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Local perturbations due to rare-earth (R^{3+}) doping

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Abstract

The origin of some complex structure in the absorption and emission spectra of rare-earth ions in different host lattices were analyzed in terms of local perturbations caused by doping. The modifications in the strength of the crystal field effect resulting from the doping were investigated in the rare-earth oxide, oxyfluoride, oxychloride and ethyl sulfate hosts. The size effect on the dopant ion in the cubic *C*-type rare-earth oxide hosts was discussed and a parallel was made to the pressure effect on the emission spectra of the Eu^{3+} ions. The complexity of the emission spectra of the Eu^{3+}-doped rare-earth calcium oxoborates $EuCa_4O(BO_3)_3$ and $GdCa_4O(BO_3)_3$:Eu^{3+} was used to illustrate the inhomogeneous distribution of the dopant. Another source of complex spectra, the pair formation, was discussed for the R^{3+}-doped rare-earth oxide and garnet hosts.

Keywords: Doping; Local perturbations; Size effect; Garnets; Oxides; Rare-earths

1. Introduction

The rare-earth (*R*) elements are used extensively not only in luminescent materials as solid state lasers but also in e.g., magnetic materials. Although the non-doped rare-earth compounds with well-defined stoichiometry can also be employed, most frequently the rare-earths enter as dopants into different host matrices [1]. The doping can usually occur without undesired consequences, but, even at very low dopant concentrations, the rare-earth ion embedded in a crystal host lattice can induce perturbations in its neighborhood [2]. Due to the low concentration, optical spectroscopy is among the very few tools sensitive enough to analyze these local perturbations, especially so when the R^{3+} doping occurs in isostructural series of rare-earth compounds. Stresses and strains in the lattice can be created due to the "size effect" even by a dopant with the same charge as that of the matrix cation replaced, but with different size. On the other hand, the effect of the lattice on the dopant may be non-negligible since, for example, the lattice may increase the covalent character in the *R*-ligand bonding [3]. When the R^{3+} dopant replaces the matrix cation the lattice rearrangements emerged as well as the expansion of the 4*f* wave functions due to increased covalent bonding may induce modifications in the free ion interactions and/or in the crystal field (c.f.) strength. Even the local symmetry around the R^{3+} ion may be modified and satellite lines due to R^{3+}–R^{3+} pairs or other R^{3+} associations may then be observed. The satellite lines are due to a slight modification of the single ion energy levels.

This work presents different quantitative data to demonstrate the dopant–host effects in selected R^{3+}-doped and non-doped rare-earth compounds. New data is reported especially for the rare-earth calcium oxoborates, $RCa_4O(BO_3)_3$ (RCOB). The data are analyzed and compared with the already known data on R^{3+} ions for rare-earth oxide (R_2O_3) [4,5], oxyfluoride (ROF) [6,7], oxychloride (ROCl) [8,9], ethyl sulfate ($R(C_2H_5SO_4) \cdot 9H_2O$) [10] and garnet ($R_3M_5O_{12}$) [11] hosts. The effect of the size difference between the dopant and the host cation on the strength of the crystal field and on the pair formation is discussed.

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2. Experimental

The rare-earth oxoborate samples used in this study were prepared by solid-state reactions both in single crystal and powder form. The single crystals were synthesized by the Czochralski technique in an iridium crucible under nitrogen atmosphere. The powders were obtained from stoichiometric $CaCO_3$, H_3BO_3 and R_2O_3 mixtures which were ground, mixed and then homogenized during 10 min. The powders were subsequently pressed by an isostatic press into disks which were first heated at 950°C for 15 h to decompose $CaCO_3$ and H_3BO_3. Then the disks were ground and pressed once again in order to obtain more homogeneous products of higher density. The disks were finally heated for 36 h at 1400°C and 1325°C for $GdCa_4O(BO_3)_3$:Eu^{3+} and $EuCa_4O(BO_3)_3$, respectively. The purity of the powder samples was verified by routine X-ray powder diffraction measurements.

The luminescence of the $EuCa_4O(BO_3)_3$ and $GdCa_4O(BO_3)_3$:Eu^{3+} samples were excited by the different lines of a 5 W Spectra Physics Ar^+ ion laser. The selective emission from the $^5D_0$ level was obtained with a Spectra Physics 375/376 continuous wave rhodamine 6G dye laser pumped by the Ar^+ ion laser.

