Crystal Structure and Fluorescence Properties of $R_2Zr_2O_7$ and $(R_{1-x}Eu_x)_2Zr_2O_7$ Compounds

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$R_2Zr_2O_7$ と $(R_{1-x}Eu_x)_2Zr_2O_7$ の結晶構造と蛍光特性

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$R_2Zr_2O_7$ and $(R_{1-x}Eu_x)_2Zr_2O_7$ ($R=La, Pr, Sm, Eu, Gd, Tb, Er, Y$) were prepared at 1600°C in air and their fluorescence properties were studied. The crystal structures of these compounds were pyrochlore-type for the light rare earths and CaF_2 -type for the heavy rare earths, respectively. However, $Gd_2Zr_2O_7$ and $Y_2Zr_2O_7$ showed broad and small (111) X-ray diffraction peaks which were characteristic of the pyrochlore-type structure. Further, annealing at 1500°C increased the intensity and the sharpness of the (111) peak of $Gd_2Zr_2O_7$. When the compounds were excited by the 254 nm line, only the Eu-doped $La_2Zr_2O_7$, $Gd_2Zr_2O_7$, and $Y_2Zr_2O_7$ showed emission spectra due to Eu^{3+} ions. These spectra and X-ray diffraction, showed that in $La_2Zr_2O_7$ almost all rare earth ions occupy D_{3d} symmetry sites, but in $Y_2Zr_2O_7$ and $Gd_2Zr_2O_7$ most rare earth ions occupy most of the O_h symmetry sites and partially the D_{3d} sites.

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1. Introduction

The preparation and crystal structures of $R_2Zr_2O_7$ (R : rare earth element) have been studied by many investigators.¹⁾⁻³⁾ The crystal structure of $R_2Zr_2O_7$ was the pyrochlore structure (space group $Fd\bar{3}m$) for the light rare earths and the fluorite-type structure (space group $Pm\bar{3}m$) for the heavy rare earths.

The emission spectra for the pyrochlore-type compounds have been reported by McCauley et al.,²⁾ and discussed on the view point of deviation from the strict O_h symmetry. However, there are some ambiguity in the assignment of emission peak.

In this study, $R_2Zr_2O_7$ and $(R_{1-x}Eu_x)_2Zr_2O_7$ are prepared and their fluorescence properties are investigated.

2. Experimental procedure

Rare earth oxides, Y_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Er_2O_3 (purity 99.9%) and zirconium oxides (purity 99.5%) were used as the starting materials. They were mixed in the desired ratio and pressed into pellets. The $R_2Zr_2O_7$ were synthesized by heating

the pellets at 1600°C in air for 12h.

The phase of products was examined by using X-ray diffractometry with $CuK\alpha$ radiation. The lattice constants were determined by using silicon as an internal standard. Magnetic measurements were carried out using a magnetic torsion balance in the temperature range from 77 to 700 K. The fluorescence spectra were measured at room temperature and liquid nitrogen temperature.

3. Results and discussion

3.1 Crystal structure

The X-ray powder diffraction patterns of $R_2Zr_2O_7$ were completely indexed on the basis of the pyrochlore-type structure for $R=La-Eu$, and the CaF_2 -type structure for $R=Gd-Er$. In the case of $R=Y$, the structure seemed to be pyrochlore-type from X-ray diffraction patterns, but the intensities of reflections such as (111), (331), (511) were rather weak.

The lattice constants of $R_2Zr_2O_7$ are shown in Fig. 1. In this figure, lattice constants of $R_2Zr_2O_7$ ($R=Gd-Er$) with fluorite-type structure were plotted as twice the actual values. The closed and open circles indicate the obtained and reported

values, respectively. The obtained values were in good agreement with the reported ones and the values decreased monotonously with increasing the atomic number of rare earth element, indicating that the rare earth ions were trivalent in these compounds.

In $Gd_2Zr_2O_7$, which was prepared at 1600°C , the intensities of X-ray diffraction peaks corresponding to the pyrochlorite-type structure were found and they increased with annealing time at 1500°C as shown in Fig. 2.

In the pyrochlorite-type structure (space group $Fd\bar{3}m$), the two kinds of cation are differently

Fig. 1. Lattice constants of $R_2Zr_2O_7$.

