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INTRODUCTION

Rare earth (RE) ions play an important role in modern optical technology as the active constituents in many novel materials. There are an increasing number of applications for these RE-activated materials and much of today's cutting-edge optical technology and future innovations are expected to rely on their unique properties. In solids some of the lanthanide ions can be present either in their divalent or trivalent state. Their electronic configurations are given by $4f^n5s^25p^6$ or $4f^{n-1}5s^25p^6$, respectively. The partially filled 4f shell is well shielded by $5s^2$ and $5p^6$ orbitals. The emission transitions, therefore, yields sharp lines in the optical spectra. The use of RE element-based phosphor, based on f-f transitions, can narrow to the visible range, resulting in both high efficiency and a high lumen equivalent. The most studied divalent lanthanide species are Eu^{2+} , Sm^{2+} and Yb^{2+} . Interest in divalent samarium doped materials was greatly enhanced after $\text{CaF}_2:\text{Sm}^{2+}$ proved to be a suitable system for lasing action. The reduction of Ln^{3+} ions to Ln^{2+} ions in the solid state generally needs a strong reducing agent, thus host of interest should be inert enough to withstand reducing in high temperature.

Further investigations on the RE ions such as $\text{Sm}^{3+}/\text{Sm}^{2+}$ are becoming more significant with the increasing demand of various fluorescent devices and visible lasers. Oxide hosts, in particular aluminates, are stable hosts for obtaining efficient luminescence of rare-earth ions [1].

EXPERIMENTAL SECTION

Polycrystalline $\text{Sr}_4\text{Al}_{14}\text{B}_x\text{O}_{25}:\text{Sm}$ (S4A7:Sm) samples were prepared using conventional solid state technique. Stoichiometric amounts of analytical grade Sm_2O_3 , SrCO_3 , nano- Al_2O_3 and H_3BO_3 , were thoroughly mixed under acetone and grounded. Boric acid acts as flux but nevertheless as proved by IR and ^{27}Al MAS NMR spectra in reference [2] incorporation of boron as BO_4 in the AlO_4 framework substitutes some aluminum. The mixtures were heated in three steps:

[I] 1000°C for 4h under air, [II] 1200-1300°C for 4h under CO, [III] 1200-1300°C for 4h under 10% H_2 /90% N_2

Samples were grounded between each annealing step. Samples were synthesized changing boron substitution level, using aluminum excess and different samarium concentration (1.0- 3.0%). XRD data were collected (step size 0.02 θ and integration time 1s) using Ni-filtered Cu K α radiation on Rigaku MiniFlex II diffractometer working in Bragg-Brentano ($\theta/2\theta$) geometry. Reflection spectra were recorded on Edinburgh Instruments FS900 spectrometer equipped with a 450W Xe arc lamp and an integration sphere. BaSO_4 (99% Sigma-Aldrich) was used as a reflectance standard. Excitation (excitation slit 1nm and emission slit 5 nm) and emission (excitation slit 10nm and emission slit 1 nm) spectra were recorded on Edinburgh Instruments FS900 fluorescence spectrometer equipped with 450W Xe arc lamp, mirror optics for powder samples. All spectra were recorded under the scan settings: step 0.5nm, dwell time 0.2s, 2 repeats.

