Luminescence properties of Li\textsuperscript{+}/Mg\textsuperscript{2+}-doped Cr\textsuperscript{3+}: ZrSiO\textsubscript{4}

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Abstract. Cr\textsuperscript{3+}: ZrSiO\textsubscript{4} ceramics with different concentrations of Cr\textsuperscript{3+}-doped were prepared by a simple solid-state reaction method, and the effect of Cr\textsuperscript{3+} concentration on the photoluminescence of ZrSiO\textsubscript{4} samples was investigated. The X-ray powder diffractometer (XRD) was used to analyze the structural characteristics of the samples. The XRD results show that zirconium silicate has been completely synthesized at 1400°C, which indicates that Cr\textsuperscript{3+} enters into the lattice of ZrSiO\textsubscript{4}, but does not change the structure of it. The emission spectra of ZrSiO\textsubscript{4} were measured by the fluorescence spectrometer. The strongest emission peak was at 689nm, which was attributed by the \textsuperscript{2}E\textsuperscript{-}A\textsuperscript{2} of Cr\textsuperscript{3+}. The influence of different concentrations of Cr\textsuperscript{3+} on the luminescence of zirconium silicate was investigated. When the concentration of Cr\textsuperscript{3+} is 0.1mol\%, the luminescence intensity of the samples is the highest. When the concentration of Cr\textsuperscript{3+} is 0.5mol\%, the intensity of the emission spectrum decreases, which is due to the concentration quenching of Cr\textsuperscript{3+} in the crystal lattice. Finally, the influence of charge compensator ions on the emission intensity of the sample is explored. The results show that the emission intensity of the zirconium silicate samples is improved when the appropriate amount of Li ion is added.

Keywords: Cr\textsuperscript{3+}:ZrSiO\textsubscript{4}, Emission spectrum, Charge compensator, Solid-state reaction.

1. Introduction
Zirconium silicate is a kind of silicate inorganic material with excellent performance. It has good physical and chemical properties, high-temperature resistance, high corrosion resistance, high thermal conductivity, simple synthesis, and good stability [1], so it is widely used in daily life and is often used as the matrix material of ceramic pigment. Zirconium silicate is a tetragonal structure, which belongs to space group I41. There are four ZrO\textsubscript{8}\textsuperscript{12-} groups and four SiO\textsubscript{4}\textsuperscript{4-} groups in one unit cell. Another significant characteristic of it is that it can accommodate a variety of doped ions. The silicon in zirconium silicate is four coordinated and zirconium is eight coordinated [2]. The crystal characteristics of zirconium silicate make it easy for rare-earth or transition elements to replace Zr\textsuperscript{4+}, resulting in defects and energy level transition, and then rare-earth or transition elements produce luminescence in the matrix. Therefore, zirconium silicate is a potential matrix material for laser materials. So, the spectroscopic study of zirconium silicate has been widely concerned by researchers.

Luminescent materials are made of matrix and doped ions. The doped ions in the matrix of luminescent materials are generally called luminescent centers. For transition metal ion luminescent...
centers, because they have unfilled d-electron shells and 3d electrons are in the outer layer, they are prone to energy level splitting. The luminescence of transition metal ions is greatly affected by the crystal field. The interaction between the d-layer electrons and the crystal field should be considered. The light emitted will be different under different crystal fields [3]. So, it is necessary to study the luminescence of transition ions in the zirconium silicate crystal field. Cr$^{3+}$, Mn$^{2+}$, Mn$^{4+}$, and other transition metal ions are commonly used as luminescence centers [4]. Cr$^{3+}$ luminescence has been widely used in real life and laser applications. In this study, zirconium silicate was used as the matrix, and the doping ion was Cr$^{3+}$.

For a long time, the conversion efficiency of solar cells is an urgent problem in the application of solar cells. A good way is to convert sunlight into a band that can be well absorbed by solar cells through adjustment. As a luminescent center, Cr$^{3+}$ can transform the ultraviolet band that can't be absorbed by solar cells into the near-infrared band that can be absorbed by solar cells, which can effectively improve the efficiency of solar cells [5]. Therefore, zirconium silicate doped with Cr$^{3+}$ is a good application in solar cells, and it is necessary to study the luminescence of Cr$^{3+}$: ZrSiO$_4$.

