Investigation on the Crystallization Process of Eu^{3+}:CaSiO$_3$ Gel Using Optical and Thermal Methods

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Alkoxy sol-gel technique is an important preparation method for production of rare-earth based phosphors. Crystallization of gel provides a way to prepare phosphors on lower working temperatures than those required for the solid state reactions. CaSiO$_3$ gel samples were obtained through hydrolysis-condensation reactions of tetraethylorthosilicate as silica source. In this work we studied the process of crystallization of Eu^{3+}-activated CaSiO$_3$ gel and decomposition of organic precursors by means of thermal analysis and infrared spectroscopy. Results of scanning electron microscopy and energy-dispersion spectrometry are used to check chemical composition and morphology of synthesized material. Emission spectra and emission lifetime measurements are performed to investigate luminescence properties of Eu^{3+} doped CaSiO$_3$ powder.

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1. Introduction

Calcium silicate CaSiO$_3$ (CSO), with its high temperature strength, creep resistance, chemical inertness, thermal stability, low thermal expansion and low thermal conductivity, is material suitable for the variety of applications [1]. Pb and Mn activated CaSiO$_3$ is typically doubly activated phosphor ("phosphor" — customary term for intensively luminescent solids) that act as yellow range lamp phosphor material. The CaSiO$_3$ containing materials are used for the production of special radio ceramics, sanitary components, porcelain materials, lining bricks, glaze and flux [2]. CaSiO$_3$ ceramics also exhibits good bioactivity and biocompatibility and finds use as biomaterial in medical industry, for the artificial bones

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and dental roots [3–6]. The most successful red phosphors were achieved with the Eu^{3+}-activated hosts, and thus the luminescence properties of Eu^{3+} in various hosts have been investigated extensively [7, 8]. Here we present a simple route for production of Eu^{3+}:$CaSiO_3$ phosphor, and observe optical and thermal properties during its evaluation from gel phase to powder form.

2. Materials and methods

The sample $CaSiO_3$ with 1at% Eu^{3+} was prepared with alkoxy sol-gel method. In brief, tetraethyl orthosilicate (TEOS, Alfa Aesar 98%), calcium oxide (CaO, Alfa Aesar 99.95%) and europium oxide (Eu_2O_3, Alfa Aesar 99.9%) were used as the starting materials, and ethanol (EtOH) as solvent. Aqueous solution containing appropriate concentrations of calcium and europium nitrates was prepared by dissolving their oxides in 6M nitric acid. Ethanol solution of equimolar tetraethoxysilane is added to the mixture. The resulting sol was stirred for 60 min at room temperature. Acidity of the obtained sol was adjusted by slowly adding ammonia solution with stirring until transparent gel is obtained. The excess of ethanol in the gel was removed at approximately 70°C and then dried in oven at 120°C for 5 days. After drying samples were heated at the 10°C/min heating rate up to 950°C and 1150°C and kept at those temperatures for 90 min. Thermo-gravimetric analysis (TGA) and differential-thermal analysis (DTA) measurements have been performed on the SETARAM SETSYS Evolution-1750 instrument. $CaSiO_3$ gel (about 20 mg) was heated from 30°C to 1500°C at the heating rate of 10°C/min in air atmosphere with the gas flow rate of 16 ml/min. FT-IR spectra of the gel and calcinated CSO samples were recorded in the wave number range of 4000–400 cm^{-1} on a Nickolet spectrophotometer (Model 380, Thermo Nickolet Corporation, Madison, USA), with 4 cm^{-1} resolution. The samples were prepared as standard KBr pellets (4% of the sample). The emission spectra and lifetime measurements were done at room temperature, on the Fluorolog-3 Model FL3-221 spectroflurometer system (HORIBA Jobin-Yvon). For emission spectra measurements a 450 W xenon lamp and R928P photomultiplier tube are used, while for the lifetime measurements 150 W pulsed xenon lamp has been utilized. The microstructure of the calcinated sample was observed by scanning electron microscope JEOL JSM 6460 LV equipped with an Oxford Instruments X-ray microanalysis unit. The purity of the sample was checked by X-ray energy-dispersion spectrometry (EDS) acquiring a spectrum for 120 s (live time) at the accelerating voltage of 25 kV.

