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Ultraviolet Luminescence of Ternary Compounds (La, Al, Ce)F_3[1]

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Luminescence of trivalent metal fluorides activated by Ce^{3+} ion has been reported by several authors.[2-4] Emission due to the Ce^{3+} center was found in the ultraviolet and/or the blue region. In these papers, however, descriptions were made only on pure CeF_3 and on binary fluorides containing CeF_3. Relations between the preparing conditions of the phosphors and their luminescence efficiency were not mentioned.

We prepared ternary (La, Al, Ce)F_3 phosphors by solid state reaction at high temperatures and found the best composition and firing conditions for these phosphors. Reflection, excitation and emission spectra were also measured.

Experimental

LaF_3 (99.999%), CeF_3 (99.99%) and other rare earth fluorides were obtained from Shin-etsu Chemical Company. AlF_3 was a C.P. reagent of Amend Drug and Chemical Co. The weighed materials were dry-mixed, placed in ceramic crucibles and fired in air for 30 min at 800°C. Firing above or below 800°C resulted in much poorer efficiency. The chemical composition of the finished phosphors was approximately the same as that before firing. X-ray diffraction data showed that the phosphors consist of two tysonite phases, one having a lattice constant slightly smaller than LaF_3, the other having a lattice constant slightly larger than CeF_3. AlF_3 diffraction lines were very weak. Thus, under the preparing conditions mentioned above, LaF_3 and CeF_3 seem to react poorly, whereas AlF_3 appears to be dissolved almost completely into two tysonite phases.

Spectroscopic measurements were made with a Perkin-Elmer Model E-1 spectrometer. A deuterium discharge lamp was used as a light source for reflection and excitation measurements. Photoluminescence was excited by 2537 Å Hg line from a low pressure mercury lamp.

Results and Discussion

Figure 1 shows the emission spectra of ($La_{0.5}Al_{0.3}Ce_{0.2}$)F_3 at 300 and 77°K. In the former, the peak is located at 2860 Å. In the latter, two well-separated peaks are observed with an energy separation of about 2000 cm^{-1}, which is close to the splitting of the ground state in a Ce^{3+} free ion, 2253 cm^{-1}. In the (La, Al, Ce)F_3 system, the feature of the emission spectrum does not depend on the chemical composition, but it shifts to the longer wavelength region when La is replaced by Y. For example, ($Y_{0.5}Al_{0.2}Ce_{0.3}$)F_3 has its emission peak at 2933 Å at 300°K.

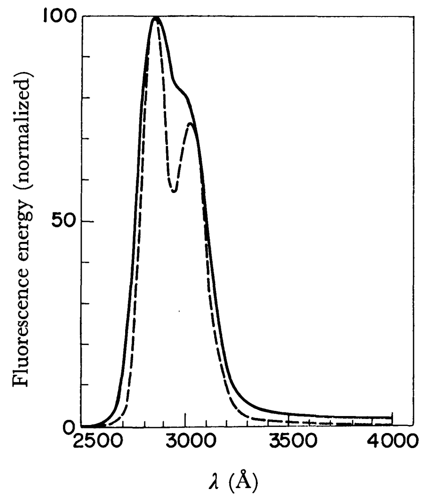

Fig. 1. Emission spectra of ($La_{0.5}Al_{0.3}Ce_{0.2}$)F_3 phosphor under 2537 Å excitation.
———: 300°K, - - - - - -: 77°K

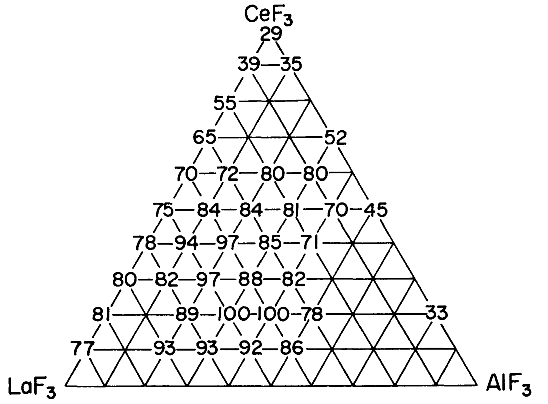

Fig. 2. Relative fluorescence efficiency of (La, Al, Ce)F_3 system.

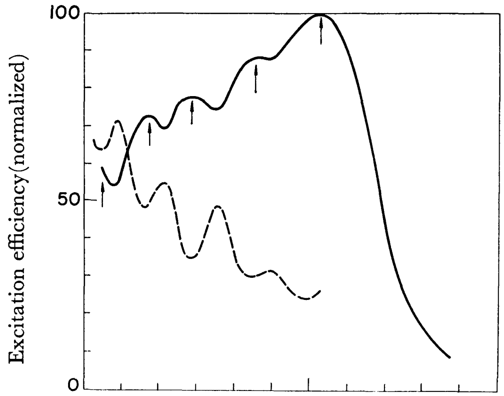

Fig. 3. Excitation and reflection spectra of ($La_{0.5}Al_{0.3}Ce_{0.2}$)F_3.
———: Excitation, ———: Reflection

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[1] Paper presented at the 26th Annual Meeting of the Chemical Society of Japan, Phosphor Section, 1972.

[2] F. A. Kroeger and J. Bakker, *Physica*, **8**, 628 (1941).

[3] J. H. Gisolf, F. A. Kroeger, and J. Bakker, U. S. 2450548 (1948).

[4] G. Blasse and A. Bril, *J. Chem. Phys.*, **51**, 3252 (1969).

Figure 2 shows the fluorescence efficiency of (La, Al, Ce)F_3 as related to phosphor compositions. The maximum efficiency is obtained for $(La_{0.5}Al_{0.3}Ce_{0.2})F_3$ and $(La_{0.4}Al_{0.4}Ce_{0.2})F_3$, which have 20% more output than the best binary solid solution $(La_{0.8}Ce_{0.2})F_3$.

Figure 3 shows the excitation as well as the diffuse reflection spectrum at 300°K. The excitation spectrum is similar to that reported by Blasse and Bril.[4] In the present spectrum, however, five bands are identified with the peaks at 1950 (51280 cm^{-1}), 2070 (48300 cm^{-1}), 2190 (45660 cm^{-1}), 2350 (42540 cm^{-1}), and 2535 (39520 cm^{-1})Å, the energy splittings between the sequent peaks being 2980, 2640, 3120, and 3020 cm^{-1}, respectively.

In the treatment of the $5d$ excited state of Ce^{3+}, the spin-orbit interaction is usually neglected and only the crystal field splitting is considered.[5,6] This approximation seems to be justified also in the case of (La, Al, Ce)F_3, since the spin-orbit coupling energy, which is 2489 cm^{-1} with the coupling constant $\zeta_{5d}=995.6$ cm^{-1} [7] in a free Ce^{3+} ion and is expected to become smaller by several tens of per cent in the crystal,[8] is too small to account for the splitting observed in the excitation and reflection spectra. The space group of tysonite structure is D_{3d}, in which the cation occupies the site with C_2 symmetry.[9] Hence, the $5d(^2D)$ state splits into five Kramer's doublets. This is in agreement with the observation.

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