

# Sm<sup>3+</sup> - doped Sc<sub>2</sub>O<sub>3</sub> polycrystalline ceramics: spectroscopic investigation

C. GHEORGHE\*, A. LUPEI, F. VOICU

National Institute for Laser, Plasma and Radiation Physics, ECS Laboratory, 077125, Magurele – Bucharest, Romania

Sm<sup>3+</sup> - doped Sc<sub>2</sub>O<sub>3</sub> translucent polycrystalline ceramics were fabricated by solid –state reaction method in order to evaluate its potential for visible emission. The optical spectra in the UV - IR range of Sm<sup>3+</sup> in these samples, at different temperatures (10-300 K), were performed. A series of data on Sm: Sc<sub>2</sub>O<sub>3</sub> system, not investigated previously, was obtained from the analysis of the absorption and visible emission spectra as well as the emission kinetics: a partial energy level scheme, lifetimes, etc.

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## 1. Introduction

The visible coherent or incoherent emission is required in many applications: technological, military, telecommunication, display, phosphors, biomedicine, etc. The visible emission could be obtained by non-linear processes or by direct emission of different ions. The studies of the visible emission of RE<sup>3+</sup> by direct pumping, due to the pumping problems with classical lamps or luminescence quenching processes, were reduced as number for many years. However, one should mention the increased recent interest in Sm<sup>3+</sup> or Dy<sup>3+</sup> ions, mainly due to the tremendous development of UV/VIS laser diodes in the last years that could be used for pumping.

The Sm<sup>3+</sup> (4f<sup>5</sup>) ion presents strong emissions from the metastable level <sup>4</sup>G<sub>5/2</sub> in visible, with long lifetimes (msec) at low concentrations, but most of the absorption bands (<sup>6</sup>H<sub>5/2</sub> → <sup>4</sup>G<sub>5/2</sub>, <sup>4</sup>F<sub>3/2</sub>, <sup>4</sup>G<sub>7/2</sub>, etc) in visible and UV have low intensity, unfavorable for efficient excitation with the existing classical sources. Thus, earlier spectroscopic studies on Sm<sup>3+</sup> have presented mainly a fundamental interest. However, in the last years, the interest in using Sm<sup>3+</sup> efficient emission in various materials, especially for phosphors in red – orange, but also for laser emission has increased in connection with the development of laser diodes in the 405 nm range, used already in many applications (lighting, optical storage, etc). One shall mention only several recent investigations of Sm<sup>3+</sup> in various materials, such as single crystals [1, 2], glasses [3, 4], phosphors [5]; many other references could be found in these citations.

Up to now, there are few studies on Sm<sup>3+</sup> ion in transparent ceramics, an interesting class of new materials. Fabrication of transparent Sm: YAG ceramics with concentrations much larger (5 at. %) than for single crystals (2-3 at. %) have been reported and Sm: YAG (used as glass of a core-doped YAG: Nd composite material) has been used to suppress the parasitic

oscillations caused by the amplified spontaneous emission of the residual luminescence of Nd<sup>3+</sup> in Nd: YAG lasers [6 - 9]. Recently, accurate spectroscopic data on Sm: YAG ceramics have been also reported [10]. Besides garnets, another interesting class of materials, fabricated by ceramic technology, are the cubic sesquioxides (Y<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>) [11, 12], but up to now no investigations on Sm<sup>3+</sup> in sesquioxide ceramics have been reported. In fact, there are few data on Sm<sup>3+</sup> in sesquioxides, they refer to Y<sub>2</sub>O<sub>3</sub> single crystals [13] and Y<sub>2</sub>O<sub>3</sub> or Lu<sub>2</sub>O<sub>3</sub> nanophosphors [14, 15].

In the present note a preliminary analysis of the spectral characteristics of the Sm<sup>3+</sup> doped Sc<sub>2</sub>O<sub>3</sub> polycrystalline ceramics is reported. The absorption and emission spectra at different temperatures (10 and 300 K) are analyzed and an energy level scheme for Sm<sup>3+</sup> in C<sub>2</sub> sites is proposed.