Previous studies suggest that Cr$^{3+}$ replaces Zr$^{4+}$ in ZrSiO$_4$ lattice [6], but when Cr$^{3+}$ enters into the lattice of ZrSiO$_4$, the charge of cations is not equal, which will cause the the problem of charge conservation in the doping area, which requires the addition of charge compensator. The types of charge compensators have a great influence on the luminescence intensity of Cr$^{3+}$: ZrSiO$_4$, so we studied the influence of two common charge compensators on the luminescence of Cr$^{3+}$: ZrSiO$_4$.

In this study, Cr$^{3+}$: ZrSiO$_4$ was synthesized by a simple solid-state method. The emission spectra of the samples were investigated and discussed. The structural properties of the samples were also analysed. More importantly, the effect of different charge compensators on the luminescence of Cr$^{3+}$: ZrSiO$_4$ was studied.

2. Experimental procedures
Cr$^{3+}$: ZrSiO$_4$ samples were prepared by high temperature solid-state method at 1400 $^\circ$C with or without 0.1mol% Li$_2$CO$_3$/MgO, in which the concentration of Cr$^{3+}$ is 0.1mol%. Cr$_2$O$_3$ (99%), SiO$_2$ (99.5%), and ZrO$_2$ (99%) powders were used as raw materials. The powder is poured into deionized water, mixed and milled for 2 hours, then taken out and poured into an agate pot, dried in the oven at 90 $^\circ$C for 10 hours in air. Finally, the samples were calcined in a high-temperature muffle furnace at 1400$^\circ$C for 4h.

The phase compositions of the samples were detected by X-ray powder diffraction (Bruker Daltonics, Germany) with Cu-K$\alpha$ radiation. The data were collected in a step scanning mode of 2$\theta$ = 20°to 80° with a step size of 0.02°and a time of 1.2s. Photoluminescence spectra were measured by using fluorescence spectrophotometer (Model FLS920, Edinburgh Instruments Ltd., United Kingdom), which was using a Xe lamp as the pump source.

3. Results and discussion
3.1. Structure studies
Figure 1 shows the XRD patterns of Cr$^{3+}$: ZrSiO$_4$ produced by calcining ZrO$_2$-SiO$_2$ powder at 1400$^\circ$C without doping or co-doped charge compensator ions Li$^+$/Mg$^{2+}$, respectively, and the standard card of ZrSiO$_4$. It can be seen from the figure that the spectrum of Cr$^{3+}$: ZrSiO$_4$ without doping or co-doped charge compensator ions are consistent with that of PDF#06-0266 [7], which indicates that ZrSiO$_4$ samples have been completely synthesized and have good crystallinity. In the spectrum of Cr$^{3+}$: ZrSiO$_4$, the peak shape does not shift, which indicates that Cr$^{3+}$ has entered into the lattice of ZrSiO$_4$ and has no obvious effect on the lattice. The peak value of Cr$^{3+}$: ZrSiO$_4$ does not change obviously after co-doped with the charge compensator. These results show that the addition of the charge compensator does not affect the synthesis of zirconium silicate. Table 1 shows the comparison of different ion radii. The ion radius of Si$^{4+}$ in zirconium silicate is 0.026nm, that of Zr$^{4+}$ is 0.072nm, and that of Cr$^{3+}$ is 0.061nm. The ionic radii of Cr$^{3+}$ and Si$^{4+}$ are quite different. If the substitution occurs, the lattice of zirconium silicate will be distorted [8], and the luminescence intensity will be very low or even no luminescence. The ionic
radius of \( \text{Cr}^{3+} \) and \( \text{Zr}^{4+} \) is very close. When \( \text{Cr}^{3+} \) replaces \( \text{Zr}^{4+} \), the lattice of zirconium silicate will not change greatly, so we think that \( \text{Cr}^{3+} \) replaces \( \text{Zr}^{4+} \) into the lattice of zirconium silicate.

\[ \text{Table 1. The radii of Li}^+, \text{Mg}^{2+}, \text{Zr}^{4+}, \text{Cr}^{3+}, \text{and Si}^{4+} \text{ ions} \]

| Ion species | Coordination number | Ion radius (nm) |
|-------------|---------------------|-----------------|
| Li\(^+\)    | 6                   | 0.076           |
| Mg\(^{2+}\) | 6                   | 0.072           |
| Zr\(^{4+}\) | 8                   | 0.072           |
| Cr\(^{3+}\) | 6                   | 0.061           |
| Si\(^{4+}\) | 4                   | 0.026           |

\[ \text{Figure 1. XRD patterns of Cr}^{3+}:\text{ZrSiO}_4 \text{ without doping or co-doped charge compensator ions Li}^+/\text{Mg}^{2+} \text{ and the standard card of ZrSiO}_4 \]

\[ \text{Figure 2. The emission spectra of Cr}^{3+}:\text{ZrSiO}_4 \text{ doped with different Cr}^{3+} \text{ concentrations} \]
3.2. Emission spectrum

