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Journal Name

ARTICLE

Upconversion luminescence of cerium-stabilized high temperature phase zirconia phosphors with a high Er^{3+} doped concentration

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Oxide upconversion (UC) materials usually have lower luminescence efficiency (LE) due to their low quenching concentration and high phonon energy. To solve this issue, we have detailly investigated the cerium-stabilized high temperature phase zirconia based phosphors $(Zr_{(0.85-x)}Ce_{0.15}O_{(2-0.5x)}:xEr^{3+})$ with different doping concentration of Er^{3+} and achieved a red phosphor with Er^{3+} concentration being as high as 10 mol%, which will have a broad prospect for application as a new UC materials. The results demonstrate that adjusting the host structure of UC materials can increase its quenching concentration and thereby the LE will be improved. The introduction of Ce^{4+} into ZrO_2 not only stabilizes its phase but also improves the LE of ZrO_2 based UC materials. The Er^{3+} coordination state changes with the increase of Er^{3+} concentration in UC phosphors based on the cerium-stabilized zirconia and the corresponding luminescence process translated into the cross relaxation from the excited state absorption, UC luminescence changes from green to red, the red emission intensity becomes more and more stronger and achieves the strongest when the Er^{3+} concentration is 10 mol%.

Introduction

Rare-earth doped UC luminescence materials have attracted a great scientific interest due to their potential applications in solid-state lasers,[1] optical fibre communication,[2] three-dimensional display,[3,4] anti-counterfeit technology,[5] bioimaging,[6,7] solar cell[8,9] and so on. UC materials not only demand high LE but also good physic and chemical properties for the practical application. Fluoride UC materials have attracted significant attention due to their lower phonon energy and higher LE,[3,6] but their poor chemical stability, mechanical strength and optical damage resistant properties have been the inevitable challenges for actual applications. Compared to the fluoride, oxide based UC materials are more suitable for industrialization and practical application due to their free pollution

fabrication process, simple manufacturing technique, excellent chemical stability and thermostability, but its lower LE blocks its further application. So, it has been a significant work to improve the LE of oxide UC materials.

Host and doped rare earth ions have important influences on the LE of UC materials under certain excitation source. Generally speaking, the lower phonon energy of substrate and higher rare earth doped concentration will bring about higher LE for UC materials, but high doping concentration will cause serious fluorescence quenching due to the lower quenching concentration for UC materials, traditional UC polycrystalline or single crystal materials are often confined to a lower concentration (for example, the doping concentration of Er^{3+} in erbium doped UC materials is about 1 mol%),[3,10] the lower quenching concentration has been the main barrier to improve the LE of many UC materials including oxide materials. To solve this bottleneck issue, taking cerium-stabilized zirconia UC phosphors as study objects, which are constituted by cerium-stabilized zirconia doped with 15 mol% Ce^{4+} (marked with 15CSZ) used as a substrate and Er^{3+} used as a active ion, related works on high rare-earth ion doping are studied to improve the LE of oxide UC materials.

To achieve the oxide UC materials doped with high concentration of rare-earth ions, the substrate must have an adjusted structure and be easy to form a good solid solution that has low phonon energy with other materials, however, few materials can satisfy this. In this paper, ZrO_2 with low phonon energy is chosen as the based materials for preparing this UC materials. ZrO_2 owns low phonon energy about 470 cm^{-1}, good chemical and photochemical stability and high melt point and so on, which is a good UC luminescence substrate.[5,11] As we all known, pure zirconia has three kinds of crystalline phase structure: monoclinic, tetragonal and cubic. The phase of zirconia changes with the

prepared temperature and used temperature, which causes the instability of physical and chemical properties and hinders its application.[12-14] To obtain the stable ZrO_2 phase, stabilizers are added into ZrO_2, which can stabilize the crystalline phase and adjust the micro-structure of ZrO_2 at the same time. Luckily, scientists did mounts of research work about the phase transition mechanism of zirconia and improving the stability, finding that the high temperature phase of zirconia can be stabilized at room temperature by adding some stabilizers (Y_2O_3, CaO, Al_2O_3, MgO, CeO_2, etc.) in the ZrO_2 . Y_2O_3, as a stabilizer, is often used in the production of zirconia ceramics, however, CaO, MgO and CeO_2 are less used. Related studies have been reported by A. Feinber's group,[15] M. V. Swain's group[16] and P. Li's group[17] and so on. We choose CeO_2 as a stabilizer in above oxides, which can form the miscible solid solution with ZrO_2, not only can stablize the tetragonal phase of ZrO_2, but also has low phonon energy(457 cm^{-1}).[17,18]

15CSZ:xEr^{3+} phosphors are prepared via reverse co-precipitation method and the influences of composition, structure and process condition on its luminescence properties are investigated in detail. Their corresponding relations and change rules and the luminescence mechanism of the phosphors are clarified. These will provide the theoretical and technical support for raising rare earth ions doping content, LE of UC materials and developing new UC luminescence materials.

