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PHASE DEPENDENCE OF LUMINESCENT EMISSION OF Eu^{2+} DOPED $SrAl_2O_4$

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In this work, we made five samples of $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, the α phase and β phase $SrAl_2O_4$:Eu^{2+},Dy^{3+} powder and pellet samples, and α phase single crystal. We have measured the emission spectra of all the samples. All the emission peaks are around 520 nm, which correspond to the transition from $4f^65d^1(^2E_g)$ to $4f^7(^8S_{7/2})$ of Eu^{2+} in $SrAl_2O_4$ host. The intensity of emission of the β phase is stronger than that of the α phase. We believe that it is because the Eu^{2+} ions have occupied the two types of sites in the α phase $SrAl_2O_4$ host and the lifetime of the transition of Eu^{2+} in the A site is longer than that in the B site. This result also proves that the β phase of the material is brighter than the α phase. In addition, the β phase can be achieved by quenching technique.

PACC: 7855; 7860; 7170C

I. INTRODUCTION

In the area of long persistent materials, there are two major interesting types of hosts, i.e., alkali earth sulfides and aluminates. The rare earth ion doped aluminates have some advantages over the sulfides. Unlike the sulfides, the alkali earth aluminates do not hydrolyze in moisture, and have a slower aging rate when exposed to UV and other radiation.

The material of $SrAl_2O_4$ host doped by Eu^{2+} and Dy^{3+} ions has a very bright brod band emission and after-glow, centered at 520 nm.[1,2] The after-glow of the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} can be longer than 20 h, thus it is a kind of super-long persistent material.[3] Because $SrAl_2O_4$ is a very good host for achieving luminescence, its structural properties have been intensively studied. Its melting point is 1960 ℃.[4] It has two phases. The β phase was clearly found to be a stuffed tridymite structure at high temperature with $a = 0.513$ nm, $c = 0.844$ nm by Blasse *et al.*[5] The α phase was found to be monoclinic. But due to the different selection of the unit cell, the cell constants were reported differently: $a = 1.020$ nm, $b = 2.026$ nm, $c = 0.842$ nm, $\gamma = 60.53°$ by Ito *et al.*[6] and $a = 0.8447$ nm, $b = 0.8816$ nm, $c = 0.5163$ nm and $\beta = 93.4°$ by Schulze *et al.*[7]

The closed inner electron shells shield the 4f outer electrons of the rare earth ions, thus the outer electrons are not sensitive to the local field. But in such exceptional ions as Ce^{3+} and Eu^{2+}, due to the d electron transition from $4f^65d^1$ to ground state[8,9], the field dependency of the emission is fairly strong. The emission peaks of Eu^{2+} in the host of $CaAl_2O_4$, $BaAl_2O_4$, $MgAl_2O_4$ and $SrAl_2O_4$ are found at 440, 460, 470 and 520 nm respectively.[10] The Sr^{2+} ions in the $SrAl_2O_4$ host have two sites, A and B, and thus the Eu^{2+} ions, which substitute for Sr^{2+} cations are in these two different field environment.[11]

We made totally five samples. Four of them are α and β phase powder and pellet samples prepared by solid-solid chemical reaction, the fifth is α phase single crystal made by laser heated pedestal growth (LHPG) method.

II. EXPERIMENTAL

$SrCO_3$ powder and Al_2O_3 powder (99.95% purity with average particle size about 10 μm) were mixed with mole ratio 1:1. Then according to the doping concentration, Eu^{2+}: Dy^{3+}: Sr^{2+}=0.01:0.01:1 (mole), powders of Eu_2O_3 and Dy_2O_3 are added and mixed. The starting materials are pressed into pellet, and then sintered at 1300 ℃ in reduction environment for about 5 h. Powder samples of $SrAl_2O_4$:Eu^{2+},Dy^{3+} are made similarly. The reduction environment is obtained by using the N_2+5%H_2 gas flow, and the environment is required in this case to ensure that all the Eu^{3+} ions in the starting material are reduced to Eu^{2+}.[12,13]

To achieve α the β phase samples, the sintered samples are annealed at 600 ℃ and 800 ℃ respectively. After annealing for 2 h, the samples are quenched. The starting materials of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} could also contain 10% mole of HBO_3, acting as a flux to enlarge the reaction cross section

so as to increase the reaction speed. The formula of the chemical reaction is similar to that without HBO_3:

$$SrCO_3+Al_2O_3+0.005Eu_2O_3 +0.005Dy_2O_3 \overset{HBO_3}{\longleftrightarrow} SrAl_2O_4{:}Eu0.01,Dy0.01+O_2$$

