

THE LUMINESCENCE OF Eu^{3+} , Tb^{3+} AND Tm^{3+} ACTIVATED $\text{Gd}_2\text{BaZnO}_5$ AND $\text{La}_2\text{BaZnO}_5$

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ABSTRACT

The luminescence of several rare-earth activators in the new compounds $\text{Gd}_2\text{BaZnO}_5$ and $\text{La}_2\text{BaZnO}_5$ is reported and discussed. Activation with the Eu^{3+} ion yields highly efficient red-emitting phosphors. Some unknown structural details can be derived from the luminescence spectra.

INTRODUCTION

Some years ago, Michel, Er-Rakho and Raveau [1] reported the existence and the crystal structure of the oxides $\text{Ln}_{4-2x}\text{Ba}_{2+2x}\text{Zn}_{2-x}\text{O}_{10-2x}$ with $\text{Ln} = \text{La}$, Nd and $0 \leq x \leq 0.25$. Recently, Michel and Raveau [2] reported the compounds $\text{Ln}_2\text{BaZnO}_5$ with $\text{Ln} = \text{Sm}$, Eu , Gd , Dy , Ho , Y . These compounds have a structure which is different from the former compounds. In their X-ray structural analysis Michel *et al.* could not distinguish between the Ba^{2+} and the Ln^{3+} ions. For both structures they proposed that the Ba^{2+} ions occupy the sites with the larger volume. This implies that the former compounds are built up of Ln_2O_5 layers, formed from face- and edge-sharing LnO_8 polyhedra, between which the Ba^{2+} and Zn^{2+} ions are inserted. In this structure there is only one crystallographic site for the lanthanide ion. Its site symmetry is C_{2v} . The structure of the other type of compounds is built up of edge- and face-sharing LnO_7 polyhedra which form a three-dimensional network. In this structure there are two crystallographic sites for the lanthanide ion. Both have site symmetry C_s .

This paper deals with the luminescence properties of two of these new compounds, *viz.* $\text{La}_2\text{BaZnO}_5$ and $\text{Gd}_2\text{BaZnO}_5$ activated with Eu^{3+} , Tb^{3+} and Tm^{3+} .

These compounds might be attractive X-ray phosphors due to the high densities of the host lattices (6.7 g/cm^3 for $\text{La}_2\text{BaZnO}_5$ and 7.7 g/cm^3 for $\text{Gd}_2\text{BaZnO}_5$).

EXPERIMENTAL

The powder samples were prepared by the usual solid state techniques using as starting materials: Ln_2O_3 ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Tm}$), Tb_4O_7 , BaCO_3 and ZnO . Mixtures of these compounds were fired twice for 12 h at temperatures between 1000 and 1200 °C. The Tb^{3+} -activated samples were fired under nitrogen, the others in air. The following samples were prepared: $\text{Gd}_2\text{BaZnO}_5$, $\text{Gd}_{1.996}\text{Eu}_{0.004}\text{BaZnO}_5$, $\text{Gd}_{1.96}\text{Eu}_{0.04}\text{BaZnO}_5$, $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{BaZnO}_5$, $\text{Gd}_{1.96}\text{Tb}_{0.04}\text{BaZnO}_5$, $\text{Gd}_{1.98}\text{Tm}_{0.02}\text{BaZnO}_5$, $\text{La}_2\text{BaZnO}_5$, $\text{La}_{1.96}\text{Eu}_{0.04}\text{BaZnO}_5$, $\text{La}_{1.84}\text{Eu}_{0.16}\text{BaZnO}_5$, $\text{La}_{3.43}\text{Eu}_{0.07}\text{Ba}_{2.5}\text{Zn}_{1.75}\text{O}_{9.5}$, $\text{La}_{1.996}\text{Tb}_{0.004}\text{BaZnO}_5$, $\text{La}_{1.96}\text{Tb}_{0.04}\text{BaZnO}_5$, $\text{La}_{1.9}\text{Tb}_{0.1}\text{BaZnO}_5$ and $\text{La}_{1.98}\text{Tm}_{0.02}\text{BaZnO}_5$. The samples were checked by X-ray powder diffraction using $\text{CuK}\alpha$ radiation.

Luminescence spectra were measured down to liquid helium temperature (LHeT) on a Perkin-Elmer MPF 3L spectrofluorometer equipped with a Xenon lamp as described in ref.[3]. $\text{La}_2\text{BaZnO}_5:\text{Tb}^{3+}$, $\text{La}_2\text{BaZnO}_5:\text{Tm}^{3+}$ and $\text{Gd}_2\text{BaZnO}_5:\text{Tm}^{3+}$ samples were also measured at room temperature on a Perkin-Elmer MPF 4 spectrofluorometer equipped with an X-ray source with a maximum voltage of 100 kV. Reflection spectra were measured at room temperature on a Perkin-Elmer EPS 3T spectrometer with MgO as a reference. Quantum efficiencies were estimated by comparison with standard phosphors.

