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Influence of high hydrostatic pressure on energetic structure and electron-lattice coupling of transition metal and rare earth related centers in solids

M. Grinberg*, J. Barzowska, W. Gryk

Institute of Experimental Physics, University of Gdansk, Wita Stwosza 57, 80-952 Gdansk, Poland

Abstract. We present the results of the photoluminescence of the crystals doped with transition metals or rare earth ions obtained under high hydrostatic pressure up to 300 kbar applied in diamond anvil cells (DAC). We have focused on Al_2O_3 , YAlO_3 LLGG and YAG garnets and LiNbO_3 , and LiTaO_3 perovskites doped with Cr^{3+} , Ti^{3+} and Ce^{3+} . We have observed the pressure induced red shift of the $d \rightarrow f$ emission in the case of materials doped with Ce and blue shift of the ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ and ${}^2\text{E} \rightarrow {}^2\text{T}_2$ emission in the case of materials doped with Cr^{3+} and Ti^{3+} , respectively. Considering our experimental data we have calculated the local compressibilities of the materials and found that almost in all cases this quantity is smaller than compressibility of the bulk.

Keywords: high pressure spectroscopy, Ce^{3+} , Cr^{3+} , Ti^{3+} , garnets, perovskites, elastic properties, electron -lattice coupling

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1. Introduction

Luminescent solid state materials comprised of insulating host lattices (normally oxides, chlorides and fluorides) activated by rare earth and transition metal ions continue to be an active area of research. These materials are desirable for practical applications for several reasons including mechanical strength, durability, chemical inertness, portability, frequent ease of chemical synthesis, and diversity of properties. All considered materials are characterized by the broad band gap (10 eV) [1]. The activity arises from the promise in areas such as solid state lasers, optical communications, scintillation, medical procedures, imaging, displays, flow cytometry, holography, and remote sensing [2–3].

Transition metals and rare earth ions contribute to the energetic structure of the system via localized states with energies inside the forbidden gap of the host materials. These states are occupied by the electrons from the unfilled internal electronic shells $3d^n$ ($1 \leq n \leq 10$) in the case of transition metals and $4f^n$ or $4f^{n-1}5d^1$ ($1 \leq n \leq 14$) in the case of rare earths. Although $3d$ and $5d$ electrons are

localized at the transition ion, they extend enough to interact with the nearest neighbor host ions. As a result, the energetic structure of transition metals and rare earths is different in different hosts.

The sensitivity of the energetic structure of transition ions on the host caused our interests in high pressure spectroscopy of these systems. The high hydrostatic pressure applied in the diamond anvil cell (DAC) diminishes the distance between the ion and ligands. As a consequence, the influence of ligands on localized electrons is stronger. High pressure spectroscopy has been extensively applied for the investigation of $3d-3d$ optical transitions in transition metal ions in solids [4–5]. One can find the review of earlier works on this topic in [4]. The author of this paper has used high pressure spectroscopy for characterization of Cr^{3+} ions in LiNbO_3 , LiTaO_3 crystals [6–9] and garnet crystals [10] as well as glasses [11]. In recent years, high pressure has been used for investigation of the emission related to $4f^{n-1}5d^1 \rightarrow 4f^n$ transitions [12–14]. In this contribution, we summarize our investigations on high pressure spectroscopy of Ti^{3+} , Ce^{3+} and Cr^{3+} ions in various materials.

2. Experimental results

2.1 High pressure spectroscopy of Ti^{3+} and Ce^{3+}

The simplest energetic structure have the Ti^{3+} and Ce^{3+} ions. It is determined by single electron that occupies the terms belonging to the $3d^1$ electronic configuration and $4f^1$ or $5d^1$ electronic configurations in the case of Ti^{3+} and Ce^{3+} , respectively. We have investigated Ti doped Al_2O_3 and $YAlO_3$ crystals. In both materials Ti^{3+} substitutes Al^{3+} ion in octahedral coordination of the six O^{2-} ligands. According to the crystal field theory [15], the $3d^1$ state is splitted into the 2E and 2T_2 states, energies of which are given by:

$$E({}^2E) = 6Dq \quad (1)$$

$$E({}^2T_2) = -4Dq \quad (2)$$

Crystal field strength parameter depends on the central ion-ligand distance according to relation $Dq \propto a^{-n}$ where exponent n depends on the nature of ligands.

