The effect of Mg$^{2+}$ ion on the optical characteristics of rare-earth ion in CaWO$_4$ polycrystal

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Abstract. The Mg$_x$Ca$_{(1-x)}$WO$_4$ polycrystals codoped with Er$^3+$ and Yb$^3+$ ions were prepared by the high temperature solid-state reaction method. The structural properties of Mg$_x$Ca$_{(1-x)}$WO$_4$ polycrystals codoped with Er$^{3+}$ and Yb$^{3+}$ ions were confirmed by the X-ray diffraction patterns. The effect of Mg$^{2+}$ ion on the optical characteristics of Er$^{3+}$ and Tm$^{3+}$ ions in CaWO$_4$ polycrystals under 980 nm excitation was investigated. The strong blue and green upconversion emissions were observed for CaWO$_4$ polycrystal doped with 30 mol% Mg$^{2+}$ ions. The Mg$^{2+}$ ions affected the optical characteristics of Er$^{3+}$ and Tm$^{3+}$ ions in CaWO$_4$ host material through tuning the rate of cross relaxation process. Studies on the upconversion emission spectra and power pump dependence of Er/Yb:Mg$_{0.3}$Ca$_{0.7}$WO$_4$ polycrystals indicated that the inefficient cross relaxation processes of $^4S_{3/2} + ^3I_{15/2}$ $\rightarrow$ $^4I_{9/2} + ^4I_{13/2}$ and $^4S_{3/2} + ^3I_{15/2}$ $\rightarrow$ $^4I_{13/2} + ^4I_{9/2}$ between Er$^{3+}$ ions were contribution to the increased green upconversion emission under 980 nm excitation.

1. Introduction
The visible luminescence can be easily obtained by use of the trivalent rare-earth ions converting the near-infrared (NIR) light into the upconversion (UC) emission under the cost-effective and high-power NIR diode laser excitation [1]. There has been considerable interest in rare-earth ions doped materials since they play an important role in the applications of the novel display technologies, optical data storage and undersea communications [2, 3]. Erbium (Er$^{3+}$) ion, which has the favorable electronic energy level structures, could emit a strong green UC emission and a weak red emission under 800 nm and 980 nm excitation [4, 5]. Doping concentration of Er$^{3+}$ ions have influence on the upconversion luminescence properties of the materials. It has been reported that the pure green or red UC emissions could be achieved by tuning the concentration of Yb$^{3+}$ ions in host materials doped with Er$^{3+}$ ions under 980 nm excitation [6-8]. The $^1G_4$ $\rightarrow$ $^3H_4$ transition of Tm$^{3+}$ ion produces the bright blue UC emission [9]. Research in this area based on rare-earth ions doped silica glasses, polymers and crystals have been widely demonstrated [10-14]. Among these host materials, calcium tungstate (CaWO$_4$) has attracted tremendous research interest since it exhibits the good chemical and physical stability. Previous works showed that CaWO$_4$ could be extensively used as X-ray phosphor, scintillating material and laser host media [15]. An efficient multiphonon relaxation, decreasing the intensity of UC emission, could be suppressed by the relatively low phonon cutoff energy of the host materials. Therefore, it is expected that a high UC efficiency could be obtained in CaWO$_4$ doped rare-earth ions...
due to its relatively low phonon cutoff energy. In order to limit the optical damage in the luminescent host materials, magnesium (Mg) ion is selected here [16].

In this paper, antiphotorefractive Mg\(^{2+}\) ions were introduced into rare earth ions doped CaWO\(_4\) polycrystals, and the effect of Mg\(^{2+}\) ions concentration on the optical characteristics of rare earth ion was investigated. Meanwhile, the effect of Er\(^{3+}\) ions on the upconversion luminescence (UCL) intensity was studied. The UC emission spectra, the pump power dependence and UC mechanism are studied.