RESULTS AND DISCUSSION

$\text{Gd}_2\text{BaZnO}_5$

At room temperature the host lattice $\text{Gd}_2\text{BaZnO}_5$ does not show any luminescence. The diffuse reflection spectrum shows an absorption edge at about 250 nm (Fig.1). For excitation into this absorption band at LHeT we observe three sharp emission lines at 315, 316 and 319 nm, which are ascribed to the $^6\text{P} - ^8\text{S}$ transition on the Gd^{3+} ion, and a broad band with a maximum at 450 nm (Fig.2). The total emission intensity of the Gd^{3+} peaks is about twice the emission intensity of the broad band. In the excitation spectrum of the broad band we observe an excitation band with a maximum at 245 nm which coincides with the measured absorption edge and a weak line at 256 nm. In the excitation spectrum of the Gd^{3+} emission we find these same bands, and also the sharp lines corresponding to transitions within the $4f^7$ shell of Gd^{3+} (Fig.1). The excitation spectrum is the same for all three Gd^{3+} emission lines.

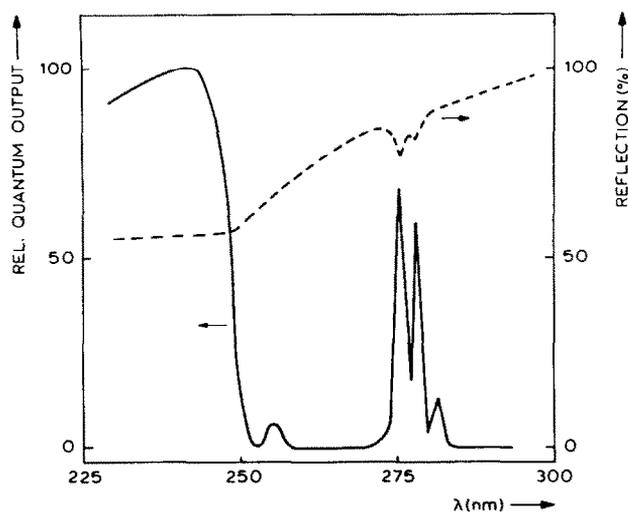


Fig. 1. Diffuse reflection spectrum of Gd_2BaZnO_5 at RT (---). Excitation spectrum of the Gd^{3+} emission of Gd_2BaZnO_5 at LHeT.

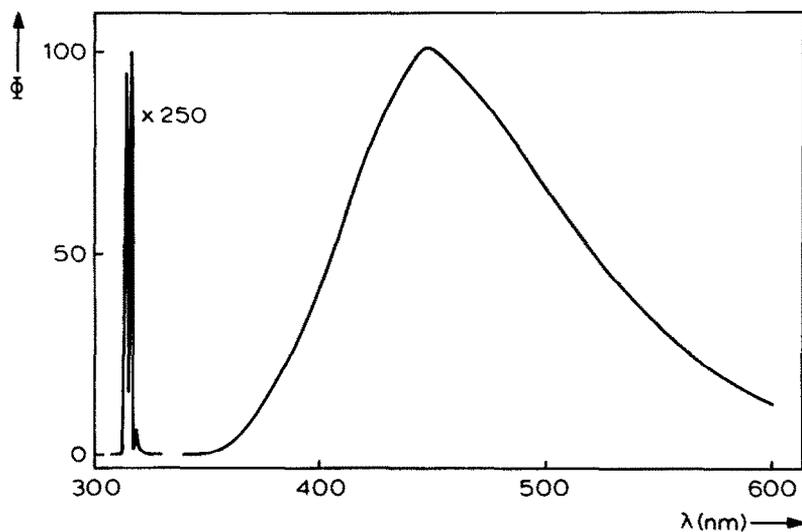


Fig. 2. Emission spectrum of unactivated Gd_2BaZnO_5 for excitation into the host lattice at LHeT. Φ gives the spectral radiant power per constant wavelength interval in arbitrary units.

The intensity of the Gd^{3+} lines and the broad band emission depends strongly on temperature. With increasing temperature, the emission intensities of all three Gd^{3+} lines decrease. The 315, 316 and 319 nm lines are quenched sequentially, *viz.* at 20, 40 and 75 K, respectively. However, the intensity of the broad band first increases with increasing temperature and reaches a maximum intensity at about 75 K which is roughly twice the LHeT intensity. The emission is quenched at about 200 K. An excitation spectrum of this broad band at 100 K shows the same features as the excitation spectrum at LHeT with the difference that the intensity of the line at 256 nm is higher.