Fig. 2. The intensity ratio of (111) peak due to pyrochlorite-type to (222) peak due to both pyrochlorite and CaF_2 -type vs. annealing time at 1500°C .

Fig. 3. Oxygen coordination for R and Zr in $R_2Zr_2O_7$ with pyrochlorite-type structure.

coordinated by oxygens as shown in Fig. 3. The R ions are coordinated by six equally spaced oxygen and two additional axial oxygen at a slightly shorter distance. On the other hand, the smaller zirconium ions were located at the center of trigonal antiprisms with six oxygen at equal distances. The site symmetry is D_{3d} for both kinds of cations.

3.2 Magnetic properties

The $R_2Zr_2O_7$ compounds were paramagnetic above 77 K, and the temperature dependence of inverse susceptibilities obeyed the Curie-Weiss law. The effective magnetic moment of $R_2Zr_2O_7$ is shown in Fig. 4. The solid line indicates the calculated values for the R^{3+} ions. The observed effective magnetic of $R_2Zr_2O_7$ were in good agreement with the calculated for R^{3+} , indicating that the rare earth ions were trivalent.

Fig. 4. Effective magnetic moments of $R_2Zr_2O_7$ compounds.

Fig. 5. Emission spectra of $(R_{0.98}Eu_{0.02})_2Zr_2O_7$ ($R = Y, \text{La and Gd}$).

Fig. 6. Effect of heat-treatment on emission spectra of $(R_{0.98}Eu_{0.02})_2Zr_2O_7$ ($R=Y, La$ and Gd).
(a) $R=Y$, (b) $R=La$, (c) $R=Gd$

3.3 Fluorescence properties

The $R_2Zr_2O_7$ showed no emission at both room temperature and liquid nitrogen temperature when excited at 254 nm. However, the samples, in which 2% of R was substituted by Eu , exhibited the fluorescence peak only for $R=La, Gd, Y$. The results are shown in Fig. 5.

When Eu^{3+} ions are located in the center of inversion symmetry, the electric dipole (E.D.) transitions are forbidden and the magnetic dipole (M.D.) transitions are allowed. However, the former transitions would be possible when they are coupled with vibration modes of the host lattice, as in the case of the compounds with the pyrochlorite-type structure.

The M.D. transitions did not split in the O_h symmetrical electric fields, but split into two lines in the D_{3d} fields. The emission peaks at 590–610 nm in Fig. 5 were due to the M.D. transition from 5D_0 to 7F_1 . The emission peaks at 610–630 nm were due to the electric dipole transitions from 5D_0 to 7F_2 .⁴⁾⁻⁶⁾ The M.D. transitions were observed in all these compounds. The splitting width of the M.D. transition levels decreased with decreasing the ionic radius of R^{3+} ions, indicating that the distortion from a cubic O_h symmetry decreased with decreasing the ionic radius of R^{3+} ion. The intensity ratio of the M.D. to the E.D. transitions decreased when the ionic radius of R^{3+} ion decreased.

The present results indicate that the rare earth ions in $(La_{0.98}Eu_{0.02})_2Zr_2O_7$ are almost located in

the D_{3d} symmetry, but in $(Y_{0.98}Eu_{0.02})_2Zr_2O_7$ and $(Gd_{0.98}Eu_{0.02})_2Zr_2O_7$ most of rare earth ions located in the O_h symmetry and partially in the D_{3d} symmetry.

3.4 Effect of heat-treatment on the emission spectra

The emission spectra of $(R_{0.98}Eu_{0.02})_2Zr_2O_7$ ($R=Y, La, Gd$) are shown in Fig. 6. The solid and dashed lines indicate the emission spectra for samples quenched from 1600°C and those for samples heated at 1600°C and followed by annealing at 1500°C, respectively. In both $(La_{0.98}Eu_{0.02})_2Zr_2O_7$ and $(Y_{0.98}Eu_{0.02})_2Zr_2O_7$, the quenched and annealed samples showed no change in emission spectra. However, in $(Gd_{0.98}Eu_{0.02})_2Zr_2O_7$ the E.D. transitions decreased by annealing at 1500°C. These results were well corresponded with the results shown in Fig. 2. The larger distortion from cubic O_h symmetry was occurred by annealing at 1500°C and rare earth ions tended to occupy the D_{3d} symmetry sites.

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