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The Luminescence of $Gd_3Sb_5O_{12}$

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Recently the existence of new oxides $R_3Sb_5O_{12}$ (R = rare earth) was reported in this journal [1]. Their crystal structure is cubic (space group $I\bar{4}3m$) with lattice parameter $a \sim 10.8$ Å. The structure has not been solved, but seems strongly related to that of Gd_2O_3, *i.e.*, a fluorite defect structure (Table III of ref. 1).

In the course of our studies on the luminescence properties of Gd^{3+} compounds [2, 3], it seemed interesting to investigate the luminescence of undoped and rare-earth ion doped $Gd_3Sb_5O_{12}$. In view of its high density it may well be suitable as an X-ray phosphor.

Experimental

Samples of $Gd_3Sb_5O_{12}$, undoped and with 1 mol% of Eu^{3+} or Tb^{3+}, were prepared as described in ref. 1. They were checked by X-ray powder diffraction. Our X-ray data are in perfect agreement with Table III of ref. 1. Luminescence measurements were performed as described elsewhere [4].

Results

None of the samples prepared shows luminescence of reasonable efficiency at room temperature. However, below 100 K an orange emission is observed under UV excitation, independent of doping. Figure 1 shows the emission and excitation spectra of this luminescence which is seen to be broad band in character. The emission band has its maximum at about 660 nm, the excitation band at about 360 nm (values at liquid helium temperature). This yields for the Stokes shift some 13 000 cm^{-1}. The excitation spectrum corresponds to the diffuse reflection spectrum only as far as the lower energy side is concerned (Fig. 1). This well-known phenomenon must be due to strong absorption at shorter absorption wavelengths which prevents the exciting radiation to enter the crystallites. The reflection spectrum shows absorption maxima at about 310, 270 and 215 nm.

In addition to the luminescence described above, we noticed in the spectra weak lines due to the dopant rare-earth ion. The activators can only be excited in their own characteristic lines, not in the broad excitation band of the orange emission. These weak lines persist up to room temperature.

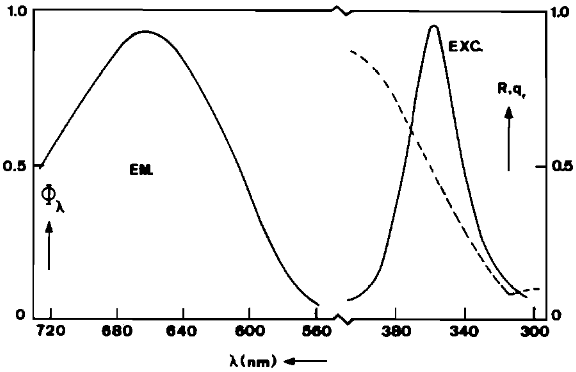

Fig. 1. Emission and excitation spectra of the luminescence of $Gd_3Sb_5O_{12}$ at LHeT. q_r gives the relative quantum output, ϕ_λ the radiant power per constant wavelength interval, both in arbitrary units. The excitation spectrum was monitored for 630 nm emission, the emission spectrum for 360 nm excitation. Note break in wavelength scale. The broken line presents the diffuse reflection spectrum of $Gd_3Sb_5O_{12}$. R indicates the reflection.

Decay measurements were performed on the Tb^{3+}-activated sample. There is a long decay time of about 2 ms which persists up to room temperature and which presents obviously the Tb^{3+} decay. However, there is also a shorter component of about 350 μs which disappears above 20 K. The signals were too weak to allow further elucidation.

Discussion

The broad-band character of the orange luminescence excludes the possibility that it is due to rare-earth ions. The absorption of the orange centre is so strong that the Gd^{3+} absorption or excitation lines cannot be observed. Its emission is situated at such a low energy that transfer to Tb^{3+} or Eu^{3+} has become impossible. This explains why we did not observe any energy transfer to the Tb^{3+} or Eu^{3+} ions.

It is obvious to ascribe this orange luminescence to the Sb^{3+} ion in $Gd_3Sb_5O_{12}$. Before we develop this assignment, some structural arguments are of relevance.

The X-ray diffraction patterns of the compounds $R_3Sb_5O_{12}$ contain, next to the strong fluorite lines, a large number of weaker lines which probably indicate a superstructure (ordering between R^{3+} and Sb^{3+} and/or between O^{2-} and the oxygen vacancies). It is interesting to note that a fluorite defect structure is common for mixed metal oxides containing $5s^2$ ions.

