

Sebastian Mahlik, PhD
Institute of Experimental Physics,
University of Gdańsk,
57 Wita Stwosza St., 80-308 Gdańsk

Summary of scientific achievements

(as attachment for a habilitation procedure proposal)

Appendix 3
(Załącznik nr 3)

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1. First and last name

Sebastian Mahlik

2. Education and scientific degrees

PhD in physics

2010, Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, thesis entitled: „Impurity-trapped Exciton States in Eu^{2+} Doped Fluorides and Pr^{3+} Doped Oxides” defended with honors, supervisor: professor Marek Grinberg, PhD.

MSc in physics

2005, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, thesis entitled: ”Optical properties of $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ thin layers obtained by laser ablation synthesis” supervisor: Przemysław Płóciennik, PhD.

3. Information on employment in scientific institutions

assistant professor
(adjunct)

01. 10. 2012 - till now

Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk.

postdoctoral

01.10.2010 - 30.09.2012

as a post-doc in the frame of project WND-POIG.01.01.02-02-006/09 *NEW LOKS new efficient phosphors for lighting and solar concentrators* Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk.

4. Scientific achievements

Indication of achievement resulting from Article 16 Section 2 of the Act on University Degrees and the University Title and on University Degrees and the University Title in the Field of Fine Arts of March 14, 2003 (Journal of Laws No. 65, item 595, with later amendments):

Monothematic series of publications [H1-H12].

a) title of scientific achievement

Influence of intermediate states on the spectroscopic properties of lanthanide ions doped dielectric lattices.

b) list of publications constituting the scientific achievement

H1. S. Mahlik, M. Behrendt, M. Grinberg, E. Cavalli, M. Bettinelli, *Pressure effects on the luminescence properties of $\text{CaWO}_4:\text{Pr}^{3+}$* , *Optical Materials* **34** (2012) 2012-2016; IF(2012)=1.918

H2. S. Mahlik, E. Cavalli, M. Bettinelli, M. Grinberg, *Luminescence of $\text{CaWO}_4:\text{Pr}^{3+}$ and $\text{CaWO}_4:\text{Tb}^{3+}$ at ambient and high hydrostatic pressures*, *Radiation Measurements*, **56** (2013) 1-5, IF(2013)=1.140

H3. S. Mahlik, M. Grinberg, E. Cavalli and M. Bettinelli, *High pressure luminescence spectra of $\text{CaMoO}_4:\text{Pr}^{3+}$* , *Journal of Physics-Condensed Matter* **24** (2012), 215402, IF(2012)=2.355

H4. S. Mahlik, M. Behrendt, M. Grinberg, E. Cavalli, M. Bettinelli, *High pressure luminescence spectra of $\text{CaMoO}_4:\text{Ln}^{3+}$ ($\text{Ln} = \text{Pr}, \text{Tb}$)*, *Journal of Physics-Condensed Matter* **25** (2013), 105502, IF(2013)=2.223

H5. S. Mahlik, A. Lazarowska, B. Grobelna, M. Grinberg, *Luminescence of $\text{Gd}_2(\text{WO}_4)_3:\text{Ln}^{3+}$ at ambient and high hydrostatic pressure*, *Journal of Physics-Condensed Matter* **24** (2012) 485501, IF(2012)=2.355

H6. S. Mahlik, A. Lazarowska, A. Speghini, M. Bettinelli, M. Grinberg, *Pressure evolution of luminescence in $\text{Sr}_x\text{Ba}_{1-x}(\text{NbO}_2)_3:\text{Pr}^{3+}$ ($x=1/2$ and $1/3$)*, *Journal of Luminescence* **152** (2014) 62-65, IF(2014)=2.719

H7. S. Mahlik, A. Lazarowska, M. Grinberg, J.-P.R.Wells, M. F. Reid, *Pressure dependence of the emission in $\text{CaF}_2:\text{Yb}^{2+}$* , Journal of Physics-Condensed Matter **27** (2015), 305501, IF(2015)=2.209

H8. S. Mahlik, A. Lazarowska, A. Speghini, M. Bettinelli, M. Grinberg, *Temperature evolution of the luminescence decay of $\text{Sr}_{0.33}\text{Ba}_{0.67}\text{Nb}_2\text{O}_6:\text{Pr}^{3+}$* , Journal of Physics-Condensed Matter **26** (2014) 165502, IF(2014)=2.346

H9. S. Mahlik, A. Lazarowska, M. Grinberg, T.-C. Liu, R.-S. Liu, *Luminescence spectra of $\beta\text{-SiAlON}/\text{Pr}^{3+}$ under high hydrostatic pressure*, The Journal of Physical Chemistry C **117** (2013), 13181-13186, IF(2013)=4.835

H10. Mahlik, S., Cavalli, E., Amer, M., Boutinaud, P., *Energy levels in $\text{CaWO}_4:\text{Tb}^{3+}$ at high pressure* Physical Chemistry Chemical Physics **17** (2015), 32341-32346, IF(2015)=4.449

H11. S. Mahlik, A. Lazarowska, J. Ueda S. Tanabe, M. Grinberg, *Spectroscopic properties and location of the Ce^{3+} energy levels in $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ at ambient and high hydrostatic pressure*, Physical Chemistry Chemical Physics **18** (2016), 6683-6690; IF(2016)=4.123

H12. M. Behrend, S. Mahlik, K. Szczodrowski, B. Kukliński, M. Grinberg *Spectroscopic properties and location of the Tb^{3+} and Eu^{3+} energy levels in $\text{Y}_2\text{O}_2\text{S}$ under high hydrostatic pressure*, Physical Chemistry Chemical Physics **18** (2016), 22266-22275; IF(2016)=4.123

From this point on, the publications selected for the habilitation process will be referred to as [H1], [H2],...[H11], [H12]

c) description of the scientific goal and the results described in the publications constituting scientific achievement

The content and scientific background of the research

Luminescent solid state materials comprising insulating host lattices activated by lanthanide ions are commonly used as laser materials, phosphors for light emitting diodes (LEDs), scintillators and persistent luminescence phosphors. In recent years, considerable attention has been paid to their potential application in the field emission displays (FEDs), phototherapy and medical photodiagnostics.[1,2]

Energetic structure and possible electronic transitions

The energetic structure of the dielectric materials doped with lanthanide (Ln) ions consists of three types of states.

The first group consists of the localized energy levels of Ln ions of the ground state $\text{Ln}^{\alpha+}$ and the excited states $\text{Ln}^{\alpha+}$ and $\text{Ln}^{(\alpha-1)+}$ (α is a valence of the ion).

The second group comprises the delocalized band states represented by the valence band (V.B.) and the conduction band (C.B.).

The intermediate states of the matrix-ion system, which constitute the third group, can be described as electron-hole pairs. These are excited states of the system in which the lanthanide ion in the matrix is in the changed charge state $\text{Ln}^{(\alpha \pm 1)+}$ relative to the $\text{Ln}^{\alpha+}$ ground state (α -represents the oxidation state, which in the case of lanthanide ions is usually: +3 or +2).

In the literature, these states are referred to as either charge transfer CT [3, 4] states in case of trapping the electron on the $\text{Ln}^{(\alpha-1)+}$ ion or IVCT intravalence charge states [5-8] in the case of ion hole location admixtures $\text{Ln} \text{Ln}^{(\alpha+1)+}$. In both cases, these states are called impurity trapped exciton (ITE) states. [9-12] The difference in the descriptions is that in the case of CT (IVCT) the location of a hole (electron) is assumed to be on the nearest matrix ions, while the ITE model assumes that the hole (electron) attracted by the long-range Coulomb potential of $\text{Ln}^{(\alpha-1)+}$ is located on the Rydberg's states.

In such a system we can distinguish three different types of transitions illustrated by the vertical arrows in Fig. 1.

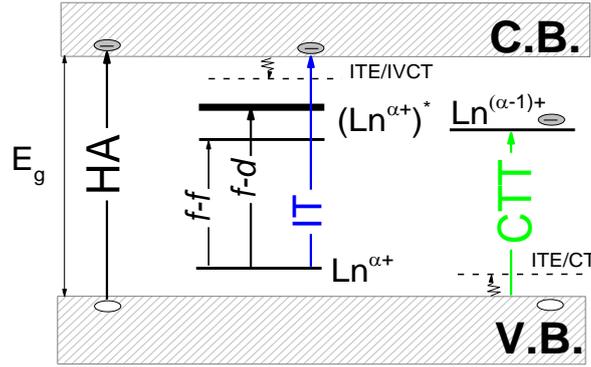


Fig. 1 Energetic structure and possible electronic transitions in the lanthanide ions activated compounds.