3. Results and discussion

The thermal decomposition behavior of the CSO sample is studied with TG-DTA technique and obtained TG-DTA curves are presented in Fig. 1. The DTA endothermic peak between room temperature and 300°C can be attributed to the vaporization of adsorbed water and residual organic molecules. The TGA

curve shows marked weight losses in the same temperature range. The second weight loss indicated by the TGA curve and endothermic effect indicated by the DTA curve, observed in the temperature range between 500°C and 600°C, may be related to the elimination of the organic compounds chemically bound to Ca and Si. The crystallization process of CSO was studied by FT-IR spectroscopy
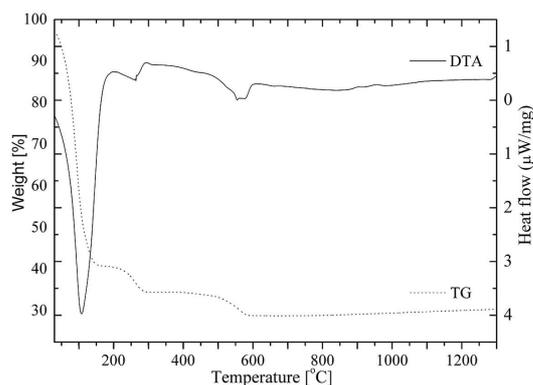
Fig. 1. TG-DTA curves of $CaSiO_3:Eu^{3+}$ gel.
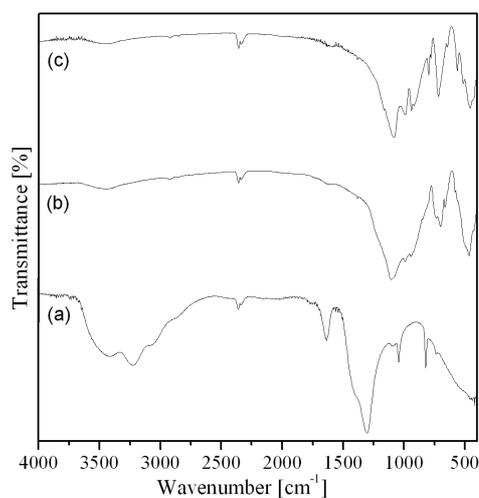
Fig. 2. FT-IR spectra of (a) $CaSiO_3:Eu^{3+}$ gel, (b) $CaSiO_3:Eu^{3+}$ powder calcinated at 950°C, and (c) $CaSiO_3:Eu^{3+}$ powder calcinated at 1150°C.

and spectra recorded for the dried gel and calcinated powders are shown in Fig. 2. Figure 2a shows FT-IR spectrum of the gel obtained after heat treatment at 120°C for 5 days. Broad band with a maximum at 3228 cm^{-1} arises from the absorption of OH$^-$ groups. Peaks at 1635 cm^{-1} and 1305 cm^{-1} originate from the absorption

of H_2O and NO_3^- groups, respectively. At the end, two lines at 1093 cm^{-1} and 1043 cm^{-1} arise from the absorption of Si–O–Si asymmetric stretching vibrations. Figure 2 also shows the infrared spectra of $CaSiO_3$:Eu^{3+} samples calcinated at 950°C (b) and 1150°C (c). One can notice that after heat treatment peaks from OH^-, H_2O and NO_3^- groups disappear completely and new bands arise, due to formation of new lattice. The high-frequency peaks in the spectral range 800–1250 cm^{-1} have been assigned to asymmetric Si–O stretching modes within a SiO_4 tetrahedron. The mid-frequency ones at 600–800 cm^{-1} are attributable to both Si–O–Si bond bending and symmetric Si–O stretching vibrations, while those in the low-frequency range (400–600 cm^{-1}) are determined by O–Si–O bond bending and Ca–O bond stretching modes. Only differences between these two spectra are broader bands in sample calcinated at lower temperature, indicating in this way that low-temperature sample is not well crystallized, while more structured peaks at high-temperature sample suggest that well crystallized silicate has formed.

Scanning electron microscopy (SEM) observations of the sample calcinated at 1150°C show agglomerates ranging from few microns to a few tens of microns. Observations at higher magnification show that they are made up of highly agglomerated sub-micron particles with flake-like morphology (see Fig. 3). The spectra obtained from energy-dispersion X-ray spectrometry (EDX) analysis in SEM qualitatively confirmed the presence of Eu dopant and the purity of the material as well, see Fig. 4. Quantitative EDX analysis verified that doping with europium is close to the expected concentration of 1 at%, see Table.
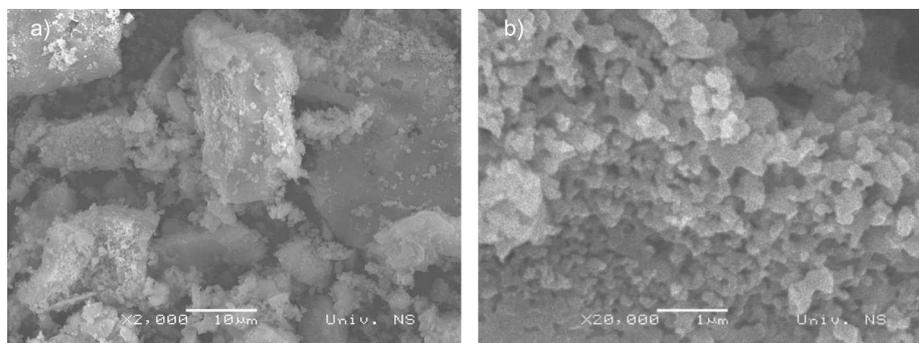
Fig. 3. SEM images taken at: (a) low magnification (2000×), (b) high magnification (20000×).

