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Yb^{3+}、Eu^{3+}共掺杂天然方纳石的上/下转换发光特性

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摘　要：利用固相法制备了 Yb^{3+}和 Eu^{3+}共掺杂天然方纳石粉末样品。978 nm 激发下获得了天然方纳石的上转换光谱，讨论了 Eu^{3+}的可见光上转换发光的合作能量传递过程。研究了荧光粉的晶体结构，该样品在 265 nm 激发下出现了主峰在 611 nm 附近较强的红色荧光，其色度坐标为(0.661，0.339)，其发光来自于 Eu^{3+}的 $^5D_0\rightarrow{}^7F_2$ 跃迁，可以用作红色荧光粉，探讨了样品发光物理机制。

关键词：三价镱离子团簇；合作敏化；合作发光；能量传递；发光材料
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Up- and Down-conversion Luminescence Properties of Natural Sodalite Doped with Europium and Ytterbium

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Abstract: The up-conversion (UC) luminescence properties of natural sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) co-doped with Europium and ytterbium (Eu^{3+} and Yb^{3+}, respectively) was studied for the first time under excitation of near infrared reflectance (NIR) light. Cooperative energy transfer process was discussed as the possible mechanism for the visible up-conversion luminescence of Eu^{3+}. The crystal structure of fluorescent powder was investigated using an X-ray powder diffraction system. The prepared phosphors radiate very strong red fluorescence with chromaticity coordinates of (0.661, 0.339) at 265 nm excitation, which consists of red light with higher purity at 611 nm due to Eu^{3+} ($^5D_0\rightarrow{}^7F_2$), so it can be used as a red phosphor. The photo physics involved in this emission is explained.

Keywords: trivalent ytterbium ion-cluster; cooperative sensitization; cooperative luminescence; energy transfer; luminescent material

1　Introduction

Natural sodalite, a typical silicate non-metal mineral containing sodium (Na), aluminium (Al), and chlorine (Cl), is plentiful in Xinjiang, China. This compound has the ideal chemical formula of $Na_8Al_6Si_6O_{24}Cl_2$ or $3(Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2){\cdot}2NaCl$ and is a non-toxic, highly water-resistant, and property-stable fluorescent mineral. Sodalite can be used to prepare photochromic materials because sodalite that contains non-stoichiometric alkali metal salts may produce a photochromic phenomenon after being doped with iron (Fe) or sulfur (S)[1]. Aierken and his co-workers[2] undertook comparative studies of sodalite from Green Island, Canada and also from China (Xinjiang). The reliable emission and excitation spectra of the S_2^- luminescence center in sodalite were recorded at 10 and 300 K and often exhibits orange-yellow luminescence duo to S_2^- under ultraviolet (UV) light. Xinjiang sodalite, after being

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heated at 800 to 1 000 ℃ for 30 min in air, has a luminescence efficiency seven times higher than the natural sodalite without heating. High luminescence efficiency of heat-treated sodalite allows observation of luminescence spectra in detail. Gaft[3] examined iron, manganese, Eu, and cerium (Fe^{3+}, Mn^{2+}, Eu^{2+}, and Ce^{3+}, respectively) luminescence centers in natural tugtupite, sodalite, and hackmanite with laser-induced time-resolved luminescence spectrograph, while van Doorn[4] observed emission and excitation spectra of ions, such as O_2^-, Mn^{2+}, Fe^{3+} in sodalite using 253.7 nm excitation at 77 K. These documents report luminescence characteristics of several luminescence centers in sodalite, but how photoluminescence (PL) properties of sodalite change if the activator is mixed with a sodalite host is an issue needing further study.

The process of photon up-conversion (UC) is a way to convert long-wavelength excitation radiation into shorter wavelength output radiation[5]. UC was discovered independently by Auzel[6–7] and Ovsyankin and Feofilov[8] in the mid-1960s. Since then, UC has been studied in great detail, both from a fundamental point of view and with different applications in mind[9–14]. Both new UC materials and processes are currently being explored. The main thrust is still in the area of lanthanide (Ln)-doped or Ln and transition metal (TM) ion co-doping systems in both crystals and glasses. However, until recently, no systematic studies of UC luminescence of most reported crystals and glasses or natural mineral up-conversion systems have been reported.

