Journal of Luminescence 168 (2015) 26–37

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Spectral characteristics of germanium compounds having apatite structure

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ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form
10 July 2015
Accepted 15 July 2015
Available online 26 July 2015

Keywords:
Photoluminescence
Excitation spectra
Judd–Ofelt parameters
Transition probabilities
Oscillator strength

ABSTRACT

In this work, solid solutions with a general formula $Ca_2La_{8(1-x)}Eu_{8x}Ge_6O_{26}$ were described and their excitation (PLE), emission (PL) and EPR spectra have been recorded. The morphology and elemental composition of the samples were studied by scanning electronic microscopy (SEM) and energy dispersive X-ray analysis (EDX) methods. Quantum yield, Judd–Ofelt intensity parameters, luminescence branching ratio, and oscillator strengths for magnetic dipole $^5D_0 \rightarrow {}^7F_1$ and electric dipole $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions are calculated for the solid solution having the largest integral intensity of emission.

1. Introduction

Recently, a large number of papers devoted to Eu^{3+} ion activated crystallophosphors were published. This ion activator is used for obtaining of luminophors that are red emission sources. One of the reasons for choosing europium is a simple scheme of energy levels, between which radiative transitions occur by UV-excitation of trivalent europium. Another reason is the possibility of studying the cationic sites in the solid phosphor crystal lattice, which is based on the presence of a line lying in the red region (614 nm) of the spectrum corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition. This electric dipole transition is parity-forbidden ($\Delta J = 0, \pm 1$), but prohibition is lifted if Eu^{3+} occupies the crystallographic positions that do not correspond to the symmetry centers, and odd terms appear in the crystal field potential expansion series. Thus, $^5D_0 \rightarrow {}^7F_2$ is supersensitive with respect to the ligand field asymmetry coordinating the cation [1].

Hosts having apatite structure are effective media for designing crystal phosphors emitting in the red region of the spectrum. A characteristic feature of these structures is the presence of two non-equivalent low-symmetry positions C_3 and C_s. Consequently, when Eu^{3+} ion is used as an activator, both the allowed magnetic dipole $^5D_0 \rightarrow {}^7F_1$ and forbidden electric dipole $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions become probable. Currently, there are numerous compounds with the general formula $M_2Ln_8(TO_4)_6I_2$, where M=Ca, Ba, Sr, Pb; Ln-trivalent ions of rare earth elements; T=P, Si, Ge, V, B, As, Ga; and I=O, S, F, Cl, Br, OH; with apatite structure. Such a variety of compositions is due to structural stability at large volume expansion [2]. All of them are characterized by the presence of two nonequivalent crystallographic positions occupied by M and Ln cations. One of these positions (6h) has a point group of symmetry C_S and is coordinated by six chemically bound oxygen ions and by one so-called "free oxygen". The second position (4f) is surrounded by 9 O^{2-} ions, that are members of the $[TO_4]^{n-}$ group. The differences in electronegativity (ΔX) between the elements P and O, Si and O, Ge and O, V and O, Ga and O, As and O, B and O are, respectively, 1.25, 1.54, 1.43, 1.81, 1.63, 1.23, and 1.4. A smaller ΔX value between the elements forming the isolated tetrahedra $[TO^4]^{n-}$ corresponds to a smaller value of the band gap [3,4]. Considering that the lower level of the conduction band in the compounds of Eu^{3+} is formed by the charge-transfer state (CTS) of $Eu^{2+}(4f^7)$–O^- ($2p^{-1}$), the crystal phosphors with the lowest energy barrier are expected to exhibit the greatest shift of the absorption band corresponding to the CTS into the long wavelength region. Therefore, for the preparation of luminescent materials with optimal excitation wavelength corresponding to the working area of industrial UV LED, matrices on the basis of phosphates and arsenates with apatite

