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Eu^{2+}-activated $Ca_5Si_2Al_2N_8$ – A novel nitridoalumosilicate red phosphor containing the special polyhedron of separated corner-shared $[Al_2N_6]$ and $[Si_2N_6]$

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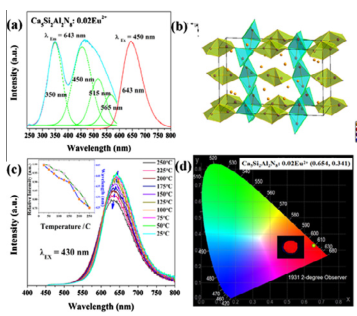
HIGHLIGHTS

- A novel nitride based phosphor $Ca_5Si_2Al_2N_8$: Eu^{2+} has been synthesized.
- $Ca_5Si_2Al_2N_8$ contains $[Al_2N_6]$ and $[Si_2N_6]$ polyhedrons and three Ca^{2+} sites.
- $Ca_5Si_2Al_2N_8$: Eu^{2+} emits a red light and has a broad excitation band.
- The $Ca_5Si_2Al_2N_8$: Eu^{2+} shows an excellent thermal stability.

GRAPHICAL ABSTRACT

Crystal structure and luminescent properties of $Ca_5Si_2Al_2N_8$: Eu^{2+} have been discussed.



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ABSTRACT

In this work, a novel nitride based Eu^{2+} activated phosphor of $Ca_5Si_2Al_2N_8$ has been successfully synthesized by the solid-state reaction at the constant pressure. The crystal structure has been refined using the Rietveld refinement. The $Ca_5Si_2Al_2N_8$ crystallizes in Orthorhombic with lattice parameters of a = 9.2336 (12) Å, b = 6.1317 (8) Å, c = 15.5049 (20) Å and V = 877.85 (31) $Å^3$, respectively. The special polyhedrons of $[Al_2N_6]$ and $[Si_2N_6]$ built up by the edge shared SiN_4 and AlN_4 tetrahedrons have been found in the $Ca_5Si_2Al_2N_8$, and the Al and Si ions are arranged in the separated sites. The three Ca^{2+} sites with the coordination number of six, seven and eight provide suitable sites for Eu^{2+} ions to occupy. The luminescence spectra of Eu^{2+} doped $Ca_5Si_2Al_2N_8$ show that a red light with the peak at 643 nm (FWHM ≈ 92 nm) can be observed, and the broad excitation band ranges from 350 nm to 565 nm. The excellent thermal stability has also been detected, which shows that the intensity at 150 °C is still beyond 90% of the initial intensity.

1. Introduction

In recent years, the warm white light emitting diodes (WLEDs) have attracted much attention because of their advantage of long service lifetime, high light efficiency and low energy consumption [1–4]. The common way to obtain the white light is the combination of the InGaN blue emitting LED and yellow emitting phosphor of $Y_3Al_5O_{12}$: Ce^{3+} (YAG: Ce^{3+}). However, this kind of white light suffers from the problem of a low color rendering index (CRI) and a high correlated color temperature due to the lack of the red component [5,6]. So the red phosphors play an important role in the WLEDs. Recently, nitride based red phosphors have attracted much attention because of their outstanding thermal stability and

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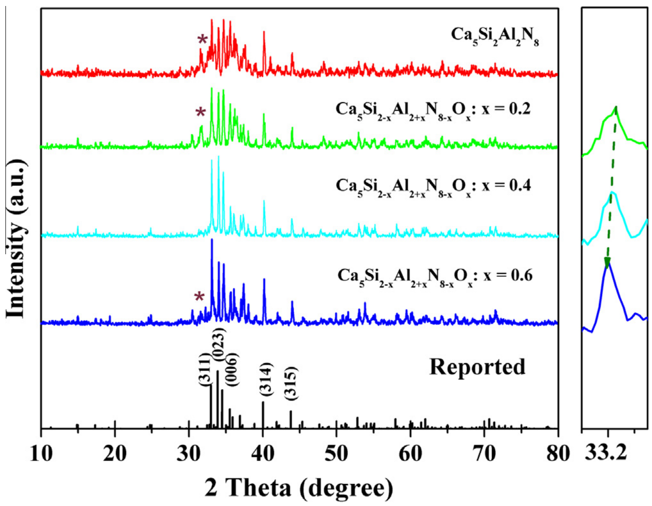

Fig. 1. The XRD patterns of $Ca_5Si_{2-x}Al_{2+x}N_{8-x}O_x$ with $x = 0$, 0.2, 0.4 and 0.6.

chemical stability, excellent luminescence properties and high quantum efficiency, such as: $Sr_2Si_5N_8$ [7], $CaAlSiN_3$ [8,9] and so on. However, the preparation of harsh conditions with high temperature and high pressure limited their application in the LEDs. Therefore, it is urgent to find new nitride based red phosphors produced under the relative low temperature and constant pressure to reduce the cost.