The broad excitation band at 245 nm is ascribed to host lattice absorption. The origin of this host lattice band is not clear, because of the complex structure of this compound. The origin of the 450 nm emission band is also not quite clear. Energy transfer from the host lattice to the Gd^{3+} ions is quite effective (see Figs.1 and 2). Since there is no spectral overlap between the 450 nm emission band and the Gd^{3+} absorption lines, and the intensity of the 450 nm emission band increases with increasing temperature, we have to suppose that the 450 nm emission is due to defect centres in the host lattice. Self-trapped exciton host lattice emission can be excluded. Since the Gd^{3+} excitation lines ($^8S \rightarrow ^6P, ^6I$) are absent in the excitation spectrum of the 450 nm emission, the increase of the 450 nm emission with temperature cannot be correlated to the corresponding decrease of the Gd^{3+} line emission. The intensity increase of the 450 nm emission has, therefore, to be ascribed to a thermal variation of the probabilities for transfer from the host lattice to the Gd^{3+} ions and the defects.

The 256 nm excitation line is ascribed to the $^8S \rightarrow ^6D$ transition on Gd^{3+} , because it occurs in the Gd^{3+} excitation spectrum. This then implies energy transfer from the 6D level of Gd^{3+} to the host lattice. This transfer has a probability which is higher than the nonradiative $^6D \rightarrow ^6P$ transition on the Gd^{3+} ion. With increasing temperature, the intensity of the $^8S \rightarrow ^6D$ line in the excitation spectrum of the 450 nm emission increases, which indicates an increasing transfer probability. Langer [4] has reported emission from 6D to 8S for $CaF_2:Gd^{3+}$, which indicates also a low probability for the $^6D \rightarrow ^6P$ transition.

As in many other Gd^{3+} compounds [5-7], the excitation energy on the Gd^{3+} sublattice is assumed to be mobile, so that concentration quenching occurs at room temperature. Only at low temperature is there Gd^{3+} emission from Gd^{3+} traps [8,9]. In our Gd_2BaZnO_5 sample there are at least three different traps. One trap is possibly due to Gd^{3+} ions on Ba^{2+} sites. In Eu^{3+} -activated Gd_2BaZnO_5 the intrinsic $^8S - ^6P$ absorption line is found at 315 nm. It seems unlikely that the 315 nm emission line is intrinsic in view of the sequential

quenching. With this assumption, the trap depths vary from a few cm^{-1} to about 400 cm^{-1} . Similar values are found for Gd^{3+} traps in $\text{GdAl}_3\text{B}_4\text{O}_{12}$ [9].

$\text{Gd}_2\text{BaZnO}_5:\text{Eu}^{3+}$

Under u.v. excitation, $\text{Gd}_2\text{BaZnO}_5$ activated with Eu^{3+} is an efficient red-emitting phosphor with a quantum efficiency of about 75%. Figure 3 presents the emission spectrum of $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{BaZnO}_5$ at LHeT for excitation in the europium-oxygen charge-transfer band. Excitation in the sharp $4f^6$ levels of Eu^{3+} yields the same spectrum. It shows the dominant $^5\text{D}_0$ emission peaks and some weak $^5\text{D}_1$ emission peaks. For C_s symmetry the following number of lines is expected (the numbers observed experimentally are shown in brackets): $^5\text{D}_0 - ^7\text{F}_0$ 1(1), $^5\text{D}_0 - ^7\text{F}_1$ 3(2), $^5\text{D}_0 - ^7\text{F}_2$ 5(5), $^5\text{D}_0 - ^7\text{F}_3$ 7(4) and $^5\text{D}_0 - ^7\text{F}_4$ 9(8). For none of the emission transitions is the observed number of lines higher than the expected number. This means that the two crystallographic Gd^{3+} sites in this structure resemble each other very much, so that there is no significant difference in the splittings of the $^7\text{F}_J$ levels. This agrees with the structure determination [2].

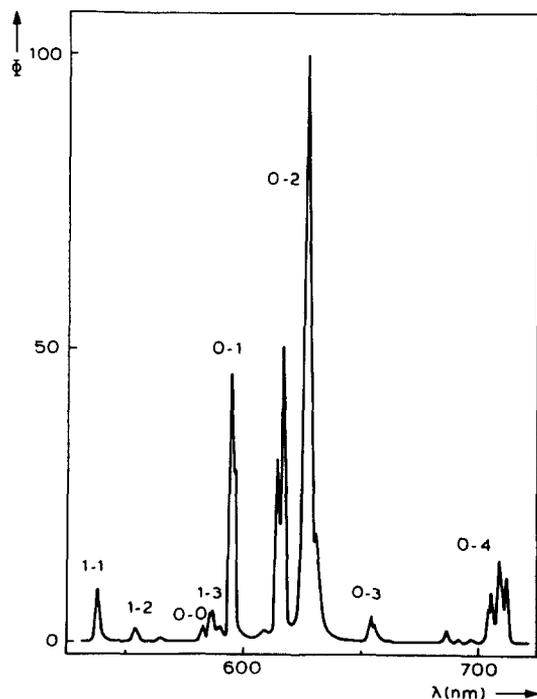


Fig. 3. Emission spectrum of $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{BaZnO}_5$ for excitation into the europium-oxygen charge-transfer band at LHeT. The notation $J \rightarrow J'$ denotes the transitions $^5\text{D}_J \rightarrow ^7\text{F}_{J'}$.

