

## Cr<sup>3+</sup> Emission in Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub> Phosphors

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### ABSTRACT

Combustion synthesis of Cr<sup>3+</sup> activated Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub> phosphors was attempted. XRD results indicated formation of alumina, while luminescence results showed profound changes from Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>. Al<sub>5</sub>SiO<sub>9.5</sub>:Cr<sup>3+</sup> did not show any photoluminescence, while Al<sub>5</sub>GeO<sub>9.5</sub>:Cr<sup>3+</sup> showed very intense luminescence; almost 150% of that shown by Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>.

### I. INTRODUCTION

alpha Alumina  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is a remarkable host material for rare earth ions because it presents excellent mechanical hardness combined with chemical stability and solubility besides a high transparency window from the ultraviolet to the infrared [1]. It plays a major role in many technologies due to its remarkable physical properties, such as a high melting point, hydrophobicity, high elastic modulus, high optical transparency, high refractive index, thermal and chemical stability, low surface acidity, and fine optical and dielectric characteristics [2–4]. The good adhesion to Si surface makes Al<sub>2</sub>O<sub>3</sub> attractive in the microelectronics and optoelectronics [5,6]. Owing to some of these properties, it is also an excellent laser host. The ruby (Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>) is the first crystal found to exhibit a laser emission as demonstrated by Maiman at the Hughes Lab in 1960 [7,8], which marked the beginning of the solid state laser technology. The wide gain and high quantum efficiency of Sapphire

(Al<sub>2</sub>O<sub>3</sub>:Ti) makes this material the optimum ultrafast laser crystal [9].

There are several double oxides involving Al<sub>2</sub>O<sub>3</sub> which might be easily prepared by combustion synthesis using exothermic reaction between aluminum nitrate and urea. From literature, we found two particular formulae quite attractive; viz. Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub>. Both these compounds contain high percentage of alumina. Their structures (orthorhombic) are different from beta alumina (hexagonal) and modification of luminescence properties of Cr<sup>3+</sup> in these hosts is expected. With these expectations, attempts were made to synthesize Cr<sup>3+</sup> activated Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub> using combustion synthesis. Results of these experiments are discussed here.

### II. METHODS AND MATERIAL

Phosphors were prepared by combustion method using metal nitrates as oxidizer and urea as a fuel [10,11]. Aluminium nitrate, SiO<sub>2</sub>/GeO<sub>2</sub> and urea were

thoroughly mixed in molar ratio 5:1:15.83. A crucible containing the mixture was inserted at 500 C in a preheated furnace. In few minutes the mixtures swells with evolution of gases and finally a flame appears. The flame lasts for about a minute. The crucible is removed from the furnace after the flame extinguishes. The foamy product is crushed to powder and used for further characterization. For preparing Cr<sup>3+</sup> doped samples Chromium nitrate in the desired quantity was added to the starting mixture.

The crystalline phases of the synthesized samples were identified by x-ray diffraction (XRD) patterns recorded on XPERT-PRO diffractometer using Cu K $\alpha$  ( $\lambda=1.54059 \text{ \AA}$ ) radiation. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on Hitachi F-7000 spectrophotometer.

### III. RESULTS AND DISCUSSION

Fig.1 shows xrd pattern of the synthesized phosphor. Surprisingly the patterns for Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub> both matched with that of Al<sub>2</sub>O<sub>3</sub>. It appears that the compounds are not formed by the combustion synthesis. Further experiments proved the contrary. EDAX analysis of Al<sub>5</sub>GeO<sub>9.5</sub> clearly showed presence of Ge (Fig.2). Further, luminescence properties of these compounds were entirely different. Fig.3 shows PL emission spectrum for Cr<sup>3+</sup> doped Al<sub>5</sub>GeO<sub>9.5</sub> and Al<sub>5</sub>SiO<sub>9.5</sub> and Al<sub>2</sub>O<sub>3</sub> excited by 413 nm. Intense line attributable to (<sup>2</sup>E $\rightarrow$ <sup>4</sup>A<sub>2g</sub>) is seen around 698 nm in the emission spectrum of Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup> with several components due to splitting of <sup>2</sup>E levels in crystal field. Similar emission peaking at 699 nm is observed for Al<sub>5</sub>GeO<sub>9.5</sub>:Cr<sup>3+</sup> with much higher intensity. On the other hand, emission was totally quenched in Al<sub>5</sub>SiO<sub>9.5</sub>:Cr<sup>3+</sup>.

Further experiments were performed on Al<sub>5</sub>GeO<sub>9.5</sub>:Cr<sup>3+</sup>. Fig.4 shows effect of Cr<sup>3+</sup> concentration on PL emission intensity. Intensity is maximum for 0.4 mol.% Cr<sup>3+</sup>. Intensity decreases for higher concentrations due to concentration quenching. From

these data critical distance for Cr<sup>3+</sup> - Cr<sup>3+</sup> transfer can be calculated using the formula [12].

$$R_c = 2 (3V/4\pi x_c N)^{1/3} (1)$$

where  $x_c$  is the critical concentration (0.004), N is the number of Al sites in the unit cell (5) and V is the volume of the unit cell (168.034  $\text{\AA}^3$ ).  $R_c$  comes out to be 25.22  $\text{\AA}$ . This is considerably greater than 17  $\text{\AA}$  observed for Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>.