The $SrAl_2O_4:Eu^{2+},Dy^{3+}$ single crystal is made by LHPG method. The seed and feeding rods are made of the starting materials without adding HBO_3 flux, which are pressed and cut into rods with diameter about 1 mm. CO_2 laser is used to heat the rod and seed. The speed of pulling the seed is 1 μm/s, and that of feeding the rod is about 2/3 speed of pulling the seed.[14]

We have measured the emission spectra of the five samples at room temperature. The results are shown in Figs.1—3. In Fig.1 the emission spectra of α and β phases of the powder samples are shown. In Fig.2 the emission spectra of α and β phases of the pellet samples are shown. Emission spectrum of the signle crystal sample is shown in Fig.3. The emission of the β phase of the pellet sample measured at 11 K and 100 K are shown in Fig.4.

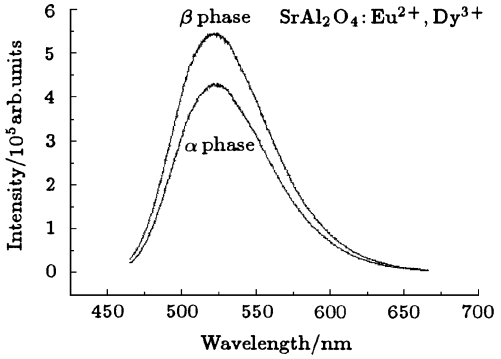


Fig.1. Emission spectra of α and β phase powder $SrAl_2O_4$ samples, measured at room temperature.

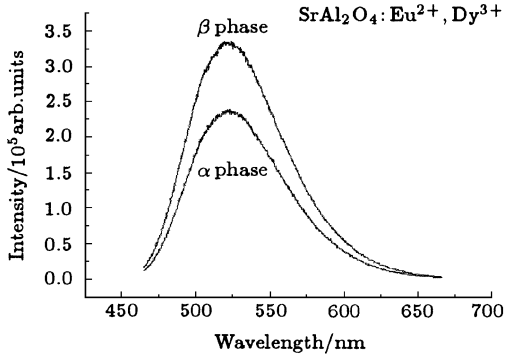


Fig.2. Emission spectra of α and β phase pellet $SrAl_2O_4$ samples, measured at room temperature.

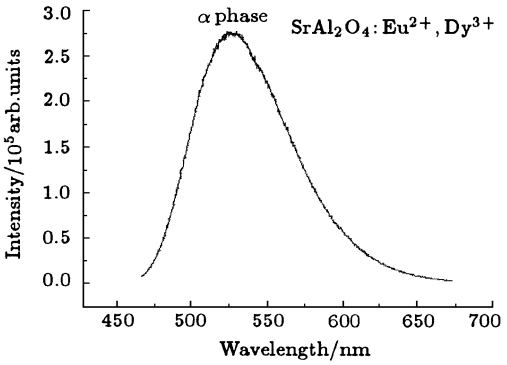


Fig.3. Emission spectra of α phase single crystal $SrAl_2O_4$ sample, measured at room temperature.

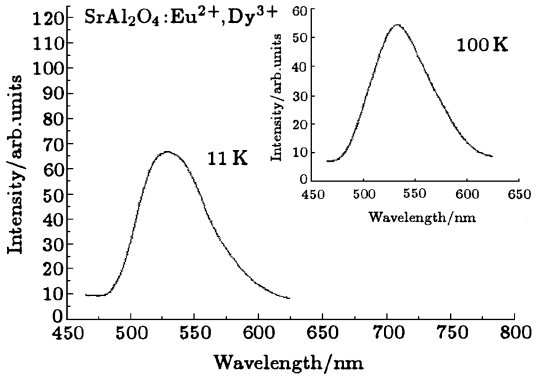


Fig.4. Emission spectra of β phase $SrAl_2O_4$ pellet sample, measured at 11 K and 100 K.

