Journal of Luminescence 197 (2018) 66–75

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Trends in Hamiltonian parameters determined by systematic analysis of f-d absorption spectra of divalent lanthanides in alkali-halides hosts: II. $CaCl_2:Ln^{2+}$ (Ln = Sm, Eu, Tm, and Yb)

Mirosław Karbowiak[a,*], Czesław Rudowicz[b,1]

[a] Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland
[b] Faculty of Chemistry, A. Mickiewicz University, Umultowska 89B, 61-614 Poznań, Poland

ARTICLE INFO

Keywords:
Rare earth alloys and compounds
Optical absorption spectroscopy
Crystal and ligand fields
$Ln^{2+}:CaCl_2$
Divalent Sm, Eu, Tm, and Yb

ABSTRACT

Systems containing divalent lanthanide elements (Ln^{2+}) are hard to synthesize and thus their characterization is still largely an unexplored area. The absorption spectra of most divalent Ln^{2+} ions were, until recently, obtained nearly exclusively for $Ln^{2+}:CaF_2$ crystals. In the first paper in a series devoted to systematic analysis of f-d absorption spectra of Ln^{2+} in alkali-halides hosts we presented new experimental data for Nd^{2+} and Dy^{2+} ions in $SrCl_2$ and reanalyzed available data for $SrCl_2$: Ln^{2+} (Ln = Sm, Eu, Tm, and Yb). The increased number of spectral data on the f-d transitions for Ln^{2+} ions makes $SrCl_2$ the second best studied matrix. The second paper in this series is devoted to $CaCl_2:Ln^{2+}$ (Ln = Sm, Eu, Tm, and Yb). The first absorption, emission, and excitation spectra for Sm^{2+}, Eu^{2+} and Yb^{2+} in $CaCl_2$ are reported. Using a uniform methodology based on a parametric Hamiltonian model proposed in Part I, a systematic analysis of the spectra is performed. This approach yields refined and consistent sets of the free-ion parameters and crystal-field (CF) ones. Systematic CF analysis of the large spectral dataset for $CaCl_2:Ln^{2+}$ consisting of a total of four ions allows revealing inherent trends across the Ln series. Our results enable partial verification of the trends uncovered in Part I for $Ln^{2+}:SrF_2$. It appears that the trends in the free-ion parameters and, to a lesser extent, CF ones observed for one Ln^{2+} ion are sufficiently systematic to allow for tentative predictions of the spectrum for any lanthanide ion based on the sets of parameters derived from the spectra obtained for another ion in the same matrix.

1. Introduction

Systematic studies of systems containing divalent lanthanide elements (Ln^{2+}) that involve analysis of spectral data performed for a series of Ln^{2+} ions in the same host have been rather scarce so far. Experimental [1–8] and theoretical [9–13] investigations of spectroscopic properties of Eu^{2+}, Yb^{2+}, Sm^{2+}, and Tm^{2+} carried out so far dealt primarily with various hosts. Until recently CaF_2 crystal [14] was a notable exception, since the absorption spectra for all divalent lanthanide (Ln^{2+}) ions, except for promethium, were obtained. However, the bands observed in the available spectra are broad and poorly resolved and therefore cannot be used for systematic analysis of Hamiltonian parameters. The second matrix in terms of the number of available experimental data on the f-d transitions for Ln^{2+} ions is $SrCl_2$ crystal. In recent years there have been reports concerning the spectral properties of divalent Ln elements: Sm^{2+} [4], Eu^{2+} [5], Tm^{2+} [15], and Yb^{2+} [16], which belong to the group of the so-called 'classic four' Ln elements that are most easily reducible from the trivalent to divalent state. Recently, the set of experimental data on absorption spectra of Ln^{2+} ions in $SrCl_2$ has been extended by two more elements, which so far have proved much more difficult to stabilize at the +2 oxidation level, i.e. Nd^{2+} [17] and Dy^{2+} [18].