Transitions of the first type occur between the Ln localized states, which belong to the $4f^n$ ($f-f$ transition) or the $4f^n$ and $4f^{n-1}5d$ electronic configurations ($f-d$ transitions). The $f-f$ transitions are parity forbidden and result in the narrow excitation and emission bands [13-16], since the electrons occupying the f orbitals are effectively shielded from the environment by the completely filled $5s^25p^6$ shells. [17-20] In contrast, the parity allowed $f-d$ transitions with typical broad bands are strongly affected by the crystalline environment. [13] [23-27]

Second, the band to band transition called the host absorption (HA) between the V.B. and C.B. states allows to define the band gap (with energy E_g) of the compound. This transition creates an electron in the C.B. and a hole in the V.B. However, because of the Coulomb attraction between these two opposite charges, an electron-hole pair can be trapped and create STE or ITE. The so-called self-trapped exciton STE [1,2] is a case, whereby the charges are trapped at the crystalline ions, whereas in the case of the ITE [9-12], the charges are trapped at the lanthanide dopant ions.

The third type of transitions are the charge transfer transitions. Among these, we can distinguish the ionization transition (IT) in which an electron is excited from the $\text{Ln}^{\alpha+}$ to the C.B. and the charge transfer transition (CTT) in which an electron is excited from the V.B. to the $\text{Ln}^{(\alpha-1)+}$ state. After IT and CTT transitions, the $\text{Ln}^{(\alpha\pm 1)+}$ ion becomes the source of the long-ranged Coulomb potential for the electron and the hole, respectively. This potential is responsible for creation of the ITE. It is worth noting that all aforementioned kinds of absorption usually lead to the intra-lanthanide emission.

It should be noted here that formally the name of the dopant (impurity) which leads to the formation of the exciton should be used. For example, the exciton trapped on praseodymium is called the praseodymium trapped exciton PTE. However, for the sake of clarity of this work, only terms ITE or ITE_{Ln} will be used (Ln- lanthanide on which the exciton is formed).

Model of impurity trapped exciton (ITE)

The model of an exciton trapped on a lanthanide ion was first proposed by Reut and Ryskin [28] for Pr^{3+} ions, followed by McClur and Pedrini [29] for Eu^{2+} ions, and assumes the location of the hole on the dopant ion, while the electron is trapped on electron states of the closest ions (on ligands). However, the ITE model suggested by Grinberg and Mahlik in 2008 [9] provides a more complete picture as it includes both the hole trapping process and the electron trapping process on the dopant.

In one electron approximation, the following Hamiltonian has been proposed to describe the lanthanide ions doped with dielectric host [9]:

$$H = \frac{-\hbar^2 \nabla^2}{2m} + V_{\text{CR}}(\mathbf{r}) + V_{\text{Ln}}(\mathbf{r})|_{r < R} - \frac{e^2}{\varepsilon \cdot r} + V_{\text{latt}}(\Delta R, \mathbf{r}) \quad (1)$$

where V_{Ln} is the local potential of the $\text{Ln}^{(\alpha \pm 1)+}$ ion, V_{CR} is the lattice periodic potential and V_{latt} represents the potential related to lattice relaxation, Δ is the shift of the ligands, which appear as the lattice response to localization or delocalization of the electron. Subscripts $r > R$ and $r < R$ denote the potential outside and inside of the first coordination sphere, respectively, R is the average distance between the $\text{Ln}^{\alpha+}$ ion and the ligands, $\frac{-e^2}{\varepsilon r}$ is a long-range Coulomb potential of $\text{Ln}^{(\alpha \pm 1)+}$, e is the electron charge and ε is the static dielectric constant of the material.

Hamiltonian (1) generates two types of states: (i) localized states ($4f^n$ and $4f^{n-1}5d$ states) related to the local potential of $\text{Ln}^{(\alpha \pm 1)+}$, $V_{\text{Ln}}(\mathbf{r})|_{r < R}$ represented by the atomic functions; $\varphi_{fd}(\mathbf{r})$, (ii) the states related to the long-range Coulomb potential and lattice relaxation potential $\frac{-e^2}{\varepsilon r} + V_{\text{latt}}(\Delta, \mathbf{r})$, represented by the functions; $F(\mathbf{r})$.

In general, these functions are orthogonal [9]:

$$\int F_{nlm}^*(\mathbf{r}) \varphi_c(\mathbf{r}) d\mathbf{r} = 0 \quad (2)$$

The approximate effective mass [30] functions of $F_{nlm}(\mathbf{r})$ are hydrogen-like functions described by n , l , m_l quantum numbers, while energies form a structure of hydrogen-like Rydberg states, which we can be presented in the following form:

$$E_{nlm}^* = \frac{1}{n^2} \text{Ry} \frac{m^*}{\varepsilon^2} \quad (3)$$

where Ry - is Rydberg constant, which is equal to $\text{Ry} = 13.6 \text{ eV}$ for the hydrogen atom,

m^* - dimensionless effective mass of the electron (hole) expressed in units of mass of electron.

The above-mentioned phenomena can be explained using a configurational coordinate diagram presented in Fig. 2.

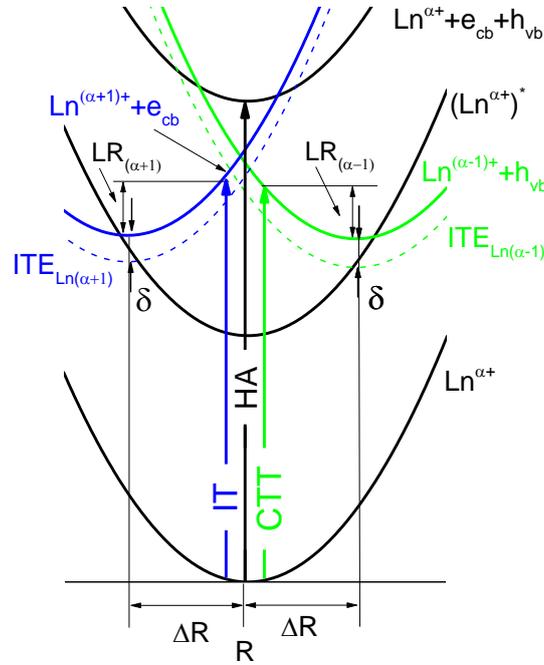


Fig.2 Configurational coordinate diagram representing the lanthanide ion doped dielectric host.

In the diagram the individual parabolas represent the electronic energies in adiabatic approximation, where configuration coordinate R represents the average distance between the Ln ion and neighboring anions (ligands).[17] The black parabolas: $\text{Ln}^{\alpha+}$ and $(\text{Ln}^{\alpha+})^*$ correspond to the ground state and excited states of Ln ion, respectively.

The black upper parabola labeled $\text{Ln}^{\alpha+} + e_{cb} + h_{vb}$ shifted from the ground state by energy E_g corresponds to the excited system: the $\text{Ln}^{\alpha+}$ ion in its ground state and a free electron and a hole, in the C.B. and V.B., respectively. The blue parabola labeled as $\text{Ln}^{(\alpha+)+} + e_{cb}$ corresponds to the case when the hole is trapped at the $\text{Ln}^{\alpha+}$ (i.e. $\text{Ln}^{(\alpha+)+}$) and the electron is in C.B. (which correspond to IT). The green parabola labeled as $\text{Ln}^{(\alpha-)+} + h_{vb}$ corresponds to the localization of the electron at the $\text{Ln}^{\alpha+}$ (i.e. $\text{Ln}^{(\alpha-)+}$) and the hole is in the V.B. (which correspond to CTT). After IT, there is one less electron in $\text{Ln}^{\alpha+}$, which causes the lattice surrounding $\text{Ln}^{(\alpha+)+}$ to shrink. In contrast, after CTT, the extra electron in $\text{Ln}^{\alpha+}$ causes the lattice expansion near $\text{Ln}^{(\alpha-)+}$. Therefore, the lattice relaxation causes the shift of the

neighboring anions (ΔR) resulting in a decrease of the ITE energy by $LR_{\alpha\pm 1}$. In the current state of the field, some relationships between the magnitude of lattice relaxation and selected crystal matrix properties have been established. However, no comprehensive model exists that takes into account all of the matrix properties. In general, one expects greater lattice relaxation energy for deeper located dopant levels and for more ionic crystals. The magnitude of lattice relaxation is certainly affected by the nearest negative ions forming the first coordination zone. The smallest lattice relaxation is expected, when the nearest surrounding of a dopant has a high symmetry and a high coordination number. The lattice relaxation can be described by the quantity $S\hbar\omega$, where $\hbar\omega$ is an effective phonon frequency and S is a Huang–Rhys parameter.[1,17] In the case of IT and CTT states, S is much larger than 10 ($2S\hbar\omega \sim 3000-8000 \text{ cm}^{-1}$). [13]

In both cases, after CTT and IT free charges in the bands are attracted by the central ions $\text{Ln}^{(\alpha\pm 1)+}$ by Coulomb potential and can be trapped creating the ITE state. The energy difference associated with the charges trapped on ITE states, which is defined as the difference between the energy of free carriers in the bands and the carriers trapped in the ITE states, is indicated in the figure by the symbol δ . This energy depends primarily on the type of lattice and weakly depends on the type of lanthanide ion on which the exciton state is formed. [12] Unfortunately there is no unambiguous procedure for quantitative calculation of δ .

