

## Synthesis and luminescent properties of $\text{Ba}_2\text{V}_2\text{O}_7:\text{Sm}^{3+}$

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**Abstract:** Samarium doped pyrovanadate  $\text{Ba}_2\text{V}_2\text{O}_7:\text{Sm}^{3+}$  phosphors were synthesized by traditional high-temperature solid-state reaction method. The phase and the structure of the samples were characterized by powder X-ray diffraction (XRD), and the luminescent properties and the energy transfer mechanism of the material were investigated using quantitative photoluminescence (PL) spectroscopy. The excitation spectrum of the sample exhibited a broad ultraviolet (UV) band with maximum at around 341 nm due to V–O charge transfer transition of the host. The emission spectrum displayed a yellow-greenish broadband (peaking at around 498 nm) coming from the host  $\text{Ba}_2\text{V}_2\text{O}_7$  and three narrow peaks (at 561, 599 and 646 nm) attributed to the dopant  $\text{Sm}^{3+}$  ions. The PL spectra revealed the energy transfer from the host to the  $\text{Sm}^{3+}$  ions. In addition, the color coordinates and the color temperature of the phosphor  $\text{Ba}_{1.95}\text{V}_2\text{O}_7:5\%\text{Sm}^{3+}$  were (0.314, 0.365) and 6135 K, respectively, under 365 nm excitation, suggesting it to be a candidate of single-phase converting phosphors for white-light-emitting diodes (WLEDs) with near-UV chips.

**Keywords:** phosphor;  $\text{Ba}_2\text{V}_2\text{O}_7:\text{Sm}^{3+}$ ; luminescence; WLED; rare earths

In recent years, white-light-emitting diodes (WLEDs) have attracted more and more attention for their advantages such as high efficiency, compactness, long operational lifetime, and environmental friendliness<sup>[1,2]</sup>. Among different kinds of WLED lamps, phosphors converted WLEDs working with a combination of phosphors and LED chips to achieve white light emission, are the most promising to replace nowadays incandescent and fluorescent lamps as major lighting sources<sup>[3]</sup>. There are two primary approaches in commercial use to obtain phosphors converted WLEDs. One is the combination of phosphors and a blue LED chip<sup>[4,5]</sup>, for example, YAG:  $\text{Ce}^{3+}$  yellow phosphor excited with a blue InGaN chip was the most typical and successful in this branch due to its high luminescence efficiency<sup>[5,6]</sup>. However, because of the lack of red-light components in this device, YAG:  $\text{Ce}^{3+}$  phosphor has disadvantages such as poor color rendering index (CRI, smaller than 80) and high correlated color temperature (CCT, higher than 7000 K)<sup>[4,7,8]</sup>. The second approach is a combination of two or three different color phosphors with a UV (or near-UV) LED chips<sup>[9–11]</sup>. However, as different hosts involved usually have different aging conditions, the combination may suffer color shift with hosts aging. In order to enhance the color stability, single-phase white phosphors excited by UV LED is proposed to be a potential solution, since different activators in only one host would experience similar aging conditions. As a result, the single-phased WLEDs have the advantages such as small color aberration,

high color rendering, and high efficiency.

As common inorganic materials, vanadates have excellent electronic, optical, and chemical properties mainly due to the 3d electrons of vanadium<sup>[12–14]</sup>. Since energy would transfer from V–O charge-transfer bands to the luminescence center, the absorption bands in many vanadates is usually quite broad and intense<sup>[15]</sup>. Besides, alkaline-earth metal pyrovanadate  $\text{M}_2\text{V}_2\text{O}_7$  (M=Ba, Sr) have a strong self-activated broadband emission<sup>[16,17]</sup>, which is induced by one-electron charge-transfer transition from the oxygen 2p orbital to the vacant 3d orbital of  $\text{V}^{5+}$  in the tetrahedral  $\text{VO}_4$  with  $T_d$  symmetry<sup>[18]</sup>. On the other hand, rare earth ions have played an important role in modern lighting and display fields due to the abundant emission colors based on their 4f–4f or 5d–4f transitions. Among rare earth ions,  $\text{Sm}^{3+}$  ( $4f^6$ ) ion is one of the most interesting rare earth ions due to its fluorescence properties. The emission of  $\text{Sm}^{3+}$  is situated in the orange spectral region and consists of three narrow characteristic peaks attributed to transitions from the excited  $^4\text{G}_{5/2}$  level to the state  $^6\text{H}_{5/2}$  (around 561 nm),  $^6\text{H}_{7/2}$  (around 590 nm) and  $^6\text{H}_{9/2}$  (around 646 nm), respectively<sup>[19,20]</sup>. Nowadays, many  $\text{Sm}^{3+}$ -doped materials have been applied in various fluorescent devices, color displays, and temperature sensors, etc.<sup>[21]</sup> In this paper,  $\text{Sm}^{3+}$  ions were doped into self-activated pyrovanadate host  $\text{Ba}_2\text{V}_2\text{O}_7$  with a yellow-green emission broadband to investigate their potential as single-phase white phosphors used for WLED.

