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Bi^{3+} Center in a Lanthanum Gallate Phosphor

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The luminescent properties of the Bi^{3+} center are investigated in $LaGaO_3$. Two excitation peaks and an ultraviolet fluorescence band are assigned, respectively, to the ${}^1S_0 \rightarrow {}^3P_1$, ${}^1S_0 \rightarrow {}^1P_1$, and ${}^3P_1 \rightarrow {}^1S_0$ transitions. From temperature dependence of decay time, it is shown that the ${}^3P_0$ level traps the electrons at very low temperature. The analogy with La_2O_3(Bi) is discussed.

I. Introduction

We have reported previously that Bi^{3+} is a good activator for lanthanide compounds such as oxides, orthovanadates or phosphates in consideration of their very similar ionic radii (*1–4*).

The present work concerns the luminescence properties of a new phosphor: $LaGaO_3$(Bi). The excitation and emission spectra together with the Bi^{3+} content, temperature dependence and decay measurements are determined. From the results, we discuss the processes involved in the Bi^{3+} luminescent center.

II. Experimental Techniques

Preparation of the Samples

Powder samples of $LaGaO_3$(Bi) with several amounts of Bi^{3+} are prepared using the method of Sallavuard, Szabo and Paris (*5*). Mixed citric complexes are easily obtained by evaporating an ammoniacal liquor of gallium citrate and lanthanum citrate in equimolecular quantities with a small amount of bismuth citrate. By firing in air up to 950°C, a decomposition takes place and the mixed oxide is formed. This oxide exhibits two crystal structures: the hexagonal and perovskite ones; but at 950°C, where the phosphor $La_{1-x}Bi_x GaO_3$ can be obtained, the only perovskite form is stable. The space group is C_{2v}^9 and the lanthanum site symmetry is triclinic C_1.

Excitation and Fluorescence Apparatus

The excitation spectra are obtained, between 2000 and 4000 Å, with a Bausch and Lomb grating monochromator. The light source is a xenon lamp (Osram XBO–450W/4) with a spectrosil quartz jacket. Maximum sensitivity in the ultraviolet spectral range is obtained with an EMI 6256 S photomultiplier tube. The spectral energy distribution is determined using a Schwarz thermopile with a quartz window.

The powders are studied in a liquid-helium cryostat (Meric) utilizing a gaseous cooling of the sample which avoids many of the problems of liquid cooling. An electric heater associated to a temperature regulator (ANVAR, MV 2000 type) and a TG 100 cryogenic sensor, gives all the temperatures between 20 and 400°K.

The fluorescence spectra are recorded on a Jobin–Yvon HRS1 grating monochromator (1200 lines/mm). The light source is the above-mentioned xenon lamp associated with a Bausch and Lomb monochromator so that the samples can be excited just in the middle of an excitation band.

Decay Time Measurements

The powder under investigation is placed in a quartz window cryostat and excited with the pulse of a deuterium flash lamp (half-height width = 4×10^{-9} sec). The exciting light passes through a

Bausch and Lomb monochromator in order to excite the phosphor in its absorption band.

The fluorescence signal is detected using a 56 DUVP Radiotechnique photomultiplier with a 50 Ω load resistance, displayed and photographed on a 545 A Tecktronix oscilloscope utilizing either an *N*-type Sampling (rise time = 0.6×10^{-9} sec) or a CA-type 24 MHz plug-in unit.

The decay time is determined by varying the temperature of the sample from 77 to 400°K.

III. Results and Discussion

Excitation and Emission Spectra

The excitation spectrum of $LaGaO_3(Bi)$ is studied varying the temperature and the Bi^{3+} amounts. At 24°K, it consists of two bands at 2400 and 3070 Å; they move to longer wavelengths (25 Å) on increasing temperature up to 295°K (Figs. 1 and 2). On the figures, for each wavelength, the energies refer to a same number of incident photons.

