



# Sm<sup>2+</sup> fluorescence and absorption in cubic BaCl<sub>2</sub>: Strong thermal crossover of fluorescence between 4f<sup>6</sup> and 4f<sup>5</sup>5d<sup>1</sup> configurations

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## ABSTRACT

The optical absorption and fluorescence spectra of polycrystalline cubic-phase barium chloride doped with divalent samarium is reported. X-ray diffraction shows that the cubic phase is stabilised at room temperature by the addition of 12.5% lanthanum trichloride; no evidence for the more common orthorhombic or hexagonal phases of barium chloride is found. Optical absorption measurements are in good agreement with a calculated spectrum for Sm<sup>2+</sup> ions at a single site of cubic symmetry, even though the material must contain a substantial fraction of chlorine interstitials and lanthanum substitutional ions. The photoluminescence spectrum shows sharp red line emission from the <sup>5</sup>D<sub>1</sub> and <sup>5</sup>D<sub>0</sub> levels of the 4f<sup>6</sup> configuration, again consistent with a single site of cubic symmetry, together with a broad emission, also in the red, which arises from the lowest levels of the 4f<sup>5</sup>5d<sup>1</sup> configuration. The relative strengths of these emissions are strongly temperature dependent; at room temperature the broad band from the lowest 4f<sup>5</sup>5d<sup>1</sup> levels peaking at 15,130 cm<sup>-1</sup> is dominant, while at low temperature (~12 K) sharp lines from the <sup>5</sup>D<sub>0</sub> level dominate. The most intense line corresponds to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition at 14,300 cm<sup>-1</sup>, but the nominally forbidden <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transition also has significant intensity. The marked temperature dependence of the intensity of the lines and bands is successfully modelled by rate equations and is explained on the basis of thermally activated crossovers between the 4f<sup>6</sup> (<sup>5</sup>D<sub>0,1</sub>) levels and the lowest levels of the 4f<sup>5</sup>5d<sup>1</sup> configuration; it is necessary to include the three lowest levels of the 4f<sup>5</sup>5d<sup>1</sup> configuration sandwiched between the <sup>5</sup>D<sub>0</sub> and <sup>5</sup>D<sub>1</sub> levels.

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## 1. Introduction

Barium chloride adopts an orthorhombic structure at room temperature, but changes to a fluorite-like structure (space group O<sub>h</sub><sup>2</sup>) between 925 °C and the melting point at 963 °C. In previous work [1,2], we have identified an interesting property of this material—when doped with ~12.5% of lanthanum or cerium trichloride, the high temperature cubic phase is stabilised at room temperature. The additional chlorine ions associated with the lanthanum or cerium can be accommodated in the empty interstitial sites in the simple cubic chlorine sub-lattice (in a fluorite lattice, one half of the interstitial sites are occupied by the cations and the other half are empty). This technique of stabilising the cubic phase means that it is possible to prepare transparent polycrystalline samples of barium chloride because the refractive index of a cubic crystal is isotropic. Since there is no grain boundary mismatch in refractive index there is minimal light scattering, and the polycrystalline samples are transparent. In this way it is possible to manufacture

transparent ceramics which are a viable cost-effective alternative to single crystals for optical applications where transparency is a key requirement, such as for scintillators and phosphors.

We have reported that europium (Eu<sup>2+</sup>) doped lanthanum-stabilised cubic barium chloride is a very efficient X-ray phosphor [2], with a similar radioluminescence output to the well known X-ray phosphor gadolinium oxysulphide:Tb. The emission arises from a strong parity-allowed 5d→4f transition at around 420 nm. The cerium-stabilised material is a good scintillator, as is the lanthanum-doped material when a small fraction of cerium is added, with conversion efficiencies of around 7200 photons/MeV and decay times of around 50 ns [3]. The emission is very well matched to the spectral response of most photomultipliers, but is a poor match to semiconductor detectors. Thus, it is of interest to consider the possibility that divalent samarium, which is frequently observed to show a 5d→4f transition in the red region of the spectrum around 700 nm, doped into cubic barium chloride might result in an efficient scintillator or phosphor material, since this emission is well-matched to silicon detector sensitivity.

