LUMINESCENCE PROPERTIES OF BaLaGa$_3$O$_7$

M.J.J. LAMMERS and G. BLASSE

Physical Laboratory, State University Utrecht, P.O. Box 80.000,
3508 TA Utrecht (The Netherlands)

ABSTRACT

The luminescence properties of undoped and Pb^{2+}-, Tb^{3+}-, and Ce^{3+}-doped BaLaGa$_3$O$_7$ have been studied. At LHeT undoped BaLaGa$_3$O$_7$ shows an emission with a maximum at 490 nm. The emission of Ba$_{0.99}$Pb$_{0.01}$LaGa$_3$O$_7$ consists of a broad band with a maximum at 400 nm, that of BaLa$_{0.98}$Tb$_{0.02}$Ga$_3$O$_7$ of the well-known ^{5}D$_3$ and ^{5}D$_4$ Tb^{3+} emission lines. The last compound shows a strong afterglow. BaLa$_{0.98}$Ce$_{0.02}$Ga$_3$O$_7$ did not luminescence; a possible explanation is presented.

INTRODUCTION

BaLaGa$_3$O$_7$ belongs to a wide group of compounds with the general formula ABC$_3$O$_7$, where A = Ca, Sr, Ba, B = La,...., Sm and C = Al, Ga [1]. The crystal structure of this group of compounds is isostructural with the mineral Sr$_2$Al$_2$SiO$_7$ of the melilite Ca$_2$(Mg,Al)[Si,Al)$_2$O$_7$] group [2]. Recently some measurements on the physical properties of BaLaGa$_3$O$_7$ have been reported: Soluch et al. [3] reported on the elastic, piezoelectric, and dielectric constants of BaLaGa$_3$O$_7$, while Berkowski et al. [4] reported on the birefringence measurements. These authors observed also that BaLaGa$_3$O$_7$ crystals are transparent from 1500 to 41000 cm^{-1}.

The large region of transparency makes BaLaGa$_3$O$_7$ a suitable host lattice for luminescent dopants, such as transition-metal or rare-earth ions. In this paper we report on the optical properties of undoped BaLaGa$_3$O$_7$ and of BaLaGa$_3$O$_7$ activated with Pb^{2+}, Ce^{3+} and Tb^{3+}.

EXPERIMENTAL

The samples were prepared by usual solid-state techniques. Starting materials were $BaCO_3$ (p.a.,99%), La_2O_3 (99.999%), GaOOH (99.99%), CeO_2 (99.999%), Tb_4O_7 (99.999%) and $PbCO_3$ (p.a.,99%). The mixtures were fired in air twice at temperatures between 1200 and 1450 °C. Ce^{3+} activated samples were also fired in a N_2/H_2 atmosphere. The cerium and terbium concentration was 2 mol%, the lead concentration was 1 mol%. Samples were checked by X-ray powder diffraction using CuKα radiation.

Luminescence spectra were measured down to liquid helium temperature on a Perkin-Elmer spectrofluorometer (MPF 3L) equipped with a Xenon lamp as described in [5] and at room temperature on a Perkin-Elmer spectrofluorometer (MPF 4) equipped with an X-ray source with a maximum voltage of 100 kV. Diffuse reflection spectra have been measured on a Perkin-Elmer Lambda 7 UV/VIS spectrophotometer.

RESULTS

In Fig. 1 the diffuse reflection spectrum of undoped $BaLaGa_3O_7$ is shown at room temperature (RT). In the UV a strong absorption is observed. The position of the absorption edge is at about 235nm; the tail of this absorption region depends on preparation methods. The R = 50% value varied from 260 to 280 nm. Excitation into this
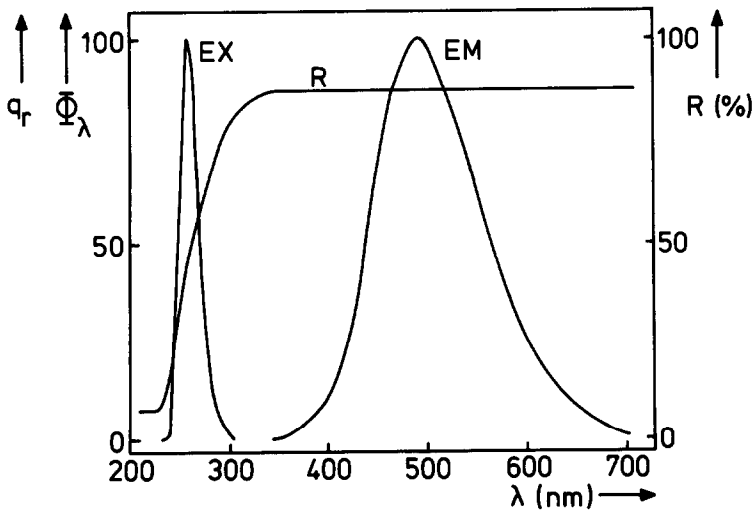