## 2. Experimental methods

Sc<sub>2</sub>O<sub>3</sub> polycrystalline ceramic samples doped with Sm<sup>3+</sup> (1 -3 at.%) were produced by solid –state reaction method, using high-purity powders (99.99 mass %) of Sc<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>, with particles size of 20-50 nm, respectively 3-7 μm. Powders were stirred in anhydrous alcohol for 48h, and the milled slurries were dried in nitrogen atmosphere, using a Mini Spray Dryer B-290 with Inert Loop B-295 from Buchi. The spray-dried powders were pressed with low pressure (12 MPa) in a metal mold in pellets with half inch diameter and 0.1 inch height and then isostatically pressed at 240 Mpa in High Pressure ISOLAB FPG 7680 from Stansted Fluid Power Ltd. Finally, after sintering for 6h at 1600 °C in Nabertherm furnace LHT 02/18, translucent ceramics were obtained.

The Sc<sub>2</sub>O<sub>3</sub> – sesquioxide at room temperature present a cubic C-type structure, belonging to the  $IA\bar{3}$  space

group [16]. The unit cell contains two types of centers with  $C_2$  and  $C_{3i}$  symmetry, in a ratio of 3/1:  $C_2$  site is an eightfold cubic structure with two oxygen vacancies on a face diagonal, while  $C_{3i}$  site corresponds to a cube with two vacancies on a body diagonal. The cationic density ( $3.338 \times 10^{22}/\text{cm}^3$ ) is rather high compared to other laser crystals. The  $\text{RE}^{3+}$  dopants are assumed to occupy randomly both sites, but the induced electric dipole transitions are allowed only for  $C_2$  centers.

The optical absorption spectra of  $\text{Sm}^{3+}$ :  $\text{Sc}_2\text{O}_3$  at 300 K and 10 K were recorded in the 400 – 1600 nm range with a setup consisting of tungsten halogen lamp, a Jarell-Ash monochromator,  $S_{20}$  and  $S_1$  photomultipliers, Ge photodiodes and a Lock-in SR830 amplifier on line with a computer. The room temperature emissions and lifetimes were measured by excitation at 405 nm with a spectrofluorometer FluoroMax 4- Horiba Jobin Yvone. The low temperature emission spectra were excited with a xenon (Bausch – Lomb) lamp with suitable filters, and the same detection system as at absorption. For the low temperature of the absorption and emission spectra a closed cycle He refrigerator ARS-2HW was used.

### 3. Results and discussion

#### 3.1. Absorption and emission data

The absorption spectra in UV-IR region for 3 at. %  $\text{Sm}$ :  $\text{Sc}_2\text{O}_3$  translucent polycrystalline ceramics, recorded at 300 K, are presented in Fig. 1. The 300K absorption spectra in near IR domain from 6000 - 11000  $\text{cm}^{-1}$  (Fig. 1a) correspond to the electric - dipole transitions, associated to  $\text{Sm}^{3+}$  in  $C_2$  centers from the  ${}^6\text{H}_{5/2}$  ground manifold to different excited  ${}^6\text{H}_j$  and  ${}^6\text{F}_j$  manifolds, split in  $(2J+1)/2$  Stark levels in  $C_2$  local symmetry.

From about  $\sim 11000 \text{ cm}^{-1}$  up to  $\sim 17452 \text{ cm}^{-1}$ , where the first Stark level of the  ${}^4\text{G}_{5/2}$  metastable level is located, there is a gap. In visible domain (Fig. 1b) a greater number of closely spaced levels are situated, they correspond to many spin - forbidden transitions  ${}^6\text{H}_{5/2} \rightarrow {}^4\text{G}_{5/2}$ ,  ${}^4\text{F}_{3/2}$ ,  ${}^4\text{G}_{7/2}$ , etc, and due to the strong level overlapping their unambiguous identification was difficult. In visible - UV domain the most intense lines with absorption peak at  $\sim 405 \text{ nm}$  (Fig. 1) contain lines that were assigned to spin - allowed  ${}^6\text{H}_{5/2} \rightarrow {}^6\text{P}_{3/2}$ ,  ${}^6\text{P}_{3/2}$  transitions that are suitable for an efficient optical pumping by laser diode working at 405 nm.