Experimental

Sample preparation

15CSZ:xEr^{3+} phosphors with different doping concentration of Er^{3+} (x=0.001,0.005,0.01,0.05,0.1,0.15,0.2) were prepared by reverse co-precipitation method. The main materials of erbium oxide (Er_2O_3, 99.99%), cerium nitrate($Ce(NO_3)_3 \cdot 6H_2O$, AR), zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, AR) and nitric acid (HNO_3,

AR) were purchased from Sinopharm Chemical Reagents Co. Ltd. Firstly, Er_2O_3 was weighed accurately according to the stoichiometric ratio, and then dissolved into concentrated HNO_3 to the transparent. The excess acid was evaporated to obtain erbium nitrate, then $ZrOCl_2 \cdot 8H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were weighed according to the stoichiometric ratio, and mixed with the previously prepared erbium nitrate, adding a proper volume deionized water to prepare a cationic solution of about 0.5 mol·L^{-1}, and vigorously stirred until homogeneous and transparent state. The mixture was slowly added to excess ammonium hydroxide $NH_3 \cdot H_2O$ (2 mol·L^{-1}), continued to stir until the titration was complete and the pH of mixture was about 9~10, continuously stirred for 2 h to react completely. The precursor in mixed solution was filtered and washed 2~3 times with deionized water. Afterwards, the precursor was dried at 105□ for 12 h and grinded in an agate mortar for 30 minutes. Then precursor powders were moved to a crucible where they would be sintered at 1200□ for 3 h in muffle furnace. Finally, the samples were obtained.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded by a Bruker/AXS D8-ADVANCE X-ray diffractometer using a copper target with Kα_1 radiation (λ=0.15406 nm). The 2θ angle ranging from 10°~90° and the working current and voltage were 40 mA and 40 kV, respectively. The UC luminescent spectra were obtained with a computer-controlled TRIAX 320 spectrofluorimeter (Jobin-Yvon Corp.) under 980 nm LD (Coherent Corp.) excitation with a power of 100 mw and a monochromator with a Hamamatsu Photonics R955 photomultiplier tube connected to a PC. The Raman spectrum was recorded on a FT-Raman spectrophotometer (Invia Raman Microscope, RENISHAW) with a Ar ion 488.0 nm laser, the output power and focus diameter are 16 mw, 2 μ m, respectively. All of the measurements were performed at room temperature.

Results and discussion

Influence of preparing temperature on the phase and UC luminescence properties of phosphors

To investigate the influence of preparing temperature on the phase and UC luminescence properties of phosphors, 15CSZ:0.1Er^{3+} phosphors were synthesized at 600□, 900□ and 1200□ for 3 h, respectively. Shown in Fig. 1 are XRD patterns of the phosphors synthesized at different temperature, it can be seen that the phosphors have the same c-ZrO_2 solid solution crystalline phase, Ce^{4+} and Er^{3+} completely replace Zr^{4+} and occupy the lattice site of ZrO_2. Patra[11] et al. reported the preparation of ZrO_2:0.005Er^{3+} nanopowders with mixture monoclinic and tetragonal phase at 800□, 900□ and 1000□, respectively. However, XRD patterns of the phosphors present no other phases except pure c-ZrO_2 phase, which also confirmed that the introduction of 15 mol% Ce^{4+} stabilizes ZrO_2 phase.
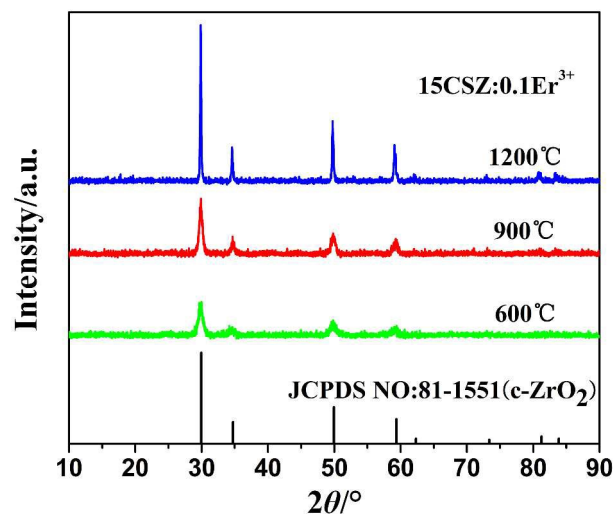
Fig. 1 XRD patterns of 15CSZ:0.1Er^{3+} phosphors prepared at different temperature.

