INTRODUCTION

Zirconates (XYO$_3$; X = Sr, Ba, Ca; Y = Zr) have high resistance to corrosion, high chemical stability and high melting points, making them popular materials in the nuclear industry and metallurgy. In addition, zirconates doped with acceptor ions, such as Lu$^{3+}$, Y$^{3+}$, Gd$^{3+}$, Ga$^{3+}$, Sc$^{3+}$ and In$^{3+}$, allow proton conduction at high temperatures. This attribute has wide industrial applications in hydrogen sensors, fuel cells, solid electrolytes, electronic ceramics and refractory materials$^{1-7}$.

Previously, calcium zirconate powder (CaZrO$_3$) was obtained using a conventional solid state reaction in which calcium carbonate and zirconium dioxide (ZrO$_2$) are ground, mixed and heated to 1850 °C$^{8}$. However, the calcium zirconate powder derived through this method is prone to inconsistencies in particle size and clusters. Accordingly, researchers developed the cellulose-citric acid method for the synthesis of powder. Previous studies have established that adding cellulose can enhance the uniformity of positive ions mixed in solutions. Moreover, the resulting powder particles are smaller and spread more evenly. Thus, we believe that the cellulose-citric acid method could be used to resolve the issue of uneven particles and clusters in the synthesis of CaZrO$_3$:Mn$^{2+}$ phosphor$^{9,10}$.

However, the light-emission and energy-transfer properties of CaZrO$_3$ phosphor doped with varying quantities of Mn$^{2+}$ have not been previously investigated. This study successfully synthesized CaZrO$_3$:Mn$^{2+}$ phosphor in a method using cellulose-citric acid to examine the light-emission properties of this material, as well as the distance and mechanism of energy transfer between Mn$^{2+}$ ions.

EXPERIMENTAL

Synthesis of CaZrO$_3$:Mn$^{2+}$ phosphor: This study utilized a novel method using cellulose-citric acid to synthesize Mn$^{2+}$-doped CaZrO$_3$ phosphor. First, quantities of calcium acetate hemihydrate [Ca(CH$_3$COO)$_2$·0.5H$_2$O] (Sigma Aldrich, 99.99 %), zirconium oxychloride octahydrate (ZrOCl$_2$·8H$_2$O) (Sigma Aldrich, 99.99 %), and manganese acetate tetrahydrate [Mn(CH$_3$COO)$_2$·4H$_2$O] (Sigma Aldrich, 99.99 %) were precisely weighed and dissolved in deionized water to obtain a clear solution containing Mn$^{2+}$, Ca$^{2+}$, and Zr$^{4+}$ ions. Precise quantities of citric acid (Riedel-de Haën, 99.99 %) and cellulose (Alfa Aesar, 99.99 %) were added to the solution and stirred thoroughly to produce a white solution. After being stirred continuously at 75 °C for 4 h, the white solution was dried in an oven at 110 °C. The resulting powder then underwent calcination at 1200 °C for 6 h to form CaZrO$_3$:Mn$^{2+}$ phosphor.

The crystal structure of CaZrO$_3$:Mn$^{2+}$ phosphor was analyzed using X-ray powder diffraction (XRD, X’Pert PRO,
RESULTS AND DISCUSSION

Crystal structure and particle appearance of CaZrO₃:Mn²⁺ phosphor: Fig. 1 presents the XRD images of CaZrO₃ phosphor with varying quantities of Mn²⁺ calcined at 1200 °C for 6 h. As shown in the figure, CaZrO₃:Mn²⁺ phosphor displays a single crystalline phase. Compared with standard powder diffraction cards, the intensity of the diffraction peak was consistent with PDF card number 35-0645. The XRD diffraction peaks for various quantities of doped Mn²⁺ were not significantly different, indicating that the doping of different Mn²⁺ contents did not influence the crystal structure of CaZrO₃:Mn²⁺ phosphor. Using XRD data and XRD comparison software, CaZrO₃:Mn²⁺ phosphor was found to exhibit an orthorhombic structure belonging to the Pnma(62) space group. The lattice parameters are a = 5.762 Å, b = 8.017 Å, c = 5.591 Å and the unit cell volume is V = 258.27 Å³. The crystalline phase was identified from the PDF: 35-0645.

Light-emission properties of CaZrO₃:Mn²⁺ phosphor: Phosphors consist primarily of a host lattice and an activator. In CaZrO₃:Mn²⁺ phosphor, CaZrO₃ is the host lattice and Mn²⁺ is the activator. The crystal structure of CaZrO₃ consists of an octahedral unit formed by six O atoms and one Zr atom ([ZrO₆]) as well as a dodecahedral unit formed by twelve O atoms and one Ca atom ([CaO₁₂]). The radii of Mn²⁺, Ca²⁺, and Zr⁴⁺ ions are 0.067 nm, 0.134 nm, and 0.072 nm, respectively. The radii of Mn²⁺ and Zr⁴⁺ ions are the closest, leading to an exchange of positions and the formation of the emission center. For this reason, doping the CaZrO₃ host lattice with Mn²⁺ ions creates a light-emitting phosphor.

