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Synthesis, Crystal Structure, and Luminescence Properties of $CaY_2Ge_3O_{10}:Ln^{3+}$, Ln = Eu, Tb

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Abstract—The crystal structure and luminescence properties of $CaY_2Ge_3O_{10}:Ln^{3+}$ (Ln = Eu, Tb) germanates synthesized via a conventional solid-state reaction and an ethylenediaminetetraacetic acid complexing process are studied. The $CaY_{2-x}Ln_xGe_3O_{10}$ (Ln = Eu, Tb; $x = 0$–1.0, 2.0; $\Delta x = 0.1$) solid solutions have a monoclinic structure (space group $P2_1/c$, $Z = 4$), in which dopant ions occupy three nonequivalent noncentrosymmetric sites with different Ca^{2+}/Ln^{3+} ratios. The effect of the synthesis methods, dopant concentrations, and excitation wavelengths on the luminescence properties of the compounds obtained is determined.

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INTRODUCTION

In recent decades, germanates doped with lanthanide ions have attracted interest as materials with a high chemical and thermal stability and a high mechanical strength for creating low-threshold lasers, crystalline phosphors, and various optical transducers [1–10]. It is known that germanium can differently coordinate oxygen atoms around itself [11–13]. Depending on the type of the germanium anion, one distinguishes ortho-, pyro-, and cyclogermanates, as well as germanates with a chain structure and a 3D framework. The compounds containing the $[Ge_3O_{10}]^{8-}$ anion in their structure were studied for the first time in 1970s in works by Smolin [14] and Maksimov [15]. The $[Ge_3O_{10}]^{8-}$ germanate anion, which is the main element of the crystal structure of numerous compounds, is a finite chain consisting of three GeO_4 tetrahedra connected to each other by bridging oxygen atoms [16, 17].

In [18], Yamane et al. described the synthesis and crystal structure of a new phase of the $CaY_2Ge_3O_{10}$ composition. The crystal lattice of this germanate consists of $[Ge_3O_{10}]$ chains and oxygen polyhedra around calcium and yttrium atoms with CN = 7. Neighboring Ca/Y polyhedra are joined via common edges and apical oxygen atoms into blocks, which, together with the $[Ge_3O_{10}]$ chains, form a three-dimensional framework. The structural formula of the $(Ca_{0.45}Y_{0.55})(Ca_{0.46}Y_{0.54})(Ca_{0.09}Y_{0.91})Ge_3O_{10}$ compound points to the existence of three cation sites with their own ratios of Y and Ca ions. Doping of this phase with rare-earth (RE) ions leads to the formation of three types of optical centers.

Of trivalent RE ions, europium is traditionally used for creating red phosphors [19–22]. The luminescence of europium-containing compounds is caused by the $^5D_0 \rightarrow {}^7F_J$ transitions. If the Eu^{3+} ion occupies a noncentrosymmetric site in the structure, then the most intense peak belongs to the $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition [23]. The compounds doped with erbium exhibit blue-green emission related to the $^5D_3 \rightarrow {}^7F_J$ and $^5D_4 \rightarrow {}^7F_J$ transitions [4, 11]. In both ions, luminescence can be excited by near-UV radiation.

In this work, we characterize the crystal structure and the optical properties of $CaY_2Ge_3O_{10}:Ln^{3+}$ compounds (Ln = Eu, Tb). The samples are synthesized using the conventional solid-state reaction and the ethylenediaminetetraacetic acid (EDTA)-complexing process. This acid forms stable coordination compounds with a large number of metal ions [24], which improves the distribution of ions in solution and prevents premature precipitation of hydroxides with changing medium acidity.

EXPERIMENTAL

The samples of $CaY_{2-x}Eu_xGe_3O_{10}$ and $CaY_{2-x}Tb_xGe_3O_{10}$ ($0 \le x \le 1.0$, $\Delta x = 0.1$, $x = 2.0$) solid solutions were synthesized by the conventional solid-state reaction and the EDTA-complexing process. As initial reagents, we used Y_2O_3 (99.98%), Eu_2O_3 (99.99%), Tb_2O_3 (99.99%), $CaCO_3$ (99.9%), and GeO_2 (99.5%).