While the synthetic temperature increases, the intensity and shape of XRD peaks are different, and the diffraction peaks become more and more higher and sharper, indicating that the grown crystalline phase becomes more and more perfect. It is noteworthy that 15CSZ is a tetragonal zirconia phase, while 15CSZ:0.1Er^{3+} is a cubic zirconia phase. It is mainly due to that the trivalent Er^{3+} ions in zirconia subtrate can produce oxygen vacancy and have coordination stable effect on zirconia substrate for this change. when the doping Er^{3+} concentration is fewer the effect is not obvious, but when the doping Er^{3+} ion concentration is higher, Er^{3+}ions produce more oxygen vacancies to make tetragonal phase of zirconia transform into cubic phase of zirconia.[12,19]
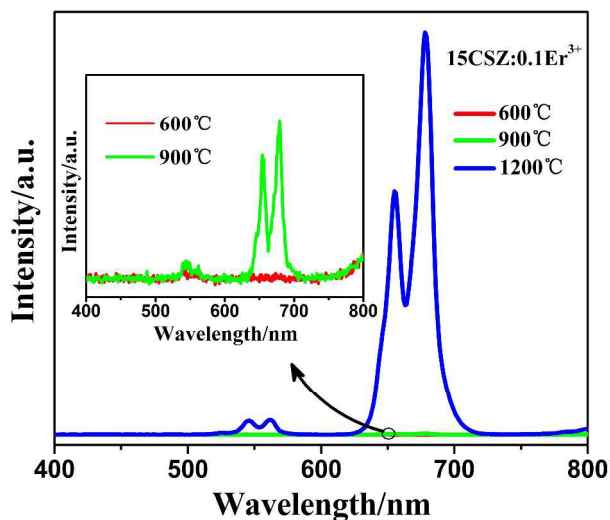

Fig. 2 UC photoluminescence spectra of 15CSZ:0.1Er^{3+} phosphors prepared at different temperature under 980 nm excitation.

Fig. 2 depicts the UC photoluminescence spectra of 15CSZ:0.1Er^{3+} phosphors prepared at 600□, 900□ and 1200□ for 3 h under 980 nm excitation. With the sintering temperature increasing, the emission intensity of the red and green become more and more stronger, especially the emission intensity at 1200□ greatly enhance compared to that at 600□ and 900□ (the green enhances by 113 and 89 times, the red enhances by 3600 and 353

times, respectively), which indicates that raising preparation temperature could enhance the UC emission intensity. The reason may be explained as above mentioned in XRD analysis, higher synthetic temperature can bring better crystalline growth and less crystalline phase defects, which thereby bring lower rate of non-radiative relaxation so as to obviously improve the UC emission intensity.[20,21]