It should be emphasized that Hamiltonian (1) describes the states after the IT as well as after the CTT. Thus the states described by $F(r)$ are the ITE states independently of whether they were created by IT or CTT process. Usually ITE is a short-lived phenomenon which decays non-radiatively leaving the impurity ion (Pr^{3+} and Tb^{3+}) in the excited state [32-34], [35], [36], [H1-H6]. However, in several compounds doped with Eu^{2+} and Yb^{2+} in fluorides the ITE states become stable and contribute to the radiative processes though anomalous luminescence. [37], [38-40], [H7]

The location of the energy levels of lanthanide ions relative to the valence and conduction bands

The information about the position of the lanthanide ions relative to the edges of the bands and exciton states is the key to understanding the optical properties of the studied systems. It is generally assumed that CTT and IT provide information on the location of lanthanide levels relative to the V.B. and C.B. edges. Positions of the ground states of all Ln^{3+} and Ln^{2+} ions in different lattices was extensively studied by Dorenbos group. [41-43] The basic result of this model is a conclusion that the differences between energies of the ground states of Ln^{2+} as

well as Ln^{3+} with different number of f electrons from Ce to Yb are fixed and independent of the lattice. Characteristic curves (zig-zag) connecting points corresponding to the ground levels of successive lanthanides [43] are consistent with the semi-empirically determined curve obtained by Nakazawa [44, 45]. Locations of the levels of Ln^{2+} and Ln^{3+} with respect to the band edges of a given lattice are schematically presented in Fig. 3.

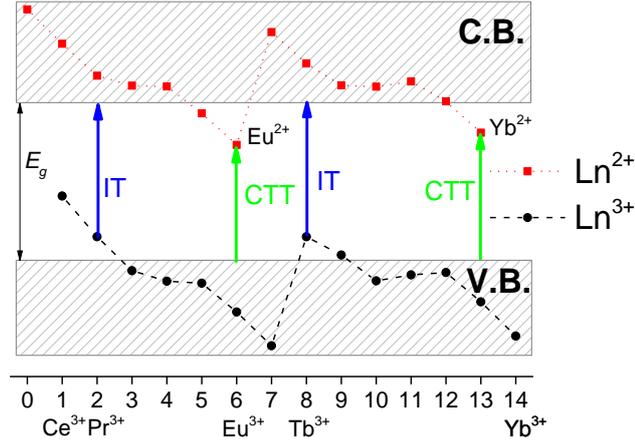


Fig. 3 The diagram representing energies of Ln^{3+} (black points) and Ln^{2+} (red points) in respect to the conduction (C.B.) and valence band (V.B.) edges. For selected ions the CTT and IT are indicated by vertical arrows; x axis values correspond to the number of electrons in the $4f$ shell of Ln^{3+} .

Location of all divalent lanthanide (Ln^{2+}) ground levels with respect to the V.B. can be estimated from the energies of the CTT (green arrows), which are responsible for the broad bands in the excitation spectra of trivalent lanthanide (Ln^{3+}) ions. In the energetic diagram it corresponds to transition from the top of the V.B. to the Ln^{2+} level. After the CTT the system consists of the Ln^{2+} ion and a hole in the V.B. (h_{vb}). Energetic distance between the top of the V.B. and the ground state of the selected Ln^{2+} is the smallest for Eu^{2+} and Yb^{2+} . Additionally, the Eu^{3+} luminescence spectrum is in the visible range (in contrast to the Yb^{3+} ion that emits light in the IR range), thus Eu^{3+} is the most widely used ion to determine the CTT energy. In other lanthanide ions CTT energies are rather large, usually exceeding the band gap energy.[46] If the Eu^{3+} CTT is known, the location of all ground state levels of the divalent lanthanides above the V.B. can be determined unambiguously.

Location below the C.B. of all trivalent lanthanide (Ln^{3+}) ground levels can be estimated if the IT (blue arrows) is known for a given ion. The IT is a transition from the localized Ln^{3+} state to the C.B. ($\text{Ln}^{3+} \rightarrow \text{Ln}^{4+} + e_{\text{cb}}$). The IT energies are most easily determined for Tb^{3+} or Pr^{3+} due

to the fact that they are the lowest for these ions and thus can be observed as broad bands in the excitation spectra, typically in the UV region. At this point, it should be noted that, compared to Tb^{3+} and Pr^{3+} ions, the ground level of Ce^{3+} is closer to C.B. However, the Ce^{3+} ion is characterized by low lying excited states of the higher 5d configuration, which impedes determination of the energy of the IT transition against a strong f-d absorption transition.

In case of doping oxide matrices with Pr^{3+} or Tb^{3+} ions, an empirical model called IVCT (Inter-Valence Charge Transfer) developed by Philippe Boutinaud et al. can be used to determine the transition energy. [5-8] This model takes into account the distance between the central ion (Pr^{3+} , Tb^{3+}) and the cations responsible for the creation of the conduction band as well as the optical electronegativity [47] and thus allows to determine the transition energy E_{IVCT} from the Pr^{3+} or Tb^{3+} ground state to the conduction band.

High pressure spectroscopy

The leading experimental technique used in this work was high-pressure spectroscopy, which included measurements of luminescence spectra, time resolved luminescence spectra with simultaneous measurement of luminescence decay time, Raman spectra and luminescence excitation spectra. High pressure experiments were performed in Merrill-Bassett type hand-operated Diamond Anvil Cells (DACs) allowing for spectral measurements at wavelength exceeding 250 nm in the temperature range up to 400 K. [48][49][12] The procedure involves placing the sample along with pressure transmitting medium in a confined space, created by drilling a small hole through a thin piece of metal sheet (gasket), and squeezing it with two opposing diamond anvils.

High hydrostatic pressure similarly to temperature and both electric and magnetic fields, is an external parameter that can alter the system and can be used to tune its physical properties. The effect of pressure on a system depends on the magnitude of pressure and on isothermal compressibility K (i.e. reciprocal bulk modulus B_0) [50,51]:

$$K = \frac{1}{B_0} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (4)$$

The values of bulk modulus B_0 of the investigated materials range from 100 GPa to 250 GPa. It is worth noting that the wide span of pressures used in our experiment (up to 40 GPa) allowed to change the interatomic distances in the studied materials from only a few percent up to about 30% This change in interatomic distances causes significant changes in the energy structure of the studied materials.

Samples

Test materials have been obtained in the framework of cooperation with international and national scientific teams led by:

- *prof. Marco Bettinelli (Laboratory of Solid State Chemistry, DB, Università a di Verona, and INSTM, UdR Verona, Verona, Italy)*
- *prof. Philippe Boutinaud (Clermont Université, ENSCCF, Laboratoire des Matériaux Inorganiques, Clermont-Ferrand and CNRS, Aubière)*
- *prof. Enrico Cavalli (Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parma, Italy)*
- *prof. Ru Shi Liu (Department of Chemistry, Taiwan National University, Taiwan)*
- *prof. Setsuhisa Tanabe (Graduate School of Human and Environmental Studies, Division of Materials Function, Kyoto University, Japan)*
- *prof. Mike Reid (MacDiarmid Institute for Advanced Materials and Nanotechnology and Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand)*
- *dr hab. Beata Grobelna (Wydział Chemii, Uniwersytet Gdański, Polska)*

Purpose of work

The aim of the study was to determine the effects of intermediate states on the luminescence properties of dielectric materials doped with lanthanide ions.