2. Experimental
The Mg\(_{x}\)Ca\(_{1-x}\)WO\(_4\) polycrystals codoped with (a) 1 mol\% Er\(^{3+}\) and 8 mol\% Yb\(^{3+}\) ions, (b) 0.5 mol\% Tm\(^{3+}\) and 8 mol\% Yb\(^{3+}\) ions were prepared by the high temperature solid-state reaction method. In order to understand the effect of Mg\(^{2+}\) ion on the optical characteristics of rare-earth ion in CaWO\(_4\) polycrystals, the values of \(x\) change from 1, 10, 30, 50 to 70 mol\%. The purities of the raw materials (CaO, WO\(_3\), MgO, Er\(_2\)O\(_3\), Yb\(_2\)O\(_3\) and Tm\(_2\)O\(_3\)) were 99.99\%. The raw materials were fully ground in an agate mortar for 4 h. The sufficient fine and fully homogenous powders were pressed into a disk under 20 MPa. The polycrystalline powders were generated via undergoing the heat treatment of 1000 °C for 6 h. Raw material compositions (mol\%) of samples are shown in Table 1.

The UC emission spectra were measured by a power-controllable 980 nm diode laser. The spectrometer (Bruker optics 500IS/SM) equipped with a semiconductor cooled charge coupled device detector (DV440, Andor) was used to record all fluorescence emissions at the same geometry.

2.1. Samples characterization
Figure 1 displays the X-ray diffraction patterns of Mg\(_{0.3}\)Ca\(_{0.7}\)WO\(_4\) polycrystals codoped with 8 mol\% Yb\(^{3+}\) and the different concentrations of Er\(^{3+}\) ions. Since the same properties are obtained in other Mg\(_{x}\)Ca\(_{1-x}\)WO\(_4\) (\(x = 0.0, 0.1, 0.3, 0.5\) and 0.7) polycrystals codoped with Tm\(^{3+}\) and Yb\(^{3+}\) ions, the measured XRD spectra of samples are not shown in Figure 1. As shown in Figure 1, there are no new peaks observed for the samples compared with the pure CaWO\(_4\) polycrystals, suggesting that Mg\(^{2+}\), Er\(^{3+}\) and Yb\(^{3+}\) ions have no influence on the structures of the samples. It is proposed that the samples are still body-centered tetragonal system. The ionic radius of Mg\(^{2+}\), Ca\(^{2+}\), Er\(^{3+}\) and Yb\(^{3+}\) are 0.57nm, 0.99nm, 0.88nm and 0.86nm, respectively. Consequently, Mg\(^{2+}\), Er\(^{3+}\) and Yb\(^{3+}\) ions may occupy the Ca-sites rather than the interstitial sites within the lattice.

Figure 1. The X-ray diffraction patterns of Mg\(_{0.3}\)Ca\(_{0.7}\)WO\(_4\) polycrystals codoped with 8 mol\% Yb\(^{3+}\) and the different concentrations of Er\(^{3+}\) ions.
3. Results and discussion

The UC emission spectra of Mg$_x$Ca$_{(1-x)}$WO$_4$ ($x = 0.0, 0.1, 0.3, 0.5$ and $0.7$) polycrystals codoped with Er$^{3+}$/Yb$^{3+}$ and Tm$^{3+}$/Yb$^{3+}$ ions under 980 nm excitation are shown in Figure 2. It can be seen that the green UC emissions centered at 525/550 nm correspond to the $^2H_{11/2}/^4S_{3/2} \rightarrow \ ^4I_{15/2}$ transitions of Er$^{3+}$ ion, respectively. The red UC emission at 660 nm arises from the $^4F_{9/2} \rightarrow \ ^4I_{15/2}$ transition [17]. As for the Tm$^{3+}$/Yb$^{3+}$-codoped Mg$_x$Ca$_{(1-x)}$WO$_4$ polycrystals, the blue UC emission at 480 nm arises from the $^1G_4 \rightarrow \ ^3H_6$ transition of Tm$^{3+}$ ion [18]. As shown in Figure 2A, the intensities of the green and red UC emissions increases with Mg$^{2+}$ ion of 1-30 mol%, and decrease at higher concentration of Mg$^{2+}$ ions. Figure 2B shows that the strongest blue UC emission is observed in M$_{0.3}$C$_{0.7}$:Tm/Yb polycrystal. These experimental results indicate that the optimal concentration of Mg$^{2+}$ ion in MgCaWO$_4$ polycrystals may be equal to 30 mol%. The effect of Mg$^{2+}$ ion on the optical characteristics of Er$^{3+}$ and Tm$^{3+}$ ions in CaWO$_4$ polycrystals will be understood in the next section.