XRD analysis of samples doped with different Er^{3+} content

Fig. 3 shows XRD patterns of the samples doped with different Er^{3+} content at 1200□ for 3 h. ZrO$_2$:0.005Er^{3+} phosphors without Ce^{4+} have *m*-ZrO$_2$ phase, which is consistent with what the related references reported.[10,13] According to the hard sphere theory, in terms of octahedral coordination structure, the cations and anions in crystal can steady exist only when their radius ratio r$^+$/r$^->$0.732, conversely, the repulsive force is stronger than electrostatic attraction, which makes the octahedral coordination structure system not steady. For zirconia, due to the r$_{Zr}$/r$_O$≈0.564, so the repulsive force between adjacent O—O bonds makes the structure not steady in the octahedral coordination structure, zirconia is easy to form monoclinic phase structure with coordination number being less than 8 under low temperature and tetragonal and cubic phase with 8 coordination number can only stably exist via the lattice vibration under high temperature.[22] However, the phase of Ce^{4+}-stabilized 15CSZ:0.005Er^{3+} phosphors is pure *t*-ZrO$_2$ solid solution phase, which demonstrates that 15 mol% Ce^{4+} well stabilizes the high temperature phase of ZrO$_2$. Owing to the smaller ion radius of Zr^{4+} (r=0.084 nm) than that of Ce^{4+} (r=0.097 nm), so the introduction of Ce^{4+} enlarges the radius ratio of cation/anion, causes the lattice distortion and weakens the repulsive force between adjacent O—O bonds, which makes the tetragonal or cubic phase of zirconia octahedral coordination structure steady exist.
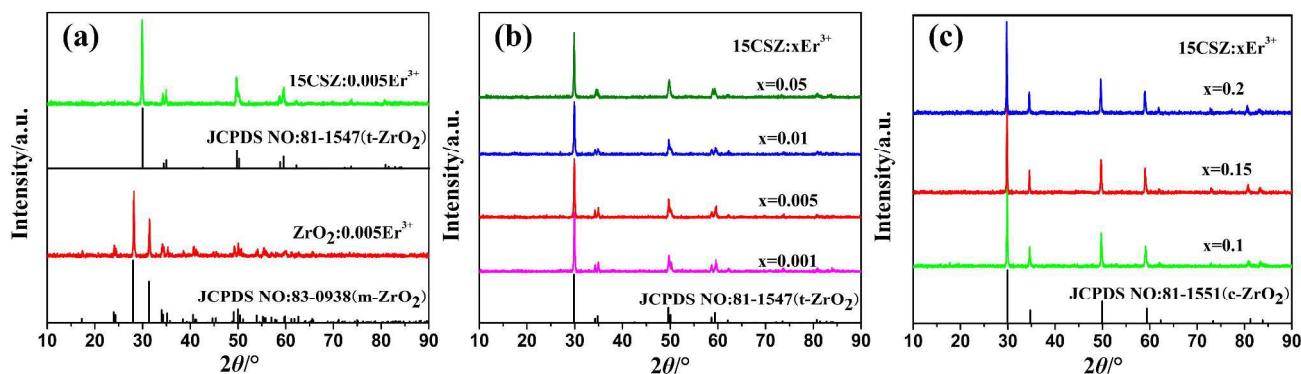
Fig. 3 (a) XRD patterns of 15CSZ:0.005Er³⁺ and ZrO₂:0.005Er³⁺ phosphors, (b) and (c) XRD patterns of 15CSZ:xEr³⁺ phosphors (x=0.001,0.005,0.01,0.05,0.1,0.15,0.2).

Seen from the Fig. 3b and 3c, it can be found that all 15CSZ:xEr³⁺ samples have no monoclinic phase. With the Er³⁺ doping concentration increasing, the phase of phosphors changes from the tetragonal phase into the cubic phase, which can be explained as a certain synergy stable effect played by Er³⁺ and Ce⁴⁺ for sample phase.[12,19]

UC photoluminescence spectra of samples doped with different Er³⁺ concent

Fig. 4 shows the UC photoluminescence spectra of 15CSZ:xEr³⁺ phosphors under 980 nm excitation. It can be seen two obvious characteristic emission bands containing the green ranging from 520~570 nm and the red ranging from 630~690 nm, which can be attributed to the ²H₁₁/₂/⁴S₃/₂ and ⁴F₉/₂→⁴I₁₅/₂ transition of Er³⁺, respectively.[10,23] To clearly observe the variation of the red and green intensity with the Er³⁺ doping content, Fig. 5 shows the variation of UC emission peaks at 560 nm (the green) and 676 nm (the red) with the Er³⁺ doping content. With Er³⁺ concentration increasing, the intensity of green emission band ranging from 520~570 nm originally increases, then gradually decreases and achieves the highest when the Er³⁺ doping content is 1 mol%.

Meanwhile, the intensity of red emission ranging from 630~690 nm originally also increases and then gradually decreases, achieving the highest when Er³⁺ concentration is 10 mol%. In all, green emission is the main luminescence for a low doping content, constantly increasing the Er³⁺ content, the luminescence changes from the green into the red , which also means the decrease of green emission and the increase of red emission. In fact, pure red UC emission is just what the researchers pursuit, for example, the red luminescence rather than green luminescence is more suitable to be applied in biological fluorescent labeling. Obviously, the emission intensity achieves the highest while the Er³⁺ concentration is 10 mol%, which indicates that the Er³⁺ doping content break the low concentration limit in traditional UC materials and the high content Er³⁺ doping is realized. Realization of high doping concentration can be explained by the following two possible reasons. On one hand, in the appropriate concentration scope, Er³⁺ substitues the site of Zr⁴⁺ to form an electron-deficient centre (also called the oxygen vacancy) due to the absent one positive charge of Er³⁺ compared with Zr⁴⁺, and each oxygen vacancy is surrounded by a pair of Er³⁺ ions, so it is highly difficult for the adjacent Er³⁺ ions to approach to form the Er³⁺ clusters, which results in the