Fig. 1. Diffuse reflection spectrum of $BaLaGa_3O_7$ at RT. Emission and excitation spectrum of the luminescence of $BaLaGa_3O_7$ at LHeT (λ_{em} = 500nm, λ_{exc} = 256nm). Φ_λ denotes the spectral radiant power per constant wavelength interval, q_r the relative quantum output, both in arbitrary units.

absorption band at RT does not yield any luminescence at all. At liquid helium temperature (LHeT) a broad emission band with a maximum at 490nm is observed. The corresponding excitation band has its maximum at 260nm (Fig. 1). The quenching temperature of this emission is at about 150K.

In addition sharp peaks with maxima at 690nm and 715nm are observed at RT for excitation into a broad excitation band with a maximum at 350nm. An additional weak, broad excitation band corresponding to this emission has its maximum at about 500nm. The intensity of the peak at 690nm decreases with decreasing temperature and vanishes at about 80K. At LHeT the spectrum consists of a prominant line at 711.5nm with weaker peaks on both sides of this line (Fig. 2). This emission is observed in all $BaLaGa_3O_7$ samples under study, independently of the dopant.
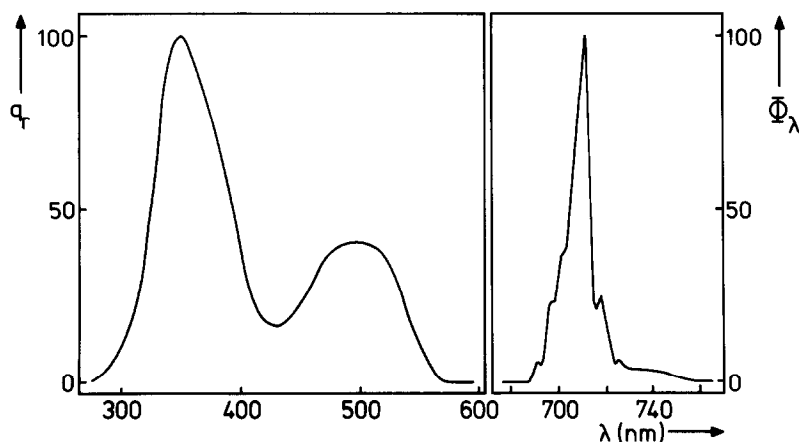

Fig. 2. Emission and excitation spectra of the red impurity emission of $BaLaGa_3O_7$ at LHeT ($\lambda_{em} = 712$nm, $\lambda_{exc} = 355$nm).

At RT the luminescence of Pb^{2+}-activated $BaLaGa_3O_7$ consists of a broad emission band with a maximum at 400nm (Fig. 3). The excitation band corresponding to this emission band has its maximum at 290nm. With decreasing temperature the half width of the emission band diminishes from 5400 cm^{-1} at RT to 4300 cm^{-1} at LHeT, while its maximum shifts to longer wavelengths, viz. to about 410nm. The maximum of the excitation band shifts to shorter wavelengths, viz. to about 280nm. The intensity of the emission does not change from LHeT to RT.
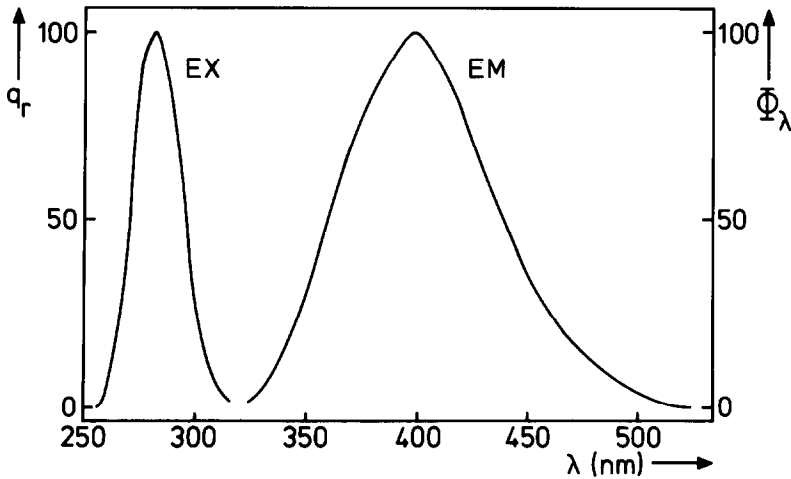
Fig. 3. Emission and excitation spectra of $Ba_{0.99}Pb_{0.01}LaGa_3O_7$ at RT (λ_{em} = 400nm, λ_{exc} = 280nm).