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## 1 Experimental

A series of  $\text{Ba}_2\text{V}_2\text{O}_7:\text{Sm}^{3+}$  phosphors with different  $\text{Sm}^{3+}$  concentration were synthesized by high-temperature solid-state reactions.  $\text{BaCO}_3$  (A.R.),  $\text{V}_2\text{O}_5$  (A.R.) and  $\text{Sm}_2\text{O}_3$  (99.99%) were used as starting materials. Stoichiometric amounts of the raw materials have been mixed and thoroughly ground in an agate mortar, and then preheated at 500 °C for 4 h in air. Subsequently, the obtained samples were ground again and then re-calcined at 1000 °C for 6 h in air. To study the influence of  $\text{Sm}^{3+}$  ions concentration on fluorescence properties of  $\text{Ba}_2\text{V}_2\text{O}_7$ : $x\text{Sm}^{3+}$ ,  $\text{Ba}_{2-x}\text{Sm}_x\text{V}_2\text{O}_7$  samples with  $x=0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07$  and  $0.08$  (molar ratio), respectively, were prepared in the experiment.

The crystal structures were analyzed by a MXPAHF rotating anode X-ray diffractometer (Cu  $K\alpha$  radiation). The XRD profiles were collected in the range  $10^\circ < 2\theta < 70^\circ$ . Photoluminescence excitation (PLE) and emission (PL) spectra were characterized on a HITACHI 850 fluorescence spectrometer with a 150 W Xe lamp as an excitation source.

## 2 Results and discussion

### 2.1 Phase and crystal structure analysis

Fig. 1 shows the XRD patterns of  $\text{Ba}_2\text{V}_2\text{O}_7:x\text{Sm}^{3+}$  samples and the standard data of  $\text{Ba}_2\text{V}_2\text{O}_7$  (PDF#76-612). Fig. 1(2), (3), (4) and (5) represent the XRD patterns of  $\text{Ba}_2\text{V}_2\text{O}_7:x\text{Sm}^{3+}$  samples with  $x=0, 0.01, 0.02$  and  $0.03$ , respectively. The XRD patterns of Fig. 1(2), (3), (4) and (5) match well with those of standard cards of  $\text{Ba}_2\text{V}_2\text{O}_7$  (PDF#76-612), indicating that single-phase phosphors  $\text{Ba}_2\text{V}_2\text{O}_7:\text{Sm}^{3+}$  were obtained and the dopant of  $\text{Sm}^{3+}$  ions had negligible effect on the lattice structure of  $\text{Ba}_2\text{V}_2\text{O}_7$  host. Besides, in  $\text{Ba}_2\text{V}_2\text{O}_7$  host,  $\text{Ba}^{2+}$  had four sites in which two sites had 7 coordination numbers, one site had 8 coordination numbers and the last site had 9

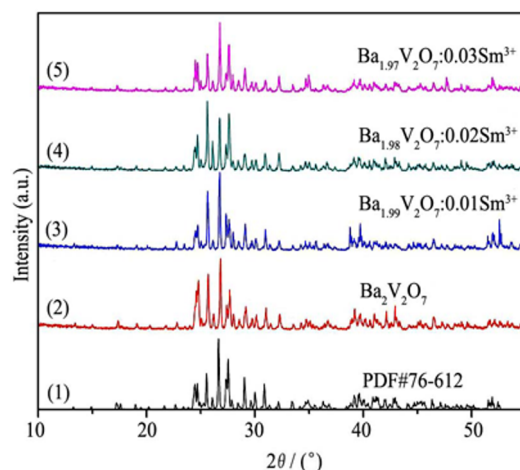


Fig. 1 Powder XRD patterns for structural analysis of samples  $\text{Ba}_2\text{V}_2\text{O}_7:x\text{Sm}^{3+}$  ( $x=0, 0.01, 0.02, 0.03$  for (2), (3), (4), (5), respectively) and the standard cards of  $\text{Ba}_2\text{V}_2\text{O}_7$  (PDF#76-612) (1)