The spectroscopy of divalent samarium has attracted considerable interest in recent years because of several unusual features. Depending on the crystal field and other energy-level parameters,

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the emission can include both sharp and slow  $4f^6 \rightarrow 4f^6$  transitions, and broad and fast  $4f^5 5d^1 \rightarrow 4f^6$  transitions. The energy-level structures of the  $4f^6$  and  $4f^5 5d^1$  configurations generally overlap for the excited states, and so thermally stimulated cross-configuration transitions can occur and which are responsible for the strong temperature dependences of the observed emissions [4]; and there have been several attempts to reconcile these temperature dependences with theories [5–7]. Another interesting aspect is that the  $^5D_0 \rightarrow ^7F_0$  fluorescence transition is a sharp singlet line which is electric and magnetic dipole forbidden in cubic sites but is nonetheless often observed. This line, also observed for the iso-electronic  $\text{Eu}^{3+}$  serves both as test of crystal field theories, and also to distinguish crystallographically different sites in a crystal without the complexities of splittings of degenerate lines [8,9].

The fluorescence spectra of orthorhombic phase barium chloride doped with divalent samarium has been described previously [4,6]. The authors report primarily sharp  $4f \rightarrow 4f$  lines originating from the  $^5D_0$  and  $^5D_1$  levels over the range 77–300 K, supplemented by a rather weak and broad  $5d \rightarrow 4f$  emission at room temperature. This was shown to originate from  $5d$  levels above the  $^5D_1$  level, and which are thermally populated at room temperature from the  $^5D_0$  and  $^5D_1$  levels. The  $4f^5 5d^1$  emission shows an initial fast decay (lifetime  $\sim 0.26 \mu\text{s}$ ), followed by a much more intense (600 times the integrated intensity) slower emission (lifetime  $\sim$  a few ms). The latter effect is attributed to a two-step decay process from the  $^5D_1$  level, which is correspondingly quenched for temperatures above about 105 K. The fluorescence spectra of  $\text{Sm}^{2+}$  hexagonal phase nanocrystals of  $\text{BaCl}_2$  has also been recently reported [10,11], and shows generally similar features to the orthorhombic phase to which it is structurally related. In both cases the lowest  $4f^5 5d^1$  level lies above the  $^5D_1$  level; in contrast we find here that for the quite different fluorite-structure cubic barium chloride, a number of  $4f^5 5d^1$  levels are sandwiched between the  $^5D_0$  and  $^5D_1$  levels which results in a more complex thermal behaviour.

In addition to the scintillation or X-ray phosphor application mentioned earlier, samarium doped materials are of interest in a range of other applications. Inhomogeneous broadening of the  $^5D_0 \rightarrow ^7F_0$  transition and the ease with which  $\text{Sm}^{2+}$  can be photo-ionised means that the samarium-doped material has been widely used in studies of persistent hole-burning [12]. The reverse process can be achieved with X-irradiation, that is  $\text{Sm}^{3+}$  can be reduced to  $\text{Sm}^{2+}$ , and this process has been proposed for applications in photoluminescence-detected X-ray storage phosphors [13], and in micro-beam radiation therapy dosimetry [14].

In this paper we describe the optical absorption and fluorescence spectroscopy of  $\text{Sm}^{2+}$ -doped lanthanum-stabilised cubic barium chloride (here abbreviated as LSCBC) from the perspective of the possible application as an X-ray phosphor or scintillator. In a preliminary report [15], we have shown that LSCBC: $\text{Sm}^{2+}$  has a red-emission scintillation efficiency of around 5% of the commercial X-ray phosphor terbium-doped gadolinium oxysulphide. The prime motivation for the present work is to understand the spectroscopy of the LSCBC:Sm system in order to optimise the X-ray phosphor performance. We find that the spectra show very strong temperature dependence which result in the  $4f^5 5d^1$  emission band dominating at room temperature, while the sharp line  $^5D_{0,1} \rightarrow ^7F_J$  emissions dominate at low temperatures. The absorption spectra and emission spectral intensity temperature dependences are calculated numerically and a consistent interpretation is given.

