Sm$^{2+}$ as a probe of crystal field in fluorides and fluorohalides: Effect of pressure and temperature

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Abstract

The luminescence of Sm$^{2+}$ substituting for Sr$^{2+}$ or Ba$^{2+}$ has been studied in SrFBr, BaFBr, BaFI and SrAlF$_5$.

The pressure induced shifts of the intra-configurational $^4D_{0,1} \rightarrow ^7F_{0,1,2}$ observed in the MFX crystals are about three times larger than those observed in ruby, confirming thus some potential of these systems as pressure sensors.

The comparison of excitation spectra in MFX shows that the position of the lowest $4f^55d^1$ band shifts strongly to the red passing from SrFBr to BaFI. In BaFI, one observes simultaneously intra-configurational and inter-configurational emission.

The non-degenerate $^4D_0 \rightarrow ^4F_0$ emission of Sm$^{2+}$ in SrAlF$_5$ confirms the presence of four crystallographic sites for Sr. Site selective spectra show clear differences for the different sites. Spectra as a function of pressure reveal different pressure shifts for the different sites.

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1. Introduction

Sm$^{2+}$-doped crystals have been shown previously to present interesting properties such as room temperature hole burning [1] or as potential pressure sensors [2]. The present study is part of a larger investigation to probe the effect of physical and chemical (by specific substitutions of ions in the host lattice) pressure on the emission properties (i.e. crystal field) experienced by the doping rare earth ion.

Crystals of the Matlockite (PbFCl-structure) family (MFX with M = Ca,Sr,Ba and X = Cl,Br,I) are an interesting subject of investigation for different reasons: they can be used for commercial applications (Eu-doped BaFBr in imaging plates), they have a relatively high symmetry (the site symmetry of the metal ion is $C_{4v}$) and they can form solid solutions such as SrFCl$_x$Br$_{1-x}$ [3]. These solid solutions lead to an important inhomogeneous broadening of the Sm$^{2+}$ emission [4]. While the spectroscopy of Sm$^{2+}$ in MFCI (M = Ca,Sr,Ba) has been studied in detail (e.g. [5]), only limited data have been published for Sm$^{2+}$ in SrFBr, BaFBr and BaFI.

SrAlF$_5$ is a potential host material for optical applications in the far UV [6] with a complex crystal structure [7].

We report in the following new results for Sm$^{2+}$ in matlockites and in SrAlF$_5$.

2. Experimental

Crystalline samples were obtained by slow cooling of stoichiometric melts of the constituent halides (e.g. SrF$_2$ + SrBr$_2$) under inert or hydrogen atmosphere in graphite crucibles. Samarium was introduced as SmF$_3$ with a nominal concentration of 1% and less with respect to Sr or Ba.

Luminescence spectra were obtained using a Bruker IFS FT instrument, a Spex 1404 monochromator, a Spex 270 monochromator, a Fluorolog 3 instrument and a Labram Raman microscope for the pressure-dependent experiments. Different lasers with emission wavelength of 405, 488, 532 nm were used as excitation sources. A New Focus external cavity diode laser was used for the site selective experiments. High-pressure experiments were done in a diamond anvil cell using silicone oil as a pressure transmitting medium. The pressure was measured using the ruby (present with the sample) luminescence.

3. Results and discussion

Fig. 1 compares the emission spectra of ruby and Sm$^{2+}$ in BaFI at ambient temperature. The pressure shifts for the sharp intra-configurational emission bands of Sm$^{2+}$ in BaFI are about 28 cm$^{-1}$/GPa, while the corresponding shift in ruby is about three times smaller. Similar shifts have been reported for Sm$^{2+}$ in SrFCl and BaFCl [2] and also observed for Sm$^{2+}$ in SrFBr. Although the reported compressibility’s are higher for BaFI...
The parameters obtained are: $p_1 = 1100 \text{ s}^{-1}$ (f–f transition), $p_2 = 8.7 \times 10^6 \text{ s}^{-1}$ (f–d transition) and $\Delta E = 1386 \text{ cm}^{-1}$. The origin of the emitting f–d state is thus calculated to be at 15,944 cm$^{-1}$, which corresponds to the intersection of excitation and emission curves in Fig. 2. The value of $p_1$ is in the range to the corresponding value observed in SrFBr (810 s$^{-1}$) and reported in CaFCl (1000 s$^{-1}$) [5], but about a factor of two larger than the values reported in SrFCl (575 s$^{-1}$) and in BaFCl (513 s$^{-1}$) [5].