The excitation in each main band leads to the same ultraviolet fluorescence (Fig. 3). With increasing temperature, it can be seen a shift of the fluorescence peak ($\lambda = 3800$ Å at 24°K and $\lambda = 3720$ Å at 295°K), a notable increasing of the half-height width and a decreasing of the emission intensity (Fig. 4). This intensity is the greatest for 5×10^{-3} at. Bi^{3+}/mole, but the gallate may be activated by

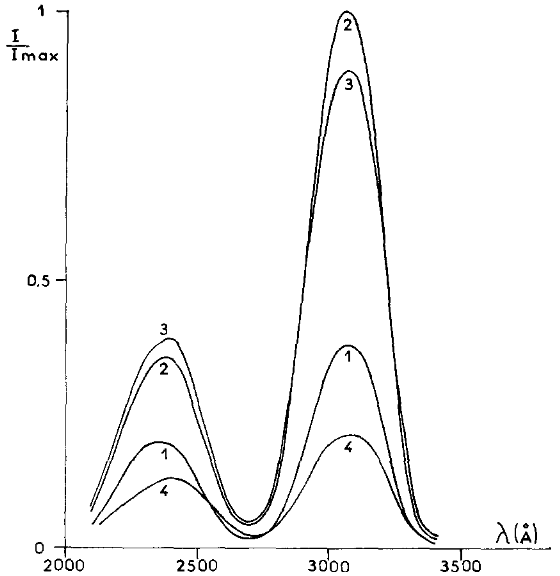

FIG. 1. The dependency of excitation spectrum on bismuth content c in $LaGaO_3(Bi)$ at 77°K. 1 ($c = 10^{-3}$); 2 ($c = 5 \times 10^{-3}$); 3 ($c = 10^{-2}$); 4 ($c = 5 \times 10^{-2}$).

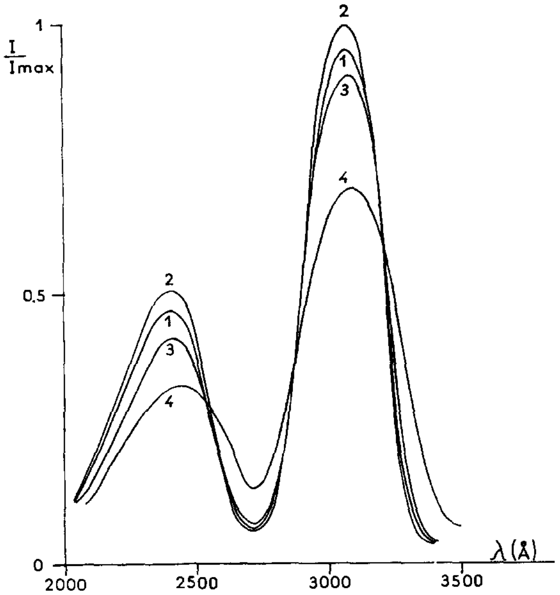

FIG. 2. Temperature dependence of the excitation spectrum in $LaGaO_3(Bi)$. 1 ($T = 24$°K); 2 ($T = 35$°K); 3 ($T = 75$°K); 4 ($T = 295$°K). (Bismuth content = 10^{-2}.)

