

Luminescence of the compounds $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$

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In this paper for the first time the compounds $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ (YLV:Eu) ($0.01 < x < 0.1$ mol) were synthesized by the simple method of solid state reaction. The technology takes much time dry low temperature and little time calcined to synthesize rare earth vanadates. Their structures were analyzed by X-ray powder diffraction experiment. The excitation and emission spectra were measured at room temperature. $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ show the characteristic missions of Eu^{3+} (${}^5D_0-{}^7F_{1,2,3,4}$ transitions dominated by ${}^5D_0-{}^7F_2$). Incorporation of Li^+ ions in the phosphors promote the crystallinity, reduce the amount of Y_2O_3 , and lower the cost of production, therefore, $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ phosphors are potentially to be one of the candidates in red-lighting materials.

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1. Introduction

Rare earth vanadates have been studied extensively. They are of interest as better hosts for luminescence and laser materials. The europium activated yttrium vanadate ($YVO_4:Eu$) has been earliest used in color television as red phosphor [1]. Bulk vanadates were prepared by high temperature solid-state reactions providing agglomerated powders, which can permit to easily change the structural characteristics of the powders. Besides this, some people obtained the nanoparticles of vanadates using the hydrothermal method [2]. Recently, a new low temperature technology based on to take much time dry low temperature and little time calcined is the most popular, which has been verified to be very useful in the synthesis of nanoparticles [3].

In the present paper for the first time we reported the new compounds of $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ (YLV:Eu) ($0.01 < x < 0.1$ mol), which were prepared by the simple method of solid state reaction.

To synthesize the new compounds, a novel synthesis technology was employed to obtain the $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ phosphors through a modified low temperature solid state reaction. The ammonium vanadate (NH_4VO_3) as source components for VO_4 and lithium nitrate ($LiNO_3$) as source components for Li. The luminescent performance and grain sizes were systematically examined. Especially, the luminescent properties of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ were discussed in detail.

2. Experimental

$Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ phosphors were prepared by the simple method of solid state reaction. The initiative

materials Y_2O_3 and Eu_2O_3 were firstly dissolved into concentrated nitric acids. Then the preparation of the precursors ($Y_{0.5-x}Li_{1.5}VO_4:Eu_x$) was described in details in the following: The rare earth nitrates solutions ($Y(NO_3)_3$ and $Eu(NO_3)_3$) were added and mixed homogenously. Then 1.0 mmol NH_4VO_3 and 1.5 mmol $LiNO_3$, the mixture was continually ground at room temperature. After 10 min of grinding, 4 ml deionized water was added to the above mixture. Under continuous stirring and heating at about $80^\circ C$. As water evaporated, the solution became viscous and finally formed a gel. Subsequently, the gel was dried at $100^\circ C$ for 4 h to yield a xerogel. That is to say, the precursors were achieved. Finally, the samples were heat-treated in a furnace at preheated to a definite temperature ($740^\circ C$) and calcined for 40 min.

X-ray diffraction (XRD) patterns were measured using a BRUKERD8 FOCUS with $Cu K\alpha$ radiation ($\lambda=0.15418$ nm), at a scanning rate of $4.0^\circ \text{min}^{-1}$. PL emission/excitation spectra were measured using an F-4500 fluorescence spectrometer (Hitachi). The sizes and morphologies of the as-synthesized samples were studied by KYKY2AMARY21000B scanning electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR, AVATAR370) were used to measure phosphors powder with the KBr pellet technique. All the measurements were carried out at room temperature.

3. Results and discussion

The crystal phases of the phosphor particles are determined by X-ray powder diffraction (Fig. 1).

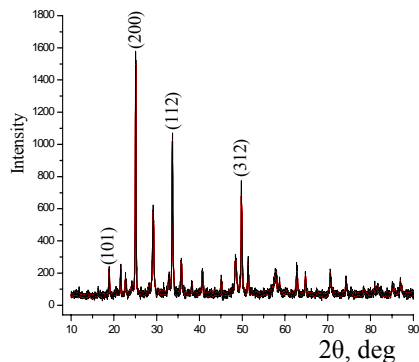


Fig. 1. X-ray diffraction (XRD) patterns of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ powders.