At RT the luminescence of $BaLa_{0.98}Tb_{0.02}Ga_3O_7$ is very weak. The emission spectrum contains lines from the $^5D_3$ and the $^5D_4$ level of the Tb^{3+} ion. The $^5D_4/^5D_3$ intensity ratio is about 4.2 for excitation at 245nm and about 1.5 for excitation at 354nm. For X-ray excitation this ratio amounts to about 1.6. The excitation spectrum consists of lines due to transitions within the $4f^8$ configuration and a broad band with a maximum at about 250nm (Fig. 4). This broad band is weaker in the excitation spectrum of the $^5D_3$ emission than in that of the $^5D_4$ emission. At LHeT we observe, in addition to the Tb^{3+} emission, the host lattice emission for excitation at wavelengths shorter than 300nm. All Tb^{3+} activated samples show a relatively long afterglow which lasts for several minutes.

The Ce^{3+} activated samples were yellow coloured. Figure 5 shows the diffuse reflection spectrum of a sample with 2% Ce^{3+}. We observe the host lattice absorption at short wavelengths, a broad absorption region which extends into the visible part of the spectrum, and a few absorption bands with the most intense one at about 335nm. High temperature treatments in air or in a reducing atmosphere changed the intensity ratio of the broad absorption region and the 335nm absorption band slightly, but the broad absorption region remained dominantly present.

The quantum efficiencies of the investigated samples were low. Only the luminescence intensity of Pb^{2+}-activated $BaLaGa_3O_7$ was of intermediate value.
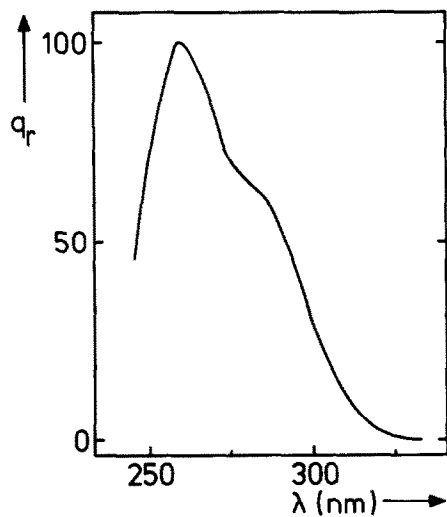
Fig. 4. Excitation spectrum of the Tb^{3+} emission of $BaLa_{0.98}Tb_{0.02}Ga_3O_7$ at RT (λ_{em} = 542nm).
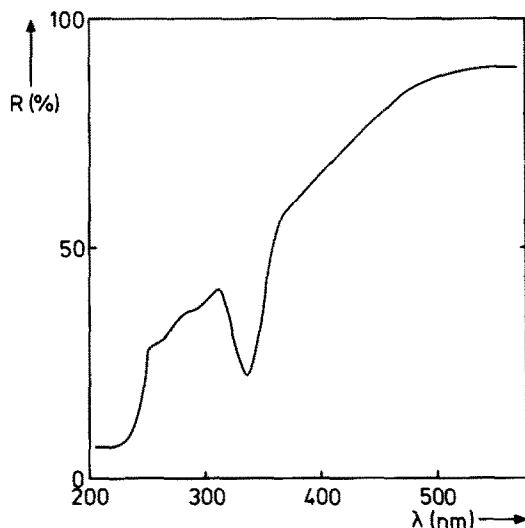

Fig. 5. Diffuse reflection spectrum of $BaLa_{0.98}Ce_{0.02}Ga_3O_7$ at RT.