The visible emission spectra of  $\text{Sm}^{3+}$  in  $\text{Sc}_2\text{O}_3$ , after lamp excitation, were recorded at 300K and 10K. The emission lines correspond to transitions to lower IR levels, the most intense lines corresponding to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$  (at  $\sim 573 \text{ nm}$  - yellow),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$  (at  $\sim 612 \text{ nm}$  orange – the strongest),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$  (at  $\sim 660 \text{ nm}$  - red),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$  (at  $\sim 730 \text{ nm}$ ) transitions, as illustrated in Fig. 2 a and b with the 300 K and 10 K spectra. At 300 K the stronger emission lines come from the first Stark level of  ${}^4\text{G}_{5/2}$  manifold, but also from the second Stark level placed at  $\sim 175 \text{ cm}^{-1}$  higher (HB).

The spectra are similar to those reported for  $\text{Sm}^{3+}$  in  $\text{Y}_2\text{O}_3$  phosphors [14]. 10 K emission spectra, given only

by first Stark of the  ${}^4\text{G}_{5/2}$ , reflect the Stark structure of the IR levels; one should mention the similar features (as relative intensities) to those of  $\text{Sm}^{3+}$  in  $\text{Y}_2\text{O}_3$  at 77 K [14]. Some additional small features were remarked, but for an unambiguous assignment further work is necessary.

The estimated room temperature lifetime for 1 at %  $\text{Sm}$ :  $\text{Sc}_2\text{O}_3$  is  $\sim 1.3 \text{ ms}$ . This value is comparable with experimental lifetimes reported for 1 mol %  $\text{Sm}$ :  $\text{Y}_2\text{O}_3$  [14, 17] of about  $\sim 1 \text{ ms}$  at 300K.

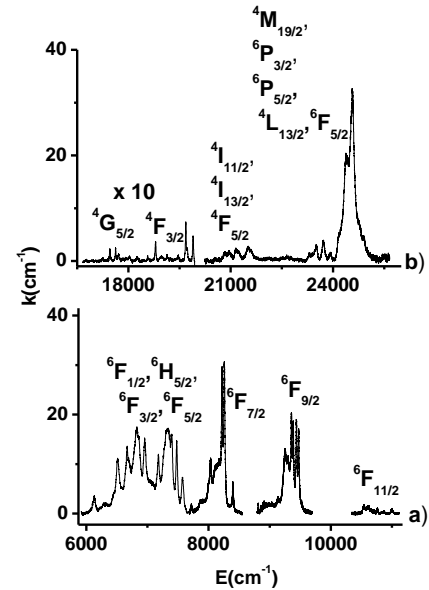


Fig. 1. The 300K absorption spectra of 3 %  $\text{Sm}$  doped  $\text{Sc}_2\text{O}_3$  in IR(a) and visible (b).

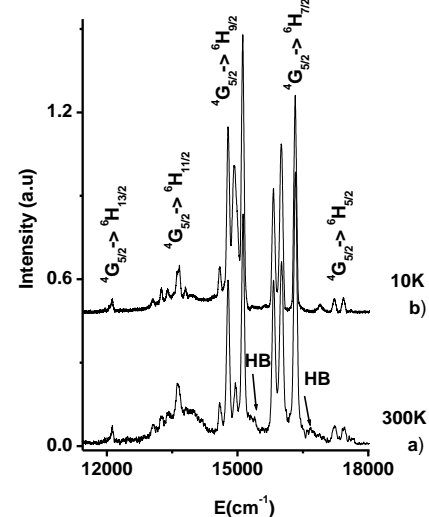


Fig. 2. 10 and 300 K emission spectrum of  $\text{Sm}$  (1at. %)  $\text{Sc}_2\text{O}_3$  under 405 nm excitation.