![Figure 2](image-url)

**Figure 2.** The UC emission spectra of Mg$_x$Ca$_{(1-x)}$WO$_4$ ($x = 0.0, 0.1, 0.3, 0.5$ and $0.7$) polycrystals codoped with Er$^{3+}$/Yb$^{3+}$ and Tm$^{3+}$/Yb$^{3+}$ ions under 980 nm excitation.

Figure 3 presents the energy level diagrams of Tm$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ ions and UC mechanisms in Er/Yb:Mg$_x$Ca$_{(1-x)}$WO$_4$ and Tm/Yb:Mg$_x$Ca$_{(1-x)}$WO$_4$ polycrystals. In the Er$^{3+}$/Yb$^{3+}$ and Tm$^{3+}$/Yb$^{3+}$ codoped systems, laser excitation of Yb$^{3+}$ ion is only considered here due to the following reasons [19, 20]. Firstly, Yb$^{3+}$ ion has a much larger absorption cross section around 980 nm and could transfer efficiently its energy to Er$^{3+}$ and Tm$^{3+}$ ions. Secondly, Tm$^{3+}$ ion has no corresponding energy level. The well-known two-photon process to populate the green and red UC emissions of Er$^{3+}$ ion can be described as follows [21]: Yb$^{3+}$ ions act as sensitizers to absorb laser photons, a 980 nm photon excites the Yb$^{3+}$ ion from the ground $^2F_{7/2}$ state to its excited $^2F_{5/2}$ state, and it transfers its excitation energy to Er$^{3+}$ ion. The energy transition (ET1) processes of ET1: $^4I_{15/2}$ (Er) + $^2F_{5/2}$ (Yb) $\rightarrow$ $^4I_{11/2}$ (Er) + $^2F_{7/2}$ (Yb) and ET2: $^4I_{11/2}$ (Er) + $^2F_{5/2}$ (Yb) $\rightarrow$ $^4F_{7/2}$ (Er) + $^2F_{7/2}$ (Yb) excite Er$^{3+}$ ions form the ground state $^4I_{15/2}$ to the upper state $^4F_{7/2}$ of Er$^{3+}$ ion. Subsequently, the green emitting $^2H_{11/2}/^4S_{3/2}$ states are populated via the nonradiatively relaxation from the $^4F_{7/2}$ state of Er$^{3+}$ ion. Er$^{3+}$ ions at the $^4I_{11/2}$ state could decay...
nonradiatively to the $^{4}I_{13/2}$ state of Er$^{3+}$ ion. ET3 process of $^{4}I_{13/2}$ (Er) + $^{2}F_{5/2}$ (Yb) → $^{4}F_{9/2}$ (Er) + $^{2}F_{7/2}$ (Yb) is contribution to the population of the red emitting $^{4}F_{9/2}$ state of Er$^{3+}$ ion. It is proposed that there are two cross relaxation (CR) processes between two neighboring Er$^{3+}$ ions (CR1: $^{3}S_{3/2} + ^{4}I_{5/2}$ → $^{4}I_{9/2}$ + $^{3}S_{3/2}$ and CR2: $^{3}S_{3/2} + ^{4}I_{5/2}$ → $^{4}I_{13/2}$ + $^{4}I_{9/2}$) in Er/Yb:Mg$_{x}$Ca$_{1-x}$WO$_{4}$ polycrystals. It is obvious that the fast CR1 and CR2 processes will lead to a reduction of the green UC emission. In the case of Tm$^{3+}$/Yb:Mg$_{x}$Ca$_{1-x}$WO$_{4}$ polycrystals, the blue emitting $^{1}G_{4}$ state of Tm$^{3+}$ ion is populated via ET4 ($^{3}H_{4}$ Tm + $^{2}F_{5/2}$ Yb → $^{3}H_{5}$ Tm + $^{3}F_{7/2}$ Yb), ET5 ($^{3}F_{4}$ Tm + $^{2}F_{5/2}$ Yb → $^{3}F_{2,3}$ Tm + $^{2}F_{7/2}$ Yb) and ET6 ($^{3}H_{4}$ Tm + $^{2}F_{5/2}$ Yb → $^{3}G_{4}$ Tm + $^{2}F_{7/2}$ Yb). Between the two neighboring Tm$^{3+}$ ions, the CR3 ($^{3}G_{4} + ^{3}H_{6}$ → $^{2}F_{2,3}$ + $^{3}F_{4}$) and CR4 ($^{3}G_{4} + ^{3}H_{6}$ → $^{3}H_{5} + ^{3}H_{6}$) processes occur in Mg$_{x}$Ca$_{1-x}$WO$_{4}$ polycrystals codoped with Tm$^{3+}$/Yb$^{3+}$ ions under 980 nm excitation. Clearly, the intensity of blue emission will be decreased with the fast rate of CR3 and CR4 processes. It is well general accepted that for the constant Er$^{3+}$ and Tm$^{3+}$ ions here, there should be a constant value for the blue, green and red UC emissions, which contradicts the experimental results shown in Figure 2. As illustrated in Figure 2, the intensities of the blue, green and red emissions change with the different concentrations of Mg$_{x}^{2+}$ ion, which indicate that the fluorescence intensities of Er$^{3+}$ and Tm$^{3+}$ ions in CaWO$_{4}$ host material are affected by Mg$^{2+}$ ions through tuning the rate of CR processes.