obvious increase of the quenching concentration. on another hand, it may be other defect species such as interstitial oxygen that compensate the unbalance of charge due to the substitution of Ce^{3+}, or Er^{3+} for Zr^{4+}.
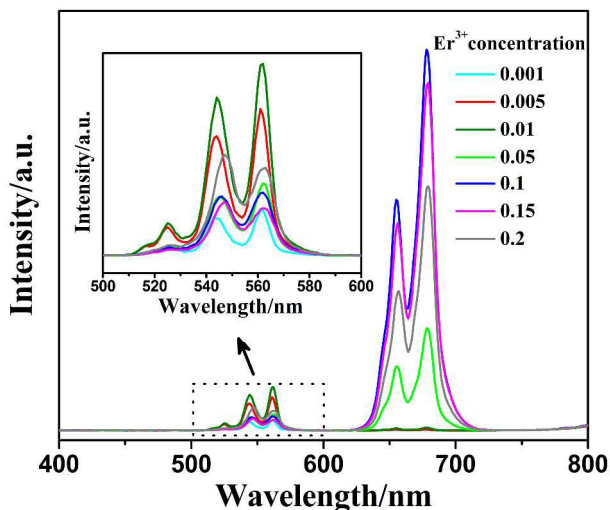

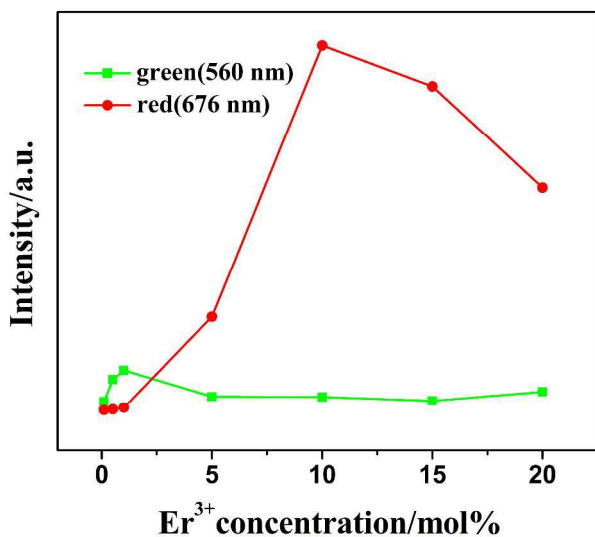**Fig. 4** UC photoluminescence spectra of 15CSZ:xEr^{3+} phosphors under 980 nm excitation.

Fig. 5 The variation of UC emission peaks at 560 nm (the green) and 676 nm (the red) with the Er^{3+} doping content.

Fig. 6 depicts the UC photoluminescence spectra of 15CSZ:0.005Er^{3+} and ZrO$_2$:0.005Er^{3+} phosphors under 980 nm

excitation. The luminesence intensity of 15CSZ:0.005Er^{3+} is far higher than that of ZrO$_2$:0.005Er^{3+} phosphors, the green and red intensity improve 56 times, 5.8 times, respectively, so the introduction of 15 mol% Ce^{4+} not only stabilizes zirconia phase but also greatly improves the UC luminescence intensity. One possible reason is that the introduction of CeO$_2$ reduces the phonon energy of substrate materials due to the low phonon energy (457 cm^{-1}) of CeO$_2$,[24] which can be explained via the raman spectra of samples doped with Ce^{4+} ions or no in Fig. 7. The highest phonon energy of ZrO$_2$:0.005Er^{3+} is about 474 cm^{-1}, which is consistent with what the previous references reported,[12] however, the highest phonon energy of ZrO$_2$:0.005Er^{3+} doped with Ce^{4+} ions is about 458 cm^{-1}, indicating that the introduction of Ce^{4+} ions does lower the phonon energy of the substrate. Another possible reason is that introduce of Ce^{4+} ions changes the phase of substrate, and different phases have great influence on upconversion luminescence.[13]

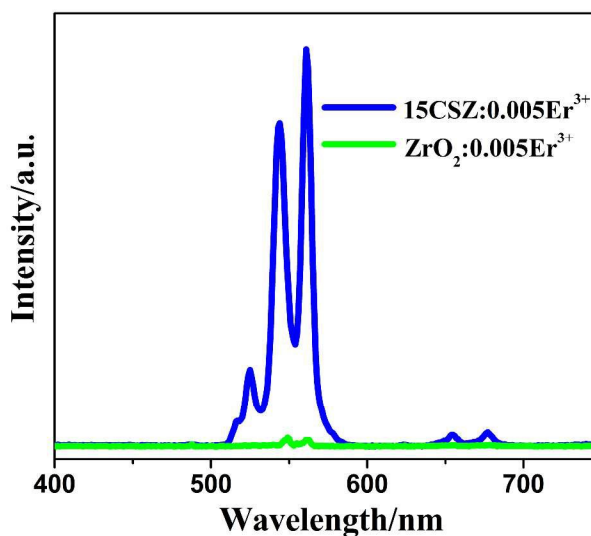**Fig. 6** UC photoluminescence spectra of 15CSZ:0.005Er^{3+} and ZrO$_2$:0.005Er^{3+} phosphors under 980 nm excitation.