The relative intensity of the f–d emission band decreases with decreasing temperature; at 80 K one observes practically only the $^2D_0 \rightarrow ^7F_3$ emission bands. Below 30 K, also $^5D_1 \rightarrow ^7F_3$ emission bands are observed. At these temperatures, both for BaFCl and SrFBr, the time resolved $^5D_0 \rightarrow ^7F_0$ emission band presents first a rise followed by a decay which results from the non-radiative decay from the $^5D_1$ level (via the 4f$^5$5d$^1$ level) to the $^5D_0$ level. This behaviour confirms the behaviour observed in SrFCl and BaFCl [4].

The non-degenerate $^5D_0 \rightarrow ^7F_0$ transition (observed more easily for Sm$^{2+}$ than for Eu$^{3+}$) can be used as a structural probe, as has been illustrated for instance in [4,10].

Fig. 3 shows the $^5D_0 \rightarrow ^7F_0$ emission observed in SrAlF$_5$ at ambient pressure and at 2.5 GPa.

The position of the $^5D_0$ level is relatively high in SrAlF$_5$ (between 14,664 and 14,686 cm$^{-1}$) compared to the values observed in the matlockites (14,476 cm$^{-1}$ in SrFCl, 14,558 cm$^{-1}$ in BaFCl). A similar high value has been found for Sm$^{2+}$ in LiBaF$_3$ (14,690 cm$^{-1}$) and explained by the relatively large crystal site with a high coordination number in an ionic lattice [11]. Note that even higher values were observed for Sm$^{2+}$ in SrMgF$_4$ (the highest value observed was 14,724 cm$^{-1}$) [10].

Four bands are clearly observed (see Fig. 3), in agreement with the four crystallographic sites reported for Sr$^{2+}$ in SrAlF$_5$ [5]. While at ambient pressure the position of the $^5D_0 \rightarrow ^7F_0$ band of sites 2 and 3 are very close, they are well separated at higher pressures.

![Fig. 1. Emission spectra of ruby and Sm$^{2+}$ in BaFCl at different pressures ($T = 300$ K) excited with 532 nm.](image1)

![Fig. 2. Excitation (grey) and emission (black) spectra of Sm$^{2+}$ in BaFCl at room temperature.](image2)

![Fig. 3. $^5D_0 \rightarrow ^7F_0$ emission observed in SrAlF$_5$ at 2.5 GPa (a) and at ambient pressure (b). The insert shows the evolution of observed band positions vs. pressure (dots) extrapolated to negative pressures (lines).](image3)
The pressure shifts observed for Sm$^{2+}$ in SrAlF$_5$ are much smaller than in the matlockites (2–5 cm$^{-1}$/GPa versus ca. 30 cm$^{-1}$/GPa). It is important to note that the pressure shifts are different for the four different bands. The insert in Fig. 3 extrapolates the observed shifts to “negative pressures” which show that a given point the four bands converge to two points. This behaviour suggests the possibility of a structural phase transition. Experimentally, a negative pressure can be achieved by replacing chemically Sr by Ba, leading thus to a bigger unit cell. The structure reported for the mixed crystal Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$ [5] has indeed a different space group than SrAlF$_5$ ($I 4/m$ instead of $I 41/amd$) with only two sites for Sr,Ba.

Another way to expand the lattice can be achieved by heating. From 15 to 300 K, the splitting of the four bands decreases from 22.2 to 21.5 cm$^{-1}$, which is the same trend as on decreasing the pressure. Recently, the observation of a phase transition at 715 K has been confirmed [12], but so far no high temperature structural data are available. The local effect of hydrostatic pressure on the crystal field will be further studied by site selective experiments as a function of pressure.

Site selective excitation experiments at ambient pressure reveal additional differences: the $^5D_0$–$^7F_1$ bands present for each site three different components, as shown in Fig. 4. If one makes a simple estimation of the crystal field parameters using the splitting between the three different components, one obtains (at 70 K) the following values (±3 cm$^{-1}$): site 1: $B_{20} = 526$ cm$^{-1}$, $B_{22} = 21$ cm$^{-1}$, sites 2 and 3: $B_{20} = $ ca. 524 cm$^{-1}$, $B_{22} = $ ca. 45 cm$^{-1}$, site 4: $B_{20} = 477$ cm$^{-1}$ and $B_{22} = 61$ cm$^{-1}$.

4. Conclusions

The pressure-dependent studies indicate that the local pressure experienced by the emitting rare earth ion is different to the global pressure applied to the crystal. It is therefore important to characterize the local environment for a quantitative understanding of the shifts observed. In the case of the matlockite (MFX) crystals, the pressure shifts are about three times stronger than the shifts observed for ruby (which is used as the standard pressure sensor).

The spectral shifts with pressure (and temperature) of the $^5D_0$–$^7F_0$ transition of Sm$^{2+}$ substituting for Sr$^{2+}$ (which has a very similar ionic radius) may be extrapolated to look for possible phase transitions of the host crystal as a function of chemical (solid solutions) or physical pressure.

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References