Figure 3. The Energy level diagrams of the Tm$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ ions. (The arrow represents the direction of the energy level transition).

Figure 4 shows the UC emission spectra of Mg$_{0.3}$Ca$_{0.7}$WO$_{4}$ polycrystals codoped with 8 mol% Yb$^{3+}$ and the different concentrations of Er$^{3+}$ ions under 980 nm excitation. It is obvious that the concentration-quenching effect of Er$^{3+}$ ions is observed in Er/Yb-codoped Mg$_{0.3}$Ca$_{0.7}$WO$_{4}$ polycrystals. The green UC emission increases with the increasing concentration of Er$^{3+}$ ions from 0.1 mol% to 2.0 mol%, whereas the intensity of green UC emission decreases at higher concentration of Er$^{3+}$ ions. Besides Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{0.1}$ polycrystal, the intensity of red UC emission remains almost constant for Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{0.5}$, Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{1.0}$, Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{2.0}$, Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{3.0}$ and Mg$_{0.3}$Ca$_{0.7}$Yb/Er$_{4.0}$ polycrystals.
Figure 4. The UC emission spectra of Mg$_{0.3}$Ca$_{0.7}$WO$_4$ polycrystals codoped with 8 mol\% Yb$^{3+}$ and the different concentrations of Er$^{3+}$ ions under 980 nm excitation.

Figure 5. Log-log plots of green emission intensity as a function of pump power of 980 nm excitation for M$_{0.3}$C$_{0.7}$:Yb/Er$_{2.0}$ polycrystal. Log-log plots of the green emission intensity as a function of pump power for M$_{0.3}$C$_{0.7}$:Yb/Er$_{2.0}$ polycrystal, shown in Figure 5, are used to better understand the UC mechanisms. In general, the relation $I \propto P^n$ is used to obtain the number of photons required to populate the upper emitting state for an unsaturated UC process [22], where $P$ is the pump intensity, $I$ is the green emission intensity, and $n$ is the number of the laser photons required. As illustrated in Figure 4, the slope value is found to be 1.97.
1.9, confirming that a two-photon process is involved to populate the green UC emission in M_{0.3}C_{0.7}:Yb/Er_{2.0} polycrystal. This is an indication that the UC mechanism of M_{0.3}C_{0.7}:Yb/Er_{2.0} polycrystal consists with the above populated path for the green emitting \(^4S_{2/2} \rightarrow \(^2H_{11/2}\) states (shown in Figure 3). In general, the fluorescence intensity is strongly dependent on the concentration and the distribution of the rare-earth ion. The fact that the intensity of green UC emission increases with the increasing concentration of Er\(^{3+}\) ions from 0.1 mol\% to 2.0 mol\% is attributed to the concentration effect. However, as the concentration of Er\(^{3+}\) ions enhances up to 3.0 mol\% and 4.0 mol\%, the distance between two neighboring Er\(^{3+}\) ion becomes short. The shortening distance makes the CR1 and CR2 processes more efficient since the CR process can readily occur when the distance between ions is small enough and is inversely proportional to the distance between two neighboring ions. It is conclusion that the CR processes play mainly role in the UC mechanism in M_{0.3}C_{0.7}:Yb/Er_{3.0} and M_{0.3}C_{0.7}:Yb/Er_{4.0} polycrystals. Consequently, the increased probabilities of CR1 and CR2 processes decrease the intensity of green UC emission in M_{0.3}C_{0.7}:Yb/Er_{3.0} and M_{0.3}C_{0.7}:Yb/Er_{4.0} polycrystals, in agreement with the experimental results shown in Figure 4.

