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Preparation and Properties of Rare-earth-doped Na2Ca3Si2O8 and BaZrSi3O9 Matrix Luminescent Materials

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To achieve higher quality temperature measurement, this paper studies the rare-earth-doped Na2Ca3Si2O8 and BaZrSi3O9 matrix luminescent materials. The paper mainly adopts sol-gel method to prepare luminescent material in the form of thin film and powder. By comparing the thermodynamic reaction of the two materials and their respective properties, the differences between the two are further distinguished. The results illustrate the temperature-dependent up-conversion luminescence mechanism of thin film and explain the relationship between the up-conversion luminescence intensity and temperature. The results show that more accurate temperature measurements can be achieved.

1. Introduction

In the field of temperature measurement, rare-earth-doped conversion luminescent materials have great advantages such as high spatial resolution, non-invasive capability, fast response, strong electromagnetic protection capability, all-optical system to avoid sparks. Therefore, the materials have a promising prospect in the optical temperature sensing field. However, from the point of view of the status quo, the conversion luminescent materials is of great concern as a temperature sensor, but quantitatively analyzing the temperature-dependent up-conversion luminescence mechanism is seldom reported. At the same time, to achieve accurate temperature measurement and to improve temperature sensitivity has been the direction of many scientific researchers.

Based on the sol-gel method, the luminescent materials of thin film and powder are prepared. By observing and recording the thermodynamic reaction data of the two, relative mathematical models have been established. Then the mathematical models are compared with each other to find out the differences so as to find out their advantages and disadvantages from the differences.

2. Literature review

Calcium barium structure material occupies an important position in many functional materials, such as piezoelectricity, ferroelectric, luminescence, catalysis, magnetoresistance and so on. It is a hot research in the field of material science. Today's global energy depletion is becoming more and more serious and the environmental climate is worsening today. The concept of green lighting proposed by Wei and other scholars at the end of twentieth Century has been paid more attention to. The main content of the concept mainly includes four indexes. It requires that the lighting project is not limited to the understanding of energy conservation. On the contrary, it needs to be improved to save energy and protect the environment, and to meet the quality of lighting and visual effects. Therefore, choosing what kind of lighting source not only has an important impact on the environment, but also on the human beings living on the earth. The suitable lighting source can not only satisfy people's life and work needs, but also contribute to the progress of human civilization (Wei et al., 2016).

Phosphors have been widely applied in many fields due to their characteristics such as photoluminescence, colorless, tasteless, non-toxic and harmless. Ni and others made fluorescent films with cellulose. At present, this kind of film, which can be converted to light, can absorb the unbeneficial ultraviolet light on the growth of the crops and transform it into the red-orange light which can promote the photosynthesis of the crops. It can

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increase the time of crop sunshine and increase the single yield, which has achieved considerable economic benefits in agriculture (Ni et al., 2016). Zhang and other scholars pointed out that fluorescent materials can also be used in anti-counterfeiting materials, road signs fluorescent coatings, color displays and fluorescent decorative materials. In addition to the above contents, the fluorescent materials also have potential application value in high-density and ultra-thin optical storage materials, molecular electronics devices, dye lasers and scintillation counting (Zhang et al., 2016).

Li and other researchers tested the scanning electron microscope (SEM), infrared spectrum (IR), afterglow properties and luminescent properties. The scanning electron microscope and infrared spectrum analysis showed that the fibers were composed of irregular particles, with independent SrAl_2O_4: Eu∽ (2 +, Dy ~ (3+) phosphor, TSHF and polypropylene structure. In addition, the highest initial afterglow intensity was observed when the TSHF concentration was 5 wt%. More interestingly, with the increase of TSHF doping, the emission peak gradually shifted to the blue region. In the CIE 1931 chromaticity map, the rare-earth doped fiber is distributed in the blue light region, showing a more obvious blue shift compared with the yellow green light of SrAl_2O_4: Eu ~ (2+), Dy ~ (3+) phosphor (Li et al., 2017). Due to the strong quenching effect of graphene oxide, synthesizing the high luminescent properties of graphene oxide rare-earth hybrid materials was a huge challenge. Zhang and so on revealed a new type of hybrid graphite oxide / rare earth complex, and Eu3 + -2- thienyl three fluoroacetone (TTA) - polymethyl methacrylate (PMA) was deposited on the surface of graphene oxide (GOSs) through a non-covalent approach between GOSs and PMA. This material showed stronger luminescence intensity, longer decay life and better thermal stability than pure Eu^{3+} complex. The results were confirmed by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and luminescence data. In addition, it was observed that PMA played an important role in improving the luminous intensity and prolonging decay life of hybrid materials (Zhang et al., 2017).