The line positions in the XRD patterns of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ are found to be consisted of YVO_4 and Li_3VO_4 phase. The structure of YVO_4 is known to belong to the tetragonal crystal system with I_{41}/amd as the space group, in which the rare earth cation is coordinated by eight oxygen atoms in an arrangement of two interpenetrating tetrahedral yielding D_{2d} as the point symmetry of the single R^{3+} site. The structure of $LiVO_4$ which lacks a center of symmetry, possesses a wurtzite-crystal type structure [1]. And mean particle size can be roughly determined from the broadening of the peaks by using the Scherrer formula [2],

$$D_{hkl} = k\lambda / [\beta(2\theta)\cos\theta]$$

where $\beta(2\theta)$ is the width of the pure diffraction profile in radians, k is 0.89, λ the wavelength of the X-rays (0.15418 nm), θ the diffraction angle and D_{hkl} is the average diameter of the crystallite. By fitting various peaks of this formula, we obtained values of about 2.0 μm for the particle diameter.

Using the scanning electron microscope we are obtained morphologies of the samples $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$, which is the largescale solid sphere-like nanocrystals. Fig. 2 shows the representative SEM micrograph of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$. It can be seen that the product mainly consists of solid micron crystalline structures, which exist with some conglomeration among the crystalline grain for the calcined of thermal decomposition. The typical crystalline grain is estimated to be around 1.0–2.0 μm in dimension. Besides this, the three-dimensional sizes of crystalline grain are very thick to afford high strength, it needs to refer that the crystalline powder and micrometer dimension for these powders with high strength would be very useful for the application to obtain high efficient phosphors because these micro crystalline materials can result in the high luminescent intensities [4].

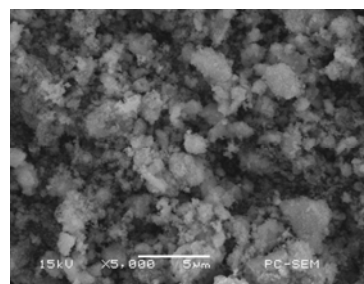


Fig. 2. Scanning electron microscope (SEM) photograph of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ powders.

All the excitation spectra of $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ have the similar features except for a difference in intensity, and, here, we chose the representative $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ excitation spectrum monitored the emission of Eu^{3+} at 618 nm was shown in Fig. 3, which consists of a broad band with high intensity from 200 to 350 nm with a maximum at 308 nm (Fig. 3a) and several narrow bands with low intensity in the range of 350–550 nm (Fig.3b). The former is due to the absorption of VO_4^{3-} group, and the absorption of VO_4^{3-} is ascribed to a charge transfer from the oxygen ligands (O^{2-}) to the central vanadium atom (V^{5+}). In crystalline YVO_4 the original T_d symmetry of VO_4^{3-} (free ion) is reduced to D_{2d} by the crystal field [5]. The latter is assigned to the f–f transitions within Eu^{3+} 4f⁶ electron configuration, the most prominent group at 538 nm being as associated with ${}^7F_0 - {}^5D_1$ transition and at 396 nm being as associated with ${}^7F_0 - {}^5L_6$ transition [6,7].

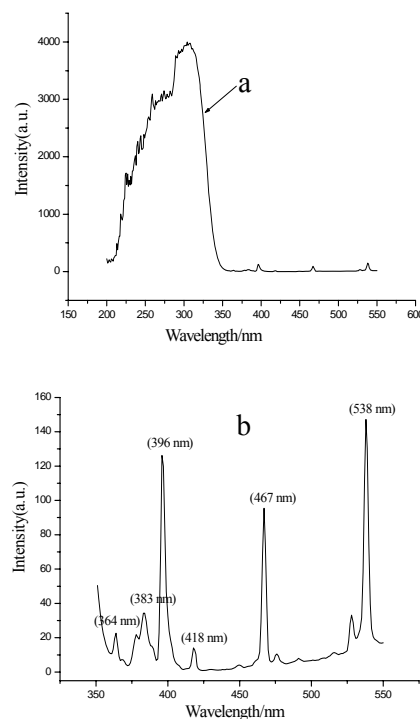


Fig. 3. Excitation spectra of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ powders under 618 nm emission: (a) 200–550 nm; (b) 350–550 nm.