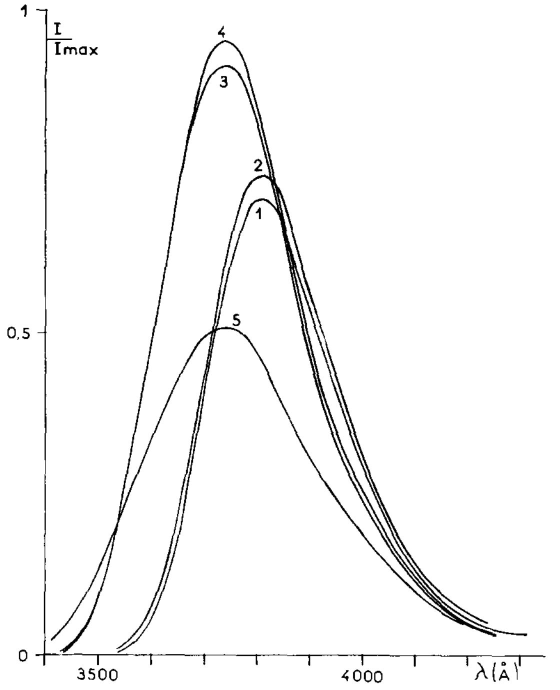

FIG. 3. Fluorescence spectrum of $LaGaO_3(Bi)$ at different temperatures ($\lambda_{exc} = 3080$ Å). 1 ($T = 24$°K); 2 ($T = 35$°K); 3 ($T = 118$°K); 4 ($T = 137$°K); 5 ($T = 295$°K). (Bismuth content = 10^{-2}.)

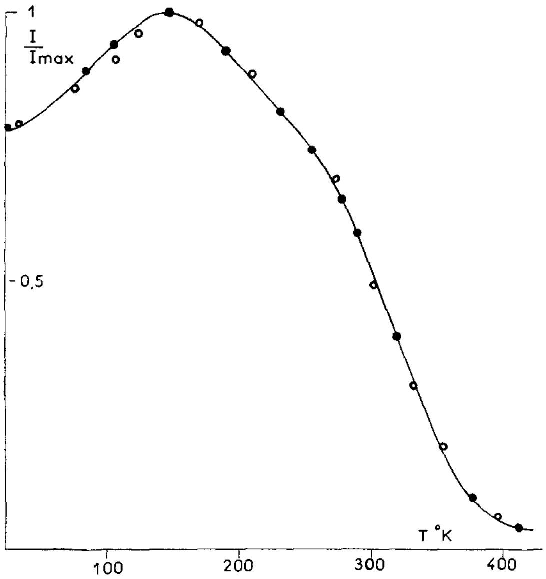

FIG. 4. Temperature dependence of the ultraviolet emission of $LaGaO_3(Bi)$. ● $\lambda_{exc} = 2450$ Å; ○ $\lambda_{exc} = 3080$ Å. (Bismuth content $= 10^{-2}$.)

very large amounts of bismuth since the concentration quenching is observed only for $c > 6 \times 10^{-2}$.

The thermal activation energy W is calculated from the energetic yield η by the Mott and Seitz formula

$$\eta = (1 + C e^{-W/KT})^{-1},$$

where C is constant and K is the Boltzmann constant. The representation of $\log [(1/\eta) - 1]$ as a function of $1/T$ is a straight line. Its slope gives $W = 0.38$ eV in the quenching range with $T > 300$°K.

Bi^{3+} Transitions

It is well known that the fluorescent properties of Bi^{3+} activated phosphors are generally due to electronic transitions of Bi^{3+}. As for other mercury-type ions, the configuration is $6s^2$ in the ground state and $6s6p$ in the first excited state. The energy levels are represented on Fig. 5. Only $^1P_1$ and $^3P_1$ lead to allowed transitions, $^3P_2$ and $^3P_0$ are metastable (*4*).

$LaGaO_3(Bi)$ presents a large analogy with $La_2O_3(Bi)$. Indeed, it can be seen on Fig. 6 that the shape and position of the excitation peaks are quite the same in both phosphors. So is the temperature dependence of the emission intensity. But the fluorescences do not peak at the same wavelength. The Stokes shift is much smaller in $LaGaO_3(Bi)$ ($\Delta = 0.78$ eV) than in $La_2O_3(Bi)$ ($\Delta = 1.40$ eV). It may be due to the difference in structure between the two hosts (hexagonal La_2O_3 and perovskite $LaGaO_3$) and in the nature of La–O bonds.

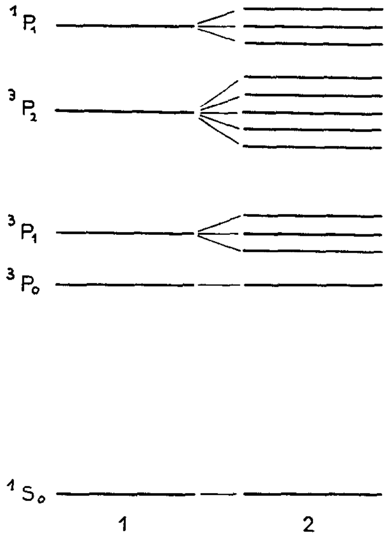

FIG. 5. Energy levels of Bi^{3+} ion. 1—free ion; 2—Bi^{3+} ion in a C_1 symmetry site.