Cheng and other scholars used XRD and Raman technology to explore the structural properties and studied the excitation of emission 980nm. The emission intensity depends on the concentration of Yb3 + ions and reaches the maximum at 7%. The logarithmic diagram of power correlation showed that the green and red emission originated from the two-photon up-conversion process. Based on photon energy and emission spectra, possible up-conversion processes and emission mechanisms were discussed. Finally, the optical temperature sensing characteristics were implemented using the fluorescence intensity ratio technology based on the green up-conversion emission. The temperature sensitivity of 300-540K was found to be higher than that of 0.0025K-1 in the whole temperature range, which revealed that the phosphor was a promising optical temperature sensing material (Cheng et al., 2016). Wang and other scholars demonstrated the preparation of Er^{3+} Doped Perovskite type ferroelectric $Na_{0.5}Bi_{0.5}TiO_3$ nano-crystals and their applications in temperature sensing. The sample was synthesized by a simple hydrothermal method. Under the excitation of a 980nm diode laser, the up-conversion emission of two thermodynamic coupled excited states from Er^{3+} at 528nm and 547nm was recorded at the temperature of 80K to 480K. The emission intensity ratio (I528 / I547) as a temperature function was studied. The sensitivity of 0.0053K-1 was observed at 400K, indicating that they are promising candidates for nano thermometers (Wang et al., 2016). Er^{3+} / Yb^{3+} co-doped phosphate glasses were successfully prepared by the traditional melt quenching technology, and the characteristics of optical, luminescence and temperature sensing were characterized by transmission spectra, photoluminescence, fluorescence attenuation and energy level diagrams. Chen and other scholars studied the temperature dependent fluorescence intensity ratio (FIR) of Yb^{3+} / Er^{3+} co-doped glass in the thermally coupled luminescent state (4S 3/2, 2H 11/2). The high relative temperature sensitivity of 1.22%O2K611 was obtained at 30302K, and the corresponding effective energy difference (62E) was 78902cm611. The maximum temperature sensitivity at 55302K was estimated to be 4.9465 x 6510613. All the results indicated that Yb^{3+} / Er^{3+} co-doped phosphate glass was an effective up-conversion material and could be used for optical temperature measurement (Chen et al., 2017).

To sum up, there are many studies on the doping of rare-earth materials and the preparation of various metal ions for luminescent materials, but there are still many obstacles to the application of luminescent materials in the optical temperature sensing field. Therefore, based on sol-gel method, the luminescent materials of thin films and powders are prepared. By observing and recording the thermodynamic response data, a mathematical model is established. Then, the mathematical models are compared with each other to find out the differences, so as to better apply them to temperature sensors.

3. Method

3.1 Photothermal effect of film and powder compression plates

Fluorescent films are prepared by the conventional sol-gel method and spin-coating method. The typical synthetic methods are as follows: 1. Under constant magnetic stirring, dissolve the identified mass of