Within the framework thereof, the influence of intermediate states on the luminescence of Pr^{3+} , Tb^{3+} , Dy^{3+} , Eu^{3+} , Ce^{3+} and Yb^{2+} ions in dielectric matrices as well as on the optical transitions related to undoped dielectric matrices have been investigated. The research has focused on spectroscopic measurements at high hydrostatic pressures obtained in DAC. Changes in pressure have induced significant changes in the energy structures of the studied systems, which has been directly observed through changes in the position of the emission and absorption/excitation bands or indirectly through the quenching or rising of luminescence. The detailed objectives of the work include:

1. Construction of an experimental workshop which allows for a number of spectroscopic studies at high hydrostatic pressures obtained in DAC comprising:
 - measurements of time resolved luminescence spectra with simultaneous measurement of decay profiles as a function of temperature
 - Raman spectra measurements

- measurements of luminescence excitation spectra
2. Determining the changes as a function of pressure:
 - excited levels of lanthanide ions relative to the ground level,
 - energies of CT and IT and intermediate states,
 - energies of lattice relaxation,
 - band gap energy E_g of dielectric matrix,
 - the depth of the traps responsible for persistent luminescence,
 3. Analysis of the obtained spectroscopic results, leading to:
 - determination of the energy level structure of the studied systems and of the nature of both radiative and non-radiative transitions.
 - determination of the nature of the energy transfer between the host and the dopant levels as well as between the dopant levels,
 4. Creation of a coherent model describing the dopant ion-matrix systems, including intermediate states

Discussion of results

Effect of the intermediate states on the Pr^{3+} ions luminescence

In the paper [H1], the optical properties of $CaWO_4$ doped with Pr^{3+} [52] have been studied as a function of hydrostatic pressure. The increase of pressure caused decrease of the intensity of f-f transitions which is accompanied by the shortening of the emission decay times. These effects have been previously observed in Pr^{3+} doped oxides and have been explained by the increased energy transfer between the local levels of Pr^{3+} through the ITE states. [32-34] [35][36] Namely, pressure induces as a decreasing in the energy of the ITE state decreases with respect to the energies of the excited states of dopant ions, causing quenching of the emission from subsequent excited states. Energy from the quenched state is transferred by ITE to the lower excited states of Pr^{3+} . In extreme cases, when the ITE energy is lower than the energy of the lowest excited state, this transfer may occur directly to the ground state of the dopant ion.

In previously studied Pr^{3+} doped oxide materials, due to the limited range of used pressures, only one of the emission levels: 3P_0 [34,36] or 1D_2 [32, 33, 35] (in systems where no 3P_0 emission is observed) was quenched. In the work [H1], the pressure-induced quenching has been observed for the first time for both emitting levels: 3P_0 at the pressure of 120 kbar and 1D_2 at the pressure of 315 kbar. This result allowed for a conclusion that for the known values

of energy of excited states as well as the respective values of pressure at which the emission from these states can be quenched, it is possible to determine the ITE as a function of pressure.

The diagram in Fig. 4a shows the change in the position of the 3P_0 and 1D_2 levels of Pr^{3+} with respect to the ITE state. In Fig.4. pressures p_1 and p_2 are the pressures at which the emission from the upper 3P_0 and lower 1D_2 emitting states is quenched. Knowing the values of p_1 and p_2 allows to calculate the pressure induced shift of the ground states with respect to the ITE state and also allows to determine the position of the lanthanide levels at ambient pressure.

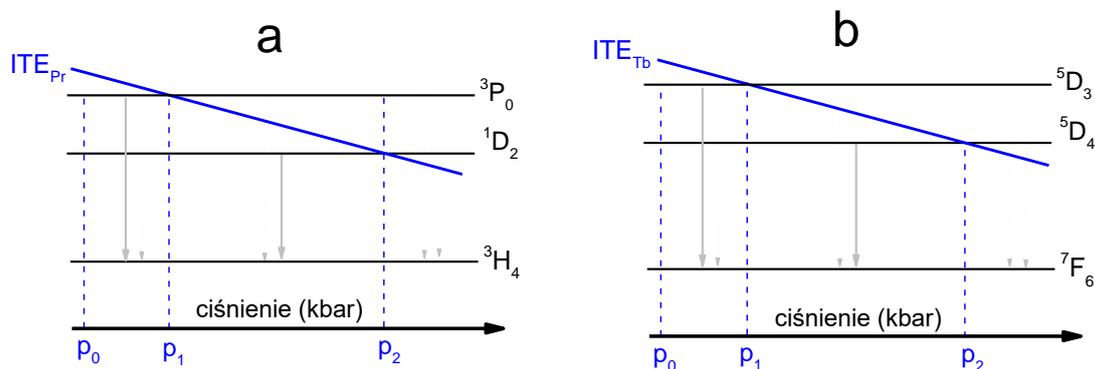


Fig. 4 Pressure dependence of the location of localized states of Pr^{3+} (a) and Tb^{3+} (b) with respect to the ITE states.

Obviously, this method can also be used for other lanthanide ions (for example for Tb^{3+} ions as shown in Fig. 4b) where quenching of the emission from the consecutive excited states is observed.

The proposed new method based on high-pressure spectroscopy allows to determine the position of the lanthanide levels is especially useful in lanthanide-doped materials where IT are not observed in the excitation spectra (for example in $CaWO_4:Pr^{3+}$).

Due to the scheelite-fergusonite phase transition in $CaWO_4$ at the pressure of 100 kbar [53, 54] it is impossible to locate the position of the Pr^{3+} ground states relative to the edge of the C.B. at ambient pressure only from the spectroscopic studies of $CaWO_4:Pr^{3+}$. However, under the assumption that the phase transition diminishes the energy of the ITE by the same quantity for Tb^{3+} and Pr^{3+} , the ambient pressure energies of the ground states can be calculated by the method described above for $CaWO_4:Ln^{3+}$ using two materials: $CaWO_4:Pr^{3+}$ and $CaWO_4:Tb^{3+}$ [55], as demonstrated in [H2].

Effect of the intermediate states on the Tb³⁺ ions luminescence

Previous studies focused exclusively on the study of the effect of the ITE on the optical properties of Pr³⁺ [32-34], [35], [36], [H1] and Eu²⁺. [37] , [38-40] In the paper [H2], **the effects of the ITE on the spectral properties of Tb³⁺ were first examined.** The optical properties of CaWO₄ doped with Tb³⁺ has been investigated and compared with the properties obtained for CaWO₄: Pr³⁺. The increase of pressure causes a decrease of the intensity of *f-f* transitions which has been accompanied by the shortening of the emission decay times. This effect has been explained by the pressure-induced decrease in energy of the ITE state relative to the energies of the ⁵D₃ and next to ⁵D₄ excited states of Tb³⁺, similarly as was the case with CaWO₄:Pr³⁺. Namely, the increase in pressure induces a decrease in the energy of the ITE state decreases with respect to the energies of the ⁵D₃ and then ⁵D₄ state, causing quenching of the emission from these states. Energy from the quenched state is transferred by ITE to the lower states of Tb³⁺. Similar results were also obtained with the CaMoO₄ matrix doped with Tb³⁺ ions as presented in [H4].

Effect of the intermediate states on the host luminescent

In the paper [H3], the influence of high pressure on the spectral properties of CaMoO₄ doped with Pr³⁺ [56] has been studied. As is the case with CaWO₄:Pr³⁺, pressure quenching of *f-f* luminescence has also been observed in CaMoO₄:Pr³⁺ and explained by the influence of the ITE states.

Apart from the sharp *f-f* transitions of Pr³⁺ ions, the CaMoO₄:Pr³⁺ is characterized by a host broadband luminescence extending in the 400–700 nm region. The increase of pressure caused a decrease of the intensity of the host emission, which was accompanied by a shortening of the luminescence decay time. Since the change in pressure did not result in a significant emission wavelengths shift, this result was quite surprising.

At this point the following questions should have been asked: What mechanism causes such strong host emission quenching with increasing pressure? What is the impact of intermediate states on the luminescent properties of dielectric hosts?

To answer these questions, it was necessary to compare the effect of high pressure on the luminescence of the undoped CaMoO₄ host and the CaMoO₄ doped with Pr³⁺ or Tb³⁺ ions, as had been done in [H4].

CaMoO₄ host is characterized by a strong broadband luminescence in the spectral range of 400-700 nm. In the case of both undoped and doped materials, a slight pressure-induced shift of the emission peak towards the higher energy was observed. Such an effect is related to

changes in the energy structure of the host (change of the band gap energy). But more importantly, the undoped host is characterized by intensive luminescence in the whole range of applied pressures up to 300 kbar. In contrast to the undoped CaMoO_4 material, in Pr^{3+} and Tb^{3+} doped CaMoO_4 , the host related luminescence decreased with increasing pressure, which was accompanied by shortening of the luminescence decay time. The host emission was completely quenched for $\text{CaMoO}_4:\text{Pr}^{3+}$ and $\text{CaMoO}_4:\text{Tb}^{3+}$ at pressures above 106 kbar and 122 kbar, respectively. The observed changes are explained by increasing energy transfer from the host to the ITE states and then to lanthanide ions. This result shows **that the ITE states can affect** not only the optical transitions between the lanthanide ion levels but also **the optical transitions associated with the host and significantly contribute to the energy transfer from the host to the dopant.**

It should be noted that Raman spectra at high hydrostatic pressures presented in [H4], were obtained on a new apparatus, adapted for measurements in diamond anvil cells. These measurements allowed to control the scheelite to fergusonite phase transition [57, 58] occurring at a pressure of 80 kbar.

