



Spectroscopy of divalent samarium in alkaline-earth fluorides

E.A. Radzhabov^{a,b,*}

^a Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a, P.O.Box 4019, 664033 Irkutsk, Russia

^b Irkutsk State University, Physics Department, Gagarin Boulevard 20, 664003 Irkutsk, Russia



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ABSTRACT

Optical spectra (absorption, luminescence, decay of emission, spectra with time resolution) of Sm²⁺ ions in alkaline-earth fluoride crystals (CaF₂, SrF₂, BaF₂) in the wavelength range 120–900 nm at 7–300 K were studied. By additive coloration of about 60% of the original Sm³⁺ is converted to Sm²⁺.

One component of the decay of the Sm²⁺ emission was observed in BaF₂ crystals with a lifetime of 16 ms (a slow component) and in CaF₂ crystals with a lifetime of 1.3 μs (fast component) at low temperature. In SrF₂ crystals, two decay of luminescence components are found in the millisecond and nanosecond time range. The luminescence spectra of the slow and fast components in CaF₂, SrF₂, BaF₂ are similar, which confirms their attribution to forbidden 4f–4f and allowed 5d–4f transitions, respectively. The results obtained made it possible to clarify the position of the excited levels of Sm²⁺ 4f(⁵D₀) and 5d(e_g) relative to the bottom of the conduction band of alkaline-earth fluorides.

1. Introduction

Samarium ions are introduced into alkaline earth fluorides in forms 2+ or 3+. Both ions effectively luminesce. The emission of Sm²⁺ is observed only at low temperatures, Sm³⁺ also luminescent at room temperature. The spectroscopy of divalent samarium was studied by several scientific groups in the 1960s [1,2] in connection with the development of laser technology. Decay of emission [3,4] and vibronic spectra were thoroughly studied. In recent studies, CaF₂-Sm²⁺ crystals were considered as effective red x-ray scintillator [5]. Formation of divalent Sm in CsBr-Sm³⁺ is expected to be use in radio-photo-luminescent dosimetry [6].

The main topic of the present paper is to establish the processes of changing the valence of Sm³⁺ ions by additive coloration and to determine the positions of the excited 4f⁶ and 4f⁵ d¹ -levels within bands gap of alkaline earth fluoride crystals.

2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method [7]. The graphite crucible contained three cylindrical cavities with a diameter of 10 mm and a length of 80 mm, which made it possible simultaneously to grow three samples with sizes Ø10 × 50 mm with different amounts of SmF₃. A few percent of CdF₂ were added into raw materials for purification from oxygen impurity

during growth.

Crystals BaF₂, SrF₂, CaF₂ with 0.01, 0.03, 0.1 mol.% of SmF₃ were grown. All samarium was in trivalent form. For the transformation of samarium ions into a divalent form, an additive coloration procedure was used.

Absorption spectra in the range 190–3000 nm were taken with spectrophotometer Perkin-Elmer Lambda-950, emission spectra were measured using grating monochromator MDR2 (LOMO). Emission, excitation spectra were measured with photomultiplier tube module Hamamatsu H6780-04 (185–850 nm). No emission spectrum correction needs to be performed as the sensitivity only weakly changed in the region of emission (400–800 nm).

3. Results

3.1. Mechanism of conversion (Sm³⁺ to Sm²⁺)

Additive colouring of the crystals was carried out in an autoclave made of stainless steel at temperatures of 700–850°C. Samples of the crystals and pieces of metallic calcium were placed in different containers or separated by metal foil in the same container. After evacuation to 10⁻²–10⁻³ Torr, the temperature increased up to 400°C. The samples were annealed at this temperature while pressure does not decrease down to 10⁻² torr again. After heating to coloration temperature, the autoclave with the samples was kept in the oven for

* Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii street 1a, P.O.Box 4019, 664033 Irkutsk, Russia.

E-mail address: eradzh@igc.irk.ru.