For lower Eu^{3+} concentrations, the relative intensities of the ${}^5\text{D}_1$, ${}^5\text{D}_2$ and ${}^5\text{D}_3$ emission lines increase. This is illustrated in Fig.4a, which shows the emission spectrum of the sample with 0.2% Eu^{3+} at LHeT for excitation in the sharp $4f^6$ levels of Eu^{3+} . The blue ${}^5\text{D}_2$ emission dominates! Obviously, the radiative ${}^5\text{D}_3$, ${}^5\text{D}_2$, ${}^5\text{D}_1 - {}^7\text{F}_J$ transitions can compete with the nonradiative relaxation processes between the ${}^5\text{D}_J$ states. Because of the low Eu^{3+} concentration of the sample, cross-relaxation can be neglected. The relaxation has to proceed via a multiphonon process. The probability of this process is determined by the number of phonons required to conserve energy. The maximum phonon frequency of this compound is low, viz. about 500 cm^{-1} [2]. With an energy gap of about 2500 cm^{-1} between ${}^5\text{D}_3$ and ${}^5\text{D}_2$, and between ${}^5\text{D}_2$ and ${}^5\text{D}_1$, at least five phonons are required for the nonradiative relaxation between these states. This makes the probabilities for these processes relatively low, so that a considerable amount of ${}^5\text{D}_3$ and ${}^5\text{D}_2$ emission can be observed. At RT the

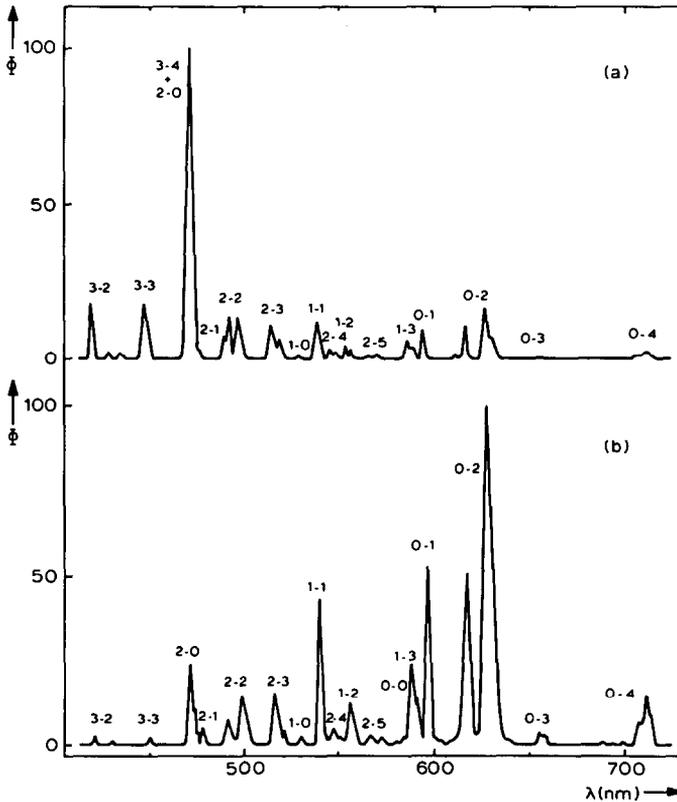


Fig. 4. Emission spectra of $\text{Gd}_{1.996}\text{Eu}_{0.004}\text{BaZnO}_5$ at LHeT, (a) for excitation into the $\text{Eu}^{3+} 4f^6$ levels ($\lambda_{\text{exc}} = 380\text{ nm}$); (b) for excitation into the europium-oxygen charge-transfer band.

intensities of the 5D_0 emission lines increase compared to the intensities of the other 5D_J emission lines. This is in agreement with the temperature dependence expected for multiphonon relaxation [10]. For excitation into the charge-transfer band the 5D_0 emission lines dominate the spectrum, even at LHeT (Fig.4b). This must be due to direct feeding of the 5D_0 state by the charge-transfer state [11].