Lattice parameters and crystal structure refinement for $CaY_2Ge_3O_{10}$, $CaEu_2Ge_3O_{10}$, $CaTb_2Ge_3O_{10}$, and $CaY_{1.2}Ln_{0.8}Ge_3O_{10}$ (Ln = Eu, Tb) synthesized via the EDTA complexing process

Unit cell parameters	$CaY_2Ge_3O_{10}$	$CaY_{1.2}Eu_{0.8}Ge_3O_{10}$	$CaY_{1.2}Tb_{0.8}Ge_3O_{10}$	$CaEu_2Ge_3O_{10}$	$CaTb_2Ge_3O_{10}$
a, Å	6.90763(6)	6.92954(14)	6.91502(10)	6.96679(16)	6.93342(15)
b, Å	6.84276(5)	6.86685(14)	6.85185(9)	6.91315(14)	6.87603(14)
c, Å	18.75830(16)	18.7977(4)	18.76706(28)	18.8713(4)	18.8049(4)
β, deg	108.9988(5)	108.8022(11)	108.8973(8)	108.4623(11)	108.7644(12)
V, Å^3	838.353(12)	846.74(3)	841.269(28)	862.11(3)	848.862(32)
$R_{wp}/R_p/R(F^2)$, %	4.98/3.68/2.63	1.88/1.47/3.24	1.69/1.31/2.61	1.08/0.83/4.47	1.30/1.01/3.41
χ^2	1.216	1.103	1.69	1.664	1.459

Solid-State Reaction Technique

The solid solutions were synthesized from a mixture of initial oxides and calcium carbonate. The mixtures were finely ground, pressed into pellets, and annealed at a temperature of 900°C for decomposition of $CaCO_3$. Then, grinding and pressing was done once again, after which the pellets of the $CaY_{2-x}Eu_xGe_3O_{10}$ composition were annealed in air at 1250°C for 72 h, while the pellets of the $CaY_{2-x}Tb_xGe_3O_{10}$ composition were annealed in argon for 20 h.

Synthesis via EDTA-Complexing Process

All the initial materials except for germanium oxide were dissolved in nitric acid (1 : 3). To dissolve GeO_2, we used a diluted solution of ammonia. The obtained acidic and alkaline solutions were poured together. The EDTA solution was used to improve the solubility of components and prevent the precipitation of metal hydroxides. The amount of EDTA was taken to be equal to the total amount of cations. The solutions obtained were stirred with a magnetic stirrer for 3 h and evaporated at a temperature of 90–95°C. As a result of the oxidation–reduction reaction, we obtained a black porous gel, which was then annealed at a temperature of 800–1000°C in air. The obtained finely dispersed white powders were pressed into pellets, which were annealed at 1100°C for 6 h (the samples with europium were annealed in air, while the samples doped with terbium were annealed in argon).

The identification of the synthesized compounds and the control of the phase purity of products were performed by X-ray diffraction analysis. All the X-ray diffraction patterns were recorded on a STADI-P (STOE) diffractometer equipped with a linear mini-PSD detector. The patterns were recorded using Cu$K\alpha_1$ radiation in the 2θ range from 5° to 120° with a step of 0.02°. As an external standard, we used polycrystalline silicon with unit cell parameter a = 5.43075(5) Å. The phases were identified using the PDF2 database (ICDD, 2009). The structure was refined using the GSAS program suite [25, 26]. The morphology of the surface of the samples was studied using a JEOL JSM-6390 LA scanning electron microscope (SEM).

The excitation and luminescence spectra were measured at room temperature on a Cary Eclipse (Varian) pulsed fluorescent spectrometer. As an excitation source, we used a 75 kW Xenon lamp (pulse length t = 2 ms, pulse frequency v = 80 Hz, wavelength resolution 0.5 nm). Prior to measurements, the samples were carefully ground and placed into a glass cell (∅10 × 1 mm) with an inner light-reflecting coating.