Changing the way of thinking

For a number of materials doped with Pr^{3+} and Tb^{3+} , it has been shown that increasing the pressure causes the emission quenching from these ions. The quenching process is explained by the influence of intermediate states and their change with increasing pressure. [32-34], [35], [36], [H1-H4] However, the question that should be answered is why the quenching process has been observed in all materials studied so far. Additionally, it should be verified if the quenching process will also be observed for other dopant ions.

It is known that for some hosts increasing pressure causes an increase in their energy band gap (e.g., YVO_4 [12]), which could suggest an increase in the energy of the C.B. edge, and thus the energy of the ITE states. In the analysis of experimental data, however, the linear energy changes of ITE as a function of pressure has been always obtained. **In order to resolve this problem, one should stop thinking about changing the energy of the ITE state, and begin to consider changing the energy level of the $4f^n$ configuration as a function of pressure.**

In the 2012 in the paper [59], Peter Dorenbos demonstrated a simple model assuming linear position change of the ground states of lanthanide ions relative to the vacuum level with the decreasing distance between the central ion and the ligands.

The starting point of this model is the determination of the electron binding energy on the f shell for free divalent $E_0(Ln^{2+}, n)$ and trivalent $E_0(Ln^{3+}, n)$ lanthanide ions; n -number of electrons on the f shell.

According to the paper [59], these energies are equal to $E_0(Ln^{2+}, 7) = -24,92$ eV and $E_0(Ln^{3+}, 6) = -42,97$ eV with respect to the vacuum level. When ions are placed in the host lattice, these energies are reduced by the electrostatic interaction of the electrons in the f -shell with the potential from the host ions. The energies of divalent $E_0(Ln^{2+}, n)$ and trivalent $E_0(Ln^{3+}, n)$ ions in the host are described by the following relationships:

$$E(Ln^{2+}, n + 1) = E_0(Ln^{2+}, n + 1) + 1440 \frac{2}{R_{2+}} \quad (5)$$

$$E(Ln^{3+}, n) = E_0(Ln^{3+}, n) + 1440 \frac{3}{R_{3+}} \quad (6)$$

In formulas (5) and (6) the energies are expressed in eV and the ionic radii R_{2+} , and R_{3+} of Ln^{2+} and Ln^{3+} in pm. Accordingly, when pressure compresses the system, the energies $E(Ln^{2+}, n + 1)$ and $E(Ln^{3+}, n)$ increase with respect to the vacuum level.

In the paper of Grinberg and Mahlik [3] it has been proposed that the energy of the ITE state can be described by a function proportional to $\frac{C}{R^m}$. The exponent m depends on the type of interaction. Specifically, $m=1$ corresponds to electrostatic Coulomb repulsion, $m=2$ corresponds to the potential of quantum well, $m=12$ corresponds to short distance Lennard Jones potential. It appears, however, that within the applied pressure range, where the relative change in distance R does not exceed tens of percent, it is sufficient to take into account only the effect of classical electrostatic potential, i.e. the $1/R$ relationship. Interestingly, the same dependency also appears in the IVCT model described by Philippe Boutinaud. [5-8]

Independently of the model, energies of the Ln^{2+} and Ln^{3+} ions should increase with pressure with respect to the energy of a free ion and with respect to the ambient pressure binding energy. This change is the same for all lanthanide ions of a given valency and is proportional to $1/R$.

The way of thinking described above can be illustrated by a simple diagram presented in Fig. 5, in which only the changes of the positions of ground levels of lanthanide ions with increasing pressure are considered. Assuming that the energies of the C.B. and V.B. edges are not changed by pressure, pressure causes the increase of the CTT (and $ITE_{Ln^{3+}}$) energies and the decrease of the IT (and $ITE_{Ln^{2+}}$) energies.

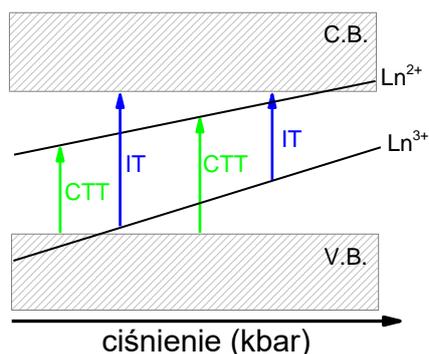


Fig. 5 Expected dependence of ground state energies of Ln^{2+} and Ln^{3+} ions on pressure. CTT are represented by green arrows and IT by blue arrows.

This approach began to appear in the work of [H1-H4] and became necessary to describe the phenomena observed in the paper [H5].

In this work the spectroscopic properties of $\text{Gd}_2(\text{WO}_4)_3$ doped with Pr^{3+} , Tb^{3+} , Eu^{3+} and Dy^{3+} were investigated. Using spectroscopic data, a diagram showing the positions of the ground levels of all di- and trivalent lanthanide ions with respect to the band edges was developed.

In contrast to $\text{Gd}_2(\text{WO}_4)_3$ doped with Pr^{3+} and Tb^{3+} which exhibited a strong f - f emission quenching, the f - f luminescence of Eu^{3+} and Dy^{3+} in $\text{Gd}_2(\text{WO}_4)_3$ remained stable over the entire range of applied pressures up to 250 kbar.

This effect was explained by the pressure-induced decrease in the energy of the ITE state relative to the energies of the excited states, similarly to how it had been done in the case of $\text{CaWO}_4:\text{Pr}^{3+}/\text{Tb}^{3+}$. The decrease of the energy of the ITE state relative to the $4f$ levels of the dopants along with the pressure increase may be considered as an increase of the energy level of the $4f^n$ configuration as a function of pressure. Since formally the CTT transition in the case of the Eu^{3+} ion is considered a transition of an electron from the V.B. to the Eu^{2+} state, the increase in CCT transition energy with increasing pressure and consequently the stabilization of the Eu^{3+} emission should be observed. In addition, an emission from a higher $^5\text{D}_3$ state of Eu^{3+} can be expected.

In the case of $\text{Gd}_2(\text{WO}_4)_3:\text{Eu}^{3+}$, the emission from the $^5\text{D}_3$ state of Eu^{3+} has not been observed, however the emission from Eu^{3+} ions is stable over the whole range of applied pressures, which may confirm the increase of the CCT energy with increasing pressure. In 2014, in the paper [60], the occurrence of pressure-induced transition from the $^5\text{D}_3$ of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$ host was demonstrated. Similar results were also obtained for other dielectric materials doped with Eu^{3+} ions. [61-63]

The ITE states may have different multiplicity

The paper [H6] is focused on the energy transfer process from matrixes $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ($x = 1/2$ and $x = 1/3$) to dopant Pr^{3+} ions. [64] It is shown that the excitation energy transfer takes place mainly through the intermediate states of ITE and not directly from the matrixes to the dopant ions. As the case has been with the previously discussed materials, the typical quenching of the f - f emission at high hydrostatic pressure has also been observed here. Knowing the pressures at which quenching of the excited states $^3\text{P}_0$ and $^1\text{D}_2$ of Pr^{3+} has been observed, allows to determine the position of the ground level of the Pr^{3+} ion at atmospheric pressure, relative to the ITE and C.B. edge.

In the paper [H6], it has been noted that ITE state can exist in either a triplet or a singlet state. The ground state of Pr^{3+} is a $^3\text{H}_4$ triplet. If the ITE singlet has lower energy, it cannot be seen in the excitation spectrum but contributes to the nonradiative processes.

The method of describing the ITE states that also takes the spin into account was used in [H7], where the spectral properties of CaF_2 doped with Yb^{2+} were investigated. [65]

As shown in the previous works [H1-H6], the intermediate ITE states in the case of doping with Pr^{3+} and Tb^{3+} ions can lead to quenching of the f - f luminescence. If the ITE state lies below the lowest excited $4f^65d^1$ level of Eu^{2+} in the Eu^{2+} ions doped dielectric lattice, a broadband emission is observed. This emission is related to the transition between the ITE state and the Eu^{2+} ground level [37], [38-40] which is known as anomalous luminescence [31]. Exactly the same kind of emission is observed in the CaF_2 doped with Yb^{2+} ions which is presented in the paper [H7].

Anomalous luminescence

$\text{CaF}_2:\text{Yb}^{2+}$ is characterized by a broadband emission in the visible range observed at atmospheric pressure only at temperatures below 200 K. This emission occurs between the ITE state and the ground level of the Yb^{2+} ion. The ground state of Yb^{2+} is a singlet $^1\text{S}_0$ ($4f^{14}$) while the excited ITE state is formed by 13 electrons in the $4f^{13}$ electronic configuration (in the ^2F state) and an additional electron bound by the Coulomb potential. Therefore, the ITE state can be either a singlet or a triplet state, labeled ^1ITE and ^3ITE , respectively.