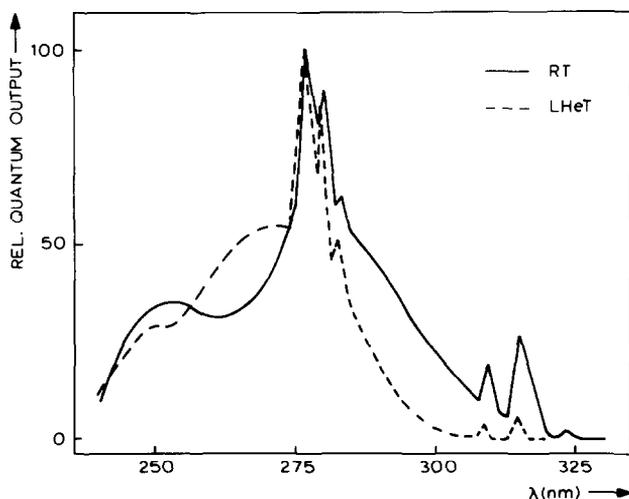


Fig. 5. Excitation spectra of the Eu^{3+} emission ($\lambda_{\text{em}} = 626 \text{ nm}$) of $\text{Gd}_{1.996}\text{Eu}_{0.004}\text{BaZnO}_5$ at RT (—) and at LHeT (---).

Figure 5 shows the excitation spectrum at RT and at LHeT of the ${}^5D_0 - {}^7F_2$ emission for the sample with 0.2% Eu^{3+} . At RT we observe a broad band with its maximum at about 280 nm, which we ascribe to the europium-oxygen charge-transfer transition, a weak broad band at about 250 nm which is due to host lattice excitation, a number of sharp lines at about 275 nm and 310 nm, which are due to the ${}^8S - {}^6I$ and ${}^8S - {}^6P$ transitions of the Gd^{3+} ion, respectively and a number of sharp lines between 350 nm and 600 nm which correspond to transitions in the $4f^6$ shell of the Eu^{3+} ion. The latter transitions are not shown in Fig.5. At LHeT the europium-oxygen charge-transfer band is narrower. Its maximum has shifted to higher energy. When the Eu^{3+} concentration is increased, the charge-transfer band shifts to lower energy. The shift of the charge-transfer band has a great effect on the intensity ratio of the $\text{Gd}^{3+} {}^6P$ and 6I excitation lines (see Fig.5). When the charge-transfer band shifts to higher energy, the intensity of the $\text{Gd}^{3+} {}^6P$ excitation lines decreases rapidly, while the intensity of the $\text{Gd}^{3+} {}^6I$ exci-

tation lines remains constant. This means that the rate for nonradiative relaxation from the 6I to the 6P level is low relative to the $Gd^{3+} {}^6I \rightarrow Gd^{3+} {}^6I$ and the $Gd^{3+} {}^6I \rightarrow Eu^{3+}$ transfer rates. So, upon excitation in the $Gd^{3+} {}^6I$ level, energy migration takes place via the 6I levels until an europium ion is reached. Since the 6I levels overlap perfectly with the allowed europium-oxygen charge-transfer transition, the Eu^{3+} is very effective in trapping the migrating $Gd^{3+} {}^6I$ energy. For the energy in the 6P level of Gd^{3+} the transfer to Eu^{3+} has to compete with trapping by Gd^{3+} traps, because the transfer rate to Eu^{3+} and to Gd^{3+} traps will be of the same order of magnitude. Similar observations have been made in gadolinium tantalates and zirconates [7,12].

For the sample activated with 0.2% Eu^{3+} , a small amount of $Gd^{3+} {}^6P$ emission was observed upon excitation at 280 nm at LHeT (7% of the total emission). This agrees with the arguments given above. For excitation into the host lattice band at 245 nm, the Gd^{3+} emission dominates the spectrum. The Eu^{3+} emission and the host lattice emission have both about half the intensity of the Gd^{3+} emission. Because of the low output of the Eu^{3+} emission, it can be concluded that for excitation into the host lattice the excitation energy is preferably transferred to Gd^{3+} , resulting in a relatively high emission intensity from Gd^{3+} traps. Transfer from the host lattice to Gd^{3+} must proceed to the 6P level, because 6I population would finally yield Eu^{3+} emission. There is no dominating direct transfer from the host lattice to Eu^{3+} , only indirect via the Gd^{3+} sublattice.

At higher Eu^{3+} concentrations, the charge-transfer band dominates the excitation spectrum in such a way that the measurements described for 0.2% Eu^{3+} are hard or even impossible to perform.

$Gd_2BaZnO_5:Tb^{3+}$

Samples of Gd_2BaZnO_5 activated with 2% Tb^{3+} are slightly brown coloured. This is ascribed to the presence of Tb^{4+} ions. Obviously this lattice incorporates Tb^{4+} ions rather easily and this possibly explains why Michel and Raveau [2] could not synthesize Tb_2BaZnO_5 . The quantum efficiency of $Gd_{1.96}Tb_{0.04}BaZnO_5$ is rather low because of the presence of the Tb^{4+} ions which act as killers for the Tb^{3+} emission.

