Luminescence of Sm$^{2+}$ Doped in BaFBr

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Abstract. The luminescence of Sm$^{2+}$-doped BaFBr has been measured as a function of temperature and pressure. The $^7F_J$ crystal field levels have been identified and the corresponding crystal field parameters evaluated. Temperature dependent lifetime measurements allow to locate the energy of the lowest 4f$^5$5d$^1$ level. Pressure dependent measurements up to 8 GPa show linear red shifts of the $^5D_{2,1,0}$ levels. These shifts are about 3 times stronger than the well known ruby pressure shifts and highlight thus the potential use as pressure sensors below 8 GPa.

Keywords: Rare-Earth Elements; Samarium; Luminescence; High pressure; Crystal Field

Introduction

Alkaline earth fluorohalides (MFX) doped with Eu$^{2+}$ and/or Sm$^{2+}$ find many applications as X-ray or neutron detectors, pressure sensors as well as optical storage by hole burning.

In this work we study the luminescence of Sm$^{2+}$ in BaFBr and related hosts as a function of pressure and temperature.

Luminescence spectra of Sm$^{2+}$

Sm$^{2+}$ has a 4f$^6$ electronic ground state configuration, but the lowest energy levels of the 4f$^5$5d$^1$ configuration are in the range of the $^5D_J$ levels (see Figure 1A). At low temperatures, emissions from the $^5D_2$ and $^5D_1$ level dominate, while at high temperature, emissions from the $^5D_0$ level and a broad emission from the lowest 4f$^5$5d$^1$ level are observed (Figure 1B).

Figure 1. A. Lowest energy levels of Sm$^{2+}$. B. Luminescence spectra of BaFBr:Sm$^{2+}$ at 10 and 453 K.

Temperature dependent spectra allowed to identify the different transitions observed and to establish an experimental energy level scheme. The experimental positions of the $^7F_J$ levels could be calculated within about 5-8 cm$^{-1}$ using the following parameters (in cm$^{-1}$): $F^2 = 332$, $\xi = 1054$, $B^{4f} = -279$, $B^{4f} = -125$, $B^{4f} = -156$, $B^{6f} = 433$ and $B^{6f} = -118$. The agreement for the $^5D_J$ levels is less satisfactory, however it is likely that these levels are subject to configuration interaction with the lowest 4f$^5$5d$^1$ levels.
Lifetime measurements as a function of temperature show a strong decrease of the lifetime of the $^5D_1$ level which is related to a non-radiative transition to the lowest $4f^6 5d^1$ level. The energy separation between these two levels could be estimated to be $2712 \pm 29$ cm$^{-1}$.

High pressure experiments were performed at room and low temperatures up to about 8 GPa. The emissions of the $^5D_1$ levels are red shifted by more than 20 cm$^{-1}$/GPa, which is an about 3 times stronger shift than the corresponding shift of the ruby $R_1$ and $R_2$ lines.

Figure 2 illustrates the splitting of the $^7F_1$ level as a function of pressure in BaFBr and SrFBr$^1$. A systematic shift can be observed, and the values of the two host materials follow a similar trend.

![Figure 2. Pressure dependent splitting of the $^7F_1$ level in BaFBr and SrFBr.](image)

**Experimental Section**

**Synthesis.** Small Sm$^{2+}$-doped BaFBr and SrFBr crystals were obtained by slow cooling of stoichiometric melts of commercial barium (strontium) fluoride and anhydrous bromide under dry nitrogen atmosphere using graphite crucibles. Samarium was added as SmF$_3$ with a mole fraction of less than 1% respective to Ba or Sr.

**Optical measurements.** To obtain the low temperature we used a closed-cycle Oxford cryostat. High temperature spectra were obtained using a home-built furnace. Different lasers with emission wavelengths of 405 nm, 488 nm and 532 nm were used as excitation sources. Luminescence spectra were obtained using a Bruker IFS66 FT instrument. Lifetime measurements were performed using a SR 430 Multichannel Scaler and a Spex 270 Monochromator.

A D’Anvils Diamond Anvil Cell (DAC) with a 4:1 methanol:ethanol mixture as pressure transmitting medium was used to generate high pressure. The pressure was monitored using the ruby (present with the sample) luminescence.

**Crystal field calculations.** The crystal field parameters were estimated using the program by Edvardsson and Aberg$^2$ which calculates all energy levels of the $4f^n$ configuration. As only $^5D_1$ and $^7F_1$ levels are observed for Sm$^{2+}$, the adjustable free ion parameters were limited to $F^2$ ($F^4$ and $F^6$ are related to $F^2$) and the spin-orbit coupling parameter $\xi$. Using an iterative routine written by D. Lovy of our department, selected parameters can be optimized by comparison with experimental data.

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