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# Investigation of the Thermoluminescent Glow Curves of Some RE-Doped Aluminate/Silicate-Based Phosphorus

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***Abstract:*** *In this paper, thermoluminescence (TL) glow curves of the $Sr_3Al_2O_6:Eu^{3+}$, $Ho^{3+}$, $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$, and $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$ phosphorus were investigated after being subjected to beta irradiation at room temperature to examine their usability in technological applications. The phosphorus $Sr_3Al_2O_6:Eu^{3+}$, $Ho^{3+}$, $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, demonstrated effective TL glow curves, even when exposed to low levels of beta radiation. The TL glow curves of these phosphors revealed the presence of a main peak alongside two minor peaks. The main peak temperatures for the europium ($Eu^{3+}$) doped holmium ($Ho^{3+}$) and dysprosium ($Dy^{3+}$) co-doped alkaline earth aluminate-based phosphors, recorded at a heating rate of 2°C/s, were observed to be in the range of 265–269 ± 2°C. Computerized glow curve deconvolution analysis show that the phosphorus have 8 individual glow peaks.*

***Keywords:*** *Aluminate-based luminescent phosphorus, silicate-based luminescent phosphorus, thermoluminescence, glow curve*

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## I. INTRODUCTION

Aluminate-based and silicate-based luminescent materials have attracted significant attention due to their excellent performance as long-lasting afterglow phosphors [1–3]. Aluminate-based materials emit light when excited by various external energy sources, including UV light, X-rays, electron beams, or visible light. This phenomenon is primarily attributed to the presence of rare-earth activator ions, which are incorporated into the aluminate crystal lattice. Aluminates typically consist of aluminum oxide combined with alkaline earth metals. Their stable crystal structures make them excellent hosts for activator ions. These ions are responsible for the emission of light when excited. Silicates are compounds containing silicon and oxygen, often combined with metals. Their complex crystal structures and chemical stability make them suitable hosts for the activator ions responsible for the luminescent properties. These materials are widely studied and used because of their efficient and long-lasting luminescence properties. Aluminate-based and silicate-based phosphors are used in emergency signage, biological imaging, security and anti-counterfeiting, lighting and displays (LEDs and other luminescent devices), and radiation detection [4–7]. However, they offer additional benefits such as improved water resistance and lower calcination temperature. These properties make RE-doped silicates particularly advantageous for applications where stability and energy efficiency in the production process are essential [8].

Rare-earth (RE) doped aluminate-based and silicate-based phosphors are attractive materials for TL applications due to their exclusive luminescence properties, such as their wide band gap (5–7 eV) [9–12]. The TL properties of the phosphors are determined by their crystal structure and chemical composition [3]. RE ions, such as $Eu^{2+}$, $Ho^{3+}$ or $Dy^{3+}$, are commonly incorporated as activators. In addition, transition metal ions (e.g., Mg…) are also used for their luminescent properties [7–9,13–15].

The first RE-doped aluminate-based phosphor, europium-doped strontium aluminates, was synthesized and studied in the late 1960s [3,16]. RE-doped aluminate phosphors have been found to have approximately ten times the luminescence efficiency of zinc sulfide, higher chemical stability, and are environmentally friendly, producing no harmful waste materials [13–15,17].

Matsuzawa et al. [3] developed $Sr\,Al_2O_4:Eu^{2+},\ Dy^{3+}$ phosphors with co-dopant additives. These phosphors have replaced traditional Zn-S based phosphors due to their successive emission intensity, chemical