RESULTS AND DISCUSSION

Crystal Structure Characterization

According to the X-ray diffraction data, solid solutions $CaY_{2-x}Ln_xGe_3O_{10}$ (Ln = Eu, Tb; $0 \le x \le 1.0$; $\Delta x = 0.1$; $x = 2.0$) have a monoclinic structure ((space group $P2_1/c$, $Z = 4$). The crystal structure refinements of the $CaEu_2Ge_3O_{10}$ and $CaTb_2Ge_3O_{10}$ samples synthesized by different methods showed that the sites are filled according to the crystal-chemical formula $(Ca_{0.45}Y_{0.55})^I(Ca_{0.46}Y_{0.54})^{II}(Ca_{0.09}Y_{0.91})^{III}Ge_3O_{10}$, which was previously proposed by Yamane et al. for the yttrium compound [18]. For solid solutions, the Y:Eu(Tb) ratio in each site was taken equal to their fractions in the initial mixtures. The substitution of Y^{3+} (CR = 1.10 Å) by Eu^{3+}(CR = 1.15 Å) or Tb^{3+}(CR = 1.12 Å) [27, 28] leads to a linear increase in the unit cell parameters and volume. The structural parameters for $CaY_2Ge_3O_{10}$, $CaEu_2Ge_3O_{10}$, $CaTb_2Ge_3O_{10}$, and $CaY_{1.2}Ln_{0.8}Ge_3O_{10}$ (Ln = Eu, Tb) compounds synthesized via the EDTA-complexing process are given in the table.

Figure 1 presents SEM images of $CaY_{1.6}Ln_{0.4}Ge_3O_{10}$ powders. The use of the EDTA-complexing process makes it possible to synthesize powders with a particle size smaller than 1 μm. The samples synthesized via the solid-state reaction exhibit a wider size distribution of particles with maxima at 4.22 ± 0.11 μm for $CaY_{1.6}Eu_{0.4}Ge_3O_{10}$ and 0.87 ± 0.08 μm for $CaY_{1.6}Tb_{0.4}Ge_3O_{10}$.

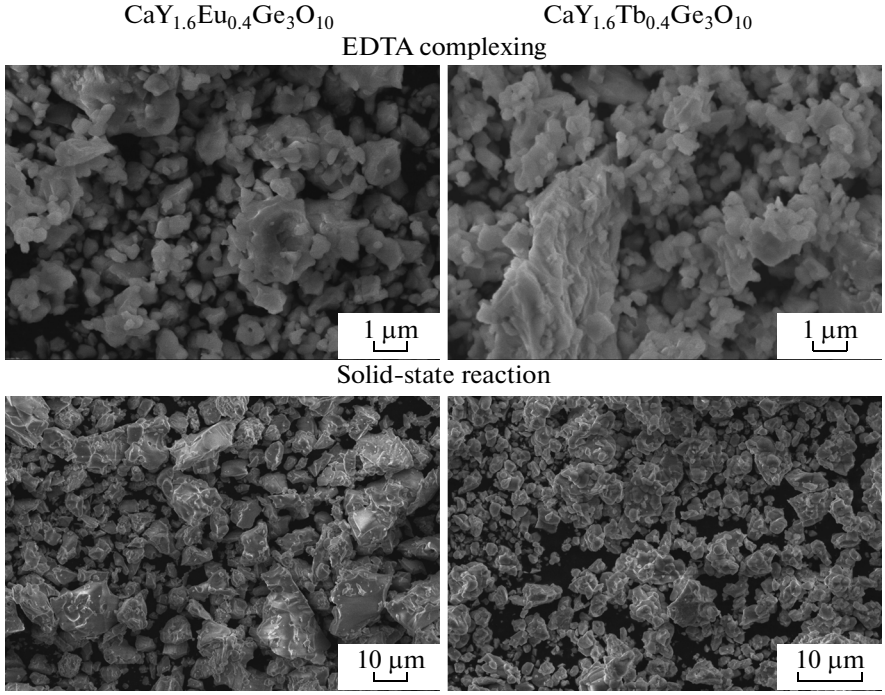

Fig. 1. SEM images of $CaY_{1.6}Ln_{0.4}Ge_3O_{10}$ (Ln = Eu, Tb) samples synthesized by different methods.

Luminescence Properties

The luminescence (λ_{ex} = 393 nm) and luminescence excitation (λ_{em} = 617 nm) spectra of the samples $CaY_{1.2}Eu_{0.8}Ge_3O_{10}$ synthesized by different methods are shown in Fig. 2. The broad band in the excitation spectra in the wavelength region of 210–300 nm belongs to photoinduced charge-transfer optical transitions from the 2*p* orbital of oxygen (O^{2-}) to the vacant 4*f* orbital of Eu^{3+} ions. The maxima in the wavelength region 310–430 nm correspond to the intraconfigurational 4*f*–4*f* transitions of dopant ions. The excitation into the charge-transfer band is more efficient for phosphors prepared using EDTA, and, vice versa, the samples synthesized by the solid-state reaction are more efficiently excited at a wavelength of 393 nm ($^7F_0 \rightarrow {}^5L_6$).