RESULTS AND DISCUSSION

Structure and XRD analysis

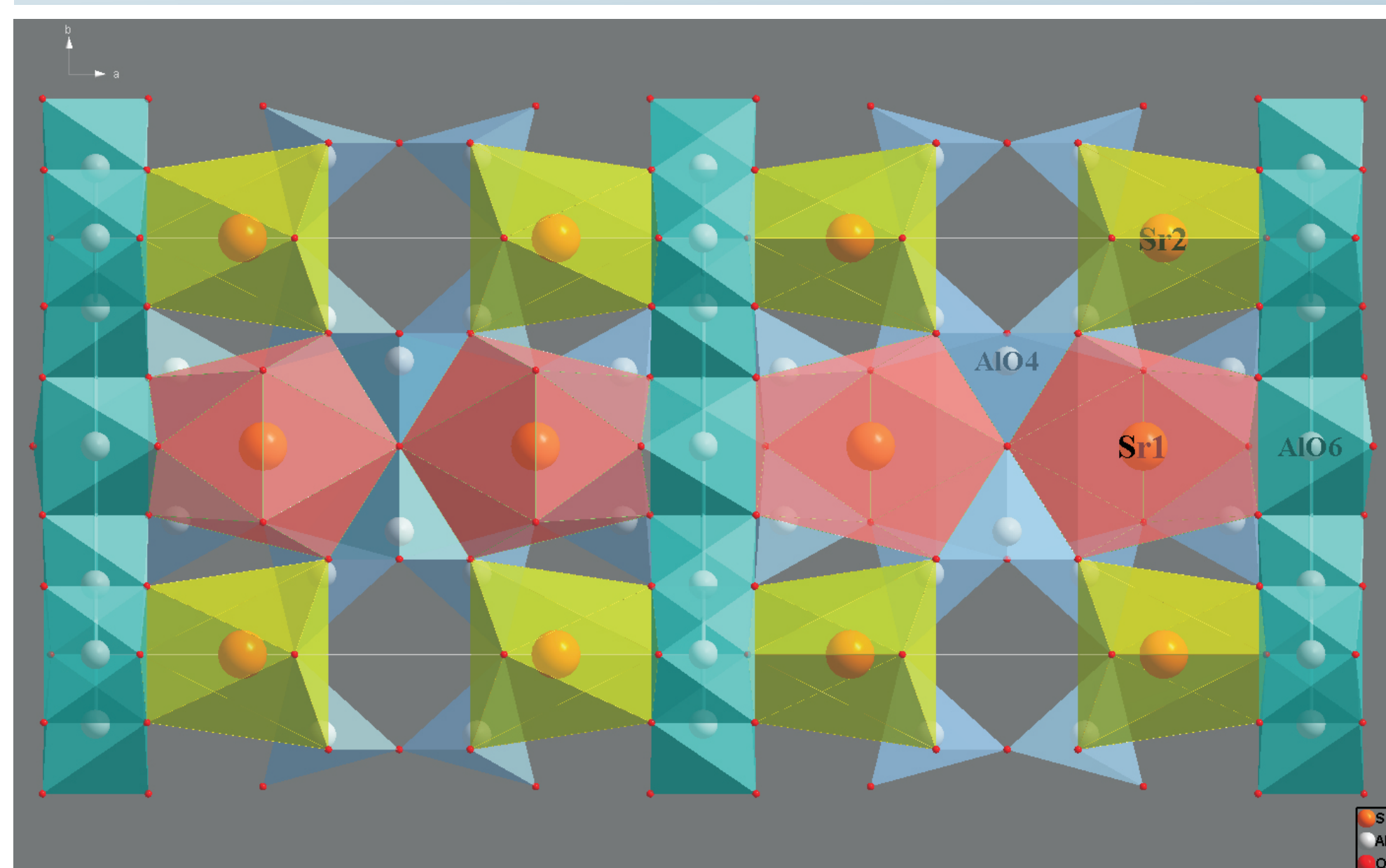


Figure 1. View towards (001) plane in the structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$