Ⅲ. RESULTS AND DISCUSSION

The structures of AB_2O_4 type materials have been studied for years, which could be labeled as defect perovskite type, tridymite type, $CaFe_2O_4$ type, etc.[15] $SrAl_2O_4$ is found to be monoclinic at low temperature and hexagonal at high temperature. The cell constant of the α phase of $SrAl_2O_4$ is given differently because of the different selection of unit cell.[6,7] We have studied the structure of the $SrAl_2O_4$ by transmission electron microscope and high resolution transmission electron microscope. From the results we obtained we are sure that the structural difference between α and β phases of $SrAl_2O_4$ is due to the small twisting of the atomic sites.[16] We thus conclude that at low temperature the α phase $SrAl_2O_4$ is in a type of modified hexagonal structure. This agrees with the report of

Blasse *et al.*[5,17]

In the $SrAl_2O_4$ host, the Eu^{2+} ion emission transition is the same as that in other host.[18—21] The transition is from the lower energy component (^2E_g) of the $4f^65d^1$ splitting in the crystal field ($^2T_{2g}$ and ^2E_g) to the $4f^7$ ($^8S_{7/2}$) ground state. In the $4f^65d^1$ configuration of the Eu^{2+} ions, spin coupling between the $4f^6$ core and the $5d^1$ electron results in a spin octet state ($5d^1$ electron spin is parallel to the total spin of the $4f^6$ core) and a spin sextet state ($5d^1$ electron spin is anti-parallel to the spin of the $4f^6$ core). Therefore, the $4f^65d^1$ electronic energy state has two different values due to the spin direction. The $4f^65d^1$ energy level of Eu^{2+} sextet is lower than that of Eu^{2+} octet. The emission transition from the Eu^{2+} octet is an allowed electronic dipole transition (typical lifetime is about 10^{-8} s), but the transition from the Eu^{2+} sextet is spin forbidden (lifetime is about 10^{-4}—10^{-6} s).

The emission spectrum of the Eu^{2+} in the α phase $SrAl_2O_4$ host at low temperature has two emission peaks relevant to two sites, as Yuan *et al.* observed (Fig.5). In our emission spectrum of the β phase sample observed at low temperature (Fig.4), shows different emission structure from the α phase. The result supports the fact that Eu^{2+}'s occupy two sites in α phase of the $SrAl_2O_4$ host.[22]

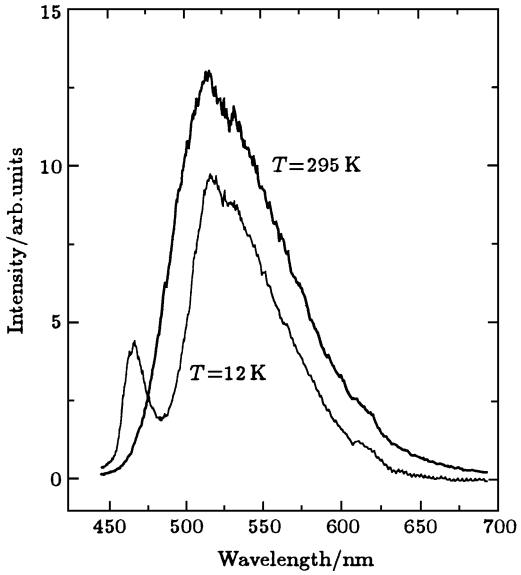


Fig.5. Emission spectra of α phase $SrAl_2O_4$:Eu^{2+}, Dy^{3+} sample, measured at 12 K and 295 K (from Ref.[11]).

From the emission spectra shown in Fig.1, Fig.2 and Fig.3, we can see that all samples' emission peaks are at 520 nm. But comparing the emission spectra of α phase with those of β phase, we find that the emission of Eu^{2+} in β phase host is stronger than in the α phase. The doping concentrations of Eu^{2+} and Dy^{3+} in all the samples are the same.

The explanation for this difference is shown in Fig.6. The sextet Eu^{2+} might have weaker field dependency than the octet one. So the sextet Eu^{2+} in

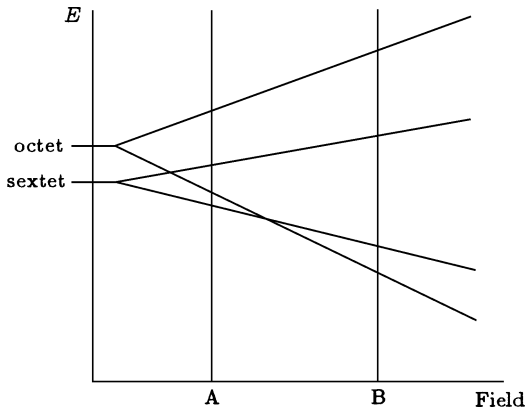


Fig.6. Energy splitting in the crystal field created by A and B sites of the α phase $SrAl_2O_4$ host.