Energy-transfer properties of CaZrO₃:Mn²⁺ phosphor: To understand the energy transfer mechanism in CaZrO₃:Mn²⁺ phosphor, the theories of Blasse and Dexter were employed to calculate the energy-transfer distance and verify the energy transfer mechanism between Mn²⁺ ions. An increase in doping content causes the Mn²⁺ ions to become more densely packed, resulting in the transfer of energy between them. The close distance between the ions under such conditions is referred to as the energy transfer distance; the distance at which the maximum intensity of light emission peaks in the phosphor is defined as the maximum energy-transfer distance. The energy-transfer distance was calculated using the Blasse-Dexter theory.
In Section (a) of the text, the wavelength (nm) is presented.

Fig. 3. Excitation spectra of CaZrO₃:Mn²⁺ phosphors (Mn²⁺ content: 0.0001 mole, 0.001 mole, 0.003 mole, 0.005 mole, 0.007 mole, 0.009 mole, 0.011 mole, 0.013 mole, 0.015 mole, 0.017 mole, 0.019 mole).

Fig. 4. Emission spectra of CaZrO₃:Mn²⁺ phosphors (Mn²⁺ content: 0.0001 mole, 0.001 mole, 0.003 mole, 0.005 mole, 0.007 mole, 0.009 mole, 0.011 mole, 0.013 mole, 0.015 mole, 0.017 mole, 0.019 mole).

The transfer distance is the content that contributes to this maximum value. In Fig. 4, emission intensity peaks at a Mn²⁺ doping level of 0.001 mole, which represents the quench threshold. The maximum value can be calculated using Blasse’s formula:

\[
\frac{I}{x} \approx \xi \left(1 + \mu \left(\frac{x}{x_c}\right)^\omega\right)^{-1}
\]

where \(I\) is the luminous intensity of the phosphorus material, \(x\) is the content of the activator ion, and \(\omega\) is the evaluation parameter of the energy-transfer mechanism between the activators. An \(\omega\) value equal to 6 indicates electric dipole interaction, an \(\omega\) value equal to 8 indicates electric dipole and electric quadrupole interaction, and an \(\omega\) value equal to 10 indicates electric quadrupole interaction. The parameters \(\xi\) and \(\mu\) are constants in identical host lattice structures under identical excitation conditions. When \(\mu \left(\frac{x}{x_c}\right)^\omega \gg 1\), eqn. 2 can be simplified to eqn. 3, in which parameter \(\xi'\) is a constant.

\[
\frac{I}{x} \approx \xi' \left(\mu \left(\frac{x}{x_c}\right)^\omega\right)^{-1}
\]

Fig. 4 shows that the critical content of Mn²⁺ in CaZrO₃: Mn²⁺ phosphor is 0.001 mole. Fig. 5 is the slope map of log \((I/x_{Mn²⁺})\) and log \((x_{Mn²⁺})\) for a Mn²⁺ content greater than 0.001 mole in Fig. 4, displaying a straight line with a slope of \(-\omega/3\). From Fig. 5, the ratio of log \((I/x_{Mn²⁺})\) to log \((x_{Mn²⁺})\) is constant with a slope of -3.636. Therefore, \(\omega = 10.908\), which is close to 10. This shows that the energy transfer mechanism between Mn²⁺ ions in CaZrO₃:Mn²⁺ phosphor is electric quadrupole interaction.

Fig. 5. log \((I/x_{Mn²⁺})\)-log \((x_{Mn²⁺})\) relationship in CaZrO₃:Mn²⁺ phosphor with Mn²⁺ content exceeding quenching threshold.

Conclusion

This study successfully synthesized CaZrO₃ phosphor doped with Mn²⁺ in a method that employed cellulose-citric acid. XRD analysis confirmed the crystal structure of CaZrO₃: Mn²⁺ phosphor as orthorhombic structure, belonging to the Pnma \{62\} space group. FE-SEM/EDX analysis revealed the appearance and element composition of CaZrO₃:Mn²⁺ particles. From a structural perspective, the light emitted by CaZrO₃: Mn²⁺ phosphor can be attributed to replacement between Mn²⁺ ions and Zr⁴⁺ ions, forming the emission center. The excitation spectrum presented an excitation peak at a wavelength of 457

\[
\left(\frac{R_M}{2}\right)^3 \approx \frac{3V}{4\pi x_c N}
\]

where \(x_c\) is the critical content of the activator; \(N\) is the number of sites per unit cell that the Mn²⁺ ion can occupy and \(V\) is the unit cell volume. By substituting the known values into the equation \((x_c = 0.001 \text{ mol}, N = 2, V = 258.27 \text{ Å}^3)\), the maximum distance for the transfer of energy (Rₐₙ) between Mn²⁺ ions was calculated to be 62.72 Å.

Dexter’s theory states that if energy transfer occurs between the same type of activator ions, the energy transfer mechanism can be determined by the intensity of the emission spectra. Dexter’s equation is as follows:

\[
\frac{I}{x} \approx \xi \left(1 + \mu \left(\frac{x}{x_c}\right)^\omega\right)^{-1}
\]

\[
\frac{I}{x} \approx \xi' \left(\mu \left(\frac{x}{x_c}\right)^\omega\right)^{-1}
\]
nm, corresponding to the $6A_1^e(6S) \rightarrow 4T_1^o(4G)$ transition in Mn$^{2+}$ ions. The emission spectrum exhibits a peak emission at 541 nm, corresponding to the $4T_1^o(4G) \rightarrow 6A_1^e(6S)$ transition in Mn$^{2+}$ ions. The maximum distance for energy transfer between Mn$^{2+}$ ions was estimated to be 62.72 Å. Finally, energy transfer between Mn$^{2+}$ ions was found to result from electric quadrupole interactions.

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