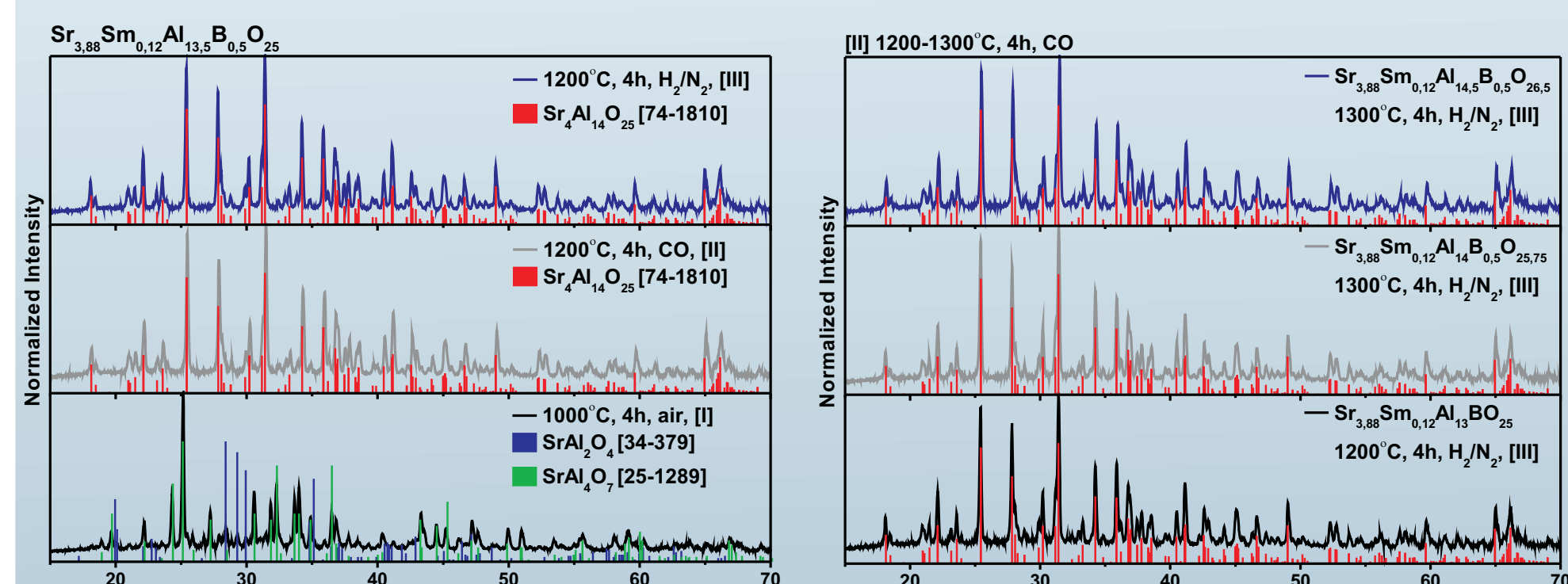


Figure 2. S4A7 phase formation dependency on annealing step (left), stoichiometry influence on XRD pattern (right)

The crystal structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ is orthorhombic, space group Pmma. The crystal structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ is shown in Fig. 1. and it is easy to find that the orthorhombic $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ consists of layers made up of AlO_6 -octahedra separated by a double layer of AlO_4 -tetrahedra and there are two different strontium sites in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: the Sr1 site lies in the complicated oxygen-polyhedron composed of eight O atoms and the Sr2 site lies in the oxygen-polyhedron composed of six O atoms. The XRD patterns of some samples, $\text{Sr}_{3.88}\text{Sm}_{0.12}\text{Al}_{14+x}\text{B}_{1-x}\text{O}_{25+y}$ ($x = 0 - 1$), are shown in Fig. 2, all peaks are assigned to the phase of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (PDF 74-1810).