3. Results and discussion

3.1. Doping and crystal field strength

The comparison of the c.f. effect of the surrounding lattice on different R^{3+} ions embedded in various hosts with different site symmetries is not an easy task. This comparison may, however, be facilitated by employing the c.f. strength parameter N_V [12,13]:

$$N_v = \left[\sum_{k,q}\left(\frac{4\pi}{2k+1}\right)\left|B_q^k\right|^2\right]^{1/2}, \tag{1}$$

where B_q^k are the individual c.f. parameters usually determined by simulating the experimental energy level schemes of the R^{3+} ions by phenomenological models.

According to the general trend well-documented in literature [10,14], the strength of the crystal field increases in a series of isomorphic non-doped compounds with increasing ionic radius of the R^{3+} cation as revealed for the rare-earth oxyfluoride and ethyl sulfate series (Fig. 1). On the other hand, an opposite evolution has been obtained for the rare-earth oxychloride series. This unconventional evolution of the c.f. strength can be due to the increasing strains in the ROCl structure which eventually lead to a structural change from ErOCl onwards [15]. The polarization effects and the strongly covalent $(REO)^+$ group present in the layered ROCl structure may have additional contributions to this evolution, as well.

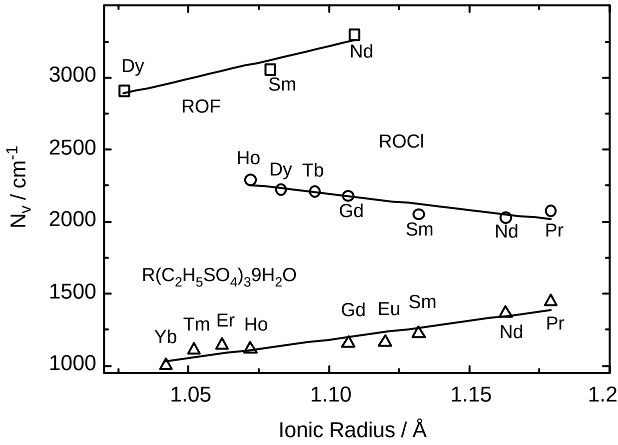

Fig. 1. Evolution of the crystal field strength in selected non-doped rare-earth compounds (□: ROF, CN = 8; ○: ROCl, CN = 9; △: $R(C_2H_5SO_4)\cdot 9H_2O$, CN = 9).

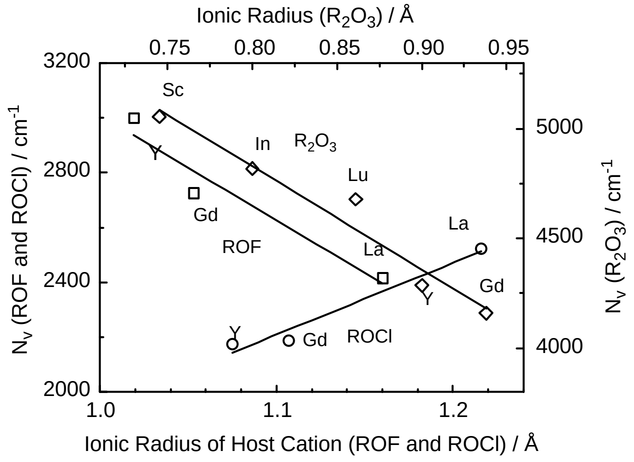

Fig. 2. Evolution of the crystal field strength in selected Eu^{3+}-doped rare-earth compounds (◇: R_2O_3, CN = 6; ○: ROCl, CN = 9; □: ROF, CN = 8).

When the dopant replaces the host cation of different ionic radius, the c.f. strength depends on the difference between the ionic radii of the two ions [16]. This size effect can be illustrated by the concept of internal pressure exerted by the host on the dopant. The comparison between the host effect in the Eu^{3+}-doped cubic C-type rare-earth oxide series (R = Gd, Y, Lu, In and Sc) and the effect of an external pressure on the $^5D_0 \rightarrow {}^7F_2$ emission line position of Y_2O_3:Eu^{3+} has shown that these effects are rather similar [16]. The resulting internal pressure in the Eu^{3+}-doped R_2O_3 ranges from −2 to 31.6 kbar (from Gd to Sc) in comparison with that in Y_2O_3. The effects created by doping on the c.f. strength can thus be significant if a large enough size difference is present.

In general, for the Eu^{3+}-doped samples with the mean R-ligand distance shorter than the corresponding distance in Eu_2O_3, the c.f. strength is increased due to the decreased distance between Eu^{3+} and the ligand. Consequently, longer Eu-ligand distances decrease the c.f. strength, which is clearly observed for the rare-earth oxides and oxyfluorides (Fig. 2). Again, the R oxychloride series shows an opposite evolution, which may be due to the contributions noted above.