The emission spectrum of this sample shows the well-known 5D_4 emission lines. In the excitation spectrum of the ${}^5D_4 - {}^7F_5$ transition three types of excitation peaks can be distinguished. A broad band with a maximum at 300 nm which can be ascribed to the $Tb^{3+} 4f-5d$ transition; two sharp lines at 308 nm and 315 nm which are due to the $Gd^{3+} 8s - 6p$ transition and a number of sharp lines corresponding to transitions within the $4f^8$ shell of Tb^{3+} . The $Gd^{3+} 8s - 6I$ transitions are not observed. For excitation in the $Gd^{3+} {}^6I$ level at LHeT hardly any Gd^{3+} emission is observed. Because the output of the

Tb³⁺ emission is low too, this means that the greater part of the excitation energy is lost nonradiatively, most likely on the Tb⁴⁺ ions.

Gd₂BaZnO₅:Tm³⁺

Gd₂BaZnO₅ activated with 1% Tm³⁺ was only measured at room temperature. The emission spectrum shows a number of sharp peaks at about 460 nm which are due to the ¹D₂ - ³F₄ transition on the Tm³⁺ ion. In the excitation spectrum of this emission, a number of excitation lines at about 360 nm are observed. These are ascribed to the ³H₆ - ¹D₂ transition on Tm³⁺. No Gd³⁺ excitation lines are observed, which means that energy transfer from the ⁶P level of Gd³⁺ to the ¹D₂ level of Tm³⁺ does not occur. This is not surprising in view of the large energy mismatch (~ 4500 cm⁻¹).

The output of the observed emission is low. For X-ray excitation at RT no emission could be detected at all.

La₂BaZnO₅

The optical absorption edge of undoped La₂BaZnO₅ is situated at about 245 nm (Fig.6). For excitation into the host lattice at LHeT a weak emission is observed with a maximum at 480 nm. Also some Tb³⁺ and Gd³⁺ emission is observed, probably due to impurities in one of the starting materials, most likely in La₂O₃.

As in Gd₂BaZnO₅, we suppose that the host lattice emission is due to defect centres. The excitation energy is transferred through the lattice until a trap or killer is reached. The defect centres, the Tb³⁺ impurities as well as the Gd³⁺ impurities act as traps. Especially the Tb³⁺ impurities are effective traps at higher temperatures.

La₂BaZnO₅:Eu³⁺ and La_{3.5}Ba_{2.5}Zn_{1.75}O_{9.5}:Eu³⁺

La₂BaZnO₅ and La_{3.5}Ba_{2.5}Zn_{1.75}O_{9.5} activated with Eu³⁺ are both efficient red-emitting phosphors under u.v. excitation. The quantum efficiency of both phosphors is about 75% compared with standard phosphors.

The emission spectra of both phosphors are the same. Figure 7 shows the emission spectrum of La_{1.96}Eu_{0.04}BaZnO₅ at LHeT for excitation into the europium-oxygen charge-transfer band. The reported site symmetry of the lanthanide ion in these structures is C_{2v}. However, for some transitions the splitting of the Eu³⁺ emission lines is higher than expected for this symmetry. This means that the Eu³⁺ ions must occupy more than one crystallographic site. Probably, La³⁺ and Eu³⁺ replace part of the Ba²⁺ ions in this structure. This becomes also clear in the Tb³⁺-activated compound (see next paragraph). The intensities of the ⁵D₁, ⁵D₂ and ⁵D₃ emission lines depend on the Eu³⁺ concentration, excitation wavelength and temperature in qualitatively the same way as in Gd₂BaZnO₅:Eu³⁺.

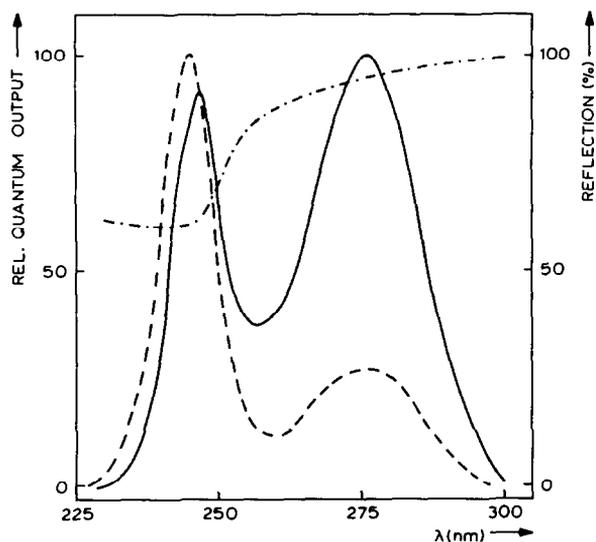


Fig. 6. Excitation spectra of the Tb^{3+} emission of $La_{1.9}Tb_{0.1}BaZnO_5$ at RT. The solid line shows the excitation spectrum of the 5D_4 emission ($\lambda_{em} = 545$ nm), the dashed line the excitation spectrum of the 5D_3 emission ($\lambda_{em} = 380$ nm). The dashed-dotted line shows the diffuse reflection spectrum of unactivated La_2BaZnO_5 .