Among the Si_3N_4–AlN system, the edge-shared SiN_4 (or AlN_4) tetrahedron pairs have first been found in the host lattice of $Ca_5Si_2Al_2N_8$ with Al and Si ions occupying different sites. And the $[Al_2N_6]$ and $[Si_2N_6]$ polyhedrons connecting with each other through the corner-shared way with alternate configuration made up the main framework of $Ca_5Si_2Al_2N_8$, which shows a tight host lattice, and the strong crystal field effect resulted by this hard host lattice is necessary for Eu^{2+} ions to emit a red light. Commonly, nitridoalumosilicate are made up of SiN_4 (or AlN_4) tetrahedron through the corner-shared way. The edge-shared SiN_4 and AlN_4 tetrahedron pairs in $Ca_5Si_2Al_2N_8$ have rarely been reported. And $Ba_2AlSi_5N_9$ [10] contains the edge-shared AlN_4 and SiN_4 tetrahedron pairs, but it shows that Al and Si ions randomly occupy the same sites, which could not be distinguished. The different ratio of Al/Si in the material synthesized have been observed in host lattice of $Ca_5Si_2Al_2N_8$ and the same phenomenon have also happen in $CaAlSiN_3$, which implies the ratio of Al/Si play an important role in the change of crystal structure of nitridoalumosilicate.

Compared with the common commercial nitride based red phosphors, the $Ca_5Si_2Al_2N_8$ can be synthesized at the constant pressure, which have been first reported by Frank Ottinger and co-workers [11]. However, the luminescence properties of Eu^{2+} activated $Ca_5Si_2Al_2N_8$ have never been reported. In this work, we have successfully synthesized the Eu^{2+} activated $Ca_5Si_2Al_2N_8$ red phosphor and analyzed its crystal structure by the Rietveld refinement. And the electronic structure of $Ca_5Si_2Al_2N_8$ has also been calculated by DFT method to show the bandgap used for Eu^{2+} ions building the luminescent center. Finally, the thermal stability of $Ca_5Si_2Al_2N_8$ has been investigated.

2. Experimental section

2.1. Material and synthesis

A series of $Ca_5Si_2Al_2N_8$: Eu^{2+} phosphors have been synthesized by the high temperature solid-state reaction. Appropriate amounts of Ca_3N_2 (Aldrich, >95.0%), Si_3N_4 (Aldrich, 99.5%), AlN (Aldrich, >98.0%) and EuF_3 (Aldrich, 99.99%) were weighted as starting materials according to nominal composition. The raw materials were fully mixed and grounded in an agate mortar, and then the final mixture was placed into a BN crucible. The former procedure was completed in a glovebox. Finally, the crucible was positioned in a horizontal tube furnace and fired at 1300 °C in a N_2 atmosphere for 12 h. When the furnace cooled to room temperature, the samples were taken out and ground again into powders for measurement.

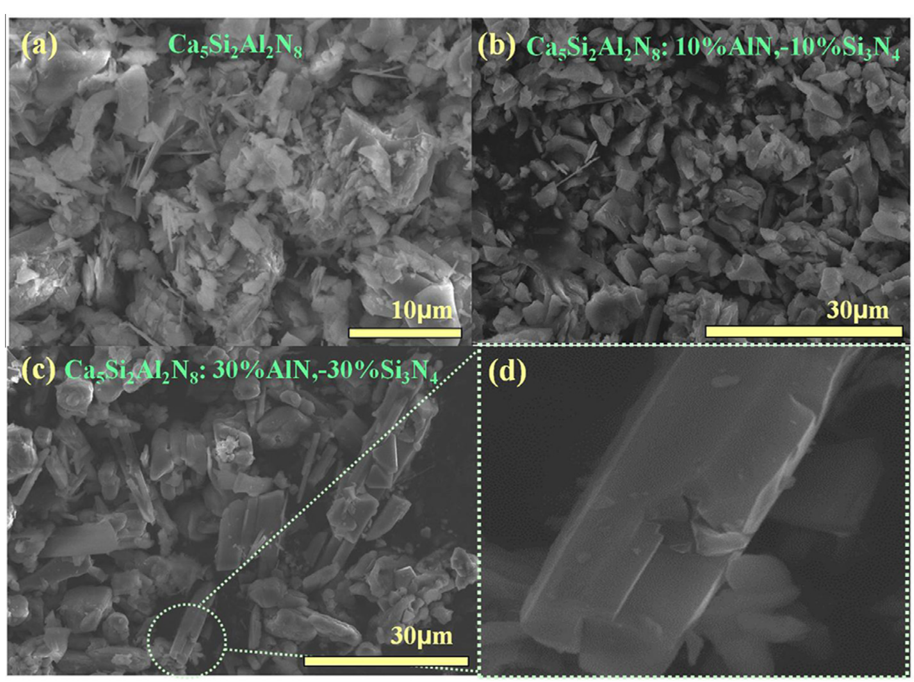

Fig. 2. SEM micrographs of $Ca_5Si_{2-x}Al_{2+x}N_{8-x}O_x$ with $x = 0$, 0.2 and 0.6, respectively.