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Preparation of the Phosphors $BaAl_2O_4$:Eu, RE (RE=Dy, Ho) by Microwave Heating Technique and Observation of Long Phosphorescence

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Abstract: The phosphors $BaAl_2O_4:Eu^{2+}$, RE (RE=Dy, Ho) have been prepared by the microwave heating technique. The long-lasting phosphorescence in the phosphors of the barium aluminate activated with europium and other rare earths has been observed for the first time.

Keywords: Barium aluminate; microwave heating technique; europium(II); Phosphorescence.

The $MAl_2O_4:Eu^{2+}$(M=Ca, Sr, Ba) have been known to be excellent phosphors under ultraviolet and cathode-ray excitation[1-3]. Studies on the phosphors were mostly performed in 1960s and early 1970s mainly for lamp and cathode-ray tube application. In 1990s the phosphor $SrAl_2O_4:Eu^{2+}$ has been found to be able to maintain its afterglow for a fairly long duration[4-6]. In these reports, $MAl_2O_4:Eu^{2+}$ were prepared mainly by a high temperature solid state method, which expended quite long reaction time of 2- 4 h at a high temperature of 1200~1500℃in a reducing atmosphere and consumed a great deal of energy. In this paper, we report the preparation of the phosphors of the barium aluminate activated with europium and other rare earths by the microwave heating technique and the observation of the long phosphorescence of the phosphors $BaAl_2O_4:Eu^{2+}$, RE (RE=Dy, Ho) for the first time.

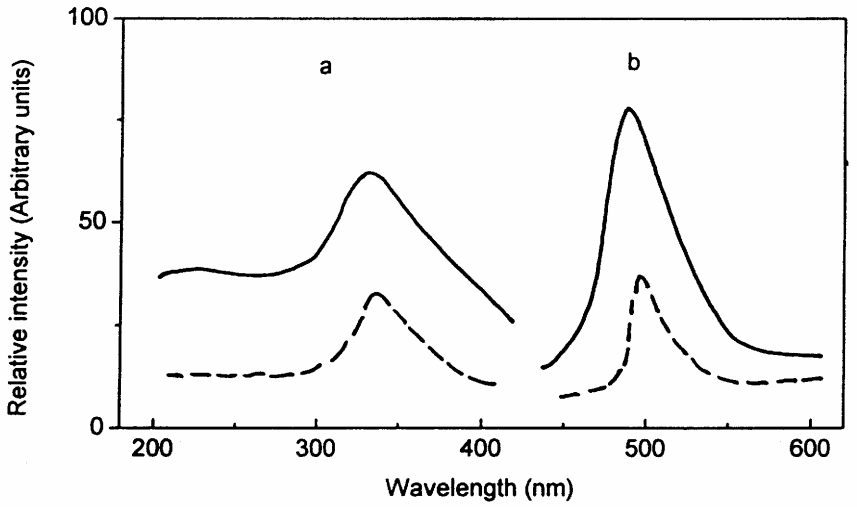
All chemicals are of analytical grade except the activator compounds, which are high purity (4N). The phosphors $BaAl_2O_4:Eu^{2+}$, RE are prepared from starting compositions consisting of $BaCO_3$, Al_2O_3, H_3BO_3, and Eu_2O_3 and RE_2O_3 (RE=Dy, Ho). The mole ratio of $BaCO_3$ and Al_2O_3 is 1:1 with 5 mol% H_3BO_3 per mole host as a flux. The concentration of europium is varied from 0.5 to 8 mol% per mole host by adding Eu_2O_3 and the concentrations of dysprosium and holmium are changed from 0.5 to 5 mol% per mole host by adding RE_2O_3. The starting compositions are well mixed by an agate mortar and pestle by adding ethyl alcohol. The mixture is placed in a covered alumina crucible and this crucible is placed into a larger covered alumina crucible. The spacing between the crucibles is filled with ferric oxide and active carbon to absorb microwave to heat the mixture and to avoid the oxidation of the products in the heating process. The crucible with chemicals is placed in a microwave oven to react about 40 minutes. Then the product is cooled to room temperature and rinsed with deionized water

and ethyl alcohol. After being dried at 100℃ for a couple of hours, final phase is checked with a conventional X-ray diffraction technique and the spectra of the phosphors are recorded at room temperature by Hitachi Model MPF–4 Fluorescence Spectrophotometer with 150W xenon lamp and the decay curves of the phosphorescence are measured by the direct current ammeter with a photronic cell receiving current signals.

Heating to materials by the microwave radiation energy depend on partly the dissipation factor of the materials, $tan\delta$, which is defined as the ratio of the dielectric loss (ε") and the dielectric constant (ε'), *i.e.* $tan\delta=\varepsilon"/\varepsilon'$, this indicates the ability of a materials to convert electromagnetic energy into heat energy at a given frequency and temperature. Due to different dielectric loss and dielectric constant for different materials, so microwave has the characteristics of selectively heating materials. For example, some materials such as C and NiO and Co_2O_3 can be heated by microwave radiation to above 1000℃, but some other materials such as CCl_4 and C_6H_{14} and NaCl can not effectively absorb microwave energy, so they can only reach a temperature of 30~80℃[7]. We find that ferric oxide is a good microwave absorber and have sucessfully applied it to prepare the phosphors of the the barium aluminate activated with europium and dysprosium and holmium by microwave heating technique.

