SPECTRAL STRUCTURES OF Al₂O₃ AND BeAl₂O₄ ACTIVATED BY Eu^{2+} *

SHI Chun-shan (石春山), MAN Shi-qing (满石清)

AND SUN Jia-yao (孙家跃)

(*Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, PRC*)

The $f \to f$ electronic emission of Eu^{2+} with configuration of $4f^7$ can bring about laser generation. Some of Eu^{2+}-activated crystals which can produce sharp line emission, are candidates for visible solid-state laser at shorter wavelengths because their threshold is low and accumulated energy high.

A necessary condition for bringing about $f \to f$ emission of Eu^{2+} is that the lowest $4f^6 5d$ level of Eu^{2+} is situated above the lowest excited $4f$ level ^6P_J, which requires host materials to meet some conditions in crystallography and spectrography. For this reason many scholars present correlative criteria from all sides[1 — 3]. Up to now, it has been found that there are several hundred Eu^{2+}-activated compounds in which the $f \to f$ line emission of Eu^{2+} has been observed. They are mostly compound fluorides, a few are oxides but simple-component oxides have not been reported yet.

A lot of experimental facts show that there are two factors that influence the spectral structure of Eu^{2+}, i.e. the strength of the crystal-field at the sites of Eu^{2+}, and the degree of covalence bond between Eu^{2+} and ligand. The type of electronic transition emission is determined by the dominator of the two factors.

I. EXPERIMENTAL

1) Starting materials. Al_2O_3, spectrographic-grade; BeO, AR and EuF_2 made by ourselves[4].

2) Sample preparation. $Al_2O_3 : Eu^{2+}$ and $BeAl_2O_4 : Eu^{2+}$ were prepared by high-temperature solid-state reaction. Al_2O_3, EuF_2 and Al_2O_3, BeO, EuF_2 were mixed and then placed in a graphite crucible, which was heated at high temperature for 6 h under the protection of nitrogen atmosphere. The resulting phosphor cakes were cooled to room

temperature, ground, then kept in a vacuum desiccator.

3) Measurements. The crystal structures of the phosphor prepared were determined by an X-ray diffractometer (Model D/MAX-II B Rigaku , Japan). All excitation and emission spectra were recorded by using a Hitachi Model MPF-4 fluorescence spectrophotometer.

II. Results and Discussion

(1) Crystal structure

The results of the analysis show that all of the phosphors prepared are single phase with definite structures. The crystallographic data obtained accord with those of ASTM 10-173 and 10-82 phases.

Al_2O_3 heated at 1300°C belongs to $\alpha\text{-}Al_2O_3$ trigonal system. Space group $R\bar{3}C$; hexagonal lattice constants: $a_H = 4.758$ Å, $c_H = 12.991$ Å. Oxygen ions are arranged into A_3 close-packed structure, represented by the symbol $\cdots ABAB \cdots$. Two-thrids of the interstices between the oxygen ions are filled with Al^{3+} ions. Three sites are filled by two Al^{3+} ions. There are three kinds of filling ways. The three arrangements of layers containing Al^{3+} ions are represented by symbol, C', C'', and C''' respectively. These layers are inserted into AB or BA oxygen close-packed ones in proper order. Along c_H axis, this arrangement may be represented by $\| AC' \ BC'' AC''' BC' \ AC'' BC''' \|$. Eu^{2+} occupies the Al^{3+} site in Al_2O_3 host, which produces an excess negative charge. It can be compensated by producing an O^{2-} vacancy, causing the part of matrix structure to distort. Because F^- has one negative charge and O^{2-} has two, the compensating charge can also be effected by replacing O^{2-} with F^- while EuF_2 is used as an activator. The latter can avoid the distortion in the crystal lattice.

$BeAl_2O_4$ belongs to olivine crystal class, orthorhombic system ($a = 9.404$ Å, $b = 5.476$ Å, $c = 4.427$ Å), and space groups is P_{nma}, the number of molecules in the unit cell is 4. Oxygen ions are arranged into distorted hexagonal closest-packed structure. Be^{2+} are in the octahedral holes of oxygen ions, and Al^{3+} in the tetrahedral holes. For the octahedral site, there are two kinds of symmetry: one is inversion symmetry (C_I), Al_I^{3+}, and the other mirror plane symmetry (C_s), Al_{II}^{3+}.

From ionic radius, Eu^{2+} should occupy octahedral site, while from the crystal-field stabilization energy, Eu^{2+} should occupies both of octahedral and tetrahedral sites with the crystal-field stabilization energies of $CFSE = 0.4\Delta_0$ and $CFSE = 0.6\Delta_t = 0.267\Delta_0$, i. e. the crystal-field stabilization energy is $4D_q$ when Eu^{2+} occupies the octahedral lattice site, and is $2.67D_q$ when Eu^{2+} occupies tetrahedral lattice site. Now we see that the octahedral site is

favourable for Eu^{2+}. When Eu^{2+} get into the octahedral site, Be^{2+} which are equal in amount to Eu^{2+} are replaced by Al^{3+} in order to meet the needs of charge balance.