coordination numbers. The ion radii with different coordination numbers in  $\text{Ba}_2\text{V}_2\text{O}_7$  are shown in Table 1<sup>[22]</sup>. Since the revised effective ionic radii of  $\text{Sm}^{3+}$  were close to those of  $\text{Ba}^{2+}$ , it was very easy for  $\text{Sm}^{3+}$  ions to substitute the  $\text{Ba}^{2+}$  of the host lattice.

Fig. 2 shows the structure of  $\text{Ba}_2\text{V}_2\text{O}_7$  and  $\text{V}_2\text{O}_7^{4-}$  dimer group. In  $\text{Ba}_2\text{V}_2\text{O}_7$  lattice, vanadium atom is tetrahedrally coordinated and two  $\text{VO}_4$  tetrahedra form dimer ( $\text{V}_2\text{O}_7$ )<sup>4-</sup> group by sharing one oxygen atom<sup>[23]</sup>. Because the emission originated from the charge-transfer (CT) of  $\text{VO}_4^{3-}$  group is strongly dependent on the structure of  $\text{VO}_4^{3-}$  group in the self-activated  $\text{Ba}_2\text{V}_2\text{O}_7$  host<sup>[16,17]</sup>, the structure of  $\text{V}_2\text{O}_7^{4-}$  group in  $\text{Ba}_2\text{V}_2\text{O}_7$  is shown in Fig. 2(b). It can be seen from Fig. 2(b) that the

Table 1 Revised effective radii ( $10^{-1}$  nm) of  $\text{Ba}^{2+}$  and  $\text{Sm}^{3+}$  ions with different coordination number (CN) in  $\text{Ba}_2\text{V}_2\text{O}_7$

Ions	CN=7	CN=8	CN=9
$\text{Ba}^{2+}$	1.38	1.42	1.47
$\text{Sm}^{3+}$	1.02	1.079	1.32

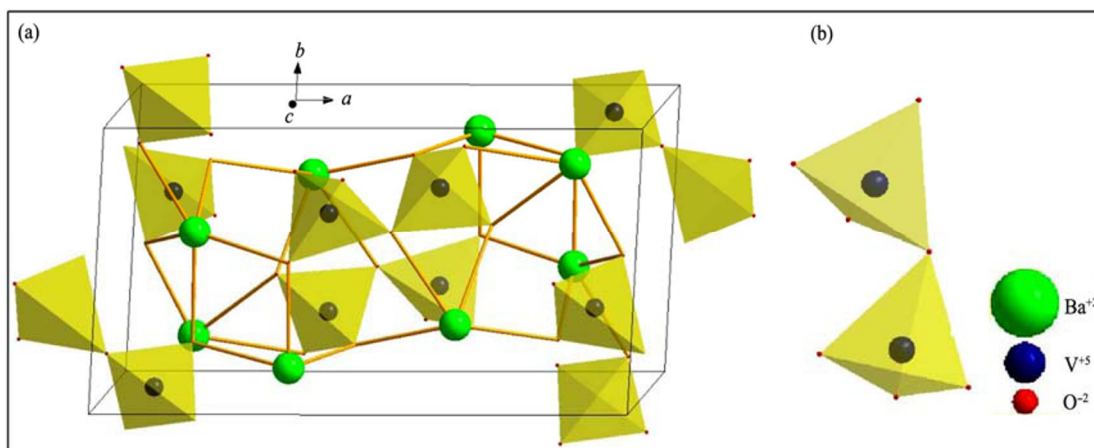


Fig. 2 Schematic crystal structure diagrams of  $\text{Ba}_2\text{V}_2\text{O}_7$

(a) The structure of  $\text{Ba}_2\text{V}_2\text{O}_7$  unit cell (consisting of four different  $\text{VO}_4$  dimers) ( $\text{V}^{5+}$  ions outside the unit cell are not plotted); (b) The structure of one  $\text{VO}_4$  dimer ( $\text{V}_2\text{O}_7^{4-}$  group)

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