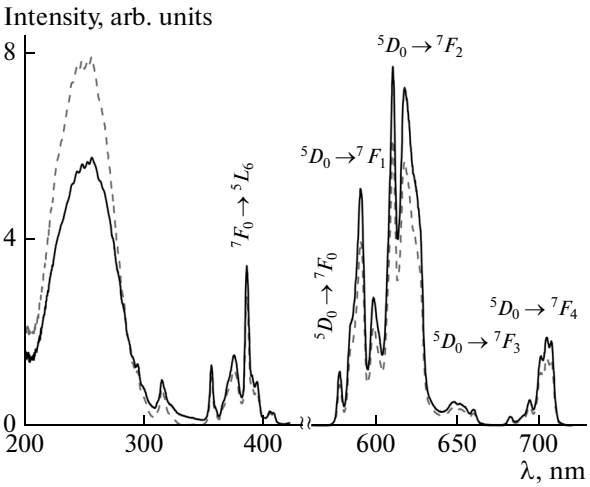

Fig. 2. Luminescence (λ_{ex} = 393 nm) and excitation (λ_{em} = 617 nm) spectra of $CaY_{1.2}Eu_{0.8}Ge_3O_{10}$ samples synthesized via (dashed line) the EDTA complexing process and (solid line) the solid-state reaction technique.

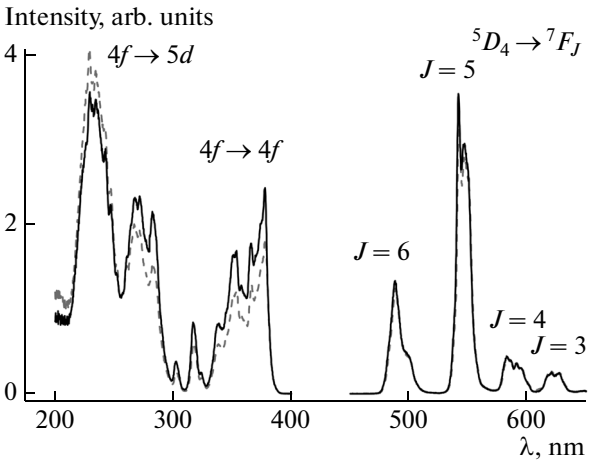

Fig. 3. Luminescence (λ_{ex} = 235 nm) and excitation (λ_{em} = 542 nm) spectra of $CaY_{1.2}Tb_{0.8}Ge_3O_{10}$ samples synthesized via (dashed line) the EDTA complexing process and (solid line) the solid-state reaction technique.

