quenching temperature low (*16*, *17*). Also asymmetrical coordination tends to shorter τ_1 (*8*).

Luminescence of the Te-rich Series

The luminescence of these samples is considerably weaker. Figure 4 shows the spectra for $La_2Te_6O_{15}$. Those for the Gd and Y samples are the same, apart from small spectral shifts. Maxima of the bands are given in Table I.

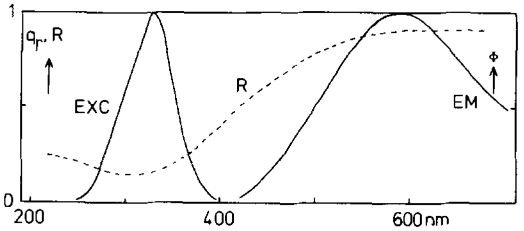

FIG. 4. Spectra of $La_2Te_6O_{15}$. See caption Fig. 2. The emission was recorded for 340-nm excitation, the excitation was recorded monitoring 600-nm emission.

The first observation to note is the difference between the excitation spectra and the diffuse reflection spectra. The latter clearly extend to much longer wavelengths. In fact the position of the excitation bands of the Ln-rich and Te-rich samples is not very different, whereas the diffuse reflection spectra are. In view of this we are inclined to ascribe the luminescence observed to centers with (overall) composition TeO_7V_O, as we did in the Ln-rich samples. Since the V_O concentration is much lower in the Te-rich samples, the longer wavelength absorption is ascribed to TeO_8 centers. Excitation into these centers does not yield luminescence, not even at 4.2 K.

In view of the considerations of one of us on the Te^{4+} coordination by O^{2-} ions (*3*), it should be realized that the Te^{4+} ion in such a center is strongly off-center. It seems reasonable to assume that a lattice with a high concentration of such groups offers the excited state of other centers a favourable condition for relaxation. In this way it can be explained why the Stokes shift of the TeO_7V_O centers is larger in the Te-rich than in the Ln-rich samples, viz., 14,500 cm^{-1} vs 10,000 cm^{-1}, respectively. This results in a lower quenching temperature of the luminescence, and, most probably, also in a lower luminescence efficiency, even at 4.2 K (*16*, *17*). These TeO_8 groups, which absorb at so low an energy, are then expected not to luminesce at all (*17*).

Although the assignments proposed are

of a tentative character only, it should be stressed that the Te^{4+} luminescence is not essentially different from that of the isoelectronic ions, like Sb^{3+} and Bi^{3+}. For these ions we have observed metal-to-metal charge-transfer transitions, for example $Bi^{3+} \rightarrow W^{6+}$ and $Bi^{3+} \rightarrow Mo^{6+}$ (*18*). These are also to be expected for Te^{4+}. Recently Baran *et al.* (*19*) observed a strong absorption band in $CdTeMoO_6$ starting at 500 nm. They ascribed this to an unspecified charge-transfer band. Actually this band must be analogous to those in the bismuth tungstates and molybdates and can be assigned as a $Te^{4+} \rightarrow Mo^{6+}$ charge-transfer transition, making the spectroscopical analogy between the several s^2 ions even more clear.

In conclusion we have observed Te^{4+} luminescence in tellurite anti-glasses and tried to explain the results not only in terms of the well-known $s^2 \rightarrow sp$ transitions, but also in terms of the regarding disordered crystal lattice.

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