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PREPARATION AND SPECTROSCOPIC PROPERTIES OF $Ca_2Al_2SiO_7$: Tb^{3+} PHOSPHOR

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Abstract. The Tb^{3+} rare-earth-ion-doped $Ca_2Al_2SiO_7$ material has a tetragonal phase structure that was successfully synthesized using the solid-state reaction method under optimal conditions: sintering temperature: 1280 °C; time: 60 minutes; and the B_2O_3 flux agent content: 4% wt. The photoluminescence spectrum of Tb^{3+} doped $Ca_2Al_2SiO_7$ phosphor consists of narrow lines with peaks at 545, 440, 462, 494, 590, and 622 nm that correspond to 4f electronic transitions of the Tb^{3+} ion. The peak at 545 nm has the highest luminescent intensity. The influence of synthesis technology and the luminescent characteristics of the phosphor are presented and discussed.

Keywords: phosphor, $Ca_2Al_2SiO_7$, Terbium, solid-state reaction

1 Introduction

Luminescent materials play an important role in lighting and display technology, fluorescent lamp, and LED manufacturing, which is highly efficient and energy-saving. Among luminescent materials, luminescent materials doped with rare-earth ions are widely used in many applications thanks to its non-toxicity, environmental friendliness, luminous efficiency, and long life [1–2]. In recent years, white LED stimulated by near-UV radiation combined with red green and blue phosphors has attracted a lot of scientists' attention. Luminescent materials that emit visible light with high efficiency when stimulated by near-UV radiation or blue light have been applied in white LED manufacturing.

Phosphors on alkaline-earth aluminosilicate ($M_2Al_2SiO_7$ with M = Ca, Sr) host the lattice doped with rare-earth ions have been studied widely thanks to its high luminescent efficiency and its luminescent characteristics [2–5]. Research on the luminescent characteristics of $Ca_2Al_2SiO_7$ phosphor doped with rare-earth ions shows that those materials have many advantages such as low cost, high thermal and chemical stability, and high absorbance to near-UV radiation [2–5]. Therefore, a technology for manufacturing the luminescent material is a topic of great concern and has great scientific significance. In recent studies, luminescent materials have been synthesized via many methods such as co-precipitation, sol-gel, solid-phase reaction, and combustion. Each method has its own advantages and disadvantages [6–9]. This paper presents the manufacturing technology for $Ca_2Al_2SiO_7$ (CAS) doped with terbium ion via the solid-state reaction method in the atmospheric environment and the luminescent characteristics of phosphor.

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2 Experiment

The Tb^{3+} ion-doped $Ca_2Al_2SiO_7$ luminescent materials are synthesized via the solid-state reaction. The chemical reagents used include $CaCO_3$ (99,9%, China), Al_2O_3 (99%, China), SiO_2 (99,9%, Korea), and Tb_4O_7 (99,9%, Merck). They were weighed according to the molar ratio and mixed with four weight percent (% wt) of B_2O_3 as a fluxing agent. The mixture was ground in an agate mortar for 1 hour before being annealed at 1280 °C for 1 hour. The structure of the material was characterized using the X-ray diffraction method on a Brucker D8-Advance diffractometer. Photoluminescent spectra of the material were acquired on an FL3-22 fluorescence spectrometer made by Horiba Jobin Yvon, USA, and a Xenon XFOR-450W lamp was used as the excitation source.

3 Results and discussion

3.1 Influence of sintering temperature on the structure of $Ca_2Al_2SiO_7$ material

The manufacturing technology is influenced by many parameters such as sintering temperature, sintering duration, and flux content. To study the influence of temperature on the structure, materials were sintered for 1 hour with 4% wt of B_2O_3 flux. The structure of materials sintered at 1120, 1150, 1180, 1250, and 1280 °C were studied. The X-ray diffraction diagrams of these materials are shown in Fig. 1.