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Other examples are $TiTe_3O_8$ [5], $SrTe_5O_{11}$ [6] and the antiglass compositions $R^{3+}Te_x{}^{4+}O_y$ with $x \sim 3$ and ~ 0.7 [7]. In these the $5s^2$ Te^{4+} ion obtains an asymmetrical one-sided coordination by displacement of the O^{2-} ions. A crystal structure determination of the compounds $R_3Sb_5O_{12}$ would be of great interest. It also seems likely here that the $5s^2$ Sb^{3+} ion is coordinated in a similar, asymmetric way [8].

The tellurite antiglasses are interesting from our point of view. This is especially the case for $Gd_2Te_6O_{15}$ and $Gd_7Te_5O_{20.5}$ [7], because they are in a sense isoelectronic with $Gd_3Sb_5O_{12}$ and, in addition, also structurally related. The luminescence of the gadolinium tellurites was reported recently [9]. The emission was quenched between 100 and 150 K, the Stokes shift amounted to 10 000 to 15 000 cm^{-1} and all spectra contained broad bands. The low temperature decay time was about 250 μs and decreased dramatically above 8 K. It was shown that these observations point to Te^{4+} luminescence.

In view of the qualitative agreement between the luminescence properties of the Gd–tellurites and $Gd_3Sb_5O_{12}$, the orange emission is ascribed to the Sb^{3+} ion. The larger Stokes shift reflects the asymmetrical coordination [4]. In terms of atomic notation, which is probably not fully adequate to describe the transitions on the asymmetrically coordinated Sb^{3+} ion, the optical transitions are assigned as follows:

(i) the emission transition is $^3P_0 \rightarrow {}^1S_0$ at low temperatures ($\tau \sim 350$ μs); above 20 K the thermally stimulated $^3P_1 \rightarrow {}^1S_0$ transition takes over [4].

(ii) the excitation band corresponds to $^1S_0 \rightarrow {}^3P_1$.

(iii) the absorption bands at 310 and 270 nm are components of $^1S_0 \rightarrow {}^3P_1$ and that at 21.5 nm is $^1S_0 \rightarrow {}^1P_1$. This yields for the $^3P_1 - {}^1P_1$ energy separation about 12 000 cm^{-1}, an acceptable value.

The difference between $Gd_3Sb_5O_{12}$ and the Gd–tellurites lies in the fact that the Sb^{3+} emission is at longer wavelength than the Te^{4+} emission (660 nm *vs.* 500–600 nm, respectively). The consequence of this is that energy transfer from Sb^{3+} to Eu^{3+} or Tb^{3+} is clearly impossible (the Sb^{3+} emitting level being far below the emitting levels of the rare earth dopants), whereas transfer from Te^{4+} to Eu^{3+} could be easily observed [9].

An accurate crystal structure determination of the compounds $R_3Sb_5O_{12}$ has to be performed before more detailed experiments and/or discussions on the luminescence of $Gd_3Sb_5O_{12}$ will become feasible.

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References

1 C. M. Marcano and I. Rasines, *Inorg. Chim. Acta, 109,* L15 (1985).
2 G. Blasse, *J. Less-Common Met., 112,* 1 (1985).
3 G. Blasse, *J. Less-Common Met., 112,* 79 (1985).
4 C. W. M. Timmermans and G. Blasse, *J. Solid State Chem., 52,* 222 (1984).
5 J. Galy, in R. S. Roth and S. J. Schneider, Jr. (eds.), 'Solid State State Chemistry', Natl. Bureau of Standards, Washington, D. C., 1972, p. 29.
6 H. G. Burckhardt and M. Trömel, *Acta Crystallogr., Sect. C, 39,* 1322 (1983).
7 M. Trömel, W. Hützler and E. Münch, *J. Less-Common Met., 110,* 421 (1985).
8 M. Trömel, *J. Solid State Chem., 35,* 90 (1980); I. D. Brown, *J. Solid State Chem., 11,* 214 (1974).
9 G. Blasse, G. J. Dirksen, E. W. J. L. Oomen and M. Trömel, *J. Solid State Chem.,* submitted for publication.