



Magneto-optical studies of valence instability in europium and terbium phosphors



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ARTICLE INFO

Available online 21 August 2015

Keywords:

Valence

Europium

Terbium

Oxysulfide and -sulfate

Phosphors

Paramagnetic susceptibility

ABSTRACT

The impurities and dopants' inappropriate valences may deteriorate the performance of luminescent materials, cause waste of the precious rare earth (R) material and thus incur financial losses. The usual methods to detect the valence of rare earths; XPS, Mössbauer and XANES spectroscopies, are not sensitive enough for low concentrations and the EPR methods are not very suitable for powders. In this work, the comparison between the theoretical and experimental temperature-dependent paramagnetic susceptibilities was used to obtain quantitatively the concentrations of the impurity valence in $\text{Eu}_2\text{O}_2\text{S}$ and $\text{Tb}_2\text{O}_2\text{SO}_4$, both containing nominally only R^{3+} . Minute (ppm level) Eu^{2+} impurities could be analyzed because of the huge difference in the paramagnetic susceptibility between Eu^{2+} and Eu^{3+} at low temperatures. However, temperatures below 50 K are then needed whilst the Tb^{IV} impurity in a Tb^{3+} matrix can be observed already at higher temperatures. The latter method based on comparing the slopes of the $\text{Tb}^{3+}/\text{Tb}^{\text{IV}}$ paramagnetic susceptibility vs temperature curves for the $\text{Tb}^{3+}/\text{Tb}^{\text{IV}}$ couple is less sensitive than for the $\text{Eu}^{2+}/\text{Eu}^{3+}$ one. Finally, the host independent temperature evolution of the paramagnetic susceptibility was calculated for Gd^{3+} (or Eu^{2+} or Tb^{IV}) to yield a simple analytical expression to be used universally.

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1. Introduction

Practically all luminescent materials (*i.e.* phosphors) are composed of a dopant and a host matrix. The former can be considered as a defect albeit regularly a beneficial one. Due to low non-radiative relaxation rates of their excited electronic levels, especially the di- and/or trivalent rare earth ($\text{R}^{2+/3+}$) doped or co-doped phosphors are widely used in such applications as plasma TV screens (*e.g.* $(\text{Y,Gd})\text{PO}_4:\text{Eu}^{3+}$), three color energy saving fluorescence lamps (*e.g.* red $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, green $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$, and blue $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$), lasers (*e.g.* $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}^{3+}$ or $\text{YPO}_4:\text{Yb}^{3+}$), X-ray intensifying screens (*e.g.* $\text{LaOBr}:\text{Tm}^{3+}$), emergency signage (*e.g.* $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ [1]), anti-forgery marking (*e.g.* $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$), *etc.* [2]. Unfortunately, the two most

common rare earth dopants, Eu and Tb, may exist with two different oxidation states, $\text{Eu}^{2+/3+}$ and $\text{Tb}^{3+/IV}$. The broad band luminescence of Eu^{2+} is usually very intense due to the parity-allowed electric dipole $4f^7 \leftrightarrow 4f^65d^1$ transitions both in absorption and emission [3]. On the other hand, the Eu^{3+} line emission is much weaker despite the very high quantum yield offset by weak absorption. Tb^{IV} does not show luminescence, but this species may absorb that of Tb^{3+} and, in addition, may facilitate non-radiative processes reducing in both cases the efficiency of Tb^{3+} doped phosphors [4]. The undesirable (impurity) valences not only deteriorate the performance of the materials but also cause considerable waste of the rare earth material and thus substantial financial losses can occur.

XANES spectroscopy is a very convenient way to distinguish between the different valence states of rare earths. This is because the white lines due to the 2p–5d transitions observed on the L_{III} edges are well separated for the different valence species, the difference being typically 8 eV as has been demonstrated for *e.g.*

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persistent luminescence materials [5]. The relative amounts of the different valence impurities are rather easy to determine by simple fitting of Gaussian (white line) and arctan (edge step) functions. Unfortunately, the method is not very sensitive for the L edges, since dopant concentrations in the parts per mille molar range are typically not observable. Moreover, a synchrotron source is required for the method and the cost of these XANES measurements is in most cases prohibitively high. Laboratory XPS methods may offer a more economical alternative, however [6].