the A site (weaker field) of the α phase host has relatively lower energy than the octet Eu^{2+}, i.e., the sextet Eu^{2+} is highly populated in the A site. The much longer lifetime of the Eu^{2+} emission of sextet in the A site then can be treated as a "flat-trap" that partially traps the excited electrons. Thus the weaker emission intensity of the Eu^{2+} in the α phase host is due to the fact that part of the emitting centers are taken away by the electron "flat-trap" in the A site. According to Blasse's atomic twisting assumption of the $SrAl_2O_4$, the Eu^{2+} site in β phase can be regarded as the same or nearly the same as the B site of the α phase $SrAl_2O_4$ host. In this case, the octet level of the Eu^{2+} is lower than the sextet, thus the emission populated to the lower octet level is initially stronger. Just as mentioned above, the emission of the β phase of $SrAl_2O_4$ being stronger than that of the α phase is due to the longer lifetime of spin sextet of the Eu^{2+} $4f^65d^1$ level in the A site of the α phase $SrAl_2O_4$ host.

IV. CONCLUSION

The α and β phase $SrAl_2O_4$:Eu^{2+},Dy^{3+} samples can be made by thermally quenching the sample at 600 ℃ and 800 ℃. The emission of the β phase sample is more than 30% over the emission of the α phase sample. This is due to the longer lifetime of spin sextet of the Eu^{2+} $4f^65d^1$ level in the A site of the α phase $SrAl_2O_4$ host.

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REFERENCES

[1] V. Abbruscato, *J. Elec. Chem. Soc.*, **118**(1971), 930.

[2] T. Matsuzawa, Y. Aoki, N. Takeuchi *et al., J. Elec. Chem. Soc.*, **143**(1996), 2670.

[3] S. Shionoya, W. M. Yen (Ed. Co-chair), Phosphor Handbook (CRC Press, Boca, Raton, Boston, London, New York, Washington D. C., 1999), p.655.

[4] F. Ganits. T. Yu. Chemekova, Yu. P. Udalov, *Z. Neorg. Khim.*, **24**(2)(1979); *Russ. J. Inorg. Chem.* (*English Trans.*), **24**(2)(1979), 260.

[5] G. Blasse, A. Bril, *Phil. Res. Rep.*, **22**(1967), 481.

[6] S. Ito, S. Banno, K. Suzuki *et al., Z. Fur. Phys. Chem.* (*Neue Folge*), **105**(1997), S173.

[7] Von A. R. Schulze *et al., Z. Anorg. Allg. Chem.*, **475**(1981), 205.

[8] J. L. Sommerdijk, A. L. N. Stevels, *Phil. Tech. Rev.*, **37**(1977), 221.

[9] A. Meijerink, J. Nuyten, G. Blasse, *J. Lumin.*, **44**(1989), 19.

[10] F. C. Palilla, A. K. Levine, M. R. Tomkus, *J. Elec. Chem. Soc.*, **115**(1968), 642.

[11] H. Yuan, Ph. D. Thesis, University of Georgia (1999).

[12] W. Jia, H. Liu, H. Yuan *et al.*, Proc. Sixth Int. Conf. on Lumin. Mat. Paris, Aug. 31, 1997.

[13] M. Pham-Thi, G. Ravaux, *J. Elec. Chem. Soc.*, **138**(1991), 1103.

[14] B. M. Tissue, L. Lu, W. M. Yen, *J. Lumin.*, **45**(1990), 20.

[15] F. P. Glasser, L. S. Dent Glasser, *J. Amer. Ceram. Soc.*, **46**(1963), 377.

[16] D. Jia, B. Wu, Y. Liu *et al.*, Proc. Chinese National MRS Conf., Dec. 1998, p.368 (in Chinese).

[17] G. Blasse, A. Bril, *J. Chen. Phys.*, **47**(1967), 5139.

[18] F. M. Ryan, W. Lehmann, D. W. Feldman *et al., J. Elec. Chem. Soc.*, **121**(1974), 1475.

[19] D. Poelman, R. Vercaemst, R. L. Meirhaeghe *et al., J. Lumin.*, **65**(1995), 7.

[20] T. J. Hsieh, R. Revay, D. Brower, *J. Vac. Sci. Tech.*, **A13**(1995), 2732.

[21] D. S. McClure, Z. Kiss, *J. Chem. Phys.*, **39**(1963), 3251.

[22] M. W. Dougill, *Nature*, **180**(1957), 292.