#### 3.2. Energy levels of $\text{Sm}^{3+}$ in $\text{Sc}_2\text{O}_3$

The crystal field levels of the  $\text{Sm}^{3+}$  in  $C_2$  sites in  $\text{Sc}_2\text{O}_3$  polycrystalline ceramic were determined from absorption and emission spectra and part are given in Table I, where the maximum splitting  $\Delta E_{\text{max}}$  of manifolds

for Sc<sub>2</sub>O<sub>3</sub> and comparatively for Y<sub>2</sub>O<sub>3</sub> [13] are also provided. The differences of the energy levels schemes of Sm<sup>3+</sup> in the two sesquioxides can be associated to

structural effects, mainly Sc<sup>3+</sup>-O<sup>2-</sup> distances that are smaller than Y<sup>3+</sup>-O<sup>2-</sup>, determining stronger covalent bonding and crystal field splittings.

Table 1. Partial energy level scheme of Sm: Sc<sub>2</sub>O<sub>3</sub> translucent polycrystalline ceramic.

<sup>2S+1</sup> L <sub>J</sub>	Energy (cm <sup>-1</sup> )	ΔE <sub>max</sub> (cm <sup>-1</sup> ) Sc <sub>2</sub> O <sub>3</sub>	ΔE <sub>max</sub> (cm <sup>-1</sup> ) Y <sub>2</sub> O <sub>3</sub> [17]
<sup>6</sup> H <sub>5/2</sub>	0, 212, 532	532	456
<sup>6</sup> H <sub>7/2</sub>	1114, 1426, 1452, 1610	496	427
<sup>6</sup> H <sub>9/2</sub>	2320, 2506, 2540, 2658, 2850	530	442
<sup>6</sup> H <sub>11/2</sub>	3631, 3770, 3823, 3894, 4039, 4180	549	447
<sup>6</sup> H <sub>13/2</sub>	4998, 5060, 5207, 5295, 5367, 5470	562	549
<sup>6</sup> F <sub>1/2</sub> , <sup>6</sup> H <sub>15/2</sub> , <sup>6</sup> F <sub>3/2</sub>	6192, 6289, 6314, 6407, 6530, 6629, 6664, 6689, 6787, 6819, 6915	723	912
<sup>6</sup> F <sub>5/2</sub>	7358, 7437, 7535	177	139
<sup>6</sup> F <sub>7/2</sub>	8212, 8251, 8276, 8393	181	152
<sup>6</sup> F <sub>9/2</sub>	9349, 9379, 9431, 9469, 9516	167	144
<sup>6</sup> F <sub>11/2</sub>	10611, 10708, 10754, 10827, 10865, 10994	383	309
<sup>4</sup> G <sub>5/2</sub>	17452, 17627, 17848	396	280

#### 4. Conclusions

In the search for materials emitting in the visible range under direct pumping, Sm<sup>3+</sup> spectroscopic characteristics in Sc<sub>2</sub>O<sub>3</sub> translucent ceramics were investigated. The absorption and emission spectra at 10 or 300 K were analyzed and a series of spectral data on Sm: Sc<sub>2</sub>O<sub>3</sub> system were obtained and compared to the published ones for Sm: Y<sub>2</sub>O<sub>3</sub> single crystals or phosphors. The intense emission lines of Sm<sup>3+</sup> in Sc<sub>2</sub>O<sub>3</sub> correspond to <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>5/2, 7/2, 9/2, 11/2</sub> transitions, the strongest intense line being in orange at ~ 612 nm at 300 K (associated to transition <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>7/2</sub> between lowest Stark levels of the manifolds). The relatively large intensity of the 612 nm line and the existence of a broad band around ~ 407 nm (cross section ~ 2.6\*10<sup>-20</sup> cm<sup>2</sup>) create a potential for this system to operate as a phosphor or laser material operating in a four level scheme (lower level is at ~ 1110 cm<sup>-1</sup>). More work on this system is in progress.

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\*Corresponding author: cristina\_gheorghe2002@yahoo.com