## 2. Experimental

Polycrystalline discs of  $\text{Ba}_{1-x-y}\text{La}_x\text{Sm}_y\text{Cl}_{2+x+y}$  were formed by melting anhydrous  $\text{BaCl}_2$ ,  $\text{LaCl}_3$  and  $\text{SmCl}_3$  powders in a platinum crucible using a RF furnace and an inert atmosphere of argon. (For

convenience, we quote values of  $x$  and  $y$  in what follows as a percentage  $100x$  or  $100y$ ). The materials were sourced from Sigma Aldrich and all had a specified purity of 99.99%. The melt was slow cooled at  $5^\circ\text{C/h}$  through the melting point of pure  $\text{BaCl}_2$  ( $963^\circ\text{C}$ ) then quickly cooled at  $30^\circ\text{C/min}$  through the cubic to orthorhombic phase transition ( $925^\circ\text{C}$ ) to optimise retention of the cubic phase, then slow cooled below  $850^\circ\text{C}$  to minimise cracking. Powder X-ray diffraction (XRD) was carried out with a Phillips PW 1730 powder diffractometer using a sealed sample holder since the material is hygroscopic. Photoluminescence (PL) measurements were performed on a HJY Fluorolog spectrometer. All reported results have been corrected for the spectral response. Absorption measurements were made on a Shimadzu UV-2100 double beam spectrometer on samples thinned to a thickness of  $250\text{--}750 \mu\text{m}$  as required to achieve sufficient light transmission. Temperatures from 12 to 350 K were attained using an RMC 22 closed cycle refrigerator.

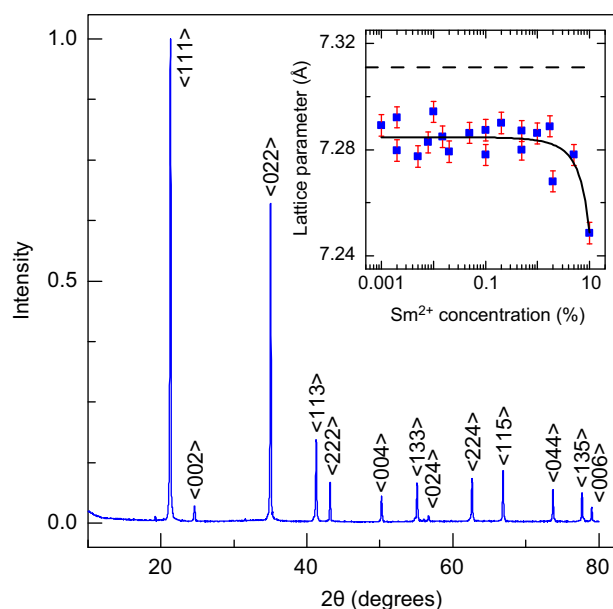
## 3. Results

### 3.1. Experimental results

#### 3.1.1. Samples and structure

The polycrystalline material as produced had a purple-red colouration, with the intensity of the colouration varying from a light red tinge in an almost transparent specimen for 0.001% doping to nearly black for 10% doping. Cooling the lightly-doped samples showed an interesting thermochromic colour change from red to green. We see no evidence for  $\text{Sm}^{3+}$  photoluminescence or optical absorption from our samples for Sm dopings below 1%, and so deduce that some reduction has occurred during the preparation process, possibly through the evaporation of a small fraction of chlorine gas. All the spectral features reported here are for samples with less than 1% doping and are attributable to divalent samarium.

Powder XRD patterns (Fig. 1) for a lanthanum content corresponding to 12.5%  $\text{La}^{3+}$  show the material has retained the high temperature cubic phase with minimal impurity phases. The very weak line at  $\sim 19^\circ$  is a  $\langle 111 \rangle K_\beta$  reflection, all other weak lines



**Fig. 1.** Powder XRD pattern of LSCBC: $\text{Sm}^{2+}$  with 12.5%  $\text{La}^{3+}$  and 0.1%  $\text{Sm}^{2+}$  recorded at room temperature with a copper tube. The broad feature evident at low angles arises from the sample holder. Inset: Variation of lattice constant with mole fraction  $\text{Sm}^{2+}$ . The dashed line indicates the lattice constant for pure  $\text{BaCl}_2$  and the solid line provides a guide to the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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