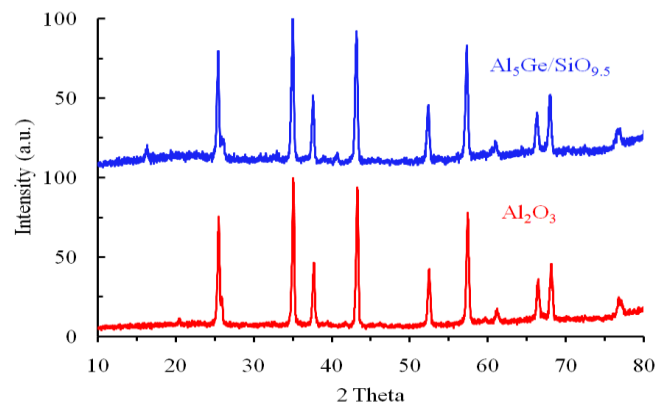


Fig.1 XRD patterns of Al<sub>5</sub>Ge/SiO<sub>9.5</sub> and Al<sub>2</sub>O<sub>3</sub>

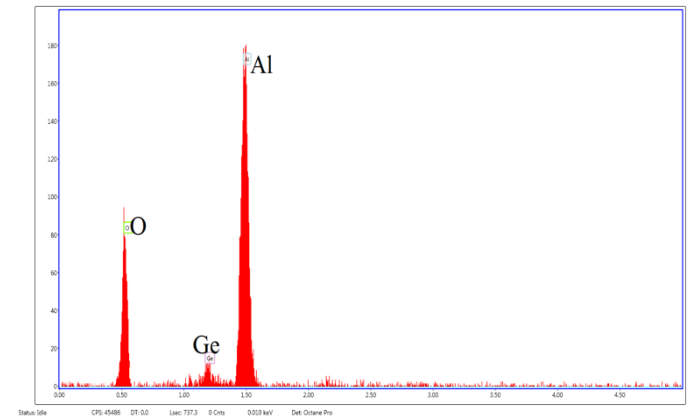


Fig.2 EDAX for Al<sub>5</sub>GeO<sub>9.5</sub>

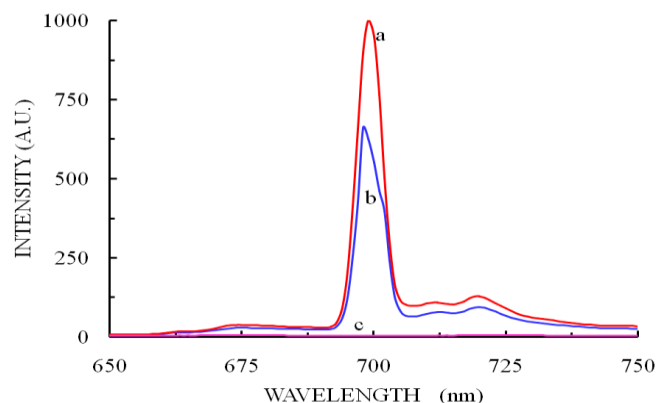


Fig.3 PL emission spectra of a) Al<sub>5</sub>GeO<sub>9.5</sub>, b) Al<sub>2</sub>O<sub>3</sub> and c) Al<sub>5</sub>SiO<sub>9.5</sub>, activated with Cr<sup>3+</sup>.

Excitation was by 413 nm light.

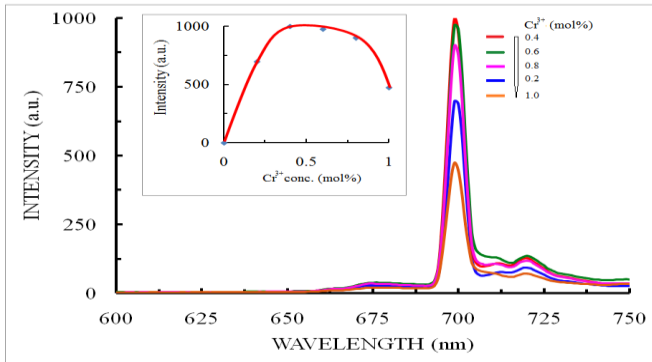


Fig.4 PL emission spectra of a)  $\text{Al}_5\text{GeO}_{9.5}:\text{Cr}^{3+}$   
Inset shows effect of  $\text{Cr}^{3+}$  concentration on intensity of 699 nm line.