We have investigated the Ce^{3+} ions incorporated in the $Y_3Al_5O_{12}$ and $Gd_3Sc_2Al_3O_{12}$. In these hosts the Ce^{3+} ions occupy the dodecahedrally coordinated Y^{3+} and Gd^{3+} positions, respectively. In both cases the ground electronic configurations $4f^1$ splits due to strong spin-orbit interaction into the ${}^2F_{7/2}$ ground state and ${}^2F_{5/2}$ excited state. It is assumed further that electron in these state is well screened from interaction with the ligands. The excited electronic configuration that is $5d^1$ interacts with the lattice in the same way as the $3d^1$, thus for dodecahedrally coordinated system the $5d^1$ splits into the 2E and 2T_2 states that energies are given by:

$$E({}^2E) = -\frac{16}{3}Dq \quad (3)$$

$$E({}^2T_2) = \frac{32}{9}Dq \quad (4)$$

The energetic structure of these two systems is presented in Fig. 1, *a* and *b*. Actually, the energy of the lowest state of the $5d^1$ electronic configuration of the Ce^{3+} ion in lattice is diminished by the quantity of depression energy E_{depr} [16]:

$$E_{depr} = -\frac{16}{3}Dq + E_{cen} \quad (5)$$

where E_{cen} is the centroid shift related to changes in the ligands polarization that accompanies $4f^1-5d^1$ transition. One considers that

$$Dq \propto \frac{1}{Q^n} \quad (6)$$

and

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$$E_{cen} \propto \frac{1}{Q^n} \quad (7)$$

In the standard crystal field model [17], $n = 5$, whereas according to the ligands polarization model [18], $n' = 6$.

According to the Fig. 1 *a* and *b*, one expects that pressure induces a blue shift of the emission of the Ti^{3+} and a red shift of the emission of the Ce^{3+} . Actually such shifts have been observed. Typical emission spectra are presented in Fig. 2, *a* and *b*. One can see that the spectral lineshape almost does not depend on pressure. One notices that maxima of the emission bands shift linearly with pressure. Thus, one can describe these shifts by respective pressure coefficients. Table 1 contains data obtained for Ce^{3+} and Ti^{3+} ions. Here the pressure shifts of the absorption maxima of the lowest absorption band for some materials are presented.

2.2. High pressure spectroscopy of Cr^{3+}

Cr^{3+} ion occupies usually octahedrally coordinated sites. Energetic structure of the lowest states of the Cr^{3+} system is presented in Fig. 1, *c*. One can see that depending on the crystal field strength the first excited state is the 4T_2 or 2E . In the low field systems, the 4T_2 state has lower energy than the 2E state and Cr^{3+} exhibits broad band emission related to the ${}^4T_2 \rightarrow {}^4A_2$ transition. In the high field case, the 2E state is lower in energy and sharp, structured (*R*-lines) emission relate to ${}^2E \rightarrow {}^4A_2$ transition is observed. Energy of the 4T_2 state with respect of the ground state is equal to $10Dq$. Thus similarly like in the case of Ti^{3+} in the case of the Cr^{3+} system one expects pressure induced blue shift of the ${}^4T_2 \rightarrow {}^4A_2$ emission band. Luminescence spectra of the $LiTaO_3:Cr^{3+}$ obtained for different pressure are presented in Fig. 2, *c*. In Table 1, the pressure blue shift of ${}^4T_2 \rightarrow {}^4A_2$ emission band in various crystals doped with Cr^{3+} are summarized.

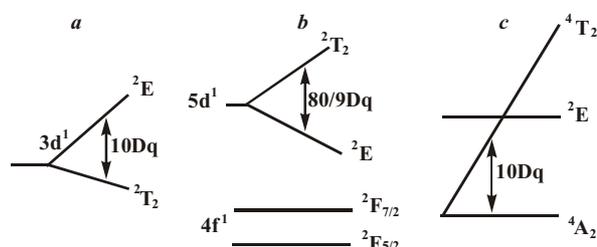


Fig. 1. Energetic structure of the Ti^{3+} ion in octahedral position (*a*), Ce^{3+} in dodecahedral position (*b*) and Cr^{3+} in the octahedral position (*c*). For the Cr^{3+} only the 4A_2 , 4T_2 and 2E states are presented.

Table 1. Spectroscopic data and calculated parameters for transition metal and rare earth ions in different materials