So we assign the main excitation band at $\lambda = 3070$ Å to the $^1S_0 \rightarrow {}^3P_1$ transition. The short wavelength excitation range may be associated either to a single transition $^1S_0 \rightarrow {}^1P_1$ or to a mixture of both transitions $^1S_0 \rightarrow {}^1P_1$ and $^1S_0 \rightarrow {}^3P_2$. The ultraviolet emission corresponds to $^3P_1 \rightarrow {}^1S_0$, the $^1P_1 \rightarrow {}^3P_1$ transition being radiationless.

Spectral Resolution

In the $LaGaO_3$ crystal, the point symmetry of bismuth site is triclinic C_1. Figure 5 shows the expected splitting of excited levels in this symmetry.

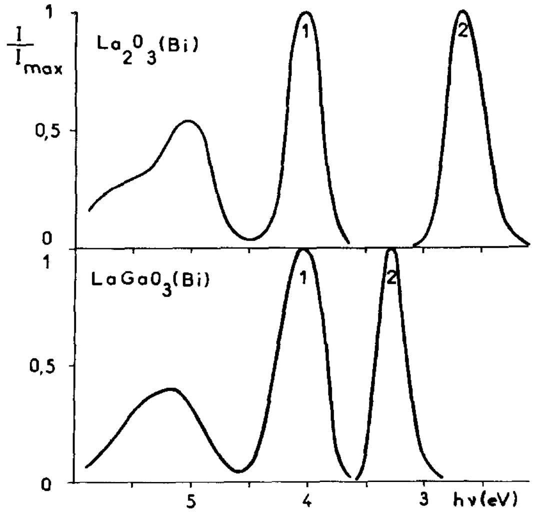

FIG. 6. $La_2O_3(Bi)$ compared with $LaGaO_3(Bi)$. 1—Excitation spectra; 2—Fluorescence spectra.

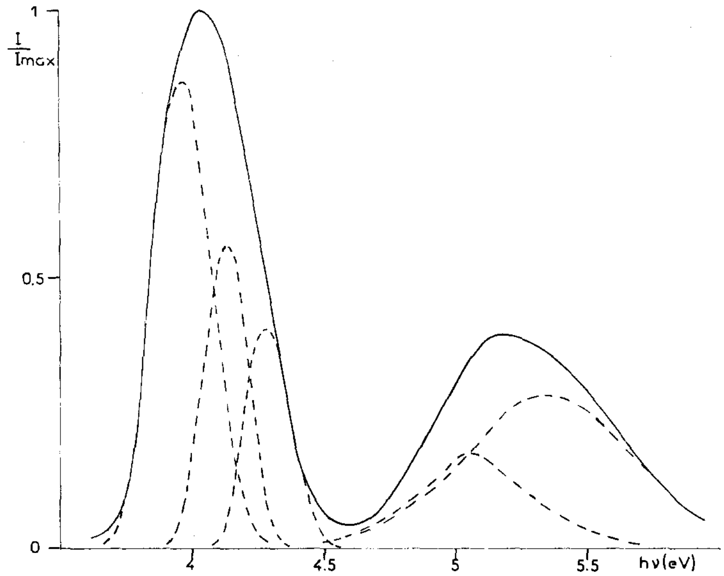

FIG. 7. Gaussian analysis of excitation spectra of $LaGaO_3$(Bi) at $T = 77°K$.

We have tried to resolve excitation and emission spectra when intensity is plotted vs frequency.

It is well known that harmonic vibrations of the O^{-2} ions around the activator lead to gaussian bands (*7*).

$$I(h\nu) = I_0(h\nu_0)\, e^{-A(h\nu - h\nu_0)^2},$$

A is a constant and $h\nu_0$ the quantum corresponding to the maximum.

