

# Persistent Phosphors Based on Alkaline-Earth Aluminate Hosts

by Uwe Happek and Anant Setlur

Prior to the mid-1990s typical, commercial persistent (or “glow-in-the-dark”) phosphors used ZnS based hosts, such as ZnS:Cu, that had relatively weak afterglow for shorter periods of time (on the order of hours) and were generally unstable in humid environments. These properties inherently limited the use of ZnS-based persistent phosphors for many

or green in the dark, these phosphor powders are incorporated into those paints or parts. These applications for luminescent and display materials were completely enabled by the discovery of the  $\text{MAl}_2\text{O}_4\text{:Eu}^{2+}$ ,  $\text{RE}^{3+}$  family of phosphors by Matsuzawa, *et al.*

Apart from the practical application of persistent phosphors, the Matsuzawa, *et al.* paper opened up the field of persistent

these persistent phosphors has led to many studies of the mechanisms behind persistent luminescence. While the initial mechanism for long persistence proposed by Matsuzawa, *et al.* has been controversial, the field has begun to move toward a greater consensus about the qualitative aspects behind persistent luminescence and the role of the  $\text{Nd}^{3+}/\text{Dy}^{3+}$  in enhancing persistent

FROM:  
T. Matsuzawa, Y. Aoki, N. Takeuchi, and  
Y. Murayama, *J. Electrochem. Soc.*, **143**,  
2670 (1996).

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## ABSTRACT

A green emitting  $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$  phosphor with very bright and long lasting phosphorescence has been newly developed. The incorporation of  $\text{Dy}^{3+}$  ion into the  $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$  system as an auxiliary activator dominates the phosphorescence, thermoluminescence, and photoconductivity characteristics of the phosphor to a large extent. Evidence is presented for the mechanism that the phosphorescence is ascribed to the photoconductivity due to holes, and to the trapping and thermal release of the holes by  $\text{Dy}^{3+}$  ions in the system. The incorporation of the  $\text{Dy}^{3+}$  ion forms a highly dense trapping level located at a suitable depth in relation to the thermal release rate at room temperature, thus producing the very bright and long phosphorescence.

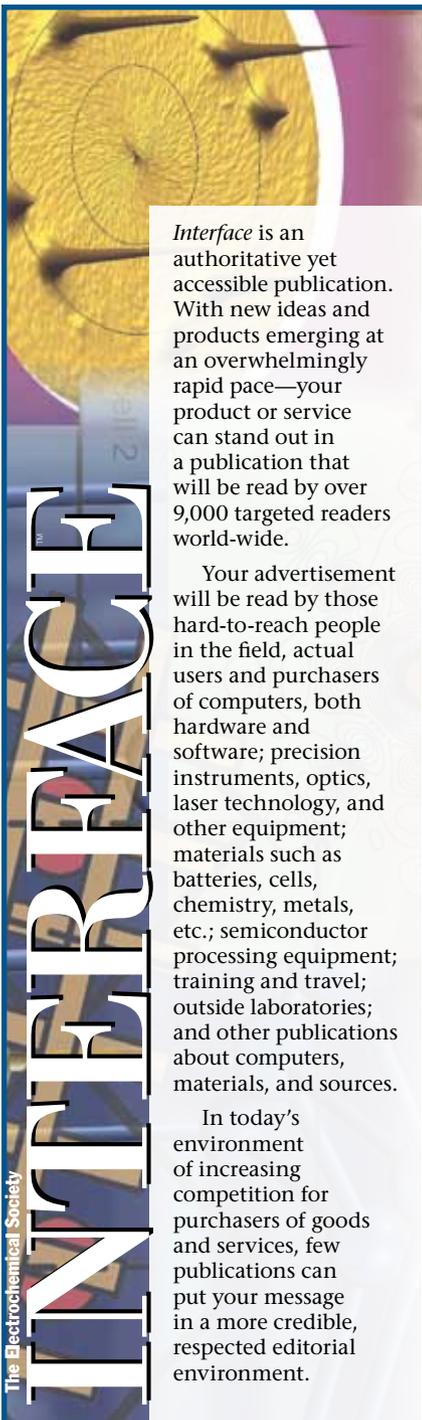
practical applications, and made these persistent phosphors more of a curiosity instead of a useful commodity. This situation changed with the publication of Matsuzawa, *et al.* (from Nemoto) in the *Journal of The Electrochemical Society* (JES) heralding the discovery of long persistence (detectable luminescence after 24 hrs) in the  $\text{MAl}_2\text{O}_4\text{:Eu}^{2+}, \text{RE}^{3+}$  ( $\text{M} = \text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ ;  $\text{RE}^{3+}$  is typically  $\text{Nd}^{3+}$  and/or  $\text{Dy}^{3+}$ ) family of phosphors (Fig. 1),<sup>1</sup> as well as the commercial introduction of these phosphors by Nemoto. The combination of long persistence with relative environmental stability has led to these materials being used as the pigments in paints and plastics for safety and security applications. For example, many of the stairwells and exits in U.S. buildings, as well as airplane cabin floors, have persistent phosphor markings to guide occupants out of the building/airplane in emergency situations. It is also likely that if you have a glow-in-the-dark paint or part that glows blue