Dopant concentration influence

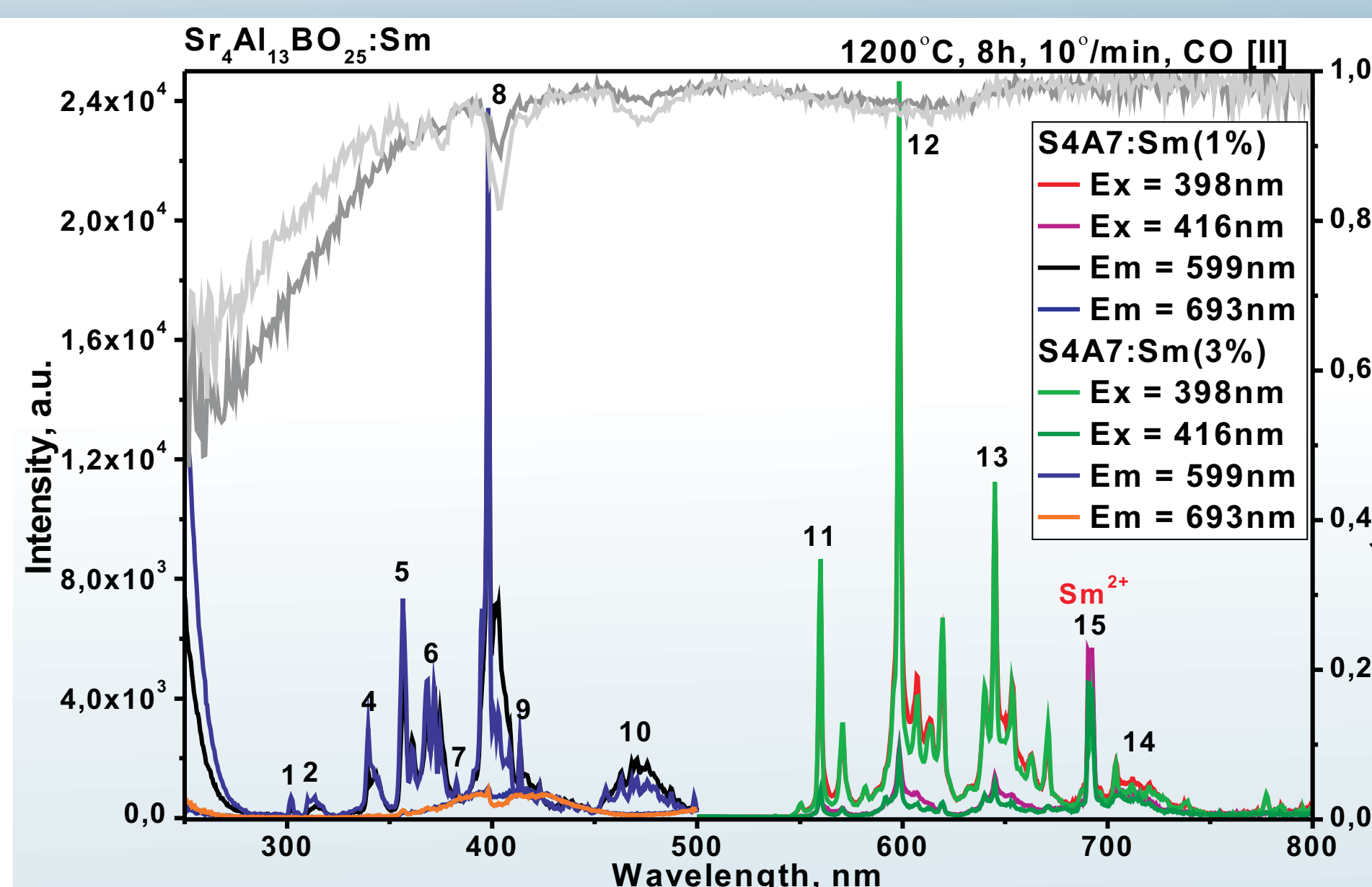


Figure 3. Samarium concentration influence on luminescence properties after second heating step under CO atmosphere