The analysis of experimental data presented in the paper [H7] showed that the lowest energy ^3ITE state is responsible for the emission. Above it, lies the ^1ITE state which causes the shortening of the luminescence decay time with increasing temperature. It means that the observed anomalous luminescence in the case of Yb^{2+} doped CaF_2 is a spin-forbidden transition. In the case of the Eu^{2+} ion, an octet level $^8\text{S}_{7/2}$ is the ground level and the excited

states are the $4f^65d$ states or the ITE states, which can be ${}^6\text{ITE}$ sextets or ${}^8\text{ITE}$ octets. According to the Hund rule, a higher multiplet ${}^8\text{ITE}$ state should be the state with lower energy. As a result, transitions are spin allowed for both d - f transitions and for ITE radiative recombination. These arguments are clearly confirmed by testing luminescence decay time at low temperatures (10 K). The ITE luminescence decay times in $\text{CaF}_2:\text{Yb}^{2+}$ are in the order of milliseconds, while the decay times of the ITE luminescence for $\text{CaF}_2:\text{Eu}^{2+}$ are in the order of microseconds.

In the paper [H7], a new method that involves observing the changes in the profiles of the luminescence decay as a function of temperature and pressure has been used. This method provides important information regarding the energy structure of the studied systems that cannot be obtained by standard spectroscopy methods.

This method allowed to determine the energy between the singlet and triplet state as well as the energy change of the ITE states in $\text{CaF}_2:\text{Eu}^{2+}$ material as a function of pressure. With increasing pressure, the luminescence from the ITE states was becoming thermally stable. Such a process is caused by a decrease of the lattice relaxation energy with increasing pressure.

It should be noted that the pressure-induced changes of the lattice relaxation energy have not been clearly determined yet, mainly due to the small number of experiments that have been performed up to date to obtain the excitation or absorption spectra at high pressures.

Another way to escape

In the examples discussed so far, it has been shown that after the excitation of the dielectric materials doped with lanthanide ions by the HA, CTT or IT process, the excitation energy is transferred through the ITEs to the dopant ions or emitted radially as exciton emission.

However, it may happen that an electron excited to the C.B. (or a hole to the V.B.), will be trapped in a trap that is not bound to the dopant but located in the crystal lattice. These traps may have different origins and their detailed analysis can be found in a number of papers [1].

In the work [H8], an analysis of the impact of intermediate states on carrier trapping mechanisms in $\text{Sr}_{0,33}\text{Ba}_{0,67}\text{Nb}_2\text{O}_6:\text{Pr}^{3+}$ material was performed. When the system is excited by the HA process, free electrons appear in the C.B., while in the V.B. holes are formed. The hole can be captured by the Pr^{3+} ion to form Pr^{4+} , which attracts the electron from the C. B. by the Coulomb potential and forms the ITE state. Exactly the same state is achieved immediately after the IT excitation. An excited electron can be trapped in another electron trap instead of being trapped on the ITE. A similar mechanism can be used to describe the

hole trapping, except that it is generally used for Eu^{3+} and Dy^{3+} dopants. This results directly from the positions of the ground levels of lanthanide ions relative to the edges of the bands (see Fig. 3).

In the paper [H8] it was shown that the traps may be filled either by the HA or the IT transitions. This result confirmed that in $\text{Sr}_{0,33}\text{Ba}_{0,67}\text{Nb}_2\text{O}_6$ doped with Pr^{3+} ions the electron traps are present. Studies of the luminescence spectra as a function of temperature were carried out in two phases: paraelectric and ferroelectric (at 76 kbar). Analysis of the results shows that the number of traps does not change with the phase transition, but their energy relative to the conduction band edge does.

The nature of the traps is not considered in the paper [H8]. It seems reasonable, however, to argue that high pressure spectroscopy can help to answer the question of the nature of traps and the nature of the trapping mechanism itself in the case of persistent luminescence in the most efficient materials doped with Eu^{2+} and Dy^{3+} . Since we can predict how the lanthanide f states change with increasing pressure, we can unambiguously answer the crucial question whether Dy^{3+} ions in such systems act as the electron traps.

The lack of a proper apparatus for measuring long decay times (of the order of minutes) as a function of pressure and temperature is now the main obstacle to resolving this issue.

Intermediate states always exist

An example of a material in which the observed ITE states have not quenched the f - f Pr^{3+} emission with increasing pressure is β -SiAlON: Pr^{3+} . [66] In the work [68], it is shown that Pr^{3+} ions can be located in two nonequivalent crystallographic sites: 2b with sixfold coordination and 2a with ninefold coordination. In the paper [H9], it was shown that the ITE states of the Pr^{3+} ions in 2a site have lower energy than the same states in 2b site. It had been anticipated that the f - f emission from Pr^{3+} ions in the 2a position would be quenched at lower pressures than the f - f emission of the Pr^{3+} in the 2b position. With increasing pressure, however, only slight luminescence quenching of the $^3\text{P}_0$ state of Pr^{3+} ions was observed, comparable at both sites. Such an effect was explained by the pressure induced increase in the probability of nonradiative multi phonon transitions from the $^3\text{P}_0$ to the lower excited state $^1\text{D}_2$ due to the increase of phonon energy.

To answer the question why the typical quenching of f - f transitions at high pressures is not observed in this material, the unusual structure of such a system should be examined. In β -SiAlON, lanthanide ions do not substitute lattice ions due to the large difference of ionic radii

between them. In the β -SiAlON, however, lanthanide ions can occupy interstitial sites in the crystalline structure [67], [68].

The occupation of the interstitial sites by the Pr^{3+} ions is different in that an additional positive charge is created and must be compensated. Therefore, to satisfy the charge neutrality requirement, Pr^{3+} ion attracts two electrons forming additional bonding–antibonding states related to the interaction between Pr^{3+} and N^{3-} . The bonds between Pr and N are covalent and are stronger than the bonds between Pr and O. As a result, the pressure does not change the length of the Pr-N bond or changes it only very slightly and therefore has little effect on the change of energy of the f states of Pr^{3+} with respect to the ITE.

It is also possible to indicate other dielectric materials (e.g. LiLuF_4 [69]) in which the levels of Pr^{3+} or Tb^{3+} ions lie so deep in the band gap, that the ITE states and their impact on the optical properties of dopant ions is not observed in the available range of pressures.

It should be noted here that the IVCT model developed by Boutinaud [5-8] assumed the existence of intermediate states only in transition metal compounds doped with Pr^{3+} or Tb^{3+} ions and thus excluding their existence in a material such as β -SiAlON. The ITE model assumes the presence of the ITE states in any dielectric lattice doped with lanthanide ions, regardless of its structure.

ITE/IVCT/CT

By means of the literature data [70], in the paper [H10], the distance between the ions forming the CaWO_4 lattice in the function of pressure was determined. Furthermore, the position of the Tb^{3+} levels relative to the ITE and the C.B. as a function of pressure was established using the known value of the band gap energy as a function of pressure as well as $1/R$ relationship (as proposed by Philippe Boutinaud in an empirical model) [7, 8]. Since the change of band positions relative to the vacuum level was unknown, the position of the V.B. edge was set at 0 and a change in the C.B. edge position was investigated.

The results corresponded to the results obtained previously in the paper [H2], when the energy of the ITE as a function of pressure had been calculated with no knowledge of the change of band gap energy during the phase transition. In the [H10] it has been clearly shown that the IVCT and ITE models in the case of $\text{CaWO}_4:\text{Tb}^{3+}$ describe exactly the same states. Since the C.B. is mainly composed of d levels derived from W^{6+} ions, the IT can be described as a charge transfer transition of an electron from Pr^{3+} ions to W^{6+} ions. The intermediate ITE/IVCT state has been named the CT state in this work.

Although not explicitly stated in [H10], one of the results turned out to be very significant, namely the change in the relative position of f states relative to the V.B. as a function of pressure in the fergusonite phase. It is clearly visible in this phase that the ground level of Tb^{3+} is approaching the V.B. edge when pressure increases.

Bearing in mind that energy of the ground states of lanthanide ions relative to the vacuum level increases with increasing pressure, this result can only mean that the V.B. edge also moves toward higher energies with increasing pressure. While there is no doubt about such a change in the C.B. edge, in the case of the V.B. edge, the energy would rather be expected to decrease or to remain unchanged. In the next work [H11] it was proved that this had not been an isolated case, and that **the pressure-induced increase of V.B. edges energy commonly occurs and is compatible with the fundamentals of quantum mechanics.**

Change of bands energy as a function of pressure

In the paper [H11] the luminescent properties of $Y_3Al_5O_{12}$ (YGG) doped with Ce^{3+} ions at high hydrostatic pressures and variable temperatures were investigated. Ce^{3+} ions in dielectric matrices are characterized by broadband emission associated with the parity allowed transition between the $5d_1$ state (the lowest state of the $5d^1$ electronic configuration) and the $^2F_{7/2}$ and $^2F_{5/2}$ states of the ground electronic configuration ($4f^1$) state ($d-f$ emission).