(2) *Spectral structure*

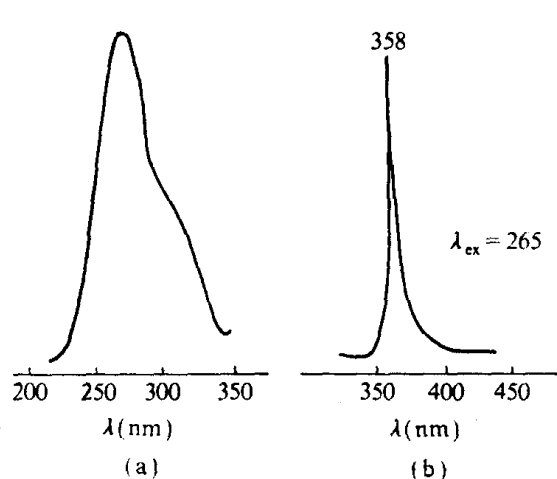The excitation and emission spectra of Eu^{2+} in Al_2O_3 and $BeAl_2O_4$, measured at 300 K are shown in Figs. 1 and 2, respectively.

Fig. 1. Excitation spectrum (a) and emission spectrum (b) of $Al_2O_3 : Eu^{2+}$ (300 K).

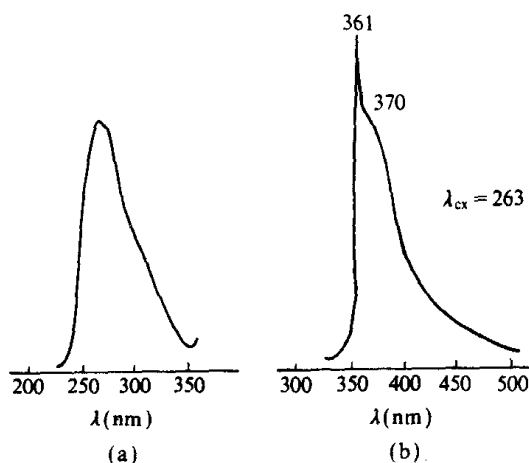Fig. 2. Excitation spectrum (a) and emission spectrum (b) of $BeAl_2O_4 : Eu^{2+}$ (300 K).

In Figs. 1 and 2, the $f \rightarrow f$ sharp line emission of Eu^{2+} is observed, and in the latter, $d \rightarrow f$ band emission of Eu^{2+} also observed. In order to explain the above spectral facts it is necessary to consider the crystal-field strength and the covalent interaction of $Eu - O$ bond at the same time.

The $4f$ electrons of Eu^{2+} are well shielded by $5s^2\ 5p^6$ configuration, so the ^6P_J levels of Eu^{2+} are not much influenced by the environment, while the $5d$ electrons in naked state are strongly influenced by the crystal-field. The environments have double influences on the luminescence properties of Eu^{2+}. The location of $4f^6 5d$ centroid of Eu^{2+} is determined by the surrounding ions or ligands (nephelauxetic effect); and the crystal-field splitting of the $5d$ level depends on the properties and distribution of these ions or ligands. The nephelauxetic effect is given by[5]

$$1 - \beta = k \cdot h.$$

The larger the product of k and h, the stronger the nephelauxetic effect $(1 - \beta)$ between the centre ion and the ligand. This implies that the covalent degree of chemical bond is strengthened. For $Eu - O$ bond, the stronger the covalence, the lower the centroid of $5d$ energy. There are $Eu - O - M$ bonds in Eu-doped compounds (M is metal ion). The h value of O^{2-} depends on the properties of the meta-position cation (M) in a large degree. When M

is a smaller, higher-charged metal ion or radical, h decreases, conversely, h increases. According to Sanderson's principle of electronegativity equalization[6], the partial charge on europium in EuO, Al_2O_3 : Eu^{2+} and $BeAl_2O_4$: Eu^{2+} can be calculated, by which the ionic blending coefficient t_i can also be calculated.

There is no electronegativity value of europium (S_{Eu}) in Sanderson's scale, so we replace the nonpolar covalent radius by the metal radius, 2.04 Å. And the relative radius of europium atom to zero charge is calculated by interpolation and extrapolation, 2.07 Å. Then

$$S_{Eu} = D_{Eu}/D_{iEu} = (r_{iEu}/r_{Eu}) = (2.07/2.04)^3 = 1.05,$$

where D_{Eu} and D_{iEu} are the average electronic densities of europium and relative radius of europium to zero charge. The partial charge on metal atom in the compounds is defined as

$$M_{p.c} = \frac{S_{int} - S_M}{2.08\sqrt{S_M}},$$

where S_{int} is the electronegativity of the compound. The calculation results are listed in Table 1.

Table 1

Partial Charge on Eu and Ionic Blending Coefficient of Eu — O Bond

Compound	Partial Charge on Eu^{2+}	Ionic Blending Coefficient of Eu — O(%)
EuO	0.60	30
$BeAl_2O_4$: Eu^{2+}	1.18	59
Al_2O_3 : Eu^{2+}	1.24	62

In $BeAl_2O_4$: Eu^{2+} and Al_2O_3 : Eu^{2+}, a few of Al^{3+} are replaced by Eu^{2+} and most of Al^{3+} and Be^{2+} are around Eu^{2+} when Eu^{2+} are doped into the crystal-lattice. Because there are smaller, higher-charged and higher-electronegative metal ions, Al^{3+} and Be^{2+}, the nephelauxetic effect of oxygen ions will be weakened, i.e. the covalent interaction of Eu — O bond is weakened. When Eu^{2+} get into the six-coordinated Al^{3+} sites, the crystal-field effect is strong, but the polarizing power of Al^{3+} and Be^{2+} can cut down the covalency of Eu — O bond, make the centroid of $4f^6 5d$ of Eu^{2+} lifted, and cause the lowest $4f^6 5d$ level of Eu^{2+} situated above the lowest excited $4f$ level P_J. So $f \to f$ emission can be observed.

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