This paper studies emission and excitation spectra of fluorine sodalite (sodalite: EuF_3, YbF_3) powders synthesized under optimum experimental conditions. To the best of our knowledge, no previous work concerning the luminance properties of EuF_3, YbF_3-activated natural sodalite has been done. Luminescence spectra revealed strong red emission of Eu^{3+} ions observed at 265 and 978 nm excitation.

2 Experimental Methods

2.1 Sample synthesis

Sodalite: x% (mass fraction) EuF_3, 10% Yb^{3+} (x=0, 1, 3, 5 and 10) phosphors were prepared *via* a solid-phase reaction by heating a mixture of Xinjiang natural sodalite and small amount of EuF_3, YbF_3. Before mixing YbF_3 and EuF_3, natural sodalite ore was ground into a powder with an agate mortar. EuF_3 (purity 99.99%) of 1%, 3%, 5%, 10% and 10% Yb^{3+} (purity 99.99%) were then mixed into the powder sodalite. The powdered samples in corundum crucibles were heated in air at 900 ℃ for 30 min using a muffle furnace. After heating, the crucibles were placed onto a metal dish and rapidly cooled to room temperature.

2.2 Sample test and characterization

The crystal structure of samples was measured using a DX-2600 variable-temperature X-ray diffraction instrument, then compared with ICDD card PDF#37-0476, and determined as $Na_8Al_6Si_6O_{24}Cl_2$ for natural sodalite.

Contents of trace elements, S, Eu, lead (Pb) Mn, Ce, samarium (Sm), and Fe in the sodalite were measured using a US VARIAN Company's VISTA-PRD ICP spectrograph located in the Analysis Center, Xinjiang Institute of Physical and Chemical Technique, Chinese Academy of Sciences. The results showed that Eu is a microelement with very low content (3.21 $mg·kg^{-1}$) in natural sodalite. The contents of trace elements in natural sodalite were determined using an inductively-coupled plasma atomic emission spectrometer (ICP-AES/Varian VISTA-PRO). The result of the ICP-AES analysis is shown in Table 1.

Table 1 Trace element contents of natural sodalite

Element	S	Eu	Pb	Mn	Ce	Sm	Fe
Content/($\mu g·g^{-1}$)	1 990.73	3.21	2.01	41.90	4.67	3.39	535.64

The down-conversion (DC) emission spectra of the samples were measured using a steady-state/transient-state fluorescence spectrometer (EDINBURGH FLS920) in the range of 200 to 800 nm. We used a 500 W deuterium lamp (HAMAMATSU, Japan) in the 200 to 320 nm region and 700 W xenon lamp (Xe 900) in the 260 to 500 nm region as excitation light sources. The excitation wavelength with an SR-500i grating monochromator was selected to measure the PL spectra. Bandpass and interference filters were placed in front of the samples to eliminate the stray light from the excitation source. The SR-750 grating monochromator was adopted to choose the observation wavelength. In addition, glass filters were set in front of the entrance slit of the observation monochromator to eliminate radiation from the excitation source.

The UC spectra of the samples were measured using a one-meter monochromator (SPEX 1 000 M; HORIBA Jobin Yvon Inc., Edison, NJ, USA) equipped with an 1 800-line mm^{-1} grating. The excitation light source was a power-adjustable continuous wave laser diode (978 nm, 10 W; BWT Beijing Ltd, Beijing, China).

Luminescence lifetimes of sample were characterized by an Edinburgh FLS 920 combined fluorescence lifetime and steady-state/transient-state spectrometer with a lifetime ranging from 50 ps to 10 s. A microsecond flash lamp with frequencies ranging from 100 to 0.1 Hz was used as the light source.

The whole measuring system was controlled by computers (popular and high-end configuration Q8400/2G/320/DVD/19) with full function control and data analysis software, steady-state data acquisition card, and quick single photon counting functions as well as 100 MHz counting rate and

calibration. To compare the PL intensities of samples, all measurements were obtained under identical conditions.