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http://dx.doi.org/10.1016/j.jlumin.2015.07.019
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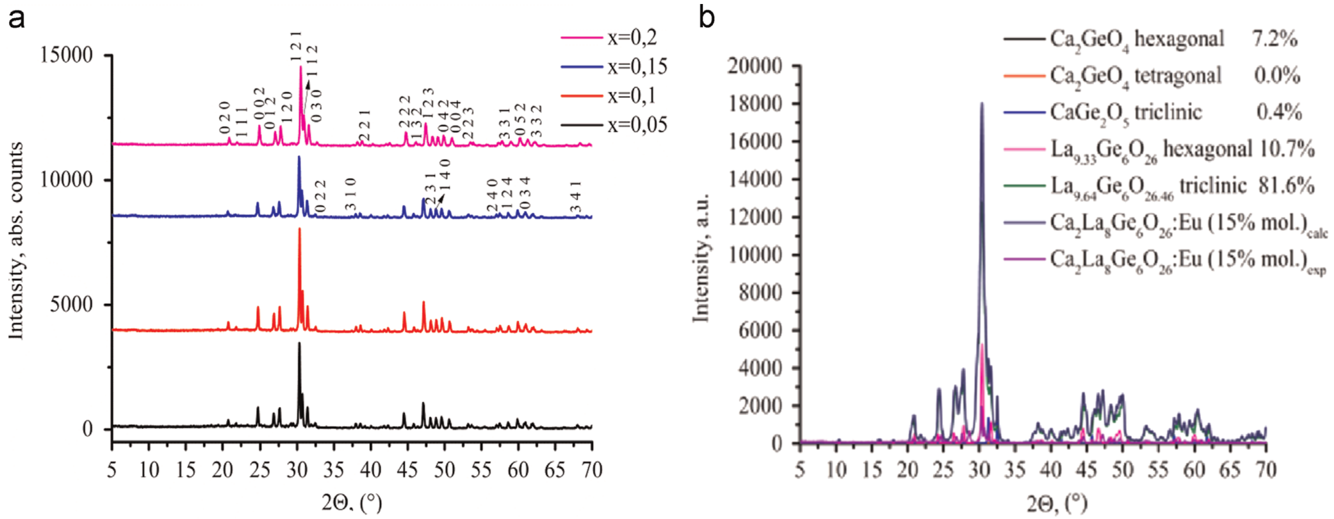

Fig. 1. (a) The XRD patterns of $Ca_2La_{8(1-x)}Eu_{8x}Ge_6O_{26-\delta}$ samples. (b) The XRD pattern and the phase composition of the intermediate sample $Ca_2La_{6.8}Eu_{1.2}Ge_6O_{26-\delta}$ ($T=1100$ °C, $t=18$ h).

structure should be used. Working with arsenic compounds is limited by their toxicity. The compounds $M_2Ln_8\ (PO_4)_6O_2$ are characterized by the presence of OH^- hydroxogroups in the oxygen channels, which reduces the reaction stability of functional materials [5]. Anion-substituted apatites with the general formula $M_{10-x}Ln_x\ (SiO_4)_x (PO_4)_{6-x}O_2$ are particular about synthesis conditions; for instance, it was found that impurity phases such as $Ca_4P_2O_7$ are precipitated if required temperature and duration of annealing are not observed [5]. The series of solid solutions $M_2Ln_8(SiO_4)_{6-x}(PO_4)_xO_2$ is limited because at $x > 0.15$ the phase $LnPO_3$ is precipitated from the basic structure [6].

2. Experimental

For synthesis of $Ca_2La_{8(1-x)}Eu_{8x}Ge_6O_{26}$ compounds, analytical grade reagents $CaCO_3$, La_2O_3, Eu_2O_3 and GeO_2 were taken as raw materials. Weighted samples of $CaCO_3$, La_2O_3 and Eu_2O_3 were dissolved in concentrated nitric acid ($\omega\%=70$, $V=10$ ml) at room temperature. The GeO_2 solution was prepared in excess of NH_4OH ($\omega\%$ not less than 25.73, $V=20$ ml) at 80 °C for 40 min. After the solution containing $Ca(NO_3)_2$, $La(NO_3)_3$ and $Eu(NO_3)_3$ was placed into ammonia solution of germanium oxide, the resulting mixture was evaporated at 120 °C until a white precipitate was formed. Then the prepared charge was heat treated in several stages. The first stage includes heating from 200 °C to 800 °C with a step of 100 °C/h to remove residual liquid phase, as well as dissociation of the complex and decomposition of $(NH_4)_3HGe_7O_{17}\cdot 4H_2O$ nitrate. The second stage is sintering at 1000 °C for 14 h and the third stage is annealing at 1200 °C for 28 h. The $Ca_2La_{6.8}Eu_{1.2}Ge_6O_{26}$ sample was further annealed at 1250 °C to dissolve impurities of foreign phases in the apatite structure.