On Fig. 7, the main excitation band of $LaGaO_3$(Bi) is resolved in three components at 3.96, 4.12 and 4.29 eV in agreement with the expected levels of Fig. 5.

The ultraviolet fluorescence peak may be resolved in two gaussian curves at least with maxima at 3.13 and 3.31 eV (Fig. 8). They might be associated to $(^3P_1)^1 \rightarrow {}^1S_0$ and $(^3P_1)^2 \rightarrow {}^1S_0$ transitions. This assignment seems to be confirmed by an anomalous temperature variation of the emission bandwidth at half-maximum intensity.

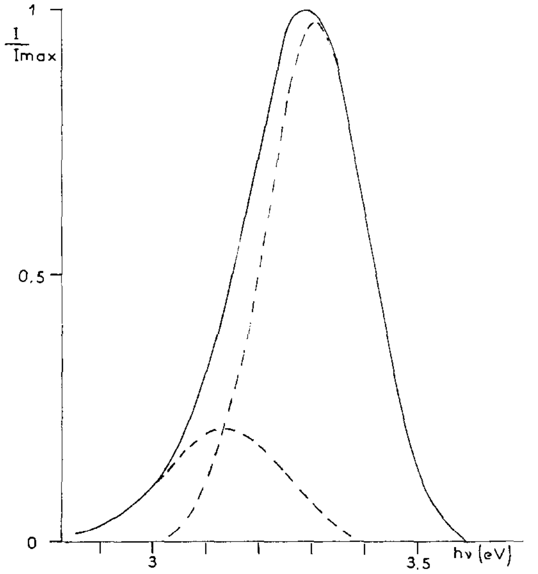

FIG. 8. Gaussian analysis of spectral energy distribution curve of $LaGaO_3$(Bi) at $T = 77°K$.

Time Life of Excited Levels

The decay times of the phosphor have been measured at various temperatures. The results are reported in Table I. We observe a very large increasing of the τ value with decreasing temperature. As for other Bi^{3+} activated phosphors, the $\tau(T)$ and $I(T)$ functions are not proportional (*4*). We think that this large increasing is due to the metastable $^3P_0$ level which traps the electrons from $^3P_1$. This trapping characteristic of the Bi^{3+} ion has been confirmed by our thermoluminescence measurements on some Bi^{3+} activated phosphors (*8*).

TABLE I

τ VALUES AT VARIOUS TEMPERATURES WITH $\lambda_{exc} = 3050$ Å AND $\lambda_{em} = 3800$ Å

T°K	77	153	213	273	295
τ (μsec)	210	6.1	1.3	0.7	0.28

At room temperature, τ is equal to 0.28 μsec. Referring to our previous work on La_2O_3(Bi) (*4*), the fluorescence probability f_{12} is greater than 10^7 sec^{-1} and can then correspond to the electric dipolar transition $^3P_1 \rightarrow {}^1S_0$. For such a transition, τ is given by the formula:

$$\tau = \frac{1}{f_{21}} = 1.5 \times 10^{-16} \frac{g_2}{g_1} \cdot \frac{g_n}{(\eta^2 + 2)^2} \cdot \frac{{\lambda_0}^2}{f}$$

with g_1 $(^1S_0) = 1$; g_2 $(^3P_1) = 3$; $n^4 \simeq 6$; $f \simeq 0.2$ and $\lambda_0 = 3070$ Å.

The calculated value, $\tau = 0.28$ μsec, well agrees with the experiment.

So, in $LaGaO_3$(Bi), the intracenter Bi^{3+} luminescence process is quite the same as in La_2O_3(Bi).

IV. Conclusion

The luminescence properties of Bi^{3+} activated lanthanum gallate possessing perovskite structure present a large analogy with those of La_2O_3(Bi). In both phosphors, excitation and fluorescence bands are due to Bi^{3+} center transitions between the ground state $^1S_0$ and the excited levels $^3P_1$ and $^1P_1$ while the metastable level $^3P_0$ is merely a trap for the electrons at low temperature.

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