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Non-rare earth doped persistent luminescence materials

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1. Introduction

Both the commercial markets as well as research and development of persistent luminescence phosphors have been dominated by materials doped with Eu^{2+} . The domination of Eu^{2+} over other rare earths (R; e.g. Ce^{3+} , Pr^{3+} , Tb^{3+}) is due to e.g. the strong and easily tunable emission (Fig. 1) as well as the favourable energy level scheme of Eu^{2+} vs. the host band structure [1]. For many reasons this situation may soon change: i) europium is needed for many other phosphor applications, ii) the recovery and recycling of europium from persistent luminescence materials is nearly impossible and iii) e.g. the biotechnical applications require strongly red emitting biomarkers. The economic pressure due to both aggressive and wildly fluctuating pricing policy of rare earths is probably the most important driving force to the change.

2. Results

The pursuit for cheaper persistent luminescence materials has already resulted in the adoption of such inexpensive host materials as the alkaline earth aluminates, MAl_2O_4 (M: Ca, Sr), $\text{Sr}_2\text{MgSi}_2\text{O}_7$ or $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ [1]. The replacement of Eu^{2+} (and R^{3+} co-) dopants with non-rare earths is ensuing at a much slower pace despite many outstanding possibilities. For example, the first persistent luminescence material, the famous Bologna Stone from the beginning of the 17th century, uses doping with Cu^{+} in BaS [2]. The 3d elements such as Ti^{3+} , Cr^{3+} and Mn^{2+} have been shown to give strong persistent luminescence, too [1,3]. Many main group metal ions such as Pb^{2+} and Bi^{3+} can also be used as dopants. To improve either the absorption of incident radiation, the efficiency of emission or its tunability, combinations with conventional dopants (e.g. Eu^{2+} - Mn^{2+} or Cr^{3+} - Pr^{3+}) or with non-rare earth ones (e.g. Cr^{3+} - Bi^{3+} or Mn^{2+} - Bi^{3+}) may be used [3]. As for the mechanism of persistent luminescence, it is necessary to consider first the redox behaviour of the dopants. It is noted at once that each dopant has an oxidized counterpart: $\text{Eu}^{2+}/\text{Eu}^{3+}$, $\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Pr}^{3+}/\text{Pr}^{4+}$, $\text{Tb}^{3+}/\text{Tb}^{4+}$, $\text{Ti}^{3+}/\text{Ti}^{4+}$, $\text{Cr}^{3+}/\text{Cr}^{6+}$, $\text{Cu}^{+}/\text{Cu}^{2+}$, $\text{Pb}^{2+}/\text{Pb}^{4+}$ and $\text{Bi}^{3+}/\text{Bi}^{5+}$. However, this does not necessarily mean that this counterpart is easily observed experimentally. The mechanism should thus be similar to the very efficient Eu^{2+} based persistent luminescence and the electrons act as charge carriers [1].

Eventually, the properties of a Eu^{2+} - Mn^{2+} dopant combination is described (Fig. 2) [4]. Efficient persistent luminescence and also tuning of emission from red to blue via e.g. magenta can be achieved. System's efficiency depends now not only on the individual dopants but also on the persistent energy transfer between them.

Are you currently a postgraduate student? (Yes/No)

N

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