Influences of phase on UC luminescence

To investigate the influences of the phase on UC luminescenc, the emission spectra of different ZrO$_2$ phases are shown in Fig. 8.

Generally speaking, there are two methods to get different ZrO_2 phases, one way is changing the doping concentration and another way is changing the calcination temperature. In our previous discussion, we have investigated the influences of the temperature on the UC luminescence and single phase was achieved under different temperature due to the addition of stabilizer. In this paper, we prepared ZrO_2 samples with different phases by changing the doping concentration. Seen from the Fig. 8 clearly, for the rare earth ions doped ZrO_2 phosphors with different phases, the intensity of UC luminescence obvious changes but the emission peak position do not change, it is obvious that different phases have great influences on the luminescence but the luminescence mechanism does not change.
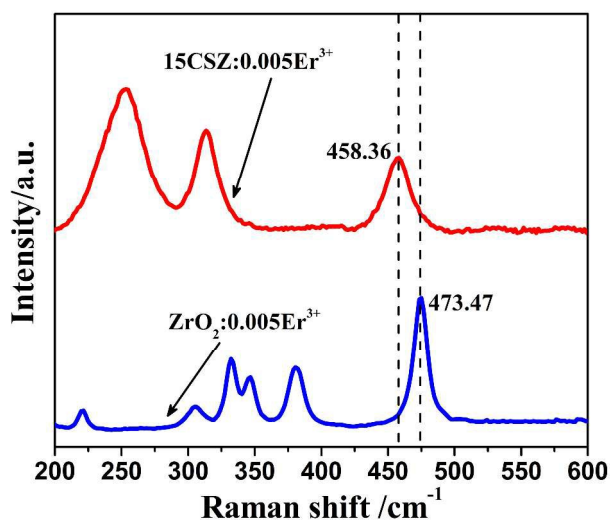

Fig. 7 Raman spectra of 15CSZ:0.005Er^{3+} and ZrO$_2$:0.005Er^{3+} phosphors.

UC luminescence mechanism analysis

Fig. 9 shows the energy level diagram of Er^{3+} and possible UC luminescence mechanism. According to the previous reports, it is well know that the UC luminescence process mainly contains the ground state absorption (GSA), excited state absorption (ESA), cross relaxation (CR) and multi-phonon nonriadiative relaxation
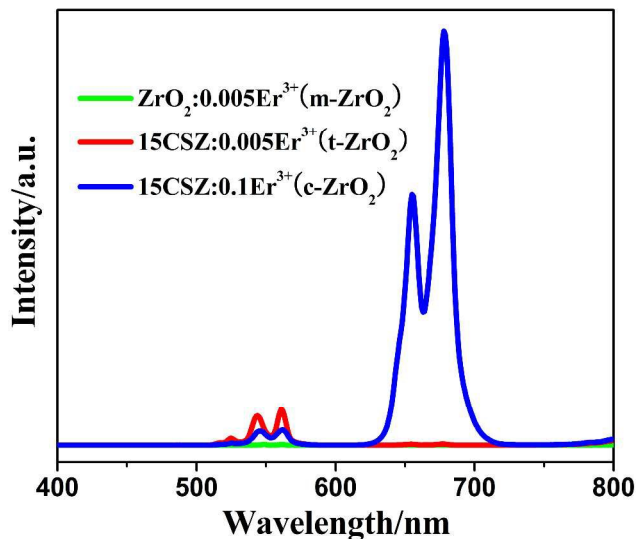
and so on.[25-27]

Fig. 8 UC photoluminescence spectra of different ZrO_2 phases under 980 nm excitation.