The scarcity of sufficient sets of data on the spectral properties of Ln^{2+} ions in the same host and usage of different methodologies for their analysis have prevented uncovering systematic changes in Hamiltonian parameters, which determine specific spectral properties of Ln^{2+} ions in several hosts. The changes in pertinent parameters, which have been defined in Eq. (1) in our recent work [19] (hereafter referred to as Part I), may represent inherent trends across the Ln series. The studies of such trends for Ln^{2+} ions remain still largely an unexplored area, unlike for Ln^{3+} ions [20] where systematic trends have been observed for the f-f transitions. For the above reasons we have set on the project aiming at obtaining more pertinent datasets that would allow for studies of possible trends in Hamiltonian parameters In Part I

---

[*] Corresponding author.
E-mail address: miroslaw.karbowiak@chem.uni.wroc.pl (M. Karbowiak).
[1] On leave of absence from: Modeling in Spectroscopy Group, Institute of Physics, West Pomeranian University of Technology Szczecin, Al. Piastów 17, 70-310 Szczecin, Poland.

https://doi.org/10.1016/j.jlumin.2018.01.011
Received 16 November 2017; Received in revised form 8 January 2018; Accepted 9 January 2018

we have critically surveyed experimental data for Ln^{2+} in $SrCl_2$ and performed a systematic analysis of the spectra using a uniform methodology based on a parametric Hamiltonian model. Usage of uniform methodology is especially important in the case of divalent ions in view of the fact that the spectra of different ions are sensitive to varying degrees to variations of different parameters. Hence, such systematic analysis carried out simultaneously for several ions in the same matrix greatly increases the probability of obtaining reliable results. Moreover, the approach proposed in Part I has allowed for revealing systematic trends in parameter values occurring in a series of divalent Nd-Sm-Eu-Dy-Tm-Yb ions in $SrCl_2$ crystals. The identified trends greatly facilitate interpretation of new experimental results. Importantly, utilizing the sets of parameters derived from the spectra obtained for another ion in the same matrix it may become possible to predict spectra for other Ln^{2+} ions in the same or even different matrix for which experimental data are not yet available. We also hypothesized that the trends in the parameters describing Coulomb interaction between nf electrons, spin-orbit interactions for f- and d-electrons as well as Coulomb direct and exchange interactions between the $(n+1)d^1$ electron and the nf^{N-1} electrons should be characteristic for given ion and should not depend strongly on the matrix.

To verify this hypothesizes, we have recently embarked on a program to synthesize $CaCl_2$ crystals doped with Ln^{2+} ions, investigate their f-d spectra, and perform the quantitative analysis. $CaCl_2$ is a convenient matrix for such comparative study, because on the one hand the environment of the central ion is similar in both cases formed by the chloride ligands, and on the other hand the geometry of the environment is distinctly different. In the case of $SrCl_2$ Sr^{2+} ion is coordinated by eight ligands forming a regular cube with the local symmetry O_h (cubic) of the node occupying $Sr^{2+}(Ln^{2+})$. In case of $CaCl_2$, the central ion is surrounded by six chlorine atoms forming a disturbed octahedron. In $CaCl_2$ the actual site symmetry of $Ca^{2+}(Ln^{2+})$ ions is C_1, however, to make the problem tractable, as an initial approach the approximation to symmetry D_{2h} (orthorhombic) or even O_h (octahedral) may be considered. This approximation would allow estimating the crystal-field (CF) parameters for Ln^{2+} ions in $CaCl_2$ based on those obtained in $SrCl_2$.

An interesting aspect is also determining to what degree a distortion in symmetry would manifest itself in electronic spectra. Based on experimental spectroscopic results, the authors found [21] that the distortion of octahedral symmetry for Tm^{2+} in $CaCl_2$ induces in the 4–4f transitions an observable splitting of a few cm^{-1}, while no such symmetry reduction effect was observed for 4f-5d transitions. This observation has formed a basis for application of the approximation to symmetry O_h for interpretation of spectra at work [21]. On the other hand, the 5d states are much more sensitive to changes in the central ion environment than the 4f states, which are shielded by 5s and 5p electrons. Hence, distortions in symmetry should have more pronounced effect on the f-d band than the f-f ones.

In $SrCl_2$ the following ions: Nd^{2+}, Sm^{2+}, Eu^{2+}, Dy^{2+}, Tm^{2+} and Yb^{2+}, were analyzed [4,5,14–19], whereas for $CaCl_2$ the experimental dataset is not so extensive. The only divalent Ln^{2+} ion for which the spectral properties of $CaCl_2{:}Ln^{2+}$ crystals have been reported to date is Tm^{2+} [21], however, no CF analysis was performed for Tm^{2+} ion. In the present study, apart from the absorption spectra for $CaCl_2{:}Tm^{2+}$, we report also, the absorption, emission, and excitation spectra for Sm^{2+}, Eu^{2+} and Yb^{2+}, which, to the best of our knowledge, are first such published spectra. Importantly, CF analysis of the dataset consisting of a total of four ions allows for identification of possible trends in Hamiltonian parameters and their comparison with the results obtained for $SrCl_2$ in Part I.