Mössbauer spectroscopy is another method to probe directly the rare earth valences, since each and every one of these elements is observable by the method. In principle, different valences show significantly different signals as reported e.g. for $\text{Yb}^{2+/3+}$ in $\text{Yb}_5(\text{Ge,Sb,Ga})_4$ intermetallics [7]. This allows the quantification of the relative amounts of the valences by fitting the theoretical Mössbauer signals to the observed ones. However, in the typical dopant concentration range (few mole % and less for the impurity valence species), very long measurement times may be needed due to the rather low sensitivity of the method [8]. Similarly, XPS (ESCA) can be used for the valence quantification of the rare earths, since different valences show significantly different signals (see e.g. Ref. [9] for Eu in $\text{Sr}_2\text{P}_2\text{O}_7$), but the sensitivity may not be sufficient, either. Finally, EPR methods are not very well suitable for powders and they are restricted to species with unpaired electrons only.

It is thus evident that there is a need for a simple non-destructive and inexpensive method for the quantification of the rare earth impurity valences. In this work, the calculation of the theoretical temperature-dependent paramagnetic susceptibilities and comparison of them with the experimental results is used to obtain quantitatively the concentration of the divalent and tetravalent impurity valence of europium and terbium, respectively. The oxysulfide and oxysulfate materials, i.e. $\text{Eu}_2\text{O}_2\text{S}$ and $\text{Tb}_2\text{O}_2\text{SO}_4$, both containing nominally only R^{3+} , are used as the target materials.

2. Experimental

2.1. Materials

The $\text{Eu}_2\text{O}_2\text{S}$ materials were prepared with thermal decomposition and reduction of $\text{Eu}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (x varies depending on e.g. the crystallization temperature). The sulfate hydrate was obtained by dissolving Eu_2O_3 into concentrated sulfuric acid and by concentrating the solution until the crystallization of the sulfate occurred. The sulfate hydrate was subsequently heated for 30 min at 830 °C in a flowing $\text{N}_2 + 12\% \text{H}_2$ gas phase to yield $\text{Eu}_2\text{O}_2\text{S}$. The $\text{Tb}_2\text{O}_2\text{SO}_4$ materials were prepared by heating $\text{Tb}_2(\text{SO}_4)_3 \cdot y\text{H}_2\text{O}$ (y is not necessarily the same as x for the europium sulfate) to 800 or 900 °C in air with a heating rate of 10 °C min^{-1} . The products were analyzed for phase purity with routine X-ray powder diffraction (XPD) measurements but no other phases than $\text{Eu}_2\text{O}_2\text{S}$ and $\text{Tb}_2\text{O}_2\text{SO}_4$ were observed with this method. However, because of the reducing (oxidizing) preparation conditions for obtaining $\text{Eu}_2\text{O}_2\text{S}$ ($\text{Tb}_2\text{O}_2\text{SO}_4$), varying amounts of divalent Eu^{2+} (tetravalent Tb^{IV}) impurities are expected. Nevertheless, small amounts of impurities – especially the amorphous ones – may not be observed with the XPD method.

2.2. Magnetic measurements

The magnetic susceptibility measurements of the $\text{Eu}_2\text{O}_2\text{S}$ materials were carried out with a Quantum Design MPMS-5S SQUID magnetometer in the temperature range from 4.5 to 300 K. The study of the magnetization curves at 4.5 K showed that the magnetic moment is proportional to the static field in the 0–0.1 T

field range. The measurement of the magnetic susceptibility was therefore carried out for an external field of 0.1 T.