Seen from the Fig. 4 and Fig. 5 can we see that the leading luminescence is green emission and red emission is relatively weak, moreover, the whole emission intensity is weak when the Er^{3+} doping content is lower in the samples. This can be explained that Er^{3+} ions absorb less photons due to their low doping content, which decreases the number of Er^{3+} in $^2H_{11/2}/^4S_{3/2}$ and $^4F_{9/2}$ levels resulting in a weak emission intensity. For the green emission excited by 980 nm infrared light, Er^{3+} firstly absorbs a photon and transits to metastable excited states $^4I_{11/2}$ level from the ground state, then transits immediately to $^4F_{7/2}$ level after absorbing another photon. Er^{3+} ions located in $^4F_{7/2}$ level quickly jump to $^2H_{11/2}$ and $^4S_{3/2}$ level via nonradiative relaxation and then the most ions transit to the ground state resulting in the green emission (Fig. 9).[13]

However, the red light can be obtained via two methods (shown in Fig. 9). The first way is that Er^{3+} ions in $^4S_{3/2}$ level transit to $^4F_{9/2}$ level through the nonradiative relaxation and then return back to the ground state with the red emission.[28] The second way is that Er^{3+} ions in $^4I_{11/2}$ level transit to the $^4I_{13/2}$ level through the

nonradiative relaxation, then jump to the $^{4}F_{9/2}$ level after absorbing another photon and finally transit to the ground state with the red emission.

Owing to the low phonon energy, the $^{4}S_{3/2}$ and $^{4}F_{9/2}$ levels, $^{4}I_{11/2}$ and $^{4}I_{13/2}$ levels both have a large energy level difference (about 3200 cm^{-1} and 3600 cm^{-1}, respectively) , the chance of nonradiative relaxation for Er^{3+} ions is very low, which leads to the weak red emission.

As shown in Fig. 4 and Fig. 5, with the Er^{3+} doping concentration increasing, the green emission decreases and red emission enhances, indicating that the number of Er^{3+} ions in $^{2}H_{11/2}/^{4}S_{3/2}$ level is decreasing and Er^{3+} ions in $^{4}F_{9/2}$ is gradually increasing. According to the previous discussion about the generation process of green and red emission, this change can happen only when the Er^{3+} ions in $^{2}H_{11/2}/^{4}S_{3/2}$ or $^{4}F_{7/2}$ levels transit to the $^{4}F_{9/2}$ level. However, this change can only happen between two Er^{3+} ions, which means that the luminescence mechanism of red emission has changed.
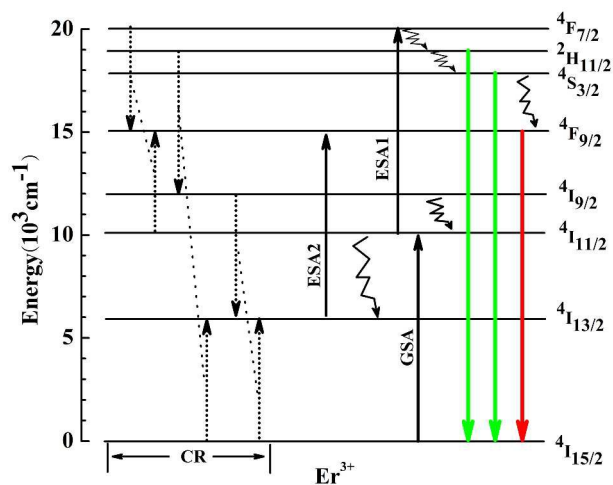

Fig. 9 The energy level diagram of Er^{3+} and the possible UC luminescence mechanism.

To clearly investigate whether the luminescence mechanism has changed, the red emission intensity of 15CSZ:0.005Er^{3+} and 15CSZ:0.1Er^{3+} phosphors were tested under the infrared light with different excitation power and the experimental results are shown in Fig. 10. Theoretically, the relation between UC emission intensity and excitation power can be described as the following:[29]

$$I_{em} \propto P^{n}$$

I_{em} represents the UC emission intensity, P represents the excitation power and n represents the absorbed photon numbers originated from the excitation light source, the calculated line slope from LogI_{em} and Log$P$ also represents n value. In Fig. 10, the curve slope of 15CSZ:0.005Er^{3+} and 15CSZ:0.1Er^{3+} phosphors at 676 nm is 1.41 and 1.71, respectively. This result indicates that the corresponding UC fluorescence processes of these two samples are both double photons absorption but have different forming mechanism.[12]
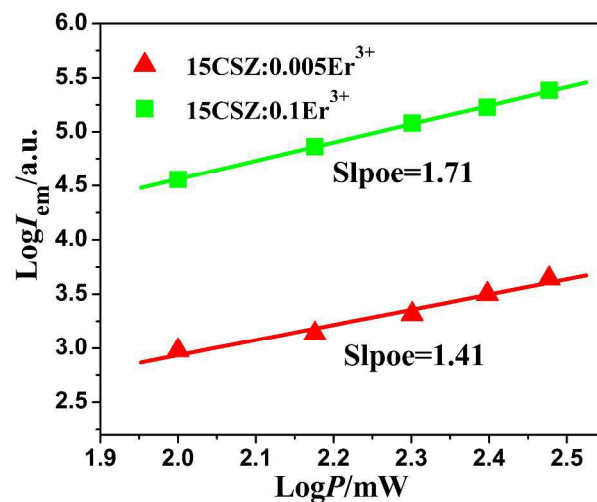
Fig. 10 The logarithmic curves of UC emission intensity of 15CSZ:0.005Er^{3+} and 15CSZ:0.1Er^{3+} phosphors at 676 nm and the corresponding excitation power.