Because of the degeneration of excited states d_1 of Ce^{3+} with C.B. at atmospheric pressure, YGG: Ce^{3+} does not exhibit a typical $d-f$ emission due to the photoionization mechanism. Also the ITE emission is not observed, which may indicate that the ITE states are not stable in the YGG matrix or that the energy from these states is transferred nonradiatively to the ground state of the Ce^{3+} ion.

With increasing pressure the $d-f$ emission was noticed to appear at a pressure of 20 kbar, although at low temperatures only. This implies that the degeneration of the lowest excited d_1 state with the C.B. is eliminated. Further increase in pressure caused the temperature stabilization of the $d-f$ emission, observed as the extension of the decay time of luminescence and the possibility to observe the luminescence at ever-increasing temperatures. At pressure above 50 kbar, the $d-f$ emission was clearly visible at room temperature. The pressure-induced occurrence of $d-f$ emission from Ce^{3+} in garnets had already been observed by A. Suchocki et al.[71, 72] and this phenomenon had been explained by the decrease of the $d-f$ transition energy under pressure (due to the increase in the crystal field as a result of the central ion-ligands distance shortening).

In [H11], it was shown that in the case of YGG: Ce³⁺ the change of the *d-f* transition energy as a function of pressure is equal to -7.2 cm⁻¹/kbar. The energy of the 5d₁ state with respect to the C.B. decreases with pressure by the quantity of 7 cm⁻¹/kbar and thus the change of the energy of the ground state of the Ce³⁺ with respect to the C.B. can easily be determined to be equal to only 0,2 cm⁻¹/kbar. This means that the energy distance between the ground state of Ce³⁺ and the C.B. is virtually independent of pressure in YGG.

However, the earlier discussion clearly suggests that the ground state of Ce³⁺ relative to the vacuum level should increase with pressure. Simple algebraic transformations presented in [H11] allowed to determine this change, which for the YGG material is equal to 49,2 cm⁻¹/kbar. This mean that the change of the C.B. edge relative to the vacuum level, as a function of pressure, is 49,4 cm⁻¹/kbar. It should be noted that this result is consistent with the theoretical ab initio calculation presented by Montesuegro et al. [73] Having known the band gap energy as a function of pressure, [73] it has been easy to determine the change of the position of the V.B. edge relative to the C.B. edge, and thus also to the vacuum level.

The results obtained in [H11] are summarized in Fig. 6, illustrating the change of positions of Ce³⁺ levels and bands as a function of pressure.

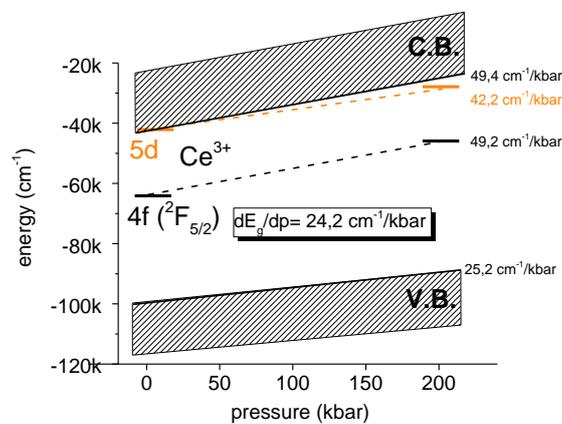


Fig. 6 Pressure dependence of the energetic structure of YGG:Ce³⁺

It should be noted that **the position of the localized levels of the lanthanide ions varies considerably with pressure.** In addition, **the energy of the V.B. increases with increasing pressure.** These two results stand in contradiction to the solid state physicists' intuition and for this reason they often attract criticism. However, they have not been refuted so far, and further experiments and preliminary theoretical calculations only seem to corroborate them.

Lattice relaxation

In the paper [H12] Y_2O_2S materials doped with Eu^{3+} and Tb^{3+} ions have been investigated. This work has been first to present the results of the research of luminescence excitation spectra at high hydrostatic pressures performed at the Institute of Experimental Physics, University of Gdansk. Such experiments has then been carried out for fluoride materials doped with Mn^{4+} ions. [74, 75]

In the case of Y_2O_2S materials doped with Eu^{3+} and Tb^{3+} , CTT and IT transitions has been clearly visible in the luminescence excitation spectra. In addition, the Dorenbos model [42], that allows to determine the relative energy of individual lanthanide ions, and the value of the band gap energy E_g calculated in the paper [76] have been used. As already mentioned, the knowledge of CTT, IT and band gap energies (E_{CTT} , E_{IT} , E_g) allows us to determine the energy structure depicting the positions of all di- and trivalent lanthanide ions in relation to the edge of the bands, as shown in Fig. 7. The diagram in Fig. 7 (a) presents the locations of the ground states of Ln^{3+} and Ln^{2+} in such a case that the V.B. and the ground states of Ln^{3+} ions are occupied and the C.B. and the ground states of Ln^{2+} ions are unoccupied.

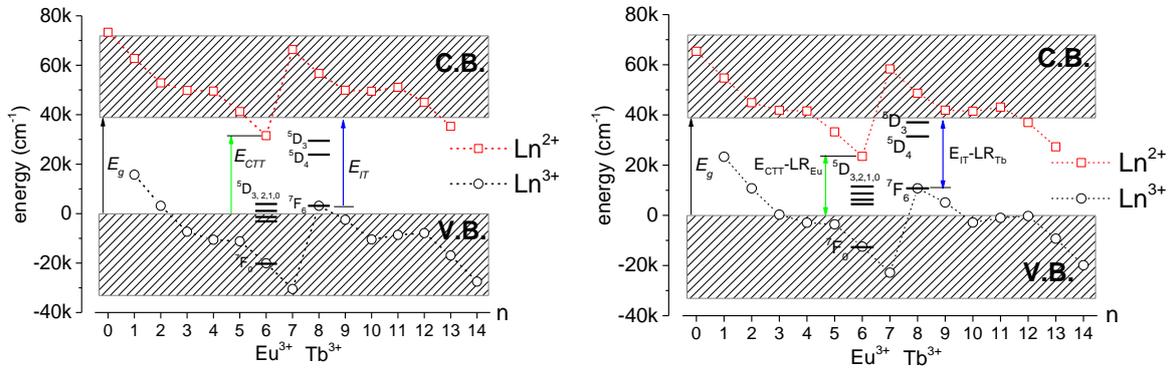


Fig. 7 The diagram representing the energies of Ln^{3+} and Ln^{2+} with respect to the C.B. and V.B. edges of Y_2O_2S obtained at ambient pressure (a) for the system in the ground state [Ln^{3+} (occupied) and Ln^{2+} (unoccupied)] (b) for the system in the excited state [Ln^{3+} (unoccupied) and Ln^{2+} (occupied)]. For Tb^{3+} and Eu^{3+} , the energies of selected states of the $4f^n$ electronic manifold are also displayed; the x-axis values correspond to the number electrons (n) in the $4f$ shell of Ln^{3+} .

In [H12], it has been shown that when creating such a diagram, attention should be paid to the lattice relaxation, i.e. the change in location of the nearest ligands around the lanthanide ion, which occurs after the changes in electron localization during an IT and a CTT. After the IT,

there is one less electron in Ln^{3+} , which causes the lattice surrounding the Ln^{4+} ion to shrink. In contrast, after the CTT, the extra electron in Ln^{3+} causes the lattice expansion near Ln^{2+} . The diagram in Fig. 7 (b) can be obtained by taking the lattice relaxation into account. It illustrates the situation of double doping with different lanthanide ions and shows the positions of the states of the lanthanide ions in the case of capturing an electron from one of the lanthanide ions by another lanthanide ion.

A system in which the ground state is Ln^{3+} and Eu^{3+} (Fig. 7 (a)) whereas the excited state is Ln^{4+} and Eu^{2+} (Fig.7 (b)) is considered. The transition from any Ln^{3+} to Eu^{3+} is considered because the Eu^{2+} ion is characterized by the lowest energy compared to other Ln^{2+} ions. After the electron transition ($\text{Ln}^{3+}, \text{Eu}^{3+} \rightarrow \text{Ln}^{4+}, \text{Eu}^{2+}$) the energy distance between the Ln^{2+} and Ln^{3+} ions is diminished by the lattice relaxation energies $\text{LR}_{\text{Tb}} + \text{LR}_{\text{Eu}}$.