The chromaticity coordinate of phosphors means the coordinate described with the Commission International de L'Eclairage (CIE) chromaticity coordinate software.

3 Results and discussion

The crystal structure of natural sodalite was examined using Cu $K_{\alpha 1}$ radiation from an X-ray powder diffractometer (D2 Phaser Bruker AXS). Fig. 1 shows the X-ray diffraction patterns of samples. The results show that (211), (222), (321) and (330) sections occur at the same position. The patterns of samples were consistent with the ICCD standard card (PDF#37-0476) of sodalite.

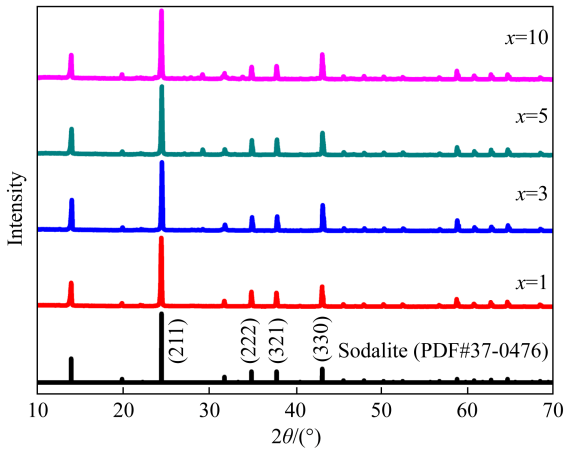


Fig. 1　X-ray diffraction patterns of Sodalite: 10% YbF3, *x*% EuF_3

Fig. 2 shows the emission spectra of Sodalite: 10% (mass fraction) YbF_3, *x*% EuF_3 (*x*=1, 3, 5, and 10) under 265 nm excitation. With rise of *x*, intensity of the narrow band with peak at 611 nm goes higher. Zhai, Yongqing et al[15] found that with higher Eu^{3+} ion concentration, the intensity of main emission peak at 618 nm continued to increase. In sodalite, Eu^{3+} replaces Na^+ to produce luminescence center, and no phenomenon of concentration quenching occurs. The crystal structure of sodalite is an ordered framework of linked AlO_4 and SiO_4 tetrahedra in which Si and Al alternate on the tetrahedral sites. The overall linkage of (Al, Si) O_4 tetrahedra results in cubo-octahedral cavities, which contain a centrally placed anion coordinated tetrahedrally to four cations.

The flexibility of the sodalite structure allows a wide range of cations and anions with potential luminescence ability to be substituted into it. The ionic radius of Eu^{3+} of 0.095 nm is close to that of Na^+ (0.097 nm), and the corresponding substitution is possible with proper charge compensation[3]. At 265 nm excitation, the emission spectrum (Fig. 2(d)) consists of several narrow bands with peaks at 580, 587, 592, 598, 611, 623, 629, 687, 693 nm and 707 nm. When the concentration of Eu^{3+} reaches 10%, the maximum and narrow band DC emission intensity is obtained. These narrow bands from 580 to 707 nm are characteristic emission bands due to Eu^{3+}[16], and can be identified to transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) using an energy diagram. The 592 nm emission corresponds to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition within Eu^{3+} and 611 nm emission to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition within Eu^{3+}. In our samples, the latter transition dominated, showing Eu^{3+} in sodalite was in the non-inversion symmetrical center in the crystal[17]. The phosphor (Fig. 2(d)) at 265 nm excitation radiated red luminescence with its main peak at 611 nm.