The XRD analysis shows that the phosphors prepared by microwave heating technique belongs to the hexagonal structure with the lattice parameter of a=0.5225 nm and c=0.8796 nm. **Figure 1** indicates the excitation and emission spectra of $BaAl_2O_4:Eu^{2+}$,RE (RE=Dy, Ho). According to the definition of the literature[6], here we describe also dysprosium and holmium as the auxiliary activators. Whether the auxiliary activators are added to the phosphors $BaAl_2O_4$:Eu or not, the samples always exhibit broad emission

Figure 1. The excitation (a) and emission (b) spectra of $BaAl_2O_4:Eu^{2+}$, RE (RE=Dy, Ho)
solid line - $BaAl_2O_4:Eu^{2+}$, Dy, Ho dotted line - $BaAl_2O_4:Eu^{2+}$



peak at about 496 nm. The emission and excitation are attributed to the 4f-5d transition of Eu^{2+}. The luminescent properties of the samples are listed in **Table 1**. As seen from **Figure 1**, within the range from 320 nm to 380 nm, the phosphors can be excited effectively and bright blue-green luminescence of Eu^{2+} is observed. It can be seen from **Table 1** and **Figure 1** that both the emission and the excitation and the half height width of Eu^{2+} do not vary with the change of doped rare earth ions in the phosphors. However, relative emission strength of Eu^{2+} in the phosphors is relatived to the type of doped rare earth ions. The experiment results show that the dysprosium and holmium not only can greatly strengthen the luminescence of the phosphors, but also greatly lengthen the afterglow of the phosphors.

Table 1. The luminescence properties of the samples

Samples	Maximum emission /nm	Maximum excitation /nm	Half height width /nm	Relative emission strength
$BaAl_2O_4$:Eu	496	341	62	40
$BaAl_2O_4$:Eu,Ho	496	341	62	85
$BaAl_2O_4$:Eu,Dy	496	341	62	90
$BaAl_2O_4$:Eu,Dy,Ho	496	341	62	100

Figure 2. The curves of phosphorescent decay of the phosphors $BaAl_2O_4:Eu^{2+}$, RE (RE=Dy,Ho)
1. $BaAl_2O_4:Eu^{2+}$, Dy, Ho 2. $BaAl_2O_4:Eu^{2+}$, Dy 3. $BaAl_2O_4:Eu^{2+}$, Ho

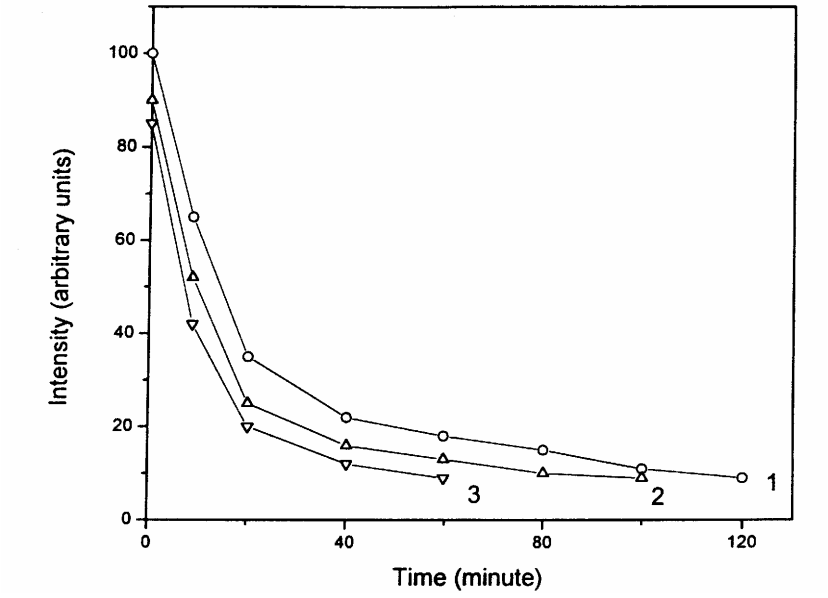


Figure 2 is the curves of the phosphorescence decay of the phosphors. It can be seen from **Figure 2** that the phosphorescence decay is rapid initially and followed by the long persistence of the afterglow after the removal of UV light. There is the longest afterglow for $BaAl_2O_4:Eu^{2+}$, Dy, Ho of the phosphors. The change of the phosphorescence strength of the phosphors with time is in good accordance with the

equation of double-curve ($I \propto t^{-n}$) and the value of n is equal to 1.1~1.2 by fitting the equation with the data from **Figure 2**, which reveals that the decay of phosphorescence of the phosphors belongs to a complex process.

In conclusion, the barium aluminate activated by europium and other rare earths has been prepared by the microwave heating method which is reliable and easy with simple equipments and the reaction time is greatly shortened, so the sources of energy is extremely economized. The very long phosphorescent phosphors $BaAl_2O_4:Eu^{2+}$, RE (RE=Dy, Ho) have been found for the first time. But what is the direct reason to make the phosphors to give off a very long phosphorescence is not clear. Further studies are in progress.

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References

1 G. Blasse and A. Bril, *Philips Res.Reps.* **1968,** *23*, 201.
2 F. C. Palilla, A. K. Levine , and M. R. Tomkus, *J.Electrochem.Soc.* **1968,** *115*, 642.
3 V. Abbruscato, *J.Electrochem.Soc.* **1971,** *118*, 930.
4 Q. M. Song, J. Y. Chen and Z. Y. Wu, *J.Fudan Univer.(Natural Science)* **1995,** *34*, 103.
5 M. D. Tang, C.K.Li, Z. W. Gao, S. H. Xu, X. Y. Jiang and K. Cai, *Chinese J.Lumin.* **1995,** *16***,** 51.
6 T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, *J.Electrochem.Soc.***1996,** *143***,** 2670.
7 D. Michael, P. Mingos and David R. Baghurst, *Chem.Soc.Rev*. **1991,** *20***,** 1.

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