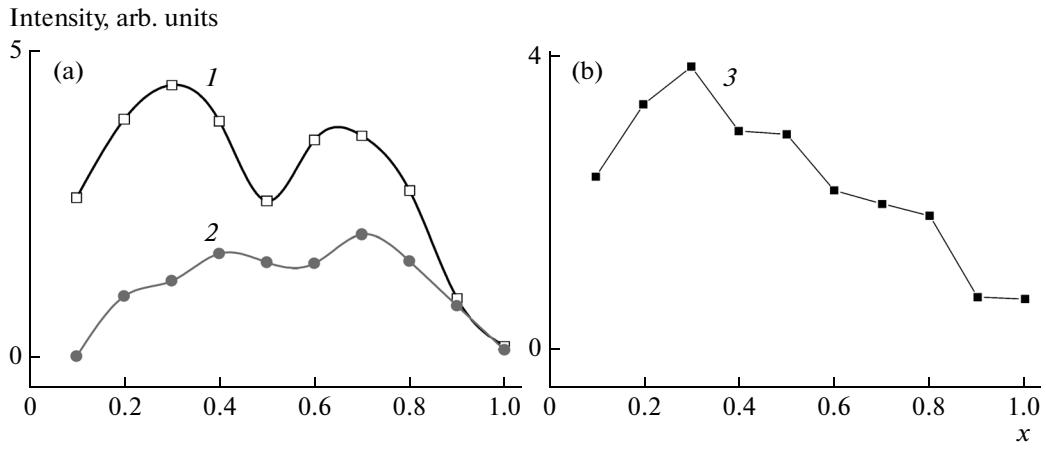

Fig. 4. Concentration dependences of the photoluminescence intensity of the solid solutions (a) $CaY_{2-x}Eu_xGe_3O_{10}$ ($\lambda_{ex} = 393$ and 250 nm) synthesized via the solid-state reaction technique and (b) $CaY_{2-x}Tb_xGe_3O_{10}$ ($\lambda_{ex} = 235$ nm) synthesized via the EDTA complexing process: (*1*) I_{617}, $\lambda_{ex} = 250$ nm; (*2*) I_{617}, $\lambda_{ex} = 393$ nm; and (*3*) I_{542}, $\lambda_{ex} = 235$ nm.

The luminescence spectra of compounds doped with europium consist of lines belonging to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions. The most intense lines correspond to the $^5D_0 \rightarrow {}^7F_2$ (604–617 nm) electric dipole transition due to the noncentrosymmetric local environment of Eu^{3+} ions [23, 29].

The excitation spectrum of $CaY_{1.2}Tb_{0.8}Ge_3O_{10}$ exhibits a broad band in the range of 220–300 nm, which corresponds to an electron transfer from the 4*f* to the 5*d* orbital of dopant ions (Fig. 3). This range can be divided into two parts: the transitions peaking at 235 nm are spin-allowed, and the transitions in the second part with maxima at 268 nm are spin-forbidden and less intense [30–32]. The maxima observed at wavelengths longer than 300 nm belong to the intraconfigurational $4f \rightarrow 4f$ transitions of Tb^{3+} ions.

At low dopant concentrations ($x \le 0.2$), the luminescence spectrum shows maxima in the blue spectral region corresponding to the $^5D_3 \rightarrow {}^7F_J$ ($J = 3$–6) transitions. With increasing dopant concentration, the blue emission becomes less intense with subsequent increase in the intensity of the green component ($^5D_4 \rightarrow {}^7F_J$ transitions), which relates to cross relaxation processes [33, 34].

The effect of the composition and the excitation wavelength on the photoluminescence intensity of $CaY_{2-x}Ln_xGe_3O_{10}$ (Ln = Eu, Tb) solid solutions is shown in Fig. 4. In the case of excitation of the Eu^{3+}-doped compounds into the charge-transfer band (250 nm), the concentration dependences exhibit two maxima at $x = 0.3$ and 0.7 nm independently of the synthesis method. In the case of excitation at $\lambda_{ex} =$ 393 nm, ($^7F_0 \rightarrow {}^5L_6$), a maximum is observed only at $x = 0.7$ (Fig. 4a). The highest luminescence intensity among the $CaY_{2-x}Tb_xGe_3O_{10}$ compounds is observed for the composition with $x = 0.3$ (Fig. 4b).

CONCLUSIONS

The Ln^{3+}:$CaY_2Ge_3O_{10}$ (Ln = Eu, Tb) germanates are synthesized via a conventional solid-state reaction and an EDTA complexing process. The crystal structure of the compounds has a monoclinic symmetry (space group $P2_1/c$, $Z = 4$) and is characterized by the existence of three optical centers, filling of which occurs in accordance with the model proposed for $CaY_2Ge_3O_{10}$ [18].

The luminescence spectra of the samples doped with Eu^{3+} ions consist of $^5D_0 \rightarrow {}^7F_J$ lines in the orange–red spectral region. The spectra of the terbium-doped samples exhibit bands in the blue–green spectral range corresponding to the $^5D_3 \rightarrow {}^7F_J$ and $^5D_4 \rightarrow {}^7F_J$ transitions. The intensity ratio of these transitions strongly depends on the dopant concentration in the lattice. At $x > 0.2$, peaks corresponding to the transitions from the $^5D_3$ level are absent, which is associated with cross relaxation.

The phosphors synthesized via the solid-state reaction have a larger grain size and exhibit brighter emission upon excitation into the charge-transfer band in the case of doping with terbium and upon excitation at $\lambda_{ex} =$393 nm in the case of germanates doped with europium. The highest luminescence intensity is observed for the composition $CaY_{2-x}Ln_xGe_3O_{10}$ (Ln = Eu, Tb) at $x = 0.3$.

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