ammonium molybdate in ethylene glycol monomethyl ether (15 m L) and glacial acetic acid (5 mL). 2. Dissolve Gd (NO_3) 3·6H2O (1.8 mmol), Yb (NO_3) 3·6H_2O (0.18 mmol) and Er (NO_3) 3. 6H_2O (0.02 mmol) with identified molar ratio into 10 mL of ethylene glycol monomethyl ether and the rare earth salt solution is added to the appealing solution gradually. 4. This solution is spin-coated on a quartz plate and the spin coater is set at 3000 rpm for 60 seconds and then dried at 60 ° C for 8 hours. 5. The sample is heated at 350 ° C for 2 hours and then calcined at 800 ° C for 2 hours. Finally, a Gd2 (MoO4) 3: 1% Er3 + / 9% Yb3 + film is prepared.
Besides, to avoid the effect of the different synthesis conditions, fluorescent materials in the form of powder are prepared under the same matching and the same conditions. The preparation method of the powder sample is the same as that of the thin film preparation. What is different is that the step 3 is directly transitioned to step 5 (skip step 4 above). Thus, a powder sample is synthesized. Figure 1 shows the film and powder sample preparation process.

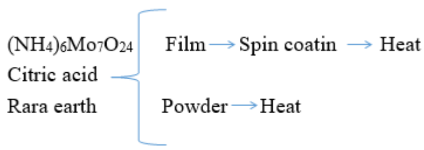

Figure 1: film and powder sample process

3.2 Up-conversion luminescence properties of thin film and powder under different excitation powers

The powder material is placed in a tablet press mold and kept at the pressure of 5 Mpa for 2 minutes to obtain a sample of powder compaction whose particles are tightly packed. In order to investigate the photothermal effect of the two forms (powder compaction and film), samples are excited with different excitation powers (0.03-3.78 W). Table 1 shows the up-conversion emission spectra of powder compacts and thin-film samples at 1.77 W, 2.56 W, 2.87 W, 3.33 W and 3.49 W powers. The experimental results show that the emission spectra of film and powder compaction samples show distinct phenomena as the excitation power increases. For the powder compaction sample, the intensity of the 525 nm emission peak is significantly greater than that of the 545 nm emission peak as the excitation power increases, while for the film sample, the intensity of the 545 nm emission peak emission is always greater than that of the 525 nm emission peak. The 525 nm and 545 nm emission peaks of Er3 + ions originate from the transitions of $^2H1_{1/2}$ and $^4S_{3/2}$ to $^4I1_{5/2}$ respectively.

Table 1: emission values

1.77 W	2.56 W	2.87 W	3.33 W	3.49 W
8.7mm	8.56mm	6.5mm	4.7mm	2.9mm

It can be seen from the calculation that the fluorescence peak value ratio corresponds to the sample temperature, indicating that the difference in fluorescence peak value ratio between the film and the powder compaction samples is caused by the temperature change caused by the photothermal effect. The fluorescence peak value ratio of the thin film sample almost keeps unchanged with the increase of the excitation power, indicating that the temperature of the thin film sample does not change with the increase of the excitation power, that is, the thin film sample is hardly affected by the photothermal effect. In contrast, the fluorescence peak value ratio of powder compaction sample continues to increase with the increase of excitation power, that is, the temperature of powder compaction samples continues to increase.

3.3 Theoretical analysis of luminescent materials

In order to clearly understand the temperature-dependent up-conversion luminescence process, the interactions of ions and ions, ions and photons, ions and phonons need to be studied quantitatively. For the interaction of ions and photons, the spontaneous emission transition probability is an indispensable optical parameter in the quantitative research. Judd-Ofelt (J-O) theory is an effective method to calculate the transition probability of 4 *f* electron orbital of rare earth ions through the absorption spectrum of rare earth ions. Based on J-O theory, the experimental oscillator strength parameter can be expressed as:

$$f_{\exp}\left(J \to J'\right) = \frac{mc^2}{N\pi e^2}\int \varepsilon(\sigma)d\sigma = \frac{2.303mc^2}{N\pi e^2 c_b \Delta x}\int A(\sigma)b\sigma$$

$$= \frac{4.318\times 10^{-9}}{c_b \Delta x}\int A(\sigma)b\sigma$$

The expression is shown in Table 2:

