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An investigation about the luminescence mechanism of $SrGa_2O_4:Eu^{3+}$ showing no detectable energy transfer from the host to the dopant ions

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ABSTRACT

Un-doped $SrGa_2O_4$ and a series of Eu^{3+} ions doped $SrGa_2O_4$ were synthesized by conventional solid state reactions. The X-ray diffraction patterns, photoluminescence excitation and photoluminescence spectra, diffuse reflection spectra of these samples were recorded and analyzed. Un-doped $SrGa_2O_4$ can emit blue-violet light in a broad band peaking at 407 nm under the excitation at 234 and 252 nm. Eu^{3+} ions doped $SrGa_2O_4$ phosphors exhibit red emission under the excitation at 274 nm. However, there is no detectable energy transfer from the host to doped Eu^{3+} ions. The further luminescence mechanism and reasons for the absence of energy transfer from the host to doped Eu^{3+} ions are discussed in detail. A novel mechanism about the luminescence of gallium compounds is proposed based on our experimental results. An energy level diagram is proposed to illustrate the luminescence mechanism of gallium compounds and reasons for the absence of energy transfer from the host to doped Eu^{3+} ions.

1. Introduction

The luminescence associated with gallium ions has been known for half a century. Blasse and Bril pointed out that the gallium compounds show a very broad emission band with a maximum at 450 nm extending from the UV region till the near infer-red region [1]. Verstegen reported that the broad band at about 450 nm can be attributed to host lattice emission in the emission curve of Mn^{2+} doped $SrGa_{12}O_{19}$ at 77 K. Efficient energy transfer from the lattice to the Mn^{2+} which occupies a tetrahedral site takes place [2,3]. Jeong et al. found that there are two fluorescence bands at 432 (corresponding to the absorption band at 260 nm) and 360 nm (corresponding to the absorption band at 246 nm) in the fluorescence spectra of $ZnGa_2O_4$, respectively. The former is originated from self-activation center of the octahedral Ga-O groups, and the latter is due to the tetrahedral Ga-O groups in the spinel lattice [4,5]. Yang and Tu reported that the emission wavelength of $SrGa_2O_4$ phosphor is ~402 nm, which is referred to the $^4T_1 \rightarrow ^4A_2$ transition of electrons in Ga d orbits. The possible excited levels of Ga^{3+} ions are $^4T_{2B}$, $^4T_1$, $^4T_{2A}$, ^2E_B and ^2E_A [6].

Although many literatures reported the luminescence of gallium compounds, the analysis of luminescence mechanism is still very simple and coarse. Some simply suggest that luminescence is related to Ga-O polyhedra [4,5], and some indicate that luminescence comes from excitation and emission of Ga^{3+} ions [6]. But the deep luminescence mechanism is not clear until now. In our recent studies, $SrGa_2O_4$ also shows host luminescence. An unusual phenomenon appears when we doped Eu^{3+} ions into $SrGa_2O_4$. That is, there is almost no energy transfer from the host to doped Eu^{3+} ions. This aroused our interest. Deep luminescence mechanism of gallium compounds and the reason for the absence of energy transfer from the host $SrGa_2O_4$ to the doped Eu^{3+} ions is revealed.

2. Experimental

2.1. Preparation

A series of un-doped and Eu^{3+} ions doped phosphors ($Sr_{1-x}Ga_2O_4$: xEu^{3+}, x = 0, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06) were synthesized by high temperature solid state reactions. The staring materials ($SrCO_3$ (99%), Ga_2O_3 (99.99%) and Eu_2O_3 (99.999%)) were weighed according to their stoichiometric ratio (It is worth noting that the amount of Ga_2O_3 needs to be increased by 2% because it volatilizes faster than

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other raw materials at high temperature), mixed together and ground thoroughly with an agate pestle in an agate mortar for 30 min. The obtained mixtures were put into corundum crucibles and sintered at 1300 °C for 6 h in a tubular furnace. The sintered powders were ground again for further measurements after their temperature was lowered to room temperature.

2.2. Characterization

Phase purity of all prepared samples was detected by a Beijing PGeneral powder X-ray diffractometer (Cu kα radiation operated at 36 kV and 20 mA, λ = 1.5406 Å). The morphology of the samples was characterized by a Hitachi S-3400N scanning electronic microscope (SEM) with an accelerating voltage of 10 kV. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded by a Hitachi F-7000 fluorescence spectrometer with a 450 W Xenon lamp (operate voltage 400 V, scanning speed 240 nm/min, in slit 2.5 nm, out silt 2.5 nm). Diffuse reflection spectra (DSR) were measured by a Shimadzu UV-2450 UV/visible spectrometer. All measurements were performed at room temperature.

3. Results and analysis

3.1. Phase formation and morphology

$SrGa_2O_4$ has two modifications, β-phase corresponding to the stable modification at room temperature and γ-$SrGa_2O_4$, a quenched high-pressure polymorph prepared at 1250 °C and 2.5 GPa. Samples prepared under normal pressure in our research belong to β-$SrGa_2O_4$. It is monoclinic, space group $\boldsymbol{P}21_1/\boldsymbol{c}1$, a = 8.3770(3) Å, b = 8.9940(2) Å, c = 10.6800(4) Å, β = 93.932(2) °, V = 802.8(5) $Å^3$, Z = 8 [7,8]. The structure of β-$SrGa_2O_4$ is characterized by layers of six-membered rings of GaO_4 tetrahedrons perpendicular to the a axis (Fig. 1). The stacking of the layers parallel to the a axis results in a three-dimensional framework containing channels that are occupied by the Sr cations for charge compensation. The relative orientation of adjacent tetrahedrons within a single ring is different. The sequence is UUDUDD (U for up and D for down) [7,8].