2. Experimental details

$CaCl_2$ single crystals doped with divalent lanthanide ions at were grown by the Bridgman method. So-obtained pure $CaCl_2$ single crystal was crushed and mixed with appropriate amount of $LnCl_2$, then placed in a vitreous carbon crucible, which was put into silica ampoule and heated for several hours at 720 K under high dynamic vacuum. After sealing under vacuum the ampoule was lowered through the vertical furnace at 1100 K at a rate of 5 mm/h. Lanthanide dichlorides used in this procedure was earlier synthesized via metallothermic route [22] in reaction of anhydrous $LnCl_3$ with Ln powder in a sealed niobium tube. Nominal concentration of Ln in $CaCl_2$ crystals was 0.25%, 0.1%, 0.5% and 0.1% w/w for Sm, Eu, Tm and Yb, respectively.

Absorption spectra were recorded in the 2500 − 200 nm range at 4.2 K on a Cary-5000 UV–Vis–NIR spectrophotometer, equipped with an Oxford Instrument model CF1204 cryostat. Emission and excitation spectra were recorded at 77 K on an Edinburgh Instruments FLSP 920 spectrofluorimeter using the Optistat DN liquid nitrogen cryostat (Oxford Instrument). For excitation stationary 450 W Xe lamp, microsecond pulsed 60 W Xe lamp or EPL-375 ps pulsed diode laser were used.

3. Crystal structure and axis systems

$CaCl_2$ crystallizes in the orthorhombic space group Pnnm [23]. The coordination polyhedron of six chloride ions around the Ca^{2+} ion may be considered as a distorted octahedron (see, Fig. 1a), whereas the actual local Ca^{2+} site symmetry is triclinic C_1. The Ca-Cl distance for the four equatorial Cl1-Cl4 atoms lying in one plane is 0.2765 nm and for the two axial Cl5 (and Cl6) ions 0.2704 nm. The angles between the axial Cl5 (or Cl6) ion and the equatorial Cl1-Cl4 ions are 90.443° for Cl5-Ca-Cl1 and Cl5-Ca-Cl2, while 89.557° for Cl5-Ca-Cl3 and Cl5-Ca-Cl4. These distances are close to those expected for a regular octahedron. The main distortion of the octahedral structure is that the angles between the equatorial Cl1-Cl4 elements should all be 90° for a perfect octahedron, while for $CaCl_2$ the angles are: 98.82° for Cl1-Ca-Cl2 and Cl3-Ca-Cl4, while 81.28° for Cl1-Ca-Cl4 and Cl2-Ca-Cl3. Importantly, the spectral analysis described below indicates that the departure from perfect octahedron is too large for application of the approximation to symmetry O_h. However, it is worth noting that if the axis system (x, y, z) is chosen as shown in Fig. 1, i.e., with the Cl5 atom lying on the z-axis and the x-axis coinciding with the bisector of Cl1-Ca-Cl2 (and Cl3-Ca-Cl4), than to obtain an approximate site symmetry D_{2h} it is enough to assume that the Cl5 and Cl6 atoms are lying on one axis. This approximation seems to be a good one because the deviation from this axis is only 0.443°. The results of calculations of the geometric coefficients in the superposition model (SPM) [24] presented in Section 6 confirm that D_{2h} is a very good approximation of the actual symmetry.

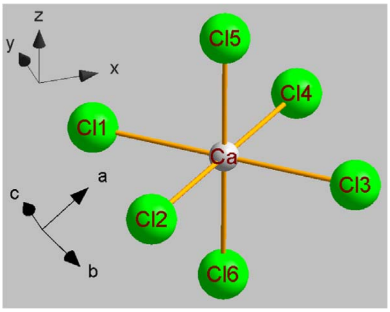

Fig. 1. The polyhedron $CaCl_6^{4-}$ in $CaCl_2$ with the orientation of the pertinent axis systems: the crystallographic axis system (a, b, c) and the Cartesian axis system (x, y, z) appropriate for the approximate symmetry D_{2h}.