DISCUSSION

Berkowski et al. [4] reported the absorption edge of $BaLaGa_3O_7$ crystals at 245nm in reasonable agreement with the edge in the reflection spectrum (Fig. 1). Their crystals showed also an absorption band with a maximum at 265nm. This band was ascribed to defect

centers connected with a deviation from stoichiometry. Such a band was not observed separately in the reflection spectrum of Fig. 1. However, the shift in the absorption tail, depending on the preparation method, is probably due to an absorption by the same kind of defect centers.

In undoped $BaLaGa_3O_7$ we observe at LHeT an emission band with a maximum at 490nm and an excitation band at 260nm. This excitation band corresponds to the absorption edge as far as the experimental data justify such an assignment. For many other gallates the excitation maximum is at the same position [6,7]. For $\beta-Ga_2O_3$ Harwig and Kellendonk [8] reported a blue emission band with a maximum at 470nm and a halfwidth equal to that in Fig. 1. They assumed that this blue emission occurs when an electron from a V_O^x or Ga_i^x center recombines with a trapped hole. Most probably a similar explanation holds also for the blue emission of $BaLaGa_3O_7$.

The red emission at about 700nm is probably due to a transition metal ion, most likely Cr^{3+} or Mn^{4+}. Both ions are $3d^3$ ions and show the same luminescence characteristics. The emission and excitation spectra shown in Fig. 2 are in excellent agreement with the analogous data for $CaZrO_3-Mn^{4+}$ [9], which in turn were similar to those for $LaAlO_3-Mn^{4+}$ [10]. This is also true for the vibrational structure observed. Therefore, the red emission is ascribed to Mn^{4+}. Since the crystal structure of $BaLaGa_3O_7$ does not offer substitutional octahedral sites and Mn^{4+} has a strong preference for such sites in view of its d^3 configuration, we ascribe the luminescence to Mn^{4+} in a second phase, most probably $LaGaO_3$. Its presence can only be detected by selective excitation of the Mn^{4+} ions. It was not observed in the X-ray diffraction patterns.

At RT the emission maximum of Pb^{2+}-activated $BaLaGa_3O_7$ is at 400nm. This emission is ascribed to the $^3P_1-^1S_0$ transition on the Pb^{2+} ion. The Stokes shift amounts to about 10000 cm^{-1}, a common value for this type of compound. The emission is at longer wavelengths than in the Pb^{2+}-activated crystallochemically related melilite compounds, $M_2M'Si_2O_7$ (M=Ca,Sr,Ba; M'=Mg,Zn), where it is situated between 300 and 350nm [11,12]. In the corresponding germanates this emission region is between 330 and 380nm [13]. The excitation peak of $BaLaGa_3O_7-Pb$ at 290nm is also at a longer wavelength than found for the Pb^{2+} activated melilite silicates (240 – 260nm). The shifts of the emission and excitation bands of $BaLaGa_3O_7-Pb$ to lower energies can be ascribed to the more covalent character of the surrounding gallate groups compared to the silicate groups. It is known that for increasing covalency of the surroundings the compression of the energy levels of the s^2 activators increases [12].

There is still another difference between $BaLaGa_3O_7-Pb$ and the Pb^{2+} activated melilites, viz. the half width of the emission bands. These are 5400 cm^{-1} and 4500 cm^{-1}, respectively. The larger value for the gallate may present its disordered nature due to the occupation of the larger cation sites by Ba^{2+} and La^{3+} ions.

The luminescence of Tb^{3+}-activated $BaLaGa_3O_7$ is weak. This is due to the low absorption strength of Tb^{3+} in this compound. In the excitation spectrum we observe only

the $4f^8$ lines and a weak broad band (Fig. 4). The origin of this band is not quite clear. Because of its position the band could be ascribed to the Tb^{3+} 4f-5d transition. However, the ban corresponds also to the excitation band of the host lattice (Fig.1). It is difficult to distinguish between these two possibilities.

The emission spectra of Tb^{3+} activated $BaLaGa_3O_7$ show the $^5D_4-^7F_J$ as well as the $^5D_3-^7F_J$ emission lines. The intensity ratio between these two emissions depends on the excitation wavelength. It has been discussed elsewhere that, in case of excitation in the sharp $4f^8$ levels of the Tb^{3+} ion, the excited ions relax nonradiatively to the $^5D_3$ level, from where they can only decay to the $^5D_4$ level by means of cross relaxation [14,15]. For excitation into the Tb^{3+} 4f-5d band the excited ion can relax directly from the $4f^75d$ state to the $^5D_4$ level resulting in a higher $^5D_4/^5D_3$ emission intensity ratio, as observed experimentally [16]. In the case of $BaLaGa_3O_7$-Tb the $^5D_4/^5D_3$ emission intensity ratio for X-ray excitation is the same as for excitation into the $4f^8$ levels. This is an indication that the broad band is due to the Tb^{3+} 4f-5d transition and not to host lattice excitation, because for X-ray excitation the same $^5D_4/^5D_3$ ratio is expected as for host lattice excitation. The low intensity of this excitation band is then due to the fact that the host lattice starts to absorb in the same spectral region and does not transfer the excitation energy efficiently to the Tb^{3+} ions.

