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Magneto-optical investigation of the cyclic redox R2O2S ↔ R2O2SO4 (R: Eu, Tb) reactions

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1. Introduction

   Impurities and dopants' inappropriate valences may deteriorate the performance of luminescent materials, cause waste of the high purity (rare earth) material and then incur significant financial losses [1]. The methods used to detect elements' valence (XPS, Mössbauer and XANES) are not sensitive enough for low concentrations and EPR is not suitable for powders. Obtaining quantitative data leaves a lot to hope for, too. To make the things worse, the two most common rare earth dopants in phosphors, Eu3+ and Tb3+, may exist in different oxidation states, Eu2+ and TbIV [1], as well. For the Eu3+ or Tb3+ doped R2O2S:Eu3+ and R 2O2SO4, the Eu2+ or TbIV may be formed since the manufacture of these phosphors involve reducing and/or oxidizing conditions. The qualitative observation of Eu2+ can usually be made based on its intense luminescence due to the parity-allowed electric dipole 4f6↔4f55d1 transitions. In contrast, the Eu3+ line emission is weaker despite the high quantum yield. TbIV does not luminesce, but this species may absorb the emission of Tb3+ and, in addition, may facilitate non-radiative processes reducing the efficiency of Tb3+ doped phosphors even further [1].

2. Results

In this work, the comparison between the experimental and calculated temperature-dependent paramagnetic susceptibilities was used to obtain quantitatively the concentrations of the valence impurity in Eu2O2S (Eu2+) and Tb2O2SO4 (TbIV), both containing nominally only R3+. The wave functions for the calculations were obtained from the analysis (Fig. 1) of the Eu3+ luminescence spectra [2,3]. Minute (ppm level) Eu2+ impurities could be defined due to the huge difference in the paramagnetic susceptibility of Eu2+ and Eu3+. However, temperatures below 50 K are then needed (Fig. 2). In contrast, the TbIV impurity in a Tb3+ host can be determined already at higher temperatures with similar susceptibility measurements. The latter method is based on comparing the slopes of the Tb3+/TbIV paramagnetic susceptibility vs. temperature curves. The results for the Tb3+/TbIV couple are less sensitive than for the Eu2+/Eu3+ one, however. Finally, the host independent temperature evolution of the paramagnetic susceptibility was calculated for Gd3+ (or Eu2+ or TbIV) to yield an analytical expression to be used universally.

1. References

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Are you currently a postgraduate student? (Yes/No)

N

Primary authors: PEDROSO, Cássio C.S. (University of São Paulo, Institute of Chemistry, São Paulo-SP, Brazil); BRITO, Hermi F. (University of São Paulo, Institute of Chemistry, São Paulo-SP, Brazil); MATOS, Jivaldo R. (University of São Paulo, Institute of Chemistry, São Paulo-SP, Brazil); Prof. HÖLSÄ, Jorma (University of Turku); RODRIGUES, Lucas C.V. (University of Turku, Turku, Finland); LASTUSAARI, Mika (University of Turku, Turku, Finland); MARYŠKO, Miroslav (The Academy of Sciences of the Czech Republic, Institute of Physics, Cukrovarnická 10, CZ-162 53 Praha 6, Czech Republic); PATURI, Petriina (University of Turku, Department of

Physics and Astronomy, Wihuri Physical Laboratory, FI-20014 Turku, Finland); RODRIGUES, Rodrigo V. (University of São Paulo, Institute of Chemistry, São Paulo-SP, Brazil)

Presenter: Prof. HÖLSÄ, Jorma (University of Turku)

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