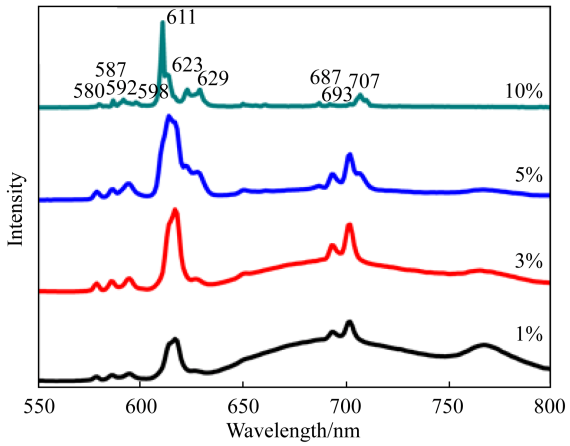


Fig. 2　Emission spectra of Sodalite: 10% YbF_3, *x*% EuF_3 (*x*= 1, 3, 5, 10) under 265 nm excitation at 300 K

Table 2 shows chromaticity coordinate values of sodalite:10% YbF_3, *A*% EuF_3 (*A*=1, 3, 5, and 10) with higher EuF_3 concentrations in which the *X* value of the chromaticity coordinate increased gradually, while the *Y* value decreased. When EuF_3 concentration is 10%, the fluorescence color became red with very high purity. Its chromaticity coordinate (0.661, 0.339) is close to the chromaticity coordinate of Y_2O_3: Eu^{3+} (0.648, 0.347), while the National Television System Committee (NTSC) standard chromaticity coordinate for red is (0.67, 0.33)[18–19]. Natural sodalite resource abounds in Xinjiang, indicating good potential for development. In addition, consumption of this type of host lattice is low and economical, and use of three-primary-colors fluorescent powder has very good research value and application prospects.

At 978 nm excitation, red emission was observed for natural sodalite co-doped with 10% YbF_3 and 10% EuF_3 as shown in Fig. 3. When the concentration of Yb^{3+} ions reached 10%, the maximum UC emission intensity was obtained. The red emission from 589 nm

to 700 nm was assigned to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, and 4) transition of Eu^{3+}, and the strongest peak at 613 nm originated from the $^5D_0 \rightarrow {}^7F_2$ transition. No luminescence could be found in the sample of Sodalite: 10%Eu^{3+} throughout the entire spectral region because the NIR excitation could not be absorbed by Eu^{3+} ions[20]. Therefore, cooperative energy transfer process from two Yb^{3+} ions to one nearby Eu^{3+} ion is the possible mechanism for the red emission.

Table 2 Chromaticity coordinate of Sodalite

Mass fraction of EuF_3/%	X	Y
1	0.619	0.380
3	0.634	0.365
5	0.642	0.358
10	0.661	0.339

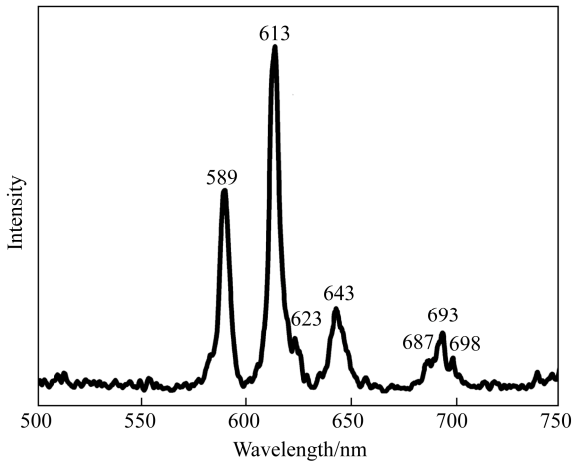


Fig. 3 Up-conversion emission spectra of Sodalite: 10% YbF_3, 10% EuF_3 upon excitation of a 978 nm laser diode

Fig. 4 shows the energy level diagram of Eu^{3+} and Yb^{3+} ions in addition to the probable UC mechanism accounting for the red emission at 978 nm excitation. In other words, two Yb^{3+} ions are first excited from $^2F_{7/2}$ to $^2F_{5/2}$ *via* 978 nm pumping. This pair of Yb^{3+} ions then transfers their total energy to one Eu^{3+} ion *via* a cooperative energy transfer process, and the Eu^{3+} ion will be excited to its $^5D_1$ level. The Eu^{3+} ion in the $^5D_1$ level can relax non-radiatively to the luminescent level $^5D_0$, which is then followed by red emission. Fig. 5 shows the NIR emission spectra of Sodalite: 10% YbF_3, 10% EuF_3 at 915 nm excitation at room temperature. The NIR emission of Yb^{3+} corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions has been previously observed between 950 nm and 1 100 nm at room temperature. The NIR emission is composed of lines corresponding to transitions from the lower Stark levels of $^2F_{5/2}$ to the various component of $^2F_{7/2}$[21].