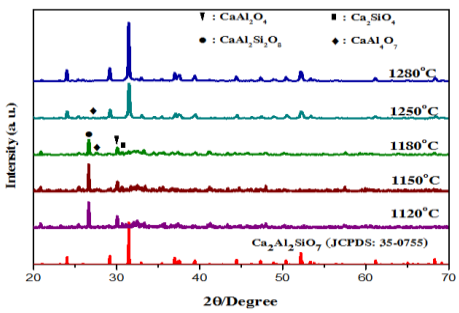

Fig. 1. The XRD diagram of CAS samples sintered at different temperatures

The results reveal that the synthesized samples have different phase structures at different sintering temperatures. When the sintering temperatures are from 1120 to 1180 °C, the samples have many undesired phases such as $Ca_2Al_2O_4$, Ca_2SiO_4, $Ca_2Al_2SiO_8$, and $CaAl_4O_7$. When the sintering temperature is 1250 °C, $CaAl_4O_7$ and $Ca_2Al_2SiO_7$ phases are observed in the material The $Ca_2Al_2SiO_7$ structure is only observed in the XRD diffraction diagram at 1280 °C. The material has a tetragonal phase with space group P-42₁m with JCPDS: 35-0755 standard card [2].

3.2 Influence of sintering duration on the structure of $Ca_2Al_2SiO_7$

The optimal sintering temperature of 1280 °C and the flux content of B_2O_3 of 4% wt were selected, and the sintering duration was set at 15, 30, 45, 60, 75, and 90 minutes. The XRD diagrams of the materials sintered at different sintering times are shown in Fig. 2.

Fig. 2 confirms that the sintering time has a strong influence on the material's phase formation. When the sintering duration is 15 minutes, $Ca_2Al_2SiO_7$ accounts for a small proportion. When the sintering duration increases to 30–45 minutes, $Ca_2Al_2SiO_7$ accounts for a more proportion but undesired phases, namely, $Ca_2Al_2O_4$, Ca_2SiO_4, $Ca_2Al_2SiO_8$, $CaAl_4O_7$ are present. When the sintering duration increases to 60–90 minutes, only $Ca_2Al_2SiO_7$ phase is observed.

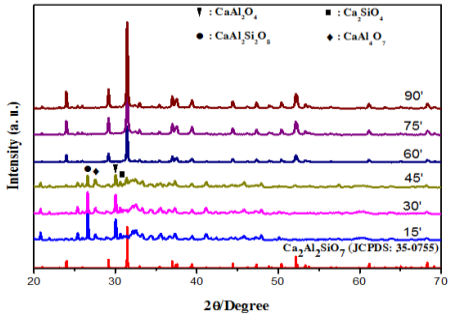

Fig. 2. The XRD diagram of CAS, sintered at different sintering durations

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3.3 Influence of B_2O_3 as a flux on the structure of $Ca_2Al_2SiO_7$

From the above results, the sintering temperature and the duration are 1280 °C and 60 minutes, respectively. The B_2O_3 flux content was selected from 0 to 5% wt. The XRD patterns of the samples are shown in Fig. 3. All samples have $Ca_2Al_2SiO_7$ phase structure. However, when the fluxing agent content is controlled from 0 to 1% wt, undesired phases Ca_2SiO_4, $CaAl_4O_7$ are still present. When the B_2O_3 flux content increases from 2 to 3% wt, $CaAl_4O_7$ stands still. The material's phase structure is optimal when the B_2O_3 fluxing agent increases to 4–5% wt. From the observation, the flux agent content plays an important role in the phase formation when using the solid-state reaction method.

The study on the influence of the sintering temperature, duration, and B_2O_3 content shows that the optimal sintering temperature, sintering duration, and B_2O_3 content is 1280 °C, 60–90 minutes and 4% wt, respectively.

3.4 Spectroscopic characteristics of $Ca_2Al_2SiO_7$ doped with Tb^{3+}

Fig. 4 shows the PL spectrum of the CAS: Tb^{3+} (0.5 % mol) material when stimulated by radiation of 368 nm. The spectrum has narrow lines, corresponding to the transitions of Tb^{3+}. The peak at 545 nm with the highest luminescent intensity corresponds to the $^5D_4$–$^7F_5$ of Tb^{3+}. Other peaks at 440, 462, 494, 590, and 622 nm have relatively weak intensity, corresponding to $^5D_3$–$^7F_4$, $^5D_3$–$^7F_3$ and $^5D_4$–$^7F_6$, $^5D_4$–$^7F_4$, $^5D_4$–$^7F_3$ [2, 8].

