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Abstract

Temperature-dependent emission spectra of Sm[2+-]doped SrMgF4 have been obtained in the temperature range from 50 to 300 K. At 50 K, six bands are observed for the very strong [5]D0→[7]F0 transition, in agreement with the reported sixfold crystal superstructure. The overall splitting of more than 70 cm[−1] highlights the important structural differences of the six Sr sites. Upon heating progressively to room temperature, the spectra change progressively with a more pronounced change between 270 and 300 K. These observations suggest the possibility of a complex structural behavior for SrMgF[4] which will require new experiments.

Reference


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Abstract

Temperature-dependent emission spectra of Sm$^{2+}$-doped SrMgF$_4$ have been obtained in the temperature range from 50 to 300 K. At 50 K, six bands are observed for the very strong 5 $D_0 \rightarrow 7 F_0$ transition, in agreement with the reported sixfold crystal superstructure. The overall splitting of more than 70 cm$^{-1}$ highlights the important structural differences of the six Sr sites. Upon heating progressively to room temperature, the spectra change progressively with a more pronounced change between 270 and 300 K. These observations suggest the possibility of a complex structural behavior for SrMgF$_4$ which will require new experiments.

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1. Introduction

Inorganic fluorides and fluorohalides have been of interest to us for some time already, in part because of their potential interest as host materials for rare earth ions for optical applications[1–3]. In particular, we have studied the luminescence of Sm$^{2+}$ in BaMgF$_4$ and in the solid solutions Ba$_{1-x}$Sr$_x$MgF$_4$ with 0 $\leq x \leq$ 0.6[4]. As an extension of this study, we have also prepared Sm$^{3+}$-doped SrMgF$_4$, but at that time, no single crystal X-ray structure of this compound was available. The crystal structure of SmMgF$_4$ has been published recently[5] and reveals a complex sixfold superstructure of the basic Cmcm lattice initially reported by Banks et al.[6].

Very recently, Abrahams[7] reanalyzed these new structural data and suggested the presence of a phase transition with a Curie temperature of ca. 450 K. Our luminescence data reported below provide additional information in relation to these structural data.

2. Experimental

Samples were prepared using solid state techniques similar to those reported by Gingl[8]. Sm was introduced as the metal with a nominal concentration of 0.2% with respect to Sr. Small orange-colored crystals (maximum size 0.3 mm $\times$ 0.3 mm $\times$ 1 mm) were obtained in addition to transparent MgF$_2$ and greenish-blue SrF$_2$ (doped with Sm). These samples are not very moisture sensitive. A crystal was chosen and placed in a glass capillary to make handling more easy, which was then introduced in an Oxford Instruments Helium flow cryostat for temperature dependent measurements. Emission spectra were excited with the 488 nm argon-ion laser line and analyzed using a Spex 1403 double monochromator (focal length 85 cm, aperture f/7.8) equipped with a Burley C31034-A20 PM tube. The 100 $\mu$m slits used in the experiments provide a spectral resolution of ca. 1.2 cm$^{-1}$.

3. Results

Sm$^{3+}$ substitutes easily for divalent Sr$^{2+}$ and Ba$^{2+}$[1,4], and therefore its emission spectrum can be used as a probe of the local environment of the substituted divalent ion. In particular, the non-degenerate $^5D_0 \rightarrow 7F_0$ transition shown in Fig. 1 illustrates this behavior for Sm$^{3+}$ in four different crystals, namely BaMgF$_4$[4], Ba$_2$Mg$_3$F$_{10}$-Ba$_{75}$Sr$_{25}$MgF$_4$[4] and SrAlF$_4$[9]. In BaMgF$_4$, there is only one Ba site in the crystal structure, while there are two in Ba$_2$Mg$_3$F$_{10}$[8]. In the case of Ba$_{75}$Sr$_{25}$MgF$_4$ with the BaMgF$_4$ structure, the substitutional disorder on the Ba site induces a significant inhomogeneous broadening of the
Sm$^{2+}$ emission bands. Finally, for SrAlF$_4$, four different bands (the third one appears as a shoulder of the central second band in Fig. 1) between 14 672 and 14 695 cm$^{-1}$ confirm the four-fold superstructure refined using single crystal X-ray diffraction [9].