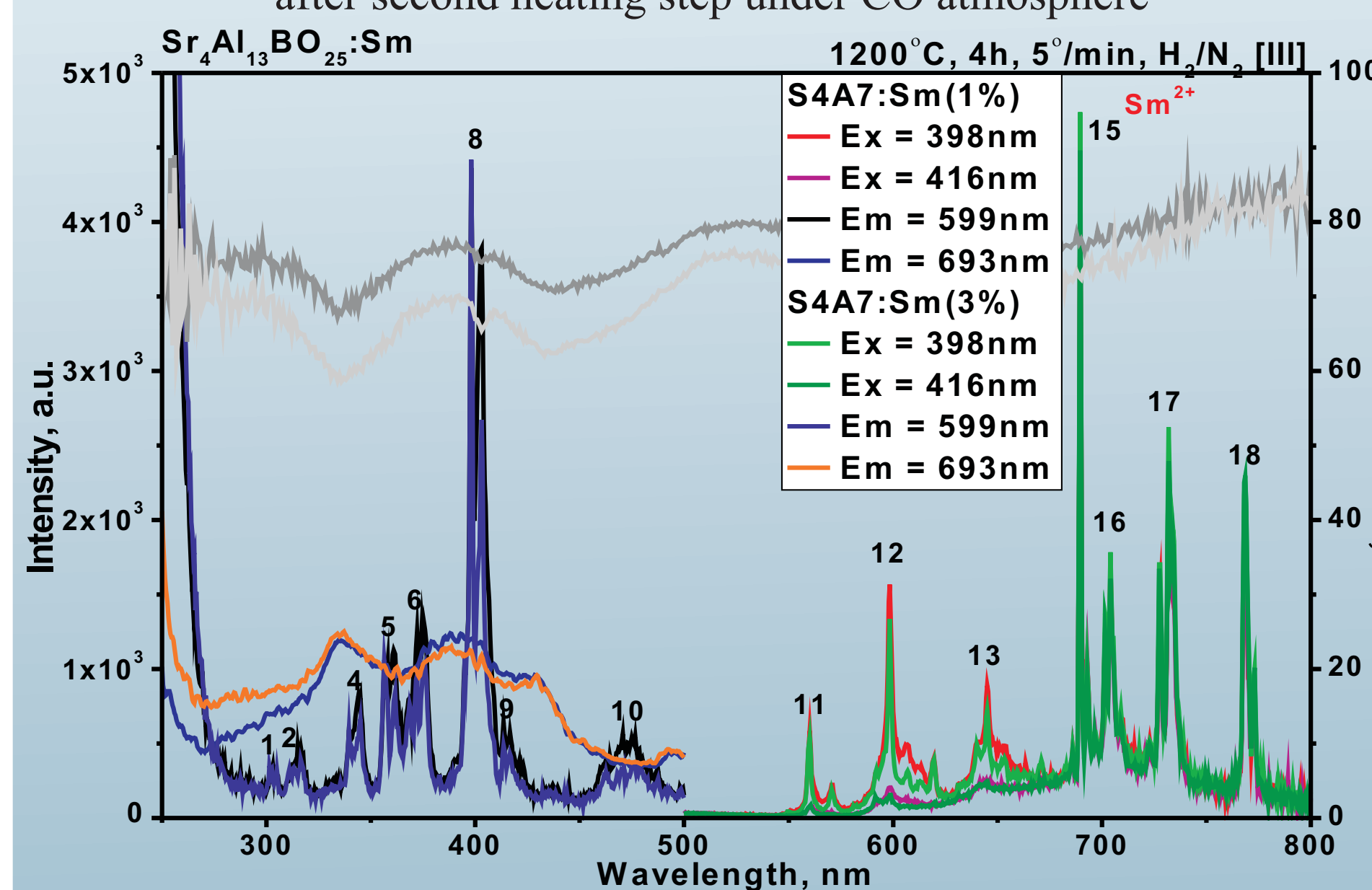


Figure 4. Samarium concentration influence on luminescence properties after third heating step under H_2/N_2 atmosphere

Samarium concentration influence on S4A7 luminescence properties is ambiguous, in figure 3 it is observable emission intensity decrease with higher concentration while in figure 4 Sm^{2+} emission intensity increases with increasing doping concentration. Possible explanation can be Sm^{2+} lower susceptibility to concentration quenching comparing to Sm^{3+} .