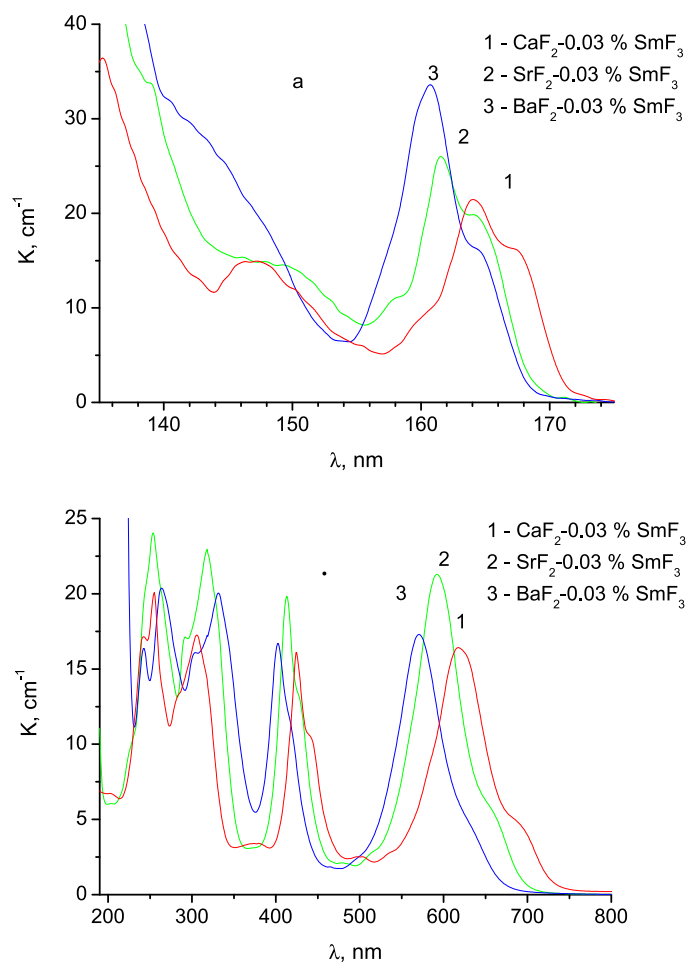


Fig. 1. Absorption spectra of initial (a) and additively coloured (b) $\text{MeF}_2\text{-}0.03 \text{ mol. \% SmF}_3$ crystals.

0.5–3 h, depending on the thickness of the samples, samarium contamination and temperature. After coloration samples were polished.

As a result of additive colouring, initially colourless crystals of alkaline-earth fluorides acquired a colour, the saturation of which increased with increasing initial concentration of trivalent samarium. In the absorption spectra (Fig. 1), characteristic bands of divalent samarium [1] appeared.

A linear dependence of the 4f-5d absorption bands of Sm^{3+} before coloration and Sm^{2+} bands after additive coloration was observed. The absorption coefficients of the allowed 4f-5d transitions of the initial Sm^{3+} and the formed Sm^{2+} are close in magnitude (see Fig. 1), which indicates that a significant fraction of initial trivalent samarium ions has become divalent.

The linear increase in the absorption coefficient of the Sm^{2+} long-wave band as a function of the concentration of the introduced SmF_3 is shown in Fig. 2. A similar dependence is also observed for other absorption bands of Sm^{2+} in the 200–500 nm region. It is known that in the crystal $\text{CaF}_2\text{-}0.01 \text{ mol. \% Sm}^{2+}$ the absorption coefficient in the Sm^{2+} long wavelength band near 600 nm is equal to 9.3 cm^{-1} [8]. From this, one can draw the lines of the complete (100%) transformation $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$ on Fig. 2. One can see that about 60% of the original trivalent samarium is converted into a divalent form by additive coloration of the alkaline-earth fluoride crystals (see Fig. 2).

The molar absorption coefficients of Sm^{2+} in SrF_2 and BaF_2 crystals are still unknown. Based on the results presented on Fig. 2 it can be assumed that the molar absorption coefficients of Sm^{2+} in three crystals of CaF_2 , SrF_2 and BaF_2 are close.

Intensive absorption bands in the vacuum ultraviolet region are found in additively coloured SmF_3 -doped CaF_2 , SrF_2 , and BaF_2 crystals

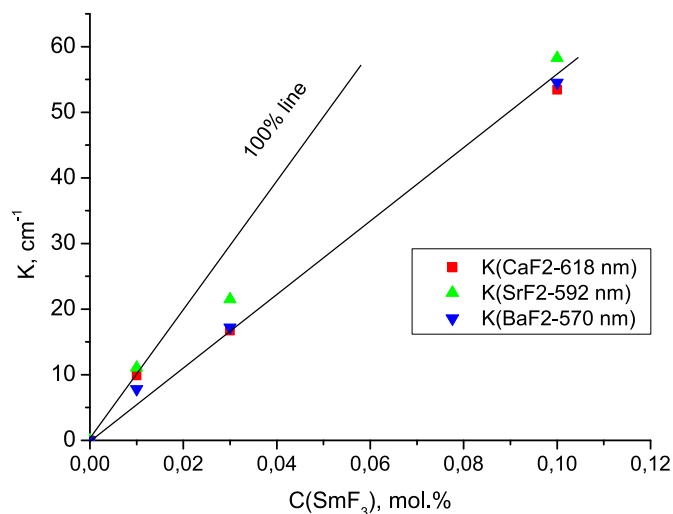


Fig. 2. The dependence of the magnitude of the long-wave Sm^{2+} band in coloured crystals on the concentration of SmF_3 in the original crystals.

at 161.0, 175.4, 206.0 nm, respectively. The bands belong to hydrogen H^- α -centres [9,10]. The formation of hydrogen centres is also confirmed by the appearance of the EPR signal of interstitial hydrogen atoms after X-ray irradiation of additively coloured crystals [10] and by infrared vibronic absorption bands near 794, 884, 957 cm^{-1} in BaF_2 , SrF_2 , CaF_2 respectively.

Additive coloration is due to the "dissolution" of metal atoms - the

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