The representative emission spectrum of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ nanocrystallites upon excitation at 310 nm was shown in Fig. 4. It is composed of the characteristic emission bands of ${}^5D_0 - {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of Eu^{3+} , with ${}^5D_0 - {}^7F_2$ transition being the most prominent band due to the absence of an inversion symmetry at the Eu^{3+} lattice site (D_{2d} symmetry) [6]. Moreover, the peak intensity of ${}^5D_0 - {}^7F_4$ transition is larger than that of ${}^5D_0 - {}^7F_3$ transition in the emission spectrum. In accordance with Judd–Ofelt theory [6], transitions to even J-numbers have much higher intensity than those to corresponding neighboring odd J-numbers. The crystal field splitting of ${}^5D_0 - {}^7F_{2,4}$ transitions of Eu^{3+} in YVO_4 host (Fig. 4) indicates that the $YVO_4:Eu$ nanocrystallites are well crystallized. The emission peaks at 614, 617, 696 and 701 nm are assigned to the ${}^5D_0(A_1) - {}^7F_2(B_2)$, ${}^5D_0(A_1) - {}^7F_2(E)$, ${}^5D_0(A_1) - {}^7F_4(B_2)$ and ${}^5D_0(A_1) - {}^7F_4(E^{(1)})$ transition, respectively [6].

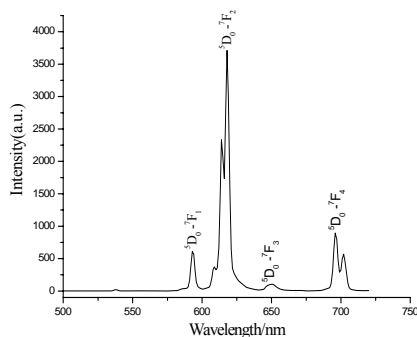


Fig. 4. Emission spectra of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ powders under 310 nm excitation.

We know that FTIR is a powerful tool for identifying different types of chemical bonds in a molecule, since each bond produces a unique infrared absorption spectrum that may be compared to its 'molecular fingerprint' [8]. Fig. 5 plots the FTIR spectra of the $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ phosphor powders.

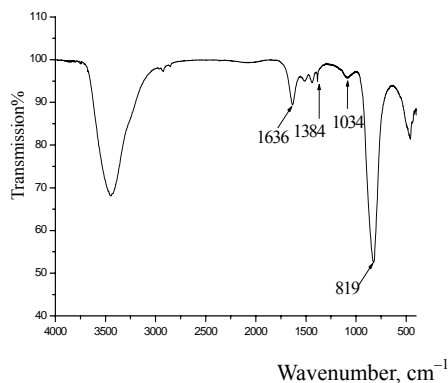


Fig. 5. FTIR patterns of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ powders.

The peaks at 1636, 1384, and 1034 cm^{-1} represent the characteristics (Y–O) metal–oxygen vibrations [9], while the absorbance peak of VO_4 in $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ sample only exhibits an peak at 819 cm^{-1} , this may be ascribed to Y^{3+} adoption 8 oxygen coordination numbers, and the VO_4 group presentation regular V-center tetrahedron with uniform bond-length and bond-angle. The equal vibrations energy of four V–O bonds makes the VO_4 group only show an vibration peak [10]. The results suggest that FTIR spectra can be regarded as an effective criterion for ascertaining the crystal category of $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$. Based on above results, we predict that FTIR spectroscopy might be a potent complementary means to identify material crystal phase. The FTIR spectroscopy of the $Y_{0.46}Li_{1.5}VO_4:Eu_{0.04}$ samples are in good agreement with the XRD analysis. It is also suggested that the Li^+ ions may serve as a self-promoter for better crystallization or as a lubricant for the complete incorporation of the Eu^{3+} ions into the $Y_{0.46}Li_{1.5}VO_4$ hosts [11].

4. Conclusions

$Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ compounds were prepared by modified low temperature solid state reaction. Its structure consists of the YVO_4 and Li_3VO_4 phase. The phosphors exhibit the characteristic fluorescence of Eu^{3+} ions. Incorporation of Li^+ ions in the phosphors can promote the crystallinity to a great extent, and thus enhance the PL emission intensity greatly, at the same time, reduce the amount of Y_2O_3 , lower the cost of production. Therefore, $Y_{0.5-x}Li_{1.5}VO_4:Eu_x$ phosphors are potentially to be one of the candidates in red-lighting materials.

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