Stoichiometry influence on luminescence

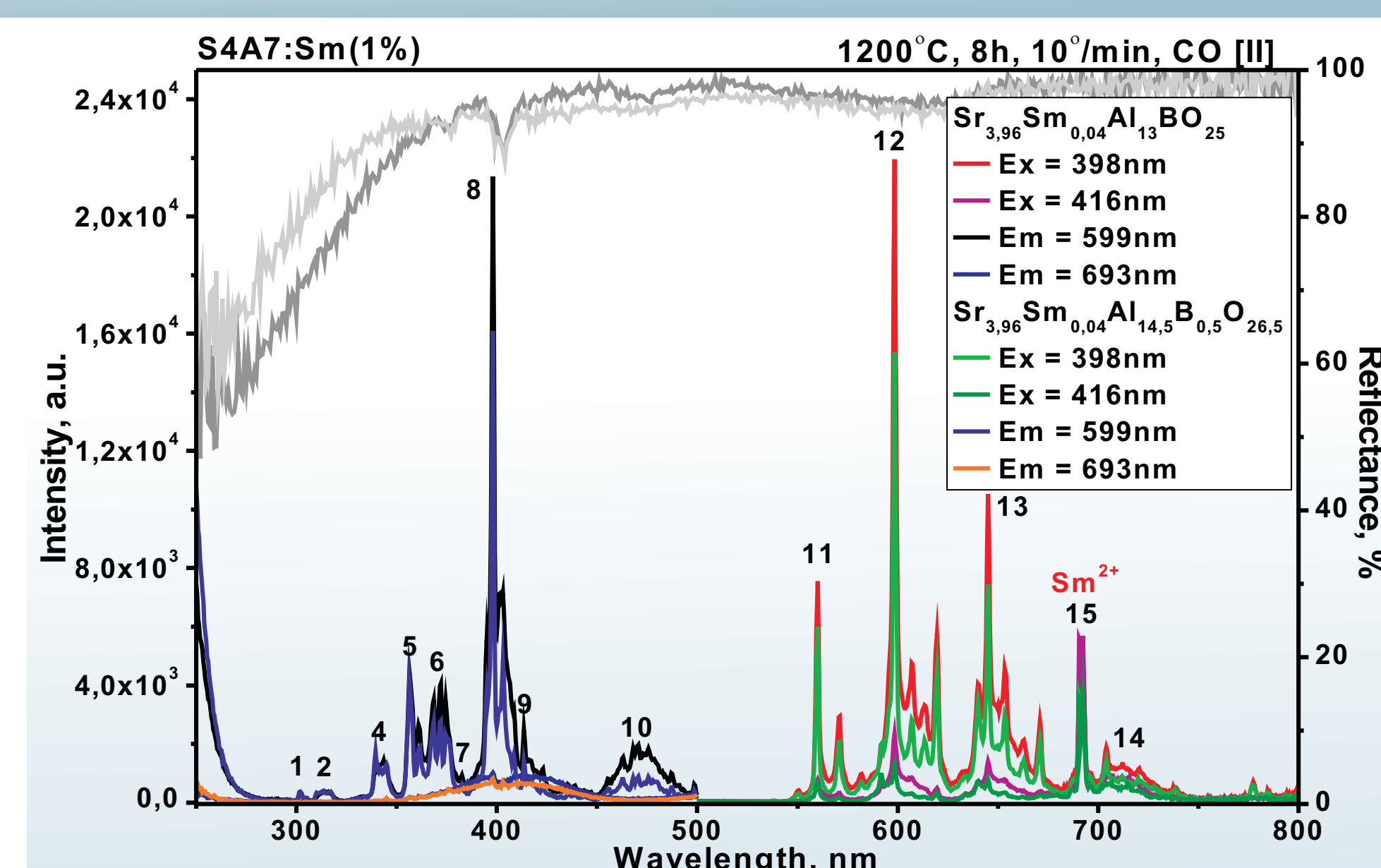


Figure 5. Stoichiometry influence on S4A7:Sm(1%) luminescence properties after second heating step under CO atmosphere