3.2. Homogeneity and distortion of local symmetry

The rare-earth calcium oxoborates, $RCa_4O(BO_3)_3$, with Nd^{3+} or Yb^{3+} as dopants are promising laser and non-linear optical materials for compact laser sources. In order to avoid power losses, very good homogeneity is required of the crystal lattice. However, at high dopant concentration the homogeneity is jeopardized as seen in the emission spectra of $EuCa_4O(BO_3)_3$ and $GdCa_4O(BO_3)_3:Eu^{3+}$ powders (Fig. 3) which show marked differences between the spectra of the non-doped and doped host lattices. The lack of homogeneity and distortions in the local symmetry in the lattice surrounding the dopant were observed also from the dependence of the luminescence spectrum on the excitation energy used. The inhomogeneous dopant distribution thus leads to a decrease in the symmetry of some R^{3+} sites [17].

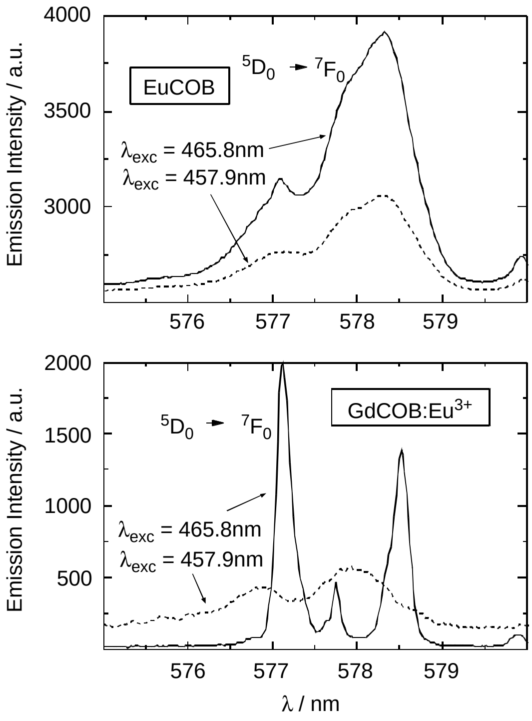

Fig. 3. Emission spectra of $EuCa_4O(BO_3)_3$ and $GdCa_4O(BO_3)_3:Eu^{3+}$ ($x_{Eu}=0.05$) powders measured at two different Ar^+ ion laser excitation energies.

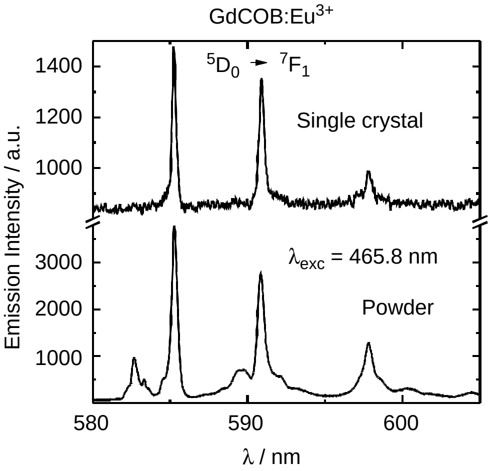

Fig. 4. Emission spectra of $GdCa_4O(BO_3)_3:Eu^{3+}$ ($x_{Eu}=0.05$) single crystal and powder.

Similar features due to local distortions were observed in the spectra of both the single crystal and powder samples, but differences were observed, as well. For the single crystal, there seems to be only one emitting R^{3+} site, whereas in the powder spectrum additional sites are observed (Fig. 4). The extra sites may be due to local defects or the R^{3+} ions occupying the two Ca^{2+} sites in addition to the lone Gd^{3+} site [14]. Also pair and higher cluster formation may lead to the complicated spectra.

3.3. R^{3+}–R^{3+} pair formation

The satellite lines observed in the absorption or emission spectra of R^{3+} dopants in single crystals have been assigned to R^{3+}–R^{3+} pairs on the grounds of several arguments: (i) the quadratic increase of the absorbance with R^{3+} concentration (for low concentrations the intensity is proportional to nC^2 where n is the number of equivalent lattice sites around a given site and C is the dopant concentration), (ii) the relative intensities of satellites in correlation with the structure and (iii) the luminescent lifetimes.