stability and afterglow. When activated by one of the lanthanide elements, the emission spectrum observed in alkaline earth aluminate phosphors is based on the 4f-5d transitions of the lanthanides [18,19]. Here, broad light absorption and emission spectra result from the high sensitivity of the 5d orbit to the external environment. More than 300 new inorganic compounds doped with $Eu^{2+}$ have been studied to observe emission spectra ranging from near ultraviolet to deep red light [20]. Strontium aluminates, one of the most suitable phosphors for use as rare earth host crystals, have attracted the attention of the scientific community in recent years due to their high luminescence efficiency and chemical stability [21]. It has been found that the location of dopant ions in the host material depends on the ionic radii of the primary crystal components and the dopant materials. In the $Eu^{2+}$-doped $Sr\,Al_2O_4$ phosphor compound, the ionic radii of the $Eu^{2+}$ and $Sr^{2+}$ doped with $Eu^{2+}$, the ionic radii of $Eu^{2+}$ and $Sr^{2+}$ ions are very close (1.20 Å and 1.21 Å, respectively). Therefore, $Eu^{2+}$ ions are very likely to replace $Sr^{2+}$ ions, as confirmed by electron paramagnetic resonance [22,23]. $Eu^{3+}$ ions have also been observed to easily reduce to $Eu^{2+}$ ions in the strontium aluminate crystals [23,24]. Engelsen et al. [25] developed pure and doped $BaAl_2O_4$ phosphors and reported their photoluminescence properties. They reported that the 460 nm band in un-doped $BaAl_2O_4$ and the 425 nm band in $BaAl_2O_4$:$Eu^{2+}$ are associated with F-center luminescence, which is a phenomenon where anionic vacancies in a crystal lattice trap electrons and subsequently emit light upon relaxation.

In this study, the thermoluminescent glow peaks of certain rare earth element-doped some aluminate and silicate-type phosphors synthesized via solid-state reaction at high temperatures were investigated, along with their suitability for use as high technological applications.

## II. EXPERIMENT AND RESULTS

In this paper, rare earth doped aluminates and silicates phosphors such as $Sr_3Al_2O_6:Eu^{3+},\ Ho^{3+}$, $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$ have been synthesized by Öztürk using the solid-state reaction method. Synthesis details, xrd, sem/edx, dta/tg, results and photoluminescence properties have been reported [26,27]. In this paper, the phosphors were exposed to beta radiation, and their TL glow curves were recorded and investigated by using computerized glow curve technique. Powdered phosphorus were spread onto thin aluminum discs, and each sample was weighed to be $2.0 \pm 0.1$ mg. Each sample was subjected to an annealing procedure at 600°C for 10 minutes before each measurement. This annealing procedure was applied after each measurement to erase any residual radiation effect. After annealing, each sample was exposed to a $^{90}Sr$–$^{90}Y$ beta radiation source for 5 minutes. The current dose rate was calculated to be 6.07 Gy/min based on the geometry of the irradiator (Type 9022A) [28]. Then, the TL glow curve was read for each sample at a linear heating rate of 2°C/s between 40°C and 400°C using an RA-04 manual thermoluminescence dosimetry reader-analyzer. Results are given in Figure 1 and 2.

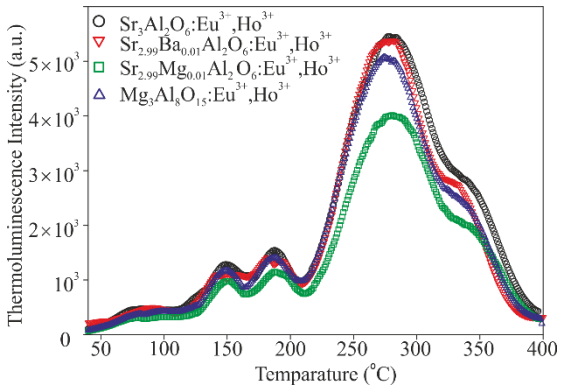


**Fig. 1. Glow curves of the $Sr_3Al_2O_6:Eu^{3+},\ Ho^{3+}$, $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$ samples**

