Accepted Manuscript

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PII: S1002-0721(18)30396-X

DOI: 10.1016/j.jre.2018.04.004

Reference: JRE 190

To appear in: *Journal of Rare Earths*

Received Date: 28 November 2017

Revised Date: 3 April 2018

Accepted Date: 9 April 2018

To tune europium valence by controlling the composition in diphase silicate phosphors[☆]

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Abstract: Commercial phosphors always require fewer impurities and higher crystallinity, but sometimes it is difficult or strict to synthesize a pure phase compound. Indeed, if the practical application is not influenced, it is acceptable to synthesize a kind of phosphors with diphase matrix that have similar structure and photoluminescence properties. In present work, we designed and synthesized a series of (1–*x*)$BaMSiO_4$·*x*$Ba_2MSi_2O_7$:Eu (M = Zn^{2+}, Mg^{2+}) diphase phosphors which contained two phases $BaMSiO_4$ (hexagonal, *P*6_3) and $Ba_2MSi_2O_7$ (monoclinic, *C*2/*c*) by a high temperature solid-state reaction in air condition. The structures and luminescence properties that are related to the phase transform from $BaMSiO_4$ to $Ba_2MSi_2O_7$ were analyzed carefully. The results show that the self-reduction ability of Eu^{3+} is not the best in above four compounds, respectively. But it reaches the maximum and gets the green emission under the UV lamp when the matrix is in a proper ratio of two phases, which suggest that the heterostructure between the two crystals ($BaMSiO_4$ and $Ba_2MSi_2O_7$) improves the self-reduction process of the diphase. The possible mechanism of the tunable europium valence and the luminescent properties in (1–*x*)$BaMSiO_4$·*x*$Ba_2MSi_2O_7$:Eu phosphors were discussed in detail.

Keywords: Diphase phosphors; Silicate; Heterostructure; Eu; Self-reduction; Rare earths

1. Introduction

White light source is necessary for room lighting, displays, monitors, solar cells, and other optical devices on a daily basis. Compared with the traditional incandescent or fluorescent lamps, white light-emitting diodes (WLEDs) lighting possess several superior properties, such as power saving, higher luminous efficiency and brightness, long operation time, and environment friendliness.[1, 2] The first and most common WLED was combined by the a blue InGaN LED chip and yellow-emitting phosphor YAG:Ce^{3+}, which is a commercial method in lighting and display areas. However, YAG:Ce^{3+} yellow phosphor suffers some weaknesses, such as a poor color rendering index and low stability of color temperature. Nowadays, the current focus of their manufacture gradually shifts from the YAG:Ce^{3+}-based excited by blue-LEDs to the single-phase white light emission phosphors excited by ultraviolet-LEDs to optimize the color rendering properties of WLEDs.

Typically, the 4f → 4f transition of Eu^{3+} ions gives sharp emission peaks of orange-red light, and the 4f → 5d transition of Eu^{2+} ions gives a wide emission band from blue to red range which are greatly influenced by the composition and structure of host matrix.[3-11] Through adjusting the ratio of Eu^{3+}/Eu^{2+}, the CIE (International Commission on illumination) and CRI (color rendering index) of the phosphors can be regulated to get the white light. The treatment on the valence states of the Eu ions in solid-state materials has vastly been researched.[12-15] The reducing atmosphere is generally necessary to reduce Eu^{3+} to Eu^{2+} in the synthesis of Eu^{3+} doped luminescent phosphors. Chen et al.[16] reported that they obtained different ratios of Eu^{3+} and Eu^{2+} concentrations within the silicate solid solution ($Sr_{1.5}Ca_{0.5}SiO_4$) by controlling the reduction time in the firing process. Obviously, the preparation of Eu^{2+} doped phosphors in air atmosphere is more convenient than in reducing atmosphere. Recently, Eu^{3+} → Eu^{2+} can be realized when Eu^{3+} doped samples were prepared in oxidizing atmosphere, e.g., air or pure O_2 gas, and this phenomenon is called the self-reduction phenomenon.[17-27] Self-reduction phenomenon is a valence change from higher valence rare-earth ions to corresponding lower valence state without reducing agent, such as from Eu^{3+} to Eu^{2+} or Ce^{4+} to Ce^{3+}, etc. This phenomenon is based on the rigid three-dimensional enclosed crystal structures. Many compounds which were observed self-reduction phenomenon have attracted much attention in not only fundamental research but also applied chemistry because it is actually much cheaper, safer and easier in

☆ **Foundation items:** Project supported by National Key Research and Development Program (2016YFB0302403), the National Natural Science Foundation of China (21571059) and Hunan Provincial Natural Science Foundation of China (2015JJ2100).

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