The lower resolution survey spectrum of Sm$^{2+}$ in SrMgF$_4$ at 50 K (shown in Fig. 2) is similar to the one observed for Sm$^{2+}$ in BaMgF$_4$ and the room temperature spectra of SrMgF$_4$ samples doped with Sm prepared under reducing atmosphere [10]. No emission of Sm$^{3+}$ was observed for our samples.

The strongest emission bands correspond to the $^5D_0 \rightarrow 7F_0$ transition, which are observed at a remarkably high frequency around 14 700 cm$^{-1}$, similarly as in BaMgF$_4$ (see Fig. 1 and [11]). In contrast to the isoelectronic Eu$^{3+}$ spectra, where the $^5D_0 \rightarrow 7F_0$ transition is very weak compared to other emission bands, a strong intensity for this transition can be observed for Sm$^{2+}$, as found experimentally for all samples in Fig. 1 or for Sm$^{2+}$ doped into MFX compounds (M = Ca, Sr, Ba; X = Cl, Br, I) [1]. This increase of intensity may be related to the close position of odd-parity states relative to $^5D_0$ and $^7F_0$.

Fig. 3 presents temperature dependent emission spectra of Sm$^{2+}$ in SrMgF$_4$. At 50 K, one observes six different bands, three weaker bands (at 14 652, 14 659 and 14 690 cm$^{-1}$) and three stronger ones (at 14 692, 14 707 and 14 724 cm$^{-1}$). This observation is perfectly in agreement with the six different Sr sites reported in [5]. The overall spread of these bands (ca. 70 cm$^{-1}$) is much larger than the one observed in SrAlF$_4$ (see Fig. 1) and indicates large structural differences of the Sr–F coordination polyhedra. Indeed, the crystal structure data [5] show quite different environments. If one sets arbitrarily two Sr–F bond length limits at 2.7 and 3.0 Å, the coordinations around the six Sr ions can be summarized as follows: Sr$_1$: five bonds < 2.7 Å; three bonds between 2.7 and 3.0 Å; three bonds between 3.0 and 3.4 Å; in short 5$^\text{+}$3$^\text{+}$3. For Sr$_2$, one obtains: 7$^\text{+}$1 + 2; Sr$_3$ and Sr$_4$: 9 bonds < 2.7 Å; Sr$_5$: 6 + 1 + 3 and Sr$_6$: 5 + 5.

Interestingly, these emission bands evolve with increasing temperature. Already at 120 K, the weak band seen as a shoulder at 50 K (at 14 690 cm$^{-1}$) cannot be distinguished anymore from the stronger emission band (at 14 692 cm$^{-1}$). The two other weak bands have merged into one broader one at ca. 270 K.

Between 270 and 300 K, there appears an important intensity redistribution of the three stronger emission bands, while the weaker large band shifts towards the other bands. These important spectral changes clearly indicate a dynamic evolution of the structure and strongly support the possibility of a higher temperature structural phase transition, as suggested by Abrahams [7].

We have attempted to reach this phase transition simply by laser heating of the small crystal, but even with laser powers of ca. 200 mW on the small crystal a spectrum similar to the one at 300 K resulted.
However, it is possible that the situation is even more complex, insofar as the reported crystal structure stemmed from a sample doped nominally with 0.06% of Ce [5]. It is not clear presently to which extent this heterovalent (Ce is trivalent, while Mg and Sr are bivalent) substitution stabilizes the reported crystal structure, and that there could be other structural varieties for pure or isovalently substituted SrMgF4.

Very recently, a superlattice structure was reported for Ce3+ doped BaMgF4 [12], while BaMgF4 doped with Eu(II) or with Sm(II) did not show any sign of rare earth site multiplication by EPR (Eu) [2] and luminescence spectroscopy [11].

In this context, it may also be interesting to note that for BaAlF5, four different crystal modifications have been reported [13] which differ by the stacking of the fluorine octahedral layers.

Further structural and spectroscopic investigations on SrMgF4 are planned for the near future.

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References