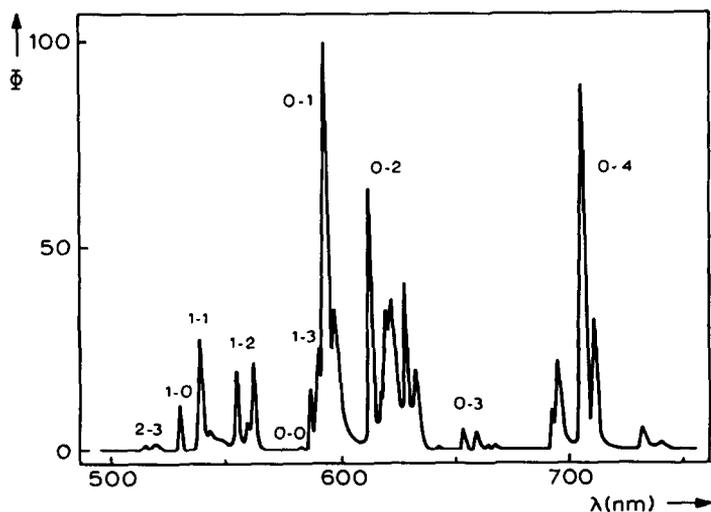


Fig. 7. Emission spectrum of $La_{1.96}Eu_{0.04}BaZnO_5$ at LHeT for excitation into the europium-oxygen charge-transfer band ($\lambda_{exc} = 320$ nm).

The charge-transfer state in $\text{La}_2\text{BaZnO}_5:\text{Eu}^{3+}$ is at lower energy than in $\text{Gd}_2\text{BaZnO}_5:\text{Eu}^{3+}$ (32300 cm^{-1} vs 37000 cm^{-1} at LHeT) (Figs.5 and 8). This is not surprising, because it is known that for coordination numbers higher than six the europium-oxygen charge-transfer band shifts usually to lower energies with increasing bond lengths [13]. In addition there is a tendency to observe the charge-transfer transition at lower energy if the number of surrounding ligands is larger [14]. The coordination number of Ln^{3+} ions in $\text{La}_2\text{BaZnO}_5$ is eight vs seven in $\text{Gd}_2\text{BaZnO}_5$ [1 and 2]. The lower charge-transfer state has influence on the temperature dependence of the ratio of the $^5\text{D}_J$ emission intensities. In $\text{La}_2\text{BaZnO}_5:\text{Eu}^{3+}$, the levels above $^5\text{D}_0$ are easier emptied via the charge-transfer level, so that the intensity of the $^5\text{D}_1$, $^5\text{D}_2$ and $^5\text{D}_3$ emission lines decreases more rapidly with increasing temperature than in $\text{Gd}_2\text{BaZnO}_5:\text{Eu}^{3+}$ [11].

If we compare $\text{La}_2\text{BaZnO}_5:\text{Eu}^{3+}$ and $\text{La}_{3.5}\text{Ba}_{2.5}\text{Zn}_{1.75}\text{O}_{9.5}:\text{Eu}^{3+}$ we observe a difference in the excitation spectra of the Eu^{3+} emission: in $\text{La}_{3.5}\text{Ba}_{2.5}\text{Zn}_{1.75}\text{O}_{9.5}:\text{Eu}^{3+}$ the charge-transfer band has a higher intensity relative to the Eu^{3+} 4f-4f lines. The latter are taken as a reference because they are not much influenced by the surroundings. Because of the higher absorption strength, the light output of this compound is higher than that of $\text{La}_2\text{BaZnO}_5:\text{Eu}^{3+}$.

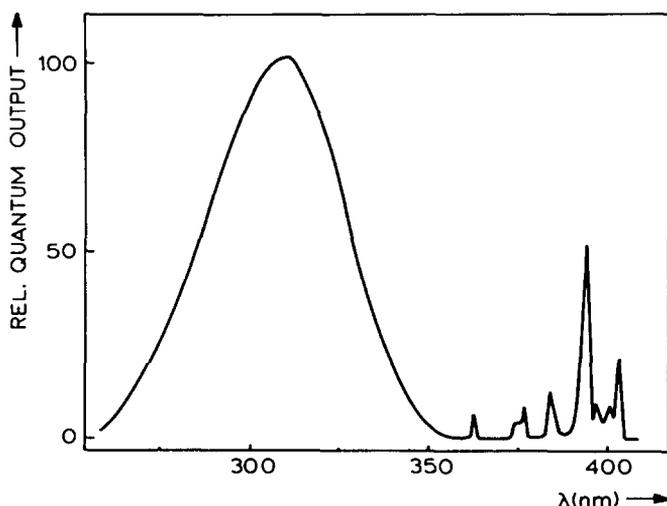


Fig. 8. Excitation spectra of the Eu^{3+} emission ($\lambda_{\text{em}} = 592\text{ nm}$) of $\text{La}_{1.96}\text{Eu}_{0.04}\text{BaZnO}_5$ at LHeT.