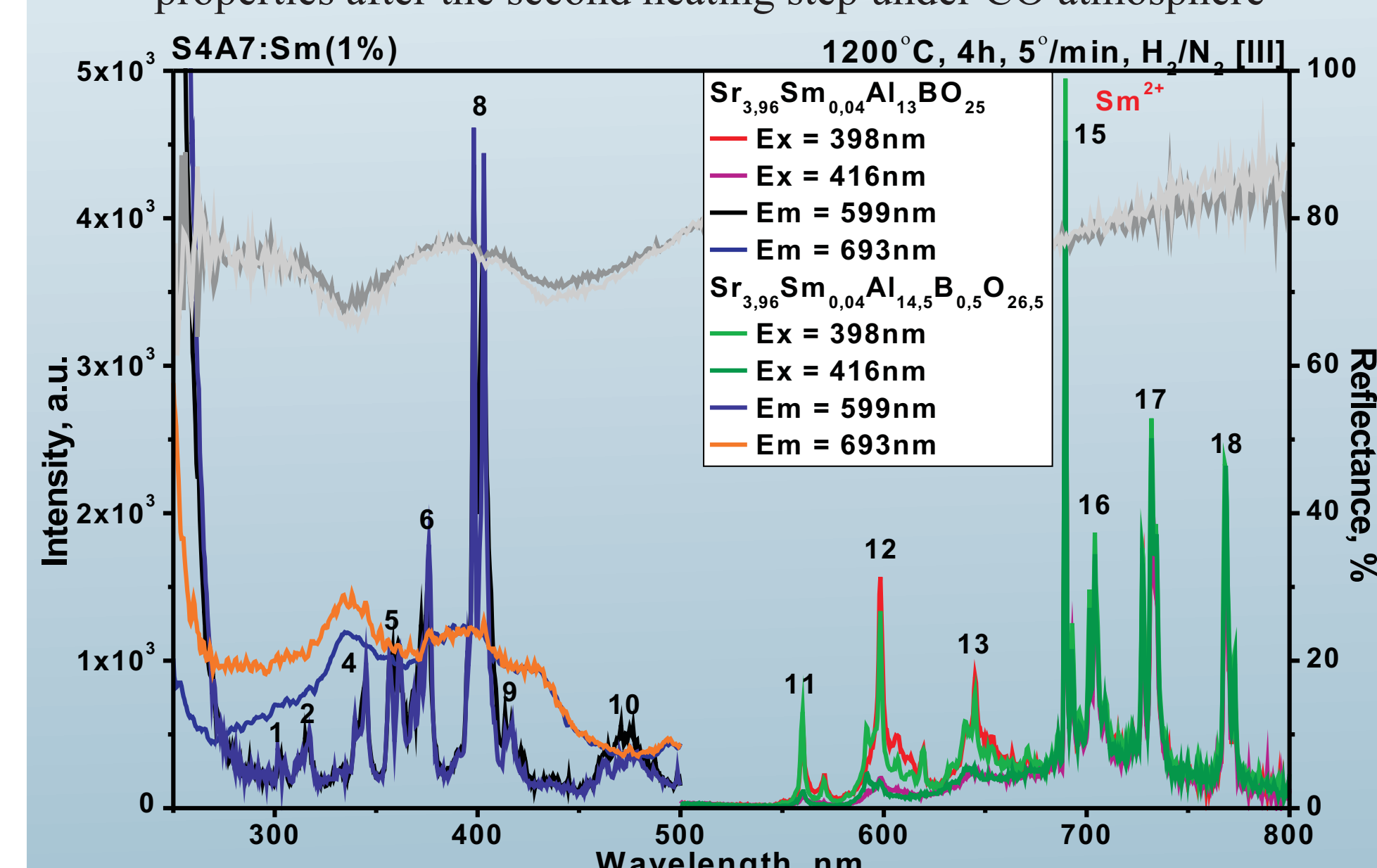


Figure 6. Stoichiometry influence on S4A7:Sm(1%) luminescence properties after the third heating step under H_2/N_2 atmosphere

As expected stoichiometry has no visible influence on shape of excitation or emission lines of samarium ion, but it is worth to mention that with higher deviation from stoichiometry emission intensity decreases. Reducing conditions (H_2/N_2) make huge influence on examined samples, it makes samples grayish and intensities decrease one order of magnitude.

$\text{Sm}^{2+}/\text{Sm}^{3+}$ 4f ENERGY LEVELS AND TRANSITIONS

The emission spectrum of trivalent samarium (Sm^{3+}) is dominated in samples after second annealing step (under CO) by transitions from the $^4\text{G}_{5/2}$ excited state located at about 17500 cm^{-1} [2]. Due to the large energy gap of about 7000 cm^{-1} to the next lower level, the $^4\text{G}_{5/2}$ decay is predominantly radiative. The strongest emission is observed in the red part of the spectrum. Figures 3 and 5 shows the excitation, emission and reflection spectra of S4A7:Sm phosphors. For the emission of Sm^{3+} ion in S4A7, prominent peak sets are observed at 562, 592 nm and 642 nm (excitation wavelength 398 nm). The peak position variation is negligible with the host lattice and are assigned to the intra-4f-shell transitions from the excited level $^4\text{G}_{5/2}$ to ground levels 11($^6\text{H}_{5/2}$), 12($^6\text{H}_{7/2}$), 13($^6\text{H}_{9/2}$). Furthermore, there is associated line structure in the excitation spectrum, corresponding to the transition within the $4f^6$ configuration from ground-level $^6\text{H}_{5/2}$ to higher energy levels of Sm^{3+} ion: 1($^3\text{H}_{9/2}$), 2($^4\text{F}_{11/2}$), 4($^3\text{H}_{7/2}$), 5($^4\text{F}_{9/2}$), 6($^3\text{D}_{5/2}$), 7($^6\text{P}_{7/2}$), 8($^4\text{K}_{11/2}$), 9($^6\text{P}_{5/2}+\text{M}_{19/2}$), 10($^4\text{G}_{9/2}+^4\text{I}_{15/2}$) [3].

However, after the third annealing step Sm^{2+} emission is dominant. The $15(^5\text{D}_0 \rightarrow ^7\text{F}_0)$ transition is at 693nm and according to the reference [4] peak position in this energy range shows weaker host influence on Sm^{2+} as in comparison more ionic systems (LiBaF_3 , CaF_2). The position of this level depends on the ionicity of the system and on the size and coordination of the Sm^{2+} site. The transitions 16, 17 and 18 are assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ respectively.

CONCLUSIONS

In this study the influence of annealing conditions on $\text{Sr}_{4-x}\text{Sm}_x\text{Al}_{14+y}\text{B}_{1-y}\text{O}_{25}$ compound luminescence prepared by conventional solid-state method is analyzed. Luminescence measurements show existence of both Sm^{2+} and Sm^{3+} cations in samples annealed at reducing atmosphere. Possible explanation for Sm^{2+} appearance in aluminate host is due to similar Sr^{2+} and Sm^{2+} radii and Sr2 site high coordination number, which enhances divalent samarium formation [5]. Up to now there are not much data on oxide lattices suitable for divalent samarium doping. Above mentioned case can extend this short list, however, more detailed study is necessary.

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