Although in garnets such as $Y_3Al_5O_{12}$ or $Gd_3Ga_5O_{12}$, the distribution of the R^{3+} dopants is random, one can have pairs even at rather low dopant concentrations. Special attention has been paid to Nd^{3+}-doped YAG, $Y_3Al_5O_{12}:Nd^{3+}$, because of its importance in laser applications. The R^{3+} dopants usually substitute for the ions in the large dodecahedral D_2 sites. Two types of Nd^{3+} satellite lines the intensities of which increase quadratically with the Nd^{3+} concentration have been identified: M_1 and M_2 corresponding to the Nd^{3+}–Nd^{3+} near neighbors and the next near neighbors at the distances of 3.67 and 5.12 Å, respectively. For different transitions shifts between pair and isolated ion lines up to 5–6 cm^{-1} for M_1 and 2–3 cm^{-1} for M_2 have been measured [11,16]. The M_2/M_1 intensity ratio equal to

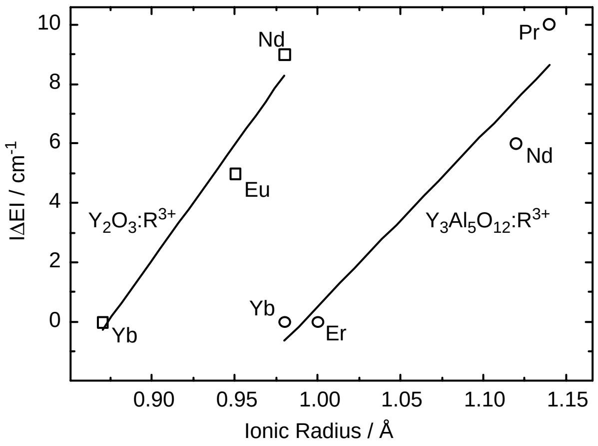

Fig. 5. Maximum shifts of pair lines from isolated ion lines in R^{3+}-doped *C*-type yttrium sesquioxide and aluminum garnet (□: Y_2O_3: R^{3+}, CN = 6; ○: $Y_3Al_5O_{12}$: R^{3+}, CN = 8).

two is in agreement with the crystal structure. The reported data on pairs usually refer to dopants with large ionic radii compared with that of the host cation [18,19] suggesting that the pairs are formed due to stress effects caused by the size mismatch.

In the *C*-type rare-earth oxides the R^{3+} ions occupy two sites with C_2 and S_6 symmetries. One can then expect several types of R^{3+}–R^{3+} pairs at the nearest distances. Though the absorption spectra of Eu^{3+} in Y_2O_3 for both sites present satellite structure, only satellites near the S_6 lines have been analyzed [20–22], and two satellites were assigned to the S_6-C_2 pairs [20]. Studies of the Nd^{3+}-doped Y_2O_3 evidenced at least two satellites in the absorption spectra [23]. They were observed near the C_2 main lines and assigned to two types of pairs: (i) two identical Nd^{3+} at nearest distances, i.e., the C_2-C_2 pairs (8 sites at distances shorter than 4 Å) and (ii) two dissimilar Nd^{3+}, i.e., the C_2-S_6 pairs (4 + 4 sites at 3.54 and 4 Å, respectively). The spectra of Eu^{3+} in Gd_2O_3 or Yb^{3+} in Y_2O_3 [24] do not present shifted lines for pairs, while Eu^{3+} and Nd^{3+} in Y_2O_3 or Yb^{3+} in Sc_2O_3 [24] present such lines, which, again, suggests that the pair formation results from the ionic radius mismatch between the dopant R^{3+} and host cation.

The effect of the ionic radius mismatch can be clearly observed in the spectra. For both the rare-earth oxides and garnets the difference between the line of the isolated ion and those resulting from pair formation increases with increasing internal pressure (Fig. 5), i.e., with the increasing size difference between the dopant and host cation.

4. Conclusions

Local perturbations resulting from the doping of rare-earth compounds by different R^{3+} ions were clearly observed in the spectroscopic data. The modifications in the strength of the crystal field were found to play an important role in the manifestation of the local perturbations. However, the evolution of the crystal field strength as a function of the host cation radius was not always easily predictable. The sample form, i.e., single crystal vs. powder, was found to influence the emission spectra since for the calcium oxyborate single crystal samples only one R^{3+} site was observed, while for the powder samples several sites were observed. The R^{3+}–R^{3+} pairs in sesquioxide and garnet hosts were observed to exist mainly when the size difference between the dopant and the host cation was positive and large enough.

Acknowledgments

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