Corresponding excitation spectrum is shown in Fig.5.  ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{1\text{g}}({}^4\text{F})$  and  ${}^4\text{T}_{2\text{g}}({}^4\text{F})$  bands can be clearly seen around 413 and 556 nm. Splitting of  ${}^4\text{T}_{1\text{g}}({}^4\text{F})$ ,  ${}^4\text{T}_{2\text{g}}({}^4\text{F})$  levels is barely visible in the spectrum recorded at room temperature.

Fig.6 shows luminescence decay curve for  $\text{Al}_5\text{GeO}_{9.5}:\text{Cr}^{3+}$  (0.2 mol.%). Single exponential is observed which can be fitted to decay constant  $\tau = 3.5$  ms which is almost same as that for  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$  (3.36 ms).

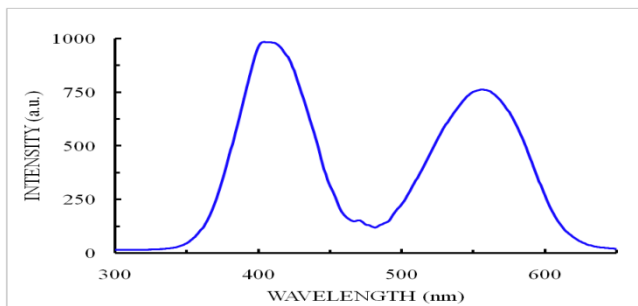


Fig.5 PL excitation spectrum for 699 nm emission of  $\text{Al}_5\text{GeO}_{9.5}:\text{Cr}^{3+}$ .

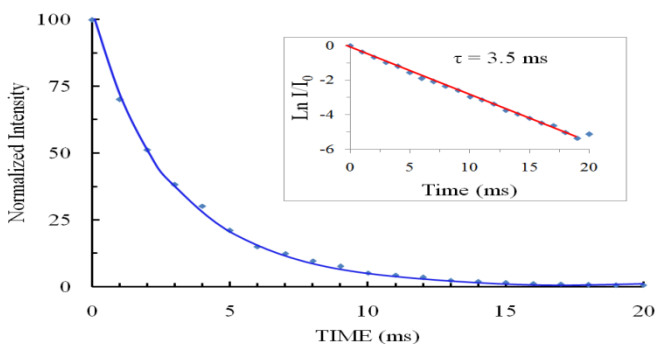


Fig.6 Luminescence decay curve for 699 nm emission of  $\text{Al}_5\text{GeO}_{9.5}:\text{Cr}^{3+}$ .

#### IV. CONCLUSION

Attempts were made to synthesize  $\text{Al}_5\text{GeO}_{9.5}$  and  $\text{Al}_5\text{SiO}_{9.5}$  compounds by combustion synthesis and obtain modification of luminescence properties of  $\text{Cr}^{3+}$  activated phosphors. XRD analysis of the combustion synthesized powders showed presence of alpha alumina phase. On the other hand, EDAX indicated presence of Ge. Luminescence properties were also changed a great deal. In  $\text{Al}_5\text{SiO}_{9.5}$ ,  $\text{Cr}^{3+}$  emission was totally quenched while luminescence increased by about 50 % in  $\text{Al}_5\text{GeO}_{9.5}$ . These inconsistencies need to be investigated further.

#### V. REFERENCES

- [1]. Glauco S. Maciel, NikiforRakov, Michael Fokine, Isabel C. S. Carvalho and Carlos B. Pinheiro, Appl Phys Lett, 89 (2006) 081109-1-3
- [2]. Y. Kim, S.M. Lee, C.S. Park, S.L. Lee, M.Y. Lee, Appl. Phys.Lett. 71 (1997) 3604–3606.
- [3]. E.P. Gusev, M. Copel, E. Cartier, I.J.R. Baumvol, C. Krug, M.A. Gribelyuk, Appl. Phys. Lett. 76 (2000) 176–178.
- [4]. A. Pillonnet-Minardi, O. Marty, C. Bovier, C. Garapon, J. Mugnier, J. Opt. Mater. 16 (2001) 9–13.
- [5]. L. Rebohle, M. Braun, R. Wutzler, B. Liu, J.M. Sun, M. Helm, W. Skorupa, Appl. Phys. Lett. 104 (2014) 251113.
- [6]. R. Serna, C.N. Afonso, Appl. Phys. Lett. 69 (1996) 1541.
- [7]. T. Maiman, Nature 187 (1960) 493.
- [8]. G. Boulon, Opt. Mater. 34 (2012) 499–512.
- [9]. V.B. Mikhailik, H. Kraus, D. Wahl, Appl. Phys. Lett. 86 (2005) 101909
- [10]. J.J. Kingsley, K. Suresh and K.C. Patil, J.Mater. Sci. 25 (1990) 1305
- [11]. J.J. Kingsley, N. Manickam and K.C. Patil, Bull. Mater. Sci. 13 (1990) 179
- [12]. G. Blasse, Philips Res. Rep. 24 (1969) 131