### Table 1. Raw material compositions (mol\%) of samples.

| Samples       | Mg\(^{2+}\) | Ca\(^{2+}\) | Er\(^{3+}\) | Yb\(^{3+}\) | Tm\(^{3+}\) |
|---------------|-------------|-------------|-------------|-------------|-------------|
| M_{0.0}C_{0.0}:Er/Yb | 0           | 100         | 1           | 8           | 0           |
| M_{0.1}C_{0.0}:Er/Yb | 10          | 90          | 1           | 8           | 0           |
| M_{0.3}C_{0.0}:Er/Yb | 30          | 70          | 1           | 8           | 0           |
| M_{0.5}C_{0.0}:Er/Yb | 50          | 50          | 1           | 8           | 0           |
| M_{0.7}C_{0.0}:Er/Yb | 70          | 30          | 1           | 8           | 0           |
| M_{0.0}C_{1.0}:Tm/Yb | 0           | 100         | 0           | 8           | 0.5         |
| M_{0.1}C_{0.0}:Tm/Yb | 10          | 90          | 0           | 8           | 0.5         |
| M_{0.3}C_{0.0}:Tm/Yb | 30          | 70          | 0           | 8           | 0.5         |
| M_{0.5}C_{0.0}:Tm/Yb | 50          | 50          | 0           | 8           | 0.5         |
| M_{0.7}C_{0.0}:Tm/Yb | 30          | 70          | 0.1         | 8           | 0           |
| M_{0.3}C_{0.0}:Tm/Yb | 30          | 70          | 0.5         | 8           | 0           |
| M_{0.5}C_{0.0}:Tm/Yb | 30          | 70          | 1.0         | 8           | 0           |
| M_{0.7}C_{0.0}:Tm/Yb | 30          | 70          | 2.0         | 8           | 0           |
| M_{0.3}C_{0.0}:Tm/Yb | 30          | 70          | 3.0         | 8           | 0           |
| M_{0.5}C_{0.0}:Tm/Yb | 30          | 70          | 4.0         | 8           | 0           |

### 4. Conclusions

The Mg_{x}Ca_{1-x}WO_{4} polycrystals codoped with Er/Yb and Tm/Yb ions are prepared by the high temperature solid-state reaction method. The optimum concentration of Mg\(^{2+}\) ions is found to be 30 mol\%. And the intensities of the blue UC emission, arising from the \(^1G_4 \rightarrow \(^1H_6\) transition of Tm\(^{3+}\) ion, and the green UC emission, corresponding to the \(^1H_{11/2} \rightarrow \(^4S_{3/2}\) \rightarrow \(^4I_{15/2}\) transitions of Er\(^{3+}\) ion, decrease at the higher concentration of Mg\(^{2+}\) ions. Meanwhile, when the concentration of Er\(^{3+}\) ion was 2 mol\%, the upconversion luminescence intensity of Er/Yb/Mg\(_{0.3}Ca_{0.7}\)WO_{4} reached the maximum. Studies on the UC emission spectra of Er/Yb-codoped Mg_{0.3}Ca_{0.7}WO_{4} polycrystals indicate that Mg\(^{2+}\) ions may affect the fluorescence intensity of rare-earth ions via tuning structural and the rate of cross relaxation process.

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