Fig. 6 shows the lg-lg plot of luminescence intensity (I) versus the pump power density (P). For the UC process, I is proportional to the nth power of P, that is $I \propto P^n$, in which n is the number of pump photons absorbed per UC photon emitted. The n values can be obtained from the slope of the linear fit. The fitting result was approximately (1.79±0.03) for emission at 613 nm. This result shows that the two-photon process was responsible for the red UC.

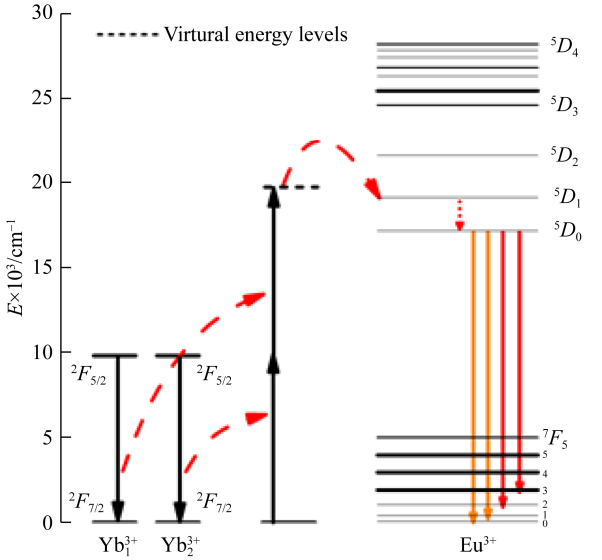


Fig. 4 Energy level diagram of Yb^{3+} and Eu^{3+} in addition to the proposed up-conversion (UC) mechanisms at 978 nm excitation

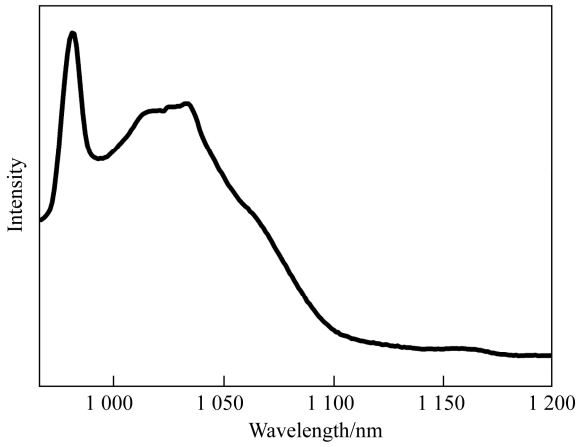


Fig. 5 Emission spectra (930–1200 nm) of Sodalite: 10% YbF_3, 10% EuF_3 upon 915 nm excitation at room temperature

The excitation spectra and the decay curves of Eu^{3+} emission were also studied. As shown in Fig. 7, the excitation spectrum consisted of an intense excitation band with peak at approximately 250 nm and weak additional narrow excitation bands with peaks at 322, 363.5, 394, 465 nm and 467 nm. The exciting spectrum while monitoring the Eu^{3+}:$^5D_0 \rightarrow {}^7F_2$ emission at 611 nm is shown in Fig. 7. A broad excitation band centered at 250 nm owing to the charge-transfer transition of O^{2-} to Eu^{3+} was detected. Several groups of sharp lines between 300 and 500 nm were due to the 4*f*–4*f* absorption transitions of Eu^{3+}. These excitation

bands could be attributed to the transitions due to Eu^{3+} in sodalite with the Eu^{3+} doping concentration increased from 1%→3%→5%.