The crystal chemical characteristics of the obtained compounds were examined with the use of a Shimadzu XRD-7000 X-ray spectrophotometer with a Cu detector. The luminescence and excitation spectra of Eu^{3+} ions were recorded on a Cary Eclipse Varian spectrofluorimeter in phosphorescence and fluorescence modes. On this facility, using the Lifetime software module, we also obtained the luminescence decay curves at emission wavelengths corresponding to the transitions $^5D_0 \rightarrow {}^7F_J$. The fluorescence spectra were measured by additional equipment LOMO-Photonics in continuous scanning mode to register the excited states with a short lifetime. The vibrational spectra were studied using a Bruker Vertex 80FT-IR spectrometer equipped with an UltraScan interferometer. The absorption spectra of the examined compounds were registered in the diffuse reflection mode in the UV–visible range (UV–vis DRS) on a Shimadzu UV-2410 spectrophotometer. The EPR spectra were recorded using a CMS-8400 ESR spectrometer. The magnetization versus magnetic field and temperature curves for apatite germanates were measured at room temperature and at the temperature of liquid helium using a vibrating sample magnetometer VSM-5T Cryogenic Ltd. Thermogravimetric analysis was carried out using a Setaram SETSYS evolution thermal mechanical analyzer providing measurements at temperatures up to 2400 °C. The surface morphology and elemental composition of the phosphor crystals were studied using a scanning electron microscope JEOL Users with a 6390 attachment to perform energy-dispersive analysis.

3. Results and discussion

3.1. X-ray analysis of $Ca_2La_{8(1-x)}Eu_{8x}Ge_6O_{26-\delta}$ compounds

Fig. 1a shows the X-ray diffraction patterns of $Ca_2La_{8(1-x)} Eu_{8x}Ge_6O_{26-\delta}$ samples.

Analysis of the X-ray powder patterns showed that the obtained compounds form a germanate apatite type phase (space group P6_3/m) with $Ca_{0.618}La_{8.942}\ (GeO_4)_6O_2$ type structure (ICDD database, card 01-073-9205). The structure of the considered germanate apatite contains three cation positions: Ca (*4f*), La (*4f*) and La (*6h*) [7]. In the (*4f*) position, Ca^{2+} and La^{3+} ions are distributed in equal amounts. Since Eu^{3+} ion is smaller than La^{3+} ion, it should preferably be located in the (*6h*) site, which is less stabilized by the surrounding oxygen ions [8]. The structure of the host is shown in Fig. 2a.

Fig. 2b shows the dependence of the crystal chemical parameters on the concentration of europium. It can be seen that the samples with apatite structure doped with ion-activator Eu^{3+} exhibit a deviation from the Vegard's rule at $0.1 \le x \le 0.15$, the magnitude of the jump at $x=0.15$ for the parameter *a* being greater than for the parameter *c*. This is explained by the influence of the substitution in the (*6h*) positions on the variation of parameter *a* [9]. As mentioned above, most of the trivalent europium enters into the (*6h*) sites; therefore the parameter *a* undergoes larger changes than the parameter *c*. The deviation from the Vegard's rule can be associated with reduction of Eu^{3+} to Eu^{2+} by the mechanism described in [9] for $Ca_2Y_8\ (SiO_4)\ _6O_2$:Eu and in Ref. [10] for $MAl_2Si_2O_8$:Eu (M=Ca, Sr, Ba): during heterovalent