The magnetic properties of the $\text{Tb}_2\text{O}_2\text{SO}_4$ materials were measured using a Quantum Design MPMS-XL-5 SQUID magnetometer. The temperature dependence of the magnetization was first measured cooling from 400 to 5 K in a 50 mT field (field cooling, FC). To focus on the low temperature range, the materials were re-measured by zero field cooling (ZFC) to 2 K and measuring magnetization in a 50 mT field with increasing temperature up to 30 K and then cooling back to 2 K. There was no difference between the ZFC and the FC measurements for any of the materials. The magnetic field dependence of the magnetization was also measured for all the materials at 5 K between –5 T and 5 T.

2.3. Theoretical calculations

The energy level structure of the R^{3+} ions may be obtained by solving the Schrödinger equation $H\Psi = E\Psi$, which states that operating the wave function (Ψ) with a Hamiltonian (H) yields the energies (E) of the levels [10]. Since the exact form of the Hamiltonian is not possible to be constructed for the rare earths, an effective Hamiltonian is used instead considering a sum of two main groups of Hamiltonians describing the interactions resulting in the removal of the degeneracy of the $4f^n$ energy levels: the free-ion and crystal field (c.f.) effects.

The free-ion part describes the R^{3+} ion without any perturbations from the surrounding ligands. In that case, the energy levels are discrete and characterized by the total orbital (L), spin (S), and angular momentum (J) values according to the Russell-Saunders coupling scheme. The composition of the free-ion Hamiltonian has been discussed in detail elsewhere [11,12]. The c.f. Hamiltonian (Eq. (1)) depicts the effect of the electric fields of the neighboring ions on the R^{3+} ion [12]. The c.f. interaction can split the free ion state with a total angular momentum J into $2J+1$ (integer J) or $J+1/2$ (half-integer J) distinct Stark levels, the number of which is determined by the crystallographic point symmetry of the R^{3+} site.

The c.f. part of the Hamiltonian can thus be expressed as follows:

$$H_{CF} = \sum_k \sum_{q=-k}^{q=k} \left\{ B_q^k \left[C_q^k + (-1)^q C_{-q}^k \right] + i S_q^k \left[C_q^k - (-1)^q C_{-q}^k \right] \right\} \quad (1)$$

where the B_q^k and S_q^k c.f. parameters are coefficients of the real and imaginary parts of the c.f. expansion, respectively, and are functions of the radial distances $\langle r^k \rangle$ (electrons) and angular contribution from the structure. C_q^k s are tensor operators related to the spherical harmonics describing the angular properties of electron wave functions; k is the rank of the tensor operator and q indicates the relevant component of this operator limited by the point group symmetry [12]. The c.f. parameters (and thus the wave functions, too), given in the Wybourne notation, are usually obtained by a phenomenological simulation of the experimental energy level schemes by minimizing the root mean square deviation between the observed and calculated energy level values. The parameter values used in the present work were adopted from the earlier results on Eu^{3+} doped $\text{Gd}_2\text{O}_2\text{S}$ [12] whilst the corresponding parameter values for Tb^{3+} in $\text{Tb}_2\text{O}_2\text{SO}_4$ were obtained from those for the Eu^{3+} doped $\text{R}_2\text{O}_2\text{SO}_4$ [13] by downscaling from Eu^{3+} to Tb^{3+} [14]. For the point symmetry of the R^{3+} site (C_{3v} in $\text{Eu}_2\text{O}_2\text{S}$, C_{2v} in $\text{Tb}_2\text{O}_2\text{SO}_4$), all c.f. parameters assume real values as follows for Eu^{3+} (Tb^{3+}) in cm^{-1} units: B_0^2 : 91 (–968), B_2^2 : –(195); B_0^4 : 1132 (–783), B_2^4 : –(348), B_4^4 : 901 (–), B_4^4 : –(–585); B_0^6 : 336 (636), B_2^6 : –(187), B_4^6 : –336 (–), B_6^6 : –(–241) and B_6^6 : 511 (–27). The free ion parameter values were obtained from the work for the rare earth oxychloride (ROCl) series [15]. The wave functions

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