La₂BaZnO₅:Tb³⁺

Under both u.v. and X-ray excitation, La₂BaZnO₅:Tb³⁺ is an efficient phosphor. The quantum efficiency is about 70%, but not stable with time.

The emission spectra of the La₂BaZnO₅ samples show the ⁵D₃ - ⁷F_J as well as the ⁵D₄ - ⁷F_J emission lines. The intensity ratio between these two emissions depends on the Tb³⁺ concentration, because of the well-known cross-relaxation process [15], and on the excitation wavelength.

In the excitation spectrum of La₂BaZnO₅:Tb³⁺, three types of excitation peaks can be distinguished (Fig.6). One is an excitation band with a maximum at 245 nm which coincides with the absorption edge in the diffuse reflection spectrum. As in pure La₂BaZnO₅, this band is ascribed to host lattice absorption. Further, we observe a broad band with a maximum at 280 nm which is ascribed to the Tb³⁺ 4f-5d transition, and a number of sharp lines between 300 and 400 nm which are due to transitions in the Tb³⁺ 4f⁸ shell. These peaks are not shown in Fig.6. Note the difference in excitation spectrum for ⁵D₃ and ⁵D₄ emission.

We now discuss the dependence of the ratio of the ⁵D₃ and ⁵D₄ emission intensities on the excitation wavelength. For comparison we mention for each excitation wavelength the value of the ⁵D₃/⁵D₄ ratio for La_{1.996}Tb_{0.004}BaZnO₅. For excitation in the Tb³⁺ 4f-5d band we observe the highest amount of ⁵D₄ emission, in agreement with Fig.6 ($\lambda_{\text{exc}} = 280 \text{ nm}$, ${}^5\text{D}_3/{}^5\text{D}_4 = 1.9$). This means that the excited ion can relax directly from the 4f⁷5d state to the ⁵D₄ level. On excitation in the sharp 4f levels of the Tb³⁺ ion, this is not possible. In that case the excited ions relax nonradiatively to the ⁵D₃ level, from where they can only decay to the ⁵D₄ level by means of cross-relaxation [15] ($\lambda_{\text{exc}} = 320 \text{ nm}$, ${}^5\text{D}_3/{}^5\text{D}_4 = 3.0$). Phenomena of this type have been reported and discussed for the first time by Struck and Fonger [16].

In most compounds, excitation in the 4f levels yields the highest amount of ⁵D₃ emission. It is therefore striking that an even higher amount of ⁵D₃ emission is observed when La₂BaZnO₅:Tb³⁺ is excited with 245 nm radiation or with X-ray radiation (${}^5\text{D}_3/{}^5\text{D}_4 = 4.0$). This high amount of ⁵D₃ emission is tentatively ascribed to nonregular Tb³⁺ ions which have no efficient cross-relaxation with the regular Tb³⁺ ions. For La₂BaZnO₅:Eu³⁺ we proposed above that part of the Ba²⁺ sites were occupied by La³⁺ and Eu³⁺ ions. To explain our results on La₂BaZnO₅:Tb³⁺ we ascribe the ⁵D₃ emission to Tb³⁺ ions on Ba²⁺ sites. Such Tb³⁺ ions have an effective positive charge. We assume that under 245 nm radiation and X-ray excitation mobile free charge carriers are created, which are preferably trapped by these effective positive sites.

La₂BaZnO₅:Tm³⁺

The emission and excitation spectra of Tm³⁺ in La₂BaZnO₅ show the same features as for Tm³⁺ in Gd₂BaZnO₅. Under X-ray radiation no Tm³⁺ emission is found. However, we observed some Tb³⁺ emission. As in undoped La₂BaZnO₅ this emission must be due to Tb³⁺ ions which are built in as impurities. Obviously Tm³⁺ cannot pick up the excitation energy from the host lattice as efficiently as Tb³⁺ does.

CONCLUSIONS

In La₂BaZnO₅ there is disorder between the Ba²⁺ and La³⁺ ions. This was not observed for Gd₂BaZnO₅. Eu³⁺-activated Ln₂BaZnO₅ (Ln = La, Gd) is an efficient red phosphor. La₂BaZnO₅:Tb³⁺ is an efficient phosphor under u.v. and X-ray excitation, but the material is not stable in air.

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