The PLE spectrum of CAS: Tb^{3+} corresponds to the emission at 545 nm is shown in Fig. 5. The spectrum spreads over a wide band in the UV region and has a few lines in the range of 310–500 nm, which corresponds to the f-f excitation transition of the Tb^{3+} ion. The peak with the highest intensity at 368 nm corresponds to the $^7F_6 \rightarrow {}^5G_5$ transition. Other weak peaks at 315, 338, 347, 376, and 481 nm correspond to the 4f-4f inner-configuration transitions that could be assigned to the $^7F_6 \rightarrow {}^5D_0$, $^7F_6 \rightarrow {}^5L_8$, $^7F_6 \rightarrow {}^5G_4$, $^7F_6 \rightarrow {}^5D_3$, $^7F_6 \rightarrow {}^5D_4$ transitions, respectively [2, 8, 10]. The color coordinate of the emission was determined from the PL spectrum of CAS: Tb^{3+} phosphor. The result in Fig. 6 indicates that the material emits green light when stimulated by a wave of 368 nm, which is suitable for the green LED manufacturing.

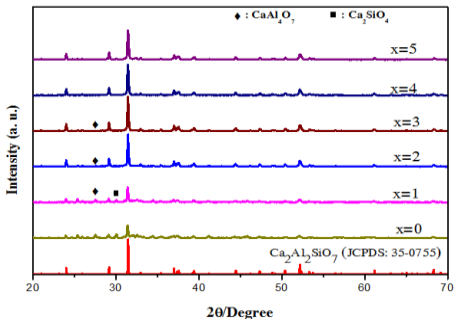

Fig. 3. The XRD diagram of CAS materials at different B_2O_3 contents (% wt)

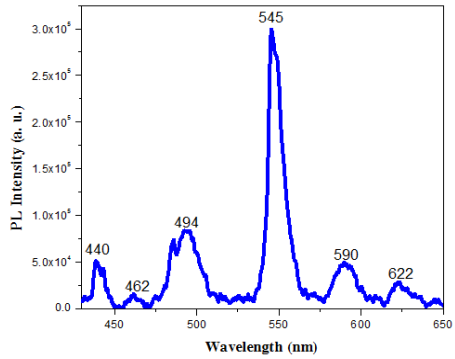

Fig. 4. PL spectra of CAS: Tb^{3+} (0.5 % mol), λ_{ex} = 368 nm

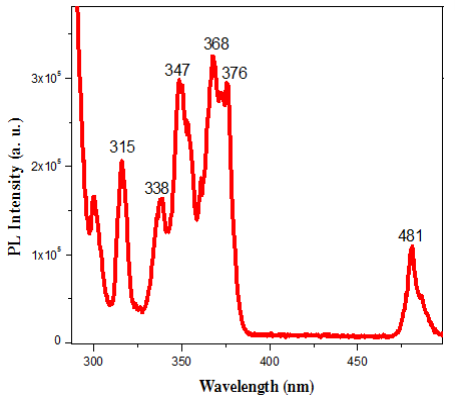

Fig. 5. PLE spectra of CAS: Tb^{3+} (0.5 %mol), λ_{em}=545 nm

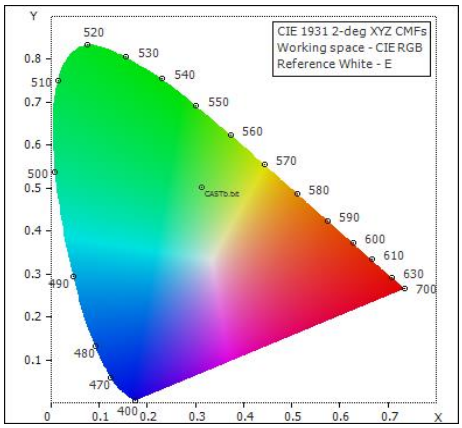

Fig. 6. CIE Color coordinate of CAS: Tb^{3+} when stimulated by radiation of 368 nm

4 Conclusion

The Tb^{3+} ion-doped $Ca_2Al_2SiO_7$ phosphor was successfully synthesized with the solid-state reaction method. The XRD diagram shows that the material has $Ca_2Al_2SiO_7$ single-phase structure when sintered at 1280 °C for 60 minutes with the fluxing agent content of 4% wt. The material's PL spectrum has narrow lines corresponding to the emission of the Tb^{3+} ion. The phosphor emits green light and CIE color coordinate of the phosphor with $x = 0.313$ and $y = 0.503$.

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