Ce^{3+} activated $BaLaGa_3O_7$ did not show any luminescence. This is surprising, since the Ce^{3+} ion is an efficient activator in this crystal structure (e.g. $Ca_2Al_2SiO_7$-Ce^{3+} [17]). In the diffuse reflection spectrum (Fig. 5) the band at 335nm is probably due to the 4f-5d transition on Ce^{3+}. It may be suggested that the broad absorption band is due to a Ce^{4+} charge-transfer transition, but these are usually situated at much higher energy [18]. However, there is a more obvious possibility. In $SrTiO_3$-Ce^{3+} a similar type of absorption has been ascribed to a transition in which the 4f electron of Ce^{3+} is promoted to the conduction band [19]. Since the gallate absorption edge transition is just the interband transition, a similar assignment is suggested here.

In this connection it is interesting to note that recently Pédrini et al. [20] have observed that in the case of $Y_3Al_5O_{12}$-Ce^{3+} the 5d levels of Ce^{3+}, except for the lowest one, are situated in the conduction band. What we propose here is that in $BaLaGa_3O_7$-Ce^{3+} all 5d levels of Ce^{3+} are situated in the conduction band. The excited Ce^{3+} ion is then ionized and will not show luminescence.

In conclusion the compound $BaLaGa_3O_7$ is not very promising as a host lattice for luminescent materials.

REFERENCES

1 A.A. Ismatov, Russ. J. Inorg. Chem., 15 (1970) 1758.

2 R.W.G. Wyckoff, Crystal Structures, Vol. 4, J.B. Wiley & Sons, New York, (1963).

3 W. Soluch, R. Ksiezopolski, W. Piekarczyk, M. Berkowski, M.A. Goodberlet and J.F. Vetelino, J. Appl. Phys., 58 (1985) 2285.

4 M. Berkowski, M.T. Borowiec, K. Pataj, W. Piekarczyk and W. Wardzynski, Physica, 123B (1984) 215.

5 H. Ronde and G. Blasse, J. Inorg. Nucl. Chem., 40 (1978) 215.

6 W.L. Wanmaker and J.W. ter Vrugt, J. Electrochem. Soc., 116 (1969) 871.

7 G. Blasse and A. Bril, J. Phys. Chem. Solids, 31 (1970) 707.

8 T. Harwig and F. Kellendonk, J. Solid State Chem., 24 (1978) 255.

9 G. Blasse and P.H.M. de Korte, J. Inorg. Nucl. Chem., 43 (1981) 1505.

10 Z.N. Zonn, V.A. Ioffe and P.P. Feofilov, Opt. Spectrosc., 19 (1965) 541.

11 H.A. Klasens, A.H. Hoekstra and A.P.M. Cox, J. Electrochem. Soc., 104 (1957) 93.

12 K.H. Butler, Fluorescent Lamp Phosphors, Technology and Theory, Pennsylvania State University Press (1980).

13 H. Koelmans and C.M.C. Verhagen, J. Electrochem. Soc., 106 (1959) 677.

14 M.J.J. Lammers, H. Donker and G. Blasse, Mater. Chem. Phys., 13 (1985) 527.

15 F. Varsanyi and G.H. Dieke, Phys. Rev. Letters, 7 (1961) 442.

16 C.W. Struck and W.H. Fonger, J. Luminescence, 1,2 (1970) 456.

17 A. Bril and H.A. Klasens, Philips Res. Rep., 7 (1952) 421.

18 H.E. Hoefdraad, J. Inorg. Nucl. Chem., 37 (1975) 1917.

19 G. Blasse and G.J. Dirksen, J. Solid State Chem., 37 (1981) 390.

20 C. Pédrini, F. Rogemond and D.S. McClure, J. Appl. Phys., 59 (1986) 1196.