So, what the luminescence mechanism of the red light has happened leads to the increase of red emission intensity and decrease of green emission intensity? It is considered that Er^{3+} substitues the Zr^{4+} to form an oxygen vacancy, each oxygen vacancy is surrounded by a pair of Er^{3+} ions with two kinds of

coordination state, when the Er^{3+} doping content is low (0.1 mol%-1 mol%), these two Er^{3+} ions are in a coordination state where the cross relaxation (CR) could not happen due to a far distance between them, however, when the Er^{3+} doping content is more than 1 mol%, the cross relaxation is able to happen due to a short distance between them,[19,30,31] which decreases the number of Er^{3+} ions in $^2H_{11/2}$ and $^4S_{3/2}$ levels but increases that in $^4F_{9/2}$ and $^4I_{13/2}$. So the red emission occupies the dominant in luminescence and becomes more stronger with the increase of Er^{3+} doping concentration.

Conclusions

15CSZ:xEr^{3+} phosphors doped with different Er^{3+} content were prepared via reverse co-precipitation method at 1200□ for 3h. A UC red phosphors with 10 mol % Er^{3+} concentration was achieved. This new UC materials has a broad prospect for application and can be directly used or used as a kind of ceramic materials at the same time, a new approach to improve the LE of UC materials is also achieved by increasing the quenching concentration through adjusting the host structure. The introduction of Ce^{4+} not only stabilizes ZrO_2 phase but also improves the LE of ZrO_2 based UC materials. The red emission processes in UC luminescence are double photons absorption, however, the luminescence mechanism varies with the Er^{3+} doping concentration. With the increase of Er^{3+} doping content, the UC luminescence process translates from the excited state absorption into the cross relaxation effect, and the luminescence changes into red emission from green emssion. The corresponding green and red emission are the strongest when the Er^{3+} doping content is 1 mol% and 10 mol%, respectively. The realization of high concentration doping for Er^{3+} may be attributed to the oxygen vacancy and interstitial oxygen to compensate the unbalance of charge in zirconia.

Notes and references

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Upconversion luminescence of cerium-stabilized high temperature phase zirconia phosphors with a high Er3+ doped concentration

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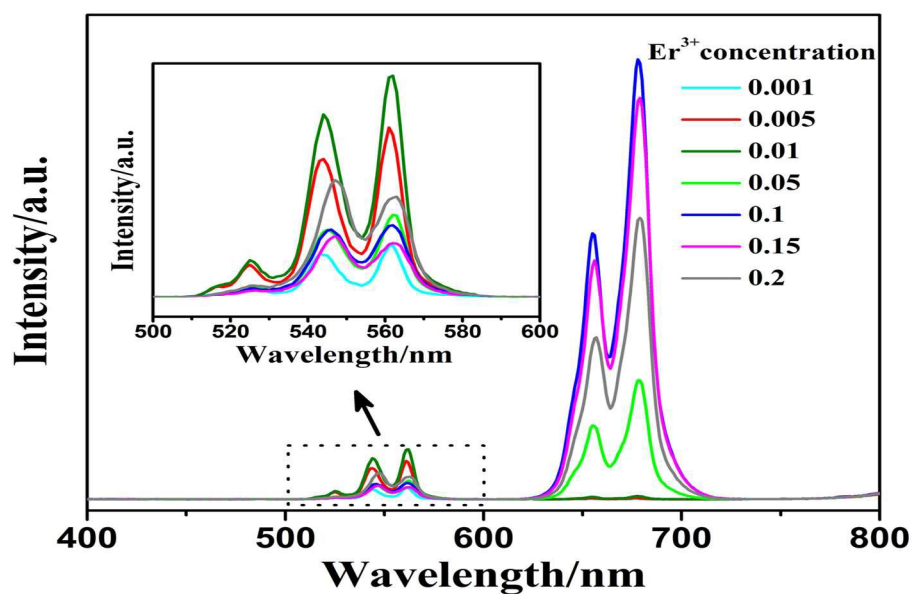
As Er^{3+} concentration increases, the luminescence can be tunable from green to red and red emission intensity reaches the maxmium with Er^{3+} concentration being as high as 10 mol%.