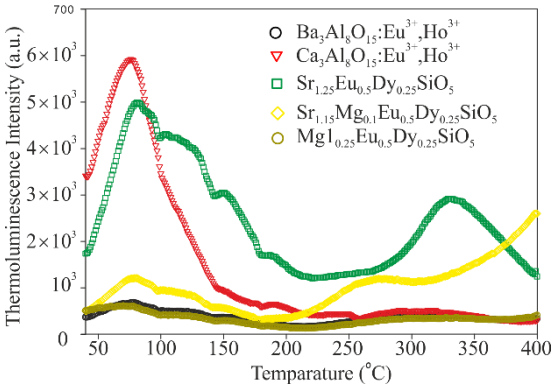


**Fig. 2. Glow curves of the $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$, and $Mg_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$ samples**

It was observed that the phosphorus $Sr_3Al_2O_6:Eu^{3+},\ Ho^{3+}$ , $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ , $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$ exhibited efficient TL emission curves even at low radiation levels. On the other hand, $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$, and $Sr_{1.25}Eu_{0.5}Dy_{0.25}SiO_5$ do not have TL glow curves that are intense and stable enough to be analyzed even at high doses.

Glow curves of the samples were analyzed by using CGCD program (TLANAL) [29]. Results are given in Figure 3-6 for $Sr_3Al_2O_6:Eu^{3+},\ Ho^{3+}$, $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$, and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, respectively.

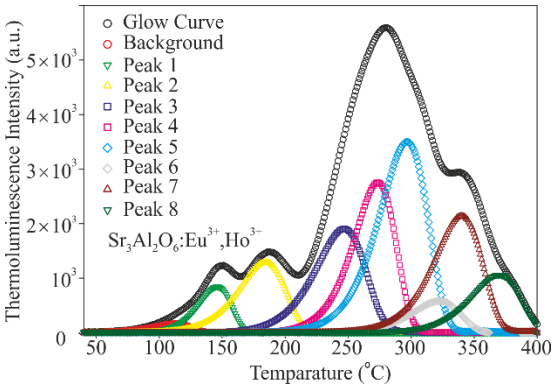


**Fig. 3. Computerized glow curve analysis of the $Sr_3Al_2O_6:Eu^{3+}$phosphorus.**

Here, it is clear that the $Sr_3Al_2O_6:Eu^{3+}$phosphorus has 8 individual glow peaks. The peak temperatures are given in Table 1.

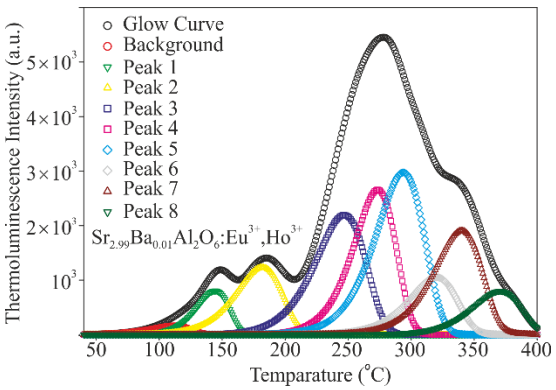


**Fig. 4. Computerized glow curve analysis of $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ phosphorus.**

One can be clearly seen that the $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ phosphorus has 8 individual glow peaks. The peak temperatures are given in Table 1.

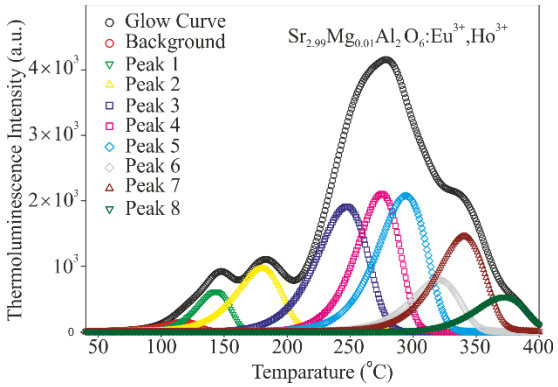


**Fig. 5. Computerized glow curve analysis of $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ phosphorus.**

It is clear from the Fig. 5 that that the $Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ phosphorus has 8 individual glow peaks. The peak temperatures are given in Table 1.