| Material | E_{depr} , [16] cm^{-1} | E_{em} , cm^{-1} | dE_{em}/dp , $\text{cm}^{-1}/\text{kbar}$ | E_{abs} , cm^{-1} | dE_{abs}/dp , $\text{cm}^{-1}/\text{kbar}$ | B , kbar | nK |
|--|--|--------------------------------|--|---------------------------------|---|---------------|-------------|
| YAG:Ce ³⁺ [14] | 27570 | 19100±100 17560±100 | -12.5±0.7 -11.8 0.7 -8.3 0.5 | 21750±100 | -12.5 0.7 | 1870 [19] | 2.85 * |
| GSAG:Ce ³⁺ | 2 7000 | 17340±100 15250±100 | -7.5 0.5 13 2[20] | 22320±100 | -15.2 0.7 | 1916** | 2.67 |
| LLGG:Cr ³⁺ | | 11700 [20] | 5.40 [5] | 15033[20,21] | 8.4 3 [24] | 1330[22,23] | 3.45 (3.88) |
| Al ₂ O ₃ :Cr ³⁺ | | 14790 *** | 5.93 [5] | 17950 50[24] | 6.96 [5] | 2420 [25] | 3.41 (3.71) |
| Al ₂ O ₃ :Ti ³⁺ | | 13670 [5] 12450 [5] | 19.6 [26] | 20590 [5] 17690 [5] | 8.52 [5] | 2420 [25] | 2.98 |
| YAlO ₃ :Ti ³⁺ | | 16330 [26] | 13.5 13.5[9] | 22880 [26] 20400 [26] | | 2004 [27] | 5.44 |
| LiNbO ₃ :Cr ³⁺ | | 10800 | | 15000 | | 1058 [28] | 2.85 (3.31) |
| LiTaO ₃ :Cr ³⁺ | | 11020 | | 15820 | | 1057 [28] | 2.7 (3.22) |
| YAG:Cr ₃ ⁺ | | | | 16500 [29] | 9****[29] | 1870 [19] | 3.06 |

* These data were calculated under assumption that pressure absorption and emission pressure coefficients are the same.

** The calculated here bulk moduli were taken from [30]

*** These data were calculated from the values of the absorption maximum and electron-lattice coupling energy $S\hbar\omega$ in accordance with the following relation

$$E_{em} = E_{abs} - 2S\hbar\omega$$

****The pressure shift was calculated from the analysis of R line lifetime dependence on pressure

3. Discussion

One considers that pressure causes an increase of crystal field according to relation

$$\frac{dDq}{dp} = -nDq \frac{1}{a} \frac{da}{dp} = nDq \frac{K}{3B}, \quad (8)$$

where B is the bulk moduli of material. The dimensionless coefficient K

$$K = \frac{a_0}{a} \frac{da}{da_0}, \quad (9)$$

where a_0 and a is the lattice constant and central ion-ligand distance, respectively, describes the way in which the macroscopic effect of pressure modifies the local environment of the central ion. $K = 1$, $K < 1$ and $K > 1$ means that the compression of the ion-ligand system is the same, smaller and larger than compression of the bulk lattice.

Since, in the excited state, the system is characterized by another distribution of electron charge than that in the ground state, after excitation the lattices ions shift a little to adapt to the new charge distribution. As a result, lattice relaxes and total energy of the system diminishes. The situation is described by configurational coordinate diagram presented in Fig. 3. The energy of lattice relaxation $S\hbar\omega$ may also depend on pressure. Thus, one obtains

$$\frac{dE_{abs}}{dp} = \frac{dE_{em}}{dp} + 2 \frac{dS\hbar\omega}{dp}. \quad (10)$$

In the case of the Ti³⁺ and Cr³⁺ systems, one can relate the pressure changes of the absorption peak to the pressure changes of the crystal field strength by

$$\frac{dE_{abs}}{dp} = 10 \frac{dDq}{dp} = 10Dq \frac{nK}{3B}. \quad (11)$$

Usually it is difficult to measure pressure dependence of the absorption spectrum. Therefore, instead of absorption we use the emission. Neglecting the dependence of the lattice relaxation energy on pressure, one obtains:

$$\frac{dE_{em}}{dp} = 10 \frac{dDq}{dp} = 10Dq \frac{nK}{3B}. \quad (12)$$

In the case of Ce³⁺, one can consider the relation:

$$\frac{dE_{abs}}{dp} \approx -E_{depr} \frac{nK}{3B}, \quad (13)$$

that is valid under condition that exponents (in relations (6) and (7)) are very similar; $n \approx n'$. Relations (11) and (13) allows to calculate quantity nK . Than assuming that the exponent value is known, one can calculate the local compressibility K . The results of calculations are listed in Table 1. One can see that almost in all the cases quantity nK is significantly smaller than 5. The exception is YAlO₃:Ti³⁺ system.