phosphors and their study, in order to improve aspects of their performance, develop new persistent phosphors, and understand the mechanisms behind the long persistence in the  $\text{MAl}_2\text{O}_4\text{:Eu}^{2+}, \text{RE}^{3+}$  materials. For example, the moisture sensitivity of  $(\text{Ca}, \text{Sr})\text{Al}_2\text{O}_4$  hosts has led to two separate fields of study: the development of protective coatings for persistent phosphor powders and the invention and development of blue and green persistent phosphors that are not as sensitive to moisture and environmental conditions. There is also interest in developing red persistent phosphors to enable a full palette of persistent phosphor colors when combined with the blue and green luminescence of  $\text{CaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{RE}^{3+}$  and  $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{RE}^{3+}$ , respectively. While there have been improved red persistent phosphors in nitride hosts,<sup>2</sup> the duration and intensity of persistence is still not comparable to that of the aluminate phosphors. Finally, the performance of

luminescence.<sup>3</sup> However, since persistent luminescence can be dependent upon both the interaction of localized levels of  $\text{Eu}^{2+}$  with extended conduction band states and the defect chemistry of a specific material (which is then dependent upon processing parameters), a full qualitative understanding of persistent luminescence is a goal for future study.

From a previously dormant topic, the field of persistent phosphors is now a vibrant field that involves and integrates aspects of chemistry, physics, and materials science, leading to the over 475 citations of Matsuzawa, *et al.* since its publication in 1996. For a more in-depth discussion about the history, sciences, and application of persistent phosphors, please refer to the Winter 2009 *Interface* article by Jorma Holsa who clearly described these aspects of persistent phosphors in far more depth. ■

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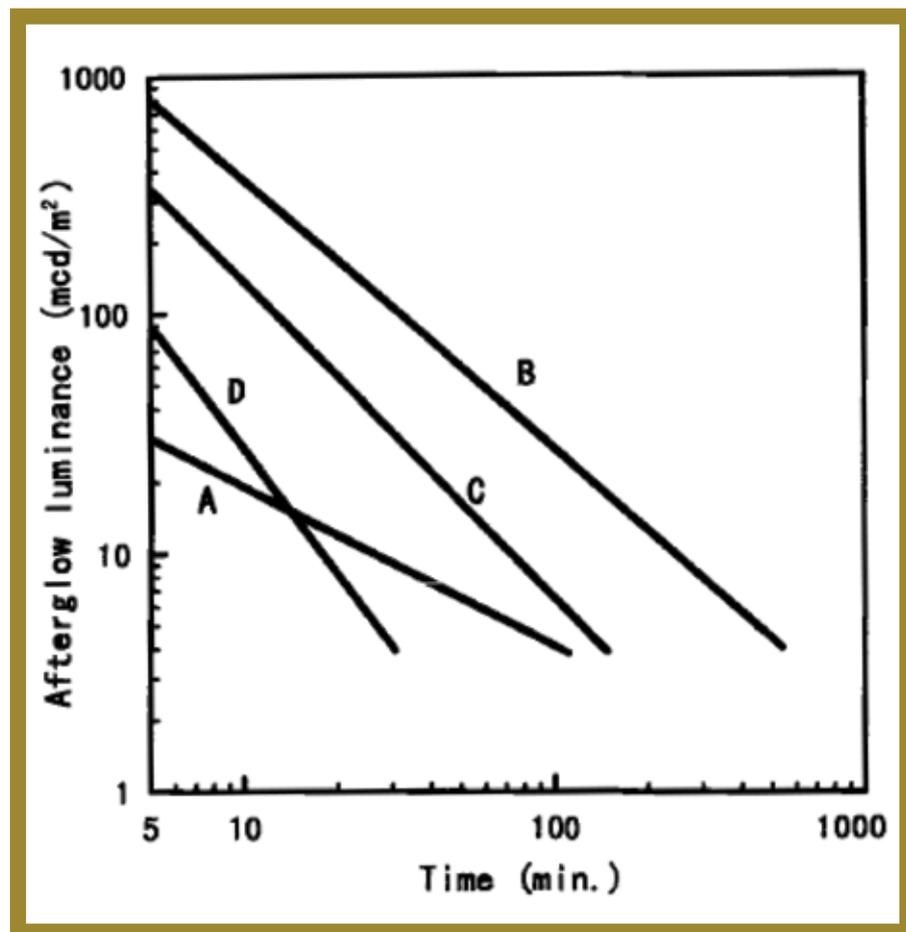
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**Fig. 1.** Persistent luminescence of (A)  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ; (B)  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ; (C)  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ ; (D) commercial  $\text{ZnS}:\text{Cu}, \text{Co}$  after 10 min exposure to 200 lx of  $D_{65}$  light at 22°C. This figure is Fig. 2 of Matsuzawa, et al.<sup>1</sup>