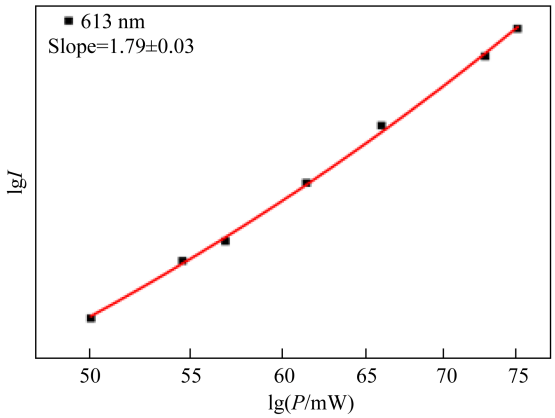


Fig. 6　Double-logarithmic plot of the pump-power dependent UC emission intensity recorded at 978 nm excitation

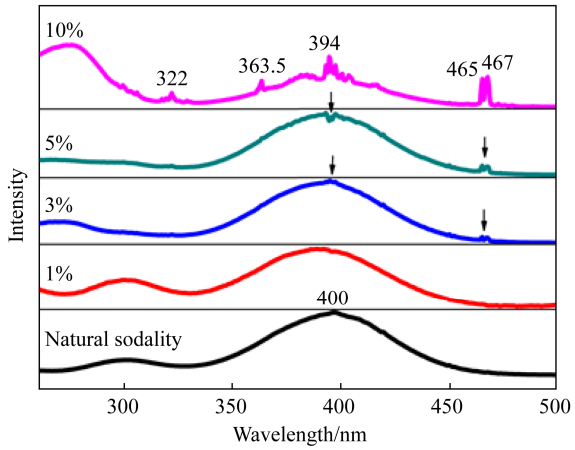
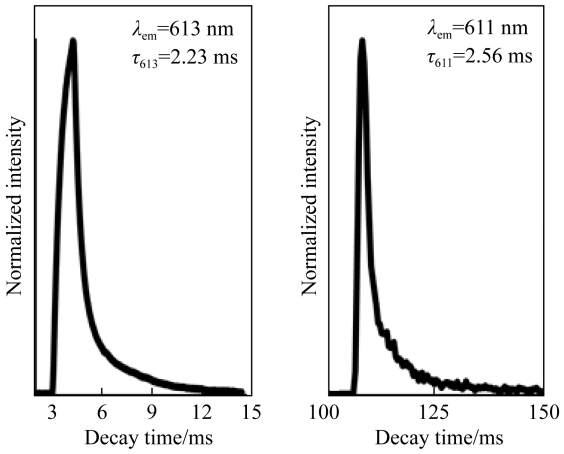


Fig. 7　Excitation spectra of sodalite and Sodalite: 10% YbF_3, x% EuF_3 (x=1, 3, 5, 10) obtained by monitoring luminescence at 611 nm.

Fig. 8 shows the luminescence decay curves of the Sodalite:10% YbF_3, 10% EuF_3 at room temperature. The curves could be fit to a single exponential curve, and the estimated lifetimes of the red luminescence (Eu^{3+}) from Sodalite:10% YbF_3, 10% EuF_3 could be estimated. Fig. 8(a) shows the decay curves of 613 nm emission from Eu^{3+} upon the excitation at 978 nm. However, the 613 nm decay curve of Eu^{3+} ions shows an increasing edge, which indicates that the excitation of Eu^{3+} originated from energy transfer. It can be seen in Fig. 8(b) that these decay curves have no increasing edge, indicating that 611 nm emission originated from the direct excitation at 265 nm, and no energy transfer process exists.

4　Conclusion

The YbF_3 and EuF_3 co-doped natural sodalite with different doping concentration were synthesized using the solid phase method. Efficient energy transfers from Yb^{3+}-dimers to Eu^{3+} were observed. The cooperative energy transfer process was discussed as the possible mechanisms for the red UC luminescence. The cooperative energy transfer process proved to contribute to the Yb^{3+} pair (Yb^{3+}-dimer)→Eu^{3+} energy transfer. Research on luminescent characteristics of sodalite would be beneficial for developing more efficient luminescent materials.



(a) Excitation of 978 nm　　(b) Excitation of 265 nm

Fig. 8　Decay curves of Eu^{3+} emission of Sodalite: 10% YbF_3, 10% EuF_3

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