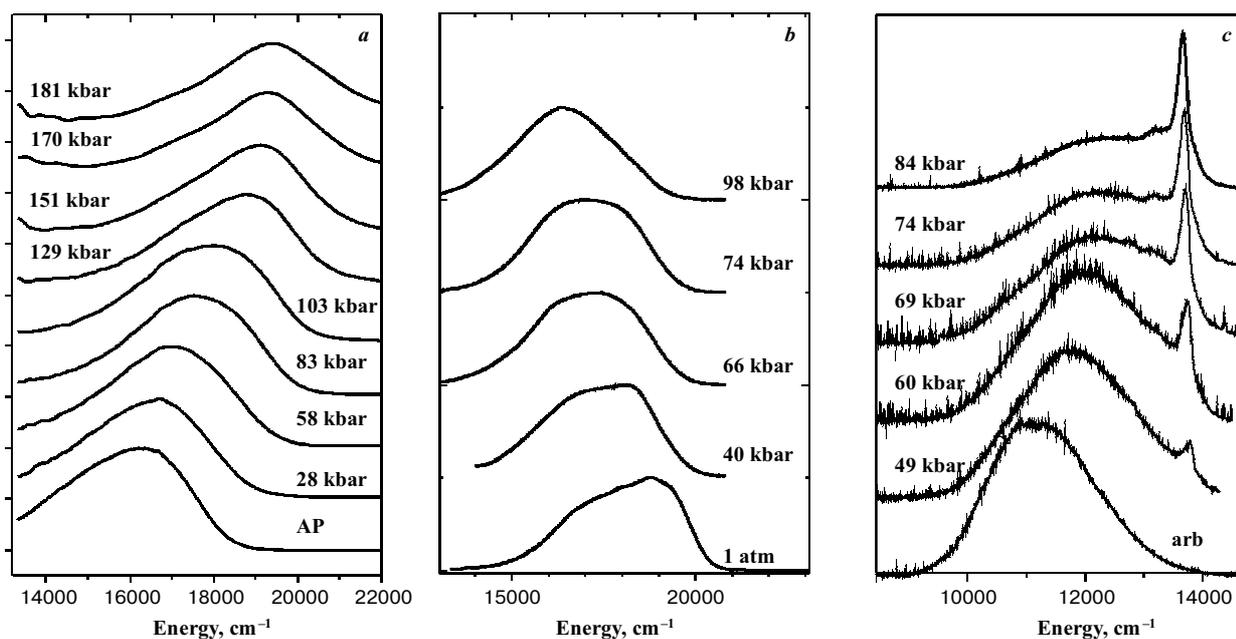


Fig. 2. Room temperature emission spectra of the $\text{YAIO}_3:\text{Ti}^{3+}$ (a), $\text{YAG}:\text{Ce}^{3+}$ (b) and $\text{LiTaO}_3:\text{Cr}^{3+}$ (c) systems obtained at different pressures applied in diamond anvil cell.

Assuming that the exponent is $n \approx 5$, the local compressibility in the vicinity of the dopant ion is significantly smaller than the bulk compressibility, $K < 1$.

4. Conclusions

We have discussed the dependence of $d-d$ and $d-f$ transition energies in the case of Ti^{3+} , Cr^{3+} and Ce^{3+} on the high hydrostatic pressure. Using the crystal field approach, we have related the pressure rates energy of the respective emission and absorption bands on compressibility (elastic moduli) of the material. In all the cases, apart of $\text{YAIO}_3:\text{Ti}^{3+}$, we have found that the compressibility of the dopant local environment is almost two times less than the compressibility of bulk materials. In the exceptional case, this local compressibility and the bulk one possess practically the same value.

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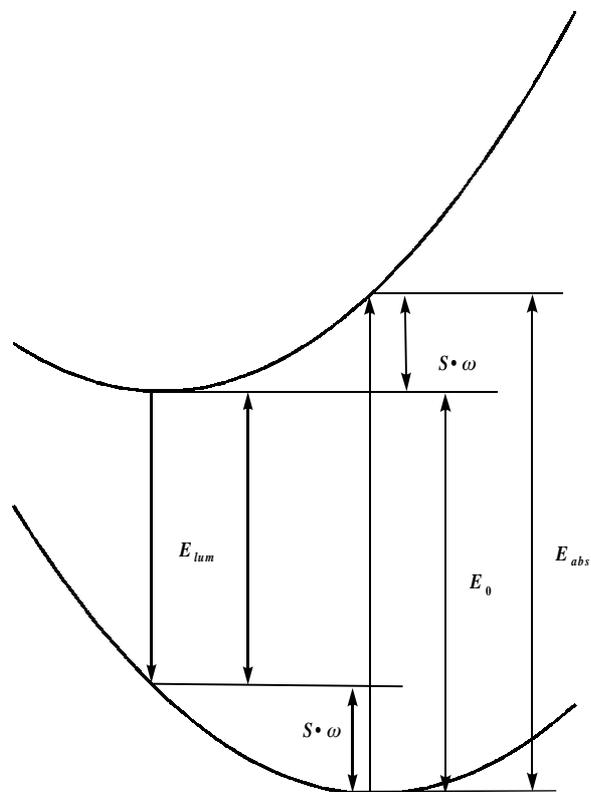


Fig. 3. Configurational coordinate model of the system strongly interacting with lattice.

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