Fig. 2 shows the emission spectra of x mol% Cr\(^{3+}\): ZrSiO\(_4\) doped with different concentrations, and excited by UV radiation (260nm), where x = 0.01, 0.05, 0.1, 0.3, 0.5. The emission peak intensity of the doped samples increases with the increase of Cr content in a certain range. When the concentration of Cr ion is 0.1%, the emission intensity reaches the maximum. If the concentration of Cr ion continues to increase, the intensity of the emission spectrum will decrease. This is because the concentration of Cr ion in the crystal lattice increases and the interaction between Cr and Cr strengthens, which makes the original emission center disappear and the concentration quenching phenomenon occurs. In the following study, we selected the sample of 0.1mol% Cr\(^{3+}\): ZrSiO\(_4\).

It can be seen from the figure that the sample has roughly the same peak shape, which indicates that the luminescence of the sample comes from the same luminescence center, and Cr ion is used as the luminescence center in the sample to cause the sample to emit light. When the excitation wavelength is 405nm, it is observed that the emission spectrum consists of a narrow band near the red region. The emission peak is located at 689nm, which belongs to \(^2\text{E} \rightarrow \text{A}_2\) of Cr\(^{3+}\), which is also consistent with the previous study [9]. Obviously, Cr\(^{3+}\) acts as the luminescence center, and chromium ions contribute near red light.

![Figure 3](image-url). Comparison of the emission spectra of 0.1mol% Cr\(^{3+}\): ZrSiO\(_4\) samples without doping or co-doped charge compensator ions

3.3. Charge compensator

Fig. 3 shows the comparison of the emission spectra of 0.1mol% Cr\(^{3+}\): ZrSiO\(_4\) samples without doping or co-doped charge compensator ions measured at room temperature. It can be seen from the figure that the luminescence intensity of Cr\(^{3+}\): ZrSiO\(_4\) is enhanced after adding charge compensator ion, which indicates that the charge compensator can enhance the luminescence performance of the samples [10]. Although the emission peak intensity is improved to some extent after co-doped with charge compensator Mg\(^{2+}\), the emission intensity is obviously improved after doping with Li\(^+\). We think that although the ionic radius of Mg\(^{2+}\) is close to that of Zr\(^{4+}\), and Mg\(^{2+}\) replaces Zr\(^{4+}\) and enters into the lattice of zirconium silicate, the lattice is still in a state of charge conservation, and the damage to the luminous intensity is greater than the improvement of charge compensation, so the enhancement of luminous intensity is not obvious [11]. After Li\(^+\) doping, the local charge conservation is eliminated and
the charge balance state is reached under the joint action of Li\(^+\) and Cr\(^{3+}\), which enhances the luminescence intensity of the samples.

4. Conclusion

In this work, Cr\(^{3+}\): ZrSiO\(_4\) samples doped without or with different concentrations of Cr\(^{3+}\) were successfully prepared by high temperature solid-state reaction. XRD results show that the ZrSiO\(_4\) sample has been completely synthesized, and the crystallinity is good. The addition of Cr\(^{3+}\) into the lattice of ZrSiO\(_4\) does not change the structure of zirconium silicate. The emission spectra of ZrSiO\(_4\) were measured by the fluorescence spectrometer. The strongest emission peak was at 689 nm, which was attributed by \(^2\)E\(-\)\(^2\)A\(_2\) of Cr\(^{3+}\). The influence of different concentrations of Cr\(^{3+}\) on the luminescence intensity of zirconium silicate samples was investigated. The results show that the luminescence intensity of zirconium silicate samples is the highest when the concentration of Cr\(^{3+}\) is 0.1mol%. When the concentration of Cr\(^{3+}\) is 0.5mol%, the intensity of the emission spectrum decreases, which is due to the concentration quenching of Cr\(^{3+}\) in the crystal lattice. Finally, the influence of different charge compensator ions on the emission intensity of the sample is also explored. The results show that the emission intensity of the zirconium silicate sample will be improved when an appropriate amount of Li ion is added.

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