Table 2: Formula represents

f_{exp}	c	N	m	e	σ	ε(σ)	A(σ)	c_b	Δx
Experimental oscillator strength	Light speed	A Fugadero constant constant	Electronic mass	Electronic charge	The energy of the absorption band corresponding to the photon	Moore extinction coefficient	Wave dependent absorbance	The concentration of rare-earth ions	Penetration depth of light

3.4 Up-conversion luminescence mechanism of temperature-dependent co-doped system

Table 3: The J-O intensity parameters and quality factor 3+doped typical host

Crystal	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6	Reference
Er:Na YF_4	2.11	1.37	1.22	1.12	[121]
Er:YAG	0.45	0.98	0.62	1.58	[122]
Er/Yb:Gd VO_4	6.47	1.51	0.91	1.66	[123]
Er/Yb:NaY(WO_4)$_2$	18.1	2.59	1.21	2.14	[124]
Er/Yb:Li La(WO_4)$_2$	9.03	2.02	0.59	3.42	[125]
Er/Yb: Gd2(MoO_4)$_3$	11.74	8.16	2.05	3.98	This work

It can be seen from Table 3 that orthorhombic material has strong covalent bonds and its spectral quality factor is 3.98, indicating that this material has great application prospect in the field of laser crystal.

4. Results and Analysis

Figure 2 shows XRD atlas of $NaLuF_4$:20%Yb^{3+}/2%Er^{3+} and $NaLuF_4$:20%Yb^{3+}/2%Er^{2+} luminescent materials and the standard data of hexagonal $NaLuF_4$ (JCPDS 27-0726); b) is SEM image of $NaLuF_4$:20%Yb^{3+}/2%Er^{3+} crystallite; c) is SEM image of $NaLuF_4$:20%Yb^{3+}/2%Er^{2+}crystallite. XRD atlas of $NaLuF_4$: 20%Yb^{3+}/2%Er^{3+} and $NaLuF_4$:20%Yb^{3+}/2%Er^{2+} luminescent materials corresponds well to the standard data of hexagonal $NaLuF_4$ as shown in the figure, and doped ions are introduced without impurities of the diffraction peaks, indicating that the prepared sample is a pure hexagonal phase. The forms of $NaLuF_4$:20%Yb^{3+}/2%Er^3 and $NaLuF_4$:20%Yb^{3+}/2%Er^{2+} luminescent materials all show irregular microrods with the length of about 1-8 μm and the diameter of about 1-3 μm.

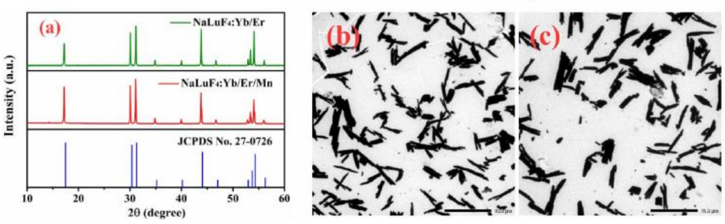

Figure 2: Standard data

Figure 3 is emission spectra of Na Lu F4:Yb3+/Er3+ and Na Lu F4:Yb3+/Er2+ material under 980 nm laser excitation.