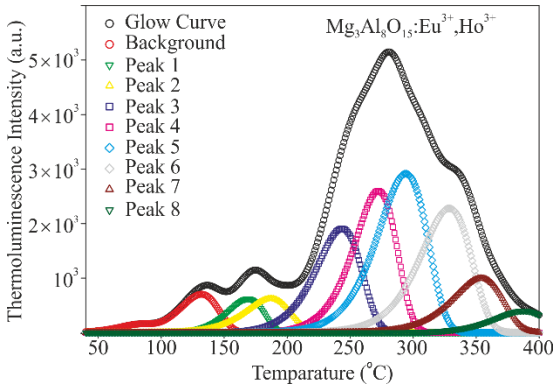


**Fig. 6. Computerized glow curve analysis of and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$ phosphorus.**

As can be easily seen from Fig. 1 that the $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$ phosphorus has 8 individual glow peaks. The peak temperatures are given in Table 1.

**Table 1 Individual peak maximum temperatures of the phosphorus.**

| Peak | $Sr_3Al_2O_6$: $Eu^{3+}$ | $Sr_{2.99}Ba_{0.01}Al_2O_6$: $Eu^{3+},Ho^{3+}(\pm2)$ | $Sr_{2.99}Mg_{0.01}Al_2O_6$: $Eu^{3+},Ho^{3+}$ | $Mg_3Al_8O_{15}$: $Eu^{3+},Dy^{3+}$ |
|---|---|---|---|---|
| | Peak Temp. $(°C)$ | Peak Temp. $(°C)$ | Peak Temp. $(°C)$ | Peak Temp. $(°C)$ |
| Peak 1 | 146±2 | 144±2 | 143±2 | 169±2 |
| Peak 2 | 184±2 | 182±2 | 180±2 | 187±2 |
| Peak 3 | 247±2 | 247±2 | 247±2 | 243±2 |
| Peak 4 | 274±2 | 273±2 | 275±2 | 272±2 |
| Peak 5 | 297±2 | 294±2 | 294±2 | 294±2 |
| Peak 6 | 322±2 | 320±2 | 320±2 | 329±2 |
| Peak 7 | 340±2 | 340±2 | 341±2 | 355±2 |
| Peak 8 | 371±2 | 371±2 | 372±2 | 387±2 |

## III. CONCLUSIONS

The phosphors doped with $Eu^{3+}$ and co-doped with $Ho^{3+}$, specifically $(Sr_{3-x}\,M_x)Al_2O_6:Eu^{3+},Ho^{3+}$ were exposed to beta radiation for the same dose, with trace amounts of barium and magnesium added. It was observed that the thermoluminescence emission intensity of the aluminum-based phosphor containing trace amounts of barium $Sr_{2.99}Ba_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$ did not significantly differ from that of the

$Sr_3Al_2O_6:Eu^{3+},Ho^{3+}$ phosphor. However, a decrease in TL emission intensity was noted for the phosphor doped with trace amounts of magnesium ($Sr_{2.99}Mg_{0.01}Al_2O_6:Eu^{3+},Ho^{3+}$). It was observed that another phosphor, $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, also responds to low beta radiation among the synthesized compounds. In the computerized glow curve deconvolution analysis, it was observed that all materials had the same number of individual TL peaks and that these peaks appeared at approximately the same temperatures. Thus, it was considered that these peaks originated from the main matrix material, aluminium oxide and that the dopes did not create new peaks. However, although the additives did not create new peaks, they did cause some changes in peak intensities. Due to their very high peak intensities, some of the materials examined are believed to be promising for technological applications. For these reasons, the authors recommend that the TL glow curves of these phosphors be investigated more intensively and in detail.

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