Fig. 2 presents the representative X-ray diffraction (XRD) patterns of un-doped $SrGa_2O_4$ and some representative samples $Sr_{1-x}Ga_2O_4$: xEu^{3+} (x = 0.02, 0.05 and 0.06). JCPDS card no. 72-0222 ($SrGa_2O_4$) is also listed for comparison. All the diffraction peaks of un-doped sample can be indexed to the standard data of $SrGa_2O_4$. When Eu^{3+} ions are doped into $SrGa_2O_4$ with a small doping concentration (no more than 5 mol%), no extra peak corresponding to impurity phase is observed, indicating that a series of $Sr_{1-x}Ga_2O_4$: xEu^{3+}(x = 0.01, 0.02, 0.03, 0.04 and 0.05) were obtained as a single phase. However, when the doping concentration reaches to 6 mol%, some extra peaks corresponding to impurity phase appear around 32° in the XRD pattern. This indicates that the doping limitation of Eu^{3+} ions in $SrGa_2O_4$ is 5 mol%.

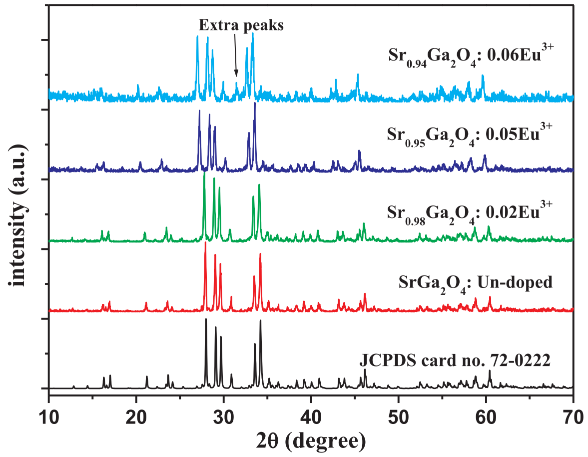

Fig. 2. XRD patterns of several representative samples $SrGa_2O_4$: xEu^{3+}(x = 0, 0.02, 0.05 and 0.06), the standard pattern of JCPDS card no. 72–0222 is also listed for comparison.

The size of particles has an effect on the PL intensity. Fig. 3 shows the SEM image of a representative sample $Sr_{0.97}Ga_2O_4$: $0.03Eu^{3+}$. The samples are consisted of aggregated particles with a size ranging from 1 to 3 μm.

3.2. DRS research

Fig. 4 plots the DRS of $SrGa_2O_4$ and $Sr_{0.95}Ga_2O_4$: $0.05Eu^{3+}$. One main drop in reflectance exists in the ultraviolet (UV) spectral range. For $SrGa_2O_4$, the drop begins at about 270 nm and for $Sr_{0.95}Ga_2O_4$: $0.05Eu^{3+}$ it begins at about 320 nm. The drop before 270 nm can be attributed to the host absorption. Also, $Sr_{0.95}Ga_2O_4$: $0.05Eu^{3+}$ presents a better absorption than un-doped $SrGa_2O_4$. Some sharp peaks appear at 360, 392 and 463 nm, which are corresponding to the transitions $^7F_{0,1}\rightarrow{}^5D_4$, $^7F_0\rightarrow{}^5L_6$, and $^7F_1\rightarrow{}^5D_2$, respectively. In the spectral region from 250 to 300 nm, the absorption of $Sr_{0.95}Ga_2O_4$: $0.05Eu^{3+}$ is enhanced compared with un-doped $SrGa_2O_4$. This spectral region is consistent

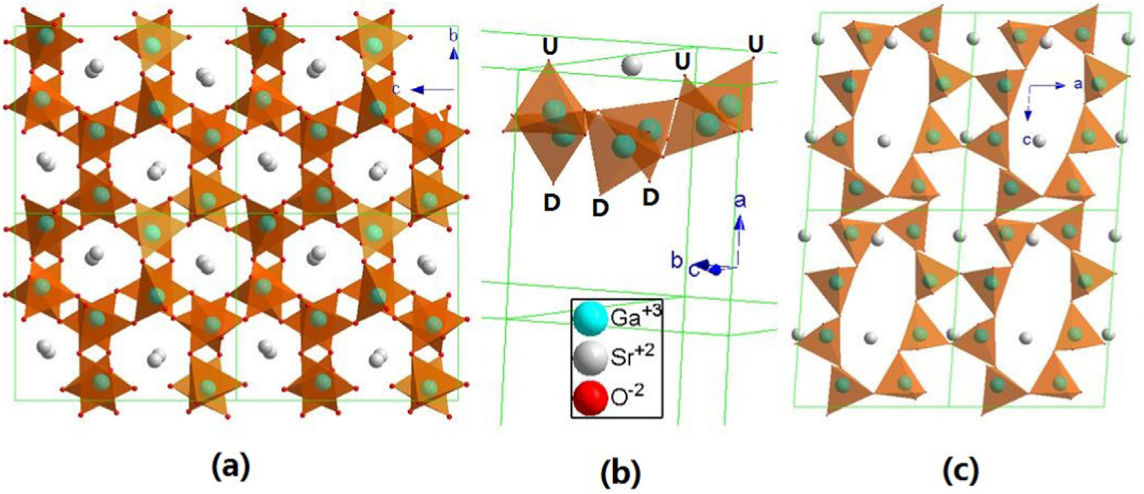

Fig. 1. Crystal structure of β-$SrGa_2O_4$ (a) a view along the a axis; (b) constitution and orientation of the a six-membered ring of GaO_4 tetrahedrons; (c) a view along the b axis.