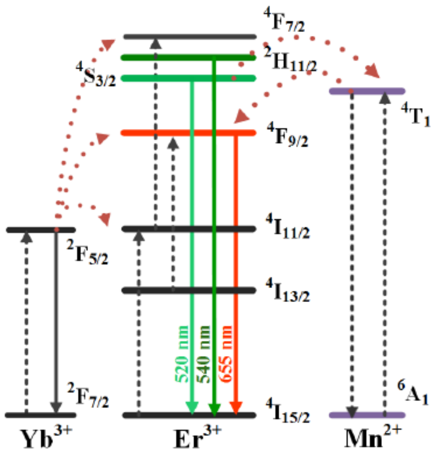

Figure 3: The emission spectra phosphors under 980 nm excitation

The characteristic emission peaks of Er3+ ions at 520 nm, 540 nm and 655 nm are observed and they derive from the transitions of 2H11/2 → 4I15/2、4S3/2→ 4I15/2 and 4F9/2 → 4I15/2 energy levels respectively. When the sample is doped with Mn2+ ions, the emission peak of Er3+ ions at 655 nm obviously increases relative to the green peak because the large energy level difference between 4S3/2 and 4F9/2 leads to non-radiation relaxation when not doped with Mn2+ ions. When Mn2+ ions are doped in the material, the 4T1 energy level of Mn2+ ions acts as a bridge of energy transfer and forms an energy transfer message between 4S3/2 and 4F9/2 energy levels of Er3+ ions, leading to an increase in the number of particles in 4F9/2 energy level, so the intensity of the 655 nm peak significantly increases relative to the green peak.

The up-conversion luminescent materials are prepared by hydrothermal method. The XRD atlas shows that the prepared materials are pure hexagonal phases. Under the excitation of 980 nm laser, the up-conversion emission peaks of Tm3+ ions at 450 nm, 475 nm and 695 nm are observed, which come from the transitions of 1D2→3F4、1G4→3H6 and 3F2→3H6 energy levels respectively, and the up-conversion emission peaks of Er3+ ions at 525 nm, 545 nm, and 660 nm are observed, which derive from the transitions of 2H11/2→4I15/2, 4S3/2→4I15/2 and 4F9/2→4I15/2 energy levels respectively.

5. Conclusions

Taking rare earth doped luminescent materials as the main research object, this paper studies the temperature-dependent up-conversion luminescence properties and analyzes the temperature-dependent up-conversion luminescence mechanism. Based on the fluorescence peak value ratio technique, optical temperature sensing performance is improved by changing the matrix materials, non-thermal coupling energy levels and energy transfer. The main results are as follows:

The photothermal effect of a thin film material of 200 nm is studied. It is found that the temperature keeps unchanged due to less light absorption and quickly dissipated heat. The properties of the thin film materials are analyzed by J-O theory. The J-O intensity parameters of the materials are Ω2 = 11.74 × 10−20 cm2、Ω4 = 8.16 × 10−20 cm2、Ω6 = 2.05 × 10−20 cm2 through calculation. Then the crystal quality factor (Ω4/Ω6) is determined to be 3.98, indicating that this material has a great application prospect in the field of laser crystals. The photophysical parameters (the transition probability of energy levels) of Er3+ ions are calculated by the J-O intensity parameter. The theoretical model has been established by the interactions of ions and ions (energy transfer, cross relaxation), ions and phonons (phonon assisted energy transfer, non-radiation relaxation), ions and photons (light absorption, spontaneous emission). The relationship between the un-conversion luminescence intensity and the temperature of the thin film material is analyzed. As the sample temperature increases, the peak intensity at 525 nm first increases and then decreases because the phonon-assisted energy transfer makes Er3+ ions transit from the4I11/2 level to 2H11/2 level (process IV of energy transfer) and the non-radiation relaxation of 2H11 / 2 level compete with each other. In the low temperature area, energy transfer dominates, resulting in an increase in the number of particles in 2H11/2 level and an increase in luminescence intensity. In the high temperature area, non-radiation relaxation dominates, leading to the decrease of in the number of particles in 2H11/2 level and the decrease of luminescence intensity. For the 545 nm luminescence peak, the non-radiation relaxation at the 4S3/2 level has been dominant and the number of particles at 4S3/2 level has continued to decrease, thus showing a continuous decrease in the luminescence peak intensity.

At present, there are many types of rare earth doped luminescent materials, so the research in this paper has some limitations. In addition, the research is based on the characteristics of non-thermal coupling energy level temperature sensing and the factors that affect the properties of temperature measurement are not elaborated, so the next subject shall focus on this. At the same time, it is a disadvantage of this paper to develop materials with higher temperature sensitivity or larger temperature range in the physiological temperature range. Finally, in theory, it is necessary to measure the temperature sensitivity and the effect of doping different ions (rare earth ions or non-rare earth ions) to further improve the material temperature sensitivity. However, this paper has not yet studied it.

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