The emission spectra of the $CaSiO_3$:Eu^{3+} sample is presented in Fig. 5. Five bands centered at around 17304, 17035, 16353, 15400, and 14255 cm^{-1} are associated to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, 4) spin-forbidden f–f transitions. The $^5D_0 \rightarrow {}^7F_1$ transition band at 17035 cm^{-1} is the parity-allowed magnetic dipole transition ($\Delta J = 1$) and its intensity does not vary with the host. Emission at around 16353 cm^{-1} corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition
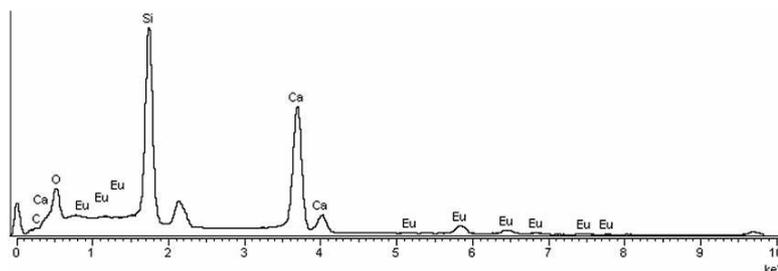
Fig. 4.   EDX spectra of CSO:Eu^{3+} sample calcinated at $1150°C$. Full Scale 12331 cts.

TABLE

Quantitative EDX analysis.

Element	Weight%	Atomic%
O	49.45	68.54
Si	24.82	19.59
Ca	19.91	11.02
Eu	5.82	0.85
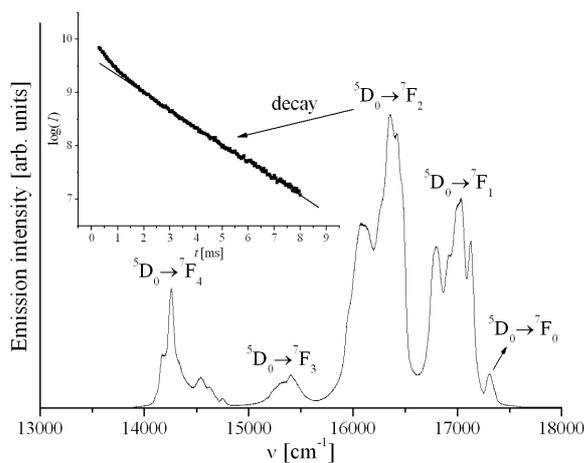
Fig. 5.   Luminescence emission spectra of $CaSiO_3$:Eu^{3+} sample annealed at $950°C$; the 3.1 ms lifetime is derived from emission decay measured at 16353 cm^{-1} (given in as inset in figure).

($\Delta J = 2$), which is very sensitive to the local environment around the Eu^{3+} ion, and its intensity depends on the symmetry of the crystal field around the europium ion. A low symmetry around the rare-earth cation increases the emission strength of the electric dipole transition. In this sense, it is generally agreed that the ratio $R = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, of the integrated intensities of the

$^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transition is a symmetry parameter of the coordinated polyhedron around the Eu^{3+} ion. The value of 1.6 measured in the present work is relatively small and indicates a moderate distortion around the europium cation. Finally, well resolved emission bands at $15400 \ cm^{-1}$ and $14255 \ cm^{-1}$ that originate from $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions can be indubitably identified on the spectrum. The fluorescence decay curve for the $^5D_0$ level at emitting $16353 \ cm^{-1}$ under excitation in $^5L_6$ energy level is shown in inset in Fig. 5. The decay profile is nearly exponential and the calculated lifetime is about 3.1 ms, which is a quite high value characteristic of europium species with low non-radiative energy transfer probability.

4. Conclusion

Phosphor powder of $CaSiO_3$:Eu^{3+} is succesfully obtained with the alkoxy sol-gel method. Thermal and infrared analysis revealed typical behavior of materials produced by sol-gel, with removal of residual water and solvents at lower, and organic compounds at higher temperatures, as well as formation of crystalline phosphor powder. Luminescence spectroscopy measurements clearly show characteristic emissions of Eu^{3+} ions and the long luminescence lifetime which can be indeed favorable for future applications.

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