The situation presented in Fig. 7 (b) is very important when considering the issue of persistent luminescence, associated with de-trapping of carriers from Dy^{3+} ions to Eu^{2+} ions, which is often erroneously explained in the literature with the aid of the diagram as shown in Fig. 7(a). However, at the moment of release of the trapped electrons, the proper approach is to take into account the diagram shown in Fig. 7 (b).

The effect of high pressure on IT and CTT

Analysis of the excitation spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ obtained at different pressures has shown that as the pressure increased, a linear shift of IT (and therefore ITE_{Tb}) towards lower energy was observed. Such a change had been repeatedly predicted in many papers before, however, only in [H12] was directly observed experimentally. As in the previously discussed materials doped with Tb^{3+} ions, also here the pressure-induced quenching of the emission from the higher excited $^5\text{D}_3$ state has been observed. Of course, the pressure-induced quenching of the transition from the $^5\text{D}_4$ state may also be expected, however, this would require high pressure, outside the available pressure range.

In the case of the CTT in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, an inverse relationship, namely, a pressure-induced shift towards the higher energies has been observed in the excitation spectra. Such a relation has been predicted earlier in [60] for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, but a direct experimental proof is presented in the paper [H12]. A similar result (the shift to the higher energy of the CTT) has then been obtained for the $\text{LaAlO}_3:\text{Eu}^{3+}$ material. [63] Additionally, the transition from the $^5\text{D}_3$ excited state at high pressure was observed in emission spectra.

The observed changes can be explained using the configuration coordinate diagrams shown in Fig. 8.

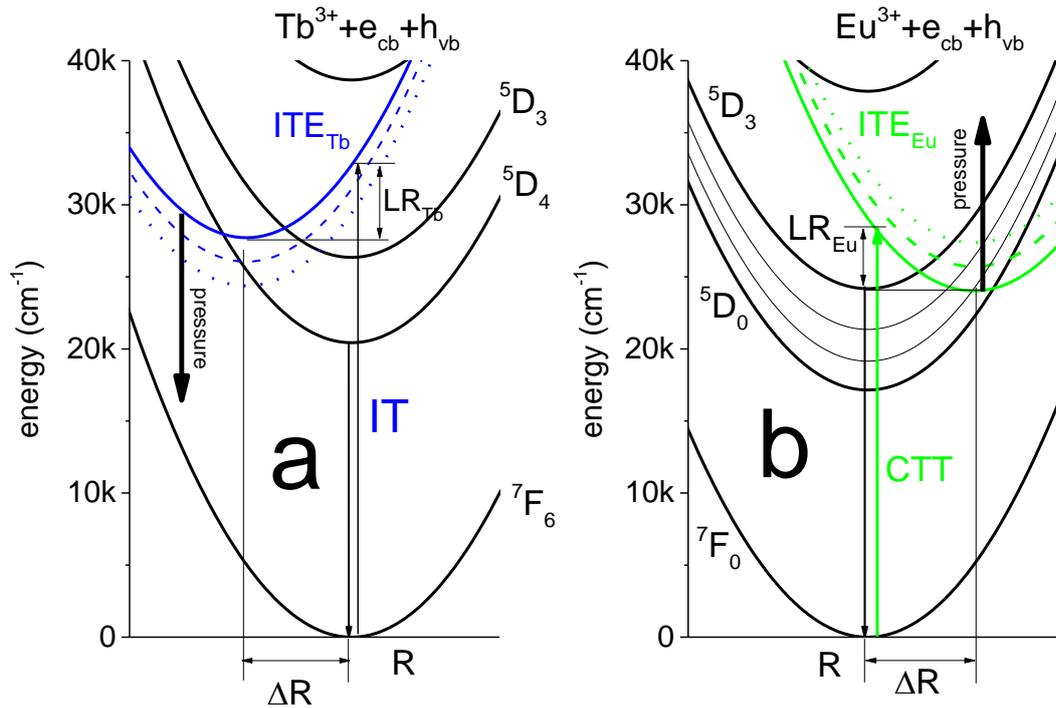


Fig. 8 Configurational coordinate diagrams of the (a) $Y_2O_2S:Tb^{3+}$ and (b) $Y_2O_2S:Eu^{3+}$ systems.

Black parabolas correspond to $4f^1$ states while blue and green parabolas correspond to ITE states (continuous line corresponds to the pressure of 1 bar, dashed line -100 kbar, dotted line -200 kbar) for Tb^{3+} and Eu^{3+} , respectively.

When an electron is transferred to the ITE state, the lattice relaxation with energy LR_{Ln} occurs. In Fig. 8 (a), illustrating the situation for $Y_2O_2S:Tb^{3+}$, it is evident that as the pressure increases, the ITE_{Tb} decreases with respect to the levels of Tb^{3+} , causing quenching of the emission from the 5D_3 state. The energy from this state is transferred by the ITE_{Tb} state to the lower lying 5D_4 state of Tb^{3+} .

In the case of $Y_2O_2S:Eu^{3+}$, as shown in Fig. 8 (b), at atmospheric pressure, the ITE_{Eu} state lies below the excited state 5D_3 of Eu^{3+} ion which causes its quenching.

As the pressure increases, the energy of the ITE_{Eu} is increased relative to the levels of Eu^{3+} , which causes the exposure of the 5D_3 state and the possibility to observe the emission from that state. It should be noted here that **the low lying ITE_{Eu} state can completely quench Eu^{3+} emission**, which is often the case in Eu^{3+} doped nitride materials. [77]

As has been already mentioned, changes of the ITE_{Tb} and ITE_E energies are related to the increase of the energy of the lanthanide ions ground levels with the increase of pressure relative to the edges of the bands as shown in Fig. 9 (and schematically shown in Fig. 5).[78]

In order to obtain a complete picture of changes in the energy structure of dielectric hosts doped with lanthanide ions as a function of pressure is necessary to know the energy bandgap changes. For $Y_2O_2S:Eu^{3+}$ such information can not, however, be found in the literature. In addition, the H.A. transitions at high pressure are only partially visible in the excitation spectra due to the limitations associated with the absorption of light above 40000 cm^{-1} by diamonds in the anvil cell. In the paper [H12], the assumption of the linear change of the $4f^n$ states energies with respect to the vacuum level was reapplied. The obtained results allowed for the construction of the diagram shown in Fig. 9, presenting the changes of the positions of the bands and the $4f^n$ local states of the selected trivalent and divalent lanthanides in relation to the vacuum level.

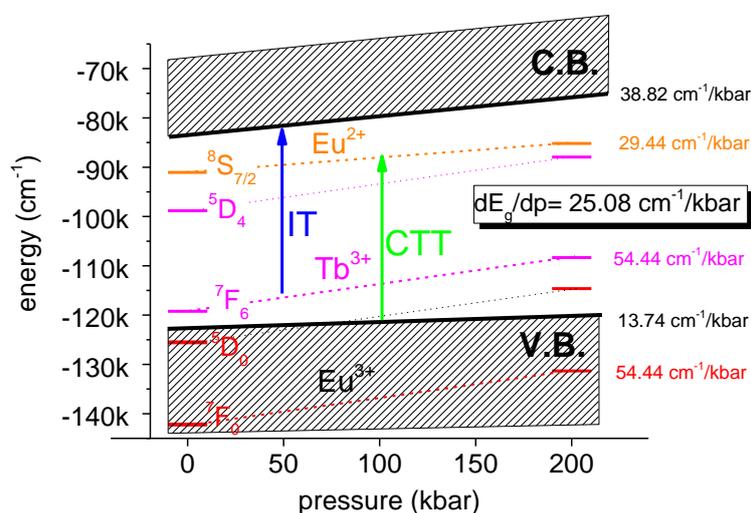


Fig. 9 Pressure dependence of the energetic structure of Y_2O_2S doped with Eu^{3+} and Tb^{3+} .

Based on the above results, it can be concluded that an **increase in pressure results in an increase in the energy of all states (local divalent and trivalent ions as well as band states), relative to the vacuum level.**

In previous experiments (regardless of whether the energy gap increases or decreases with pressure) **a decrease in the IT energy and an increase in the CTT energy with increasing pressure has always been observed.**

Summary

Unique measurement methods and detailed analysis of the experimental results have allowed for a progress in understanding of relaxation processes in luminescent materials doped with lanthanide ions. In particular, the results obtained in [H1-H12] emphasize the significant role that intermediate states play in the charge capture and recombination processes. The results in these papers have provided important information necessary to design efficient luminescent and scintillation materials.

The most important achievements include:

- proving common existence of ITE states in dielectric materials doped with lanthanide ions,
- determination of the influence of intermediate states on the excitation energy transfer mechanism,
- determination of changes in energy structure with respect to the vacuum level of the ion-matrix system with increasing pressure,
- proving that IVCT, CT, ITE are in fact the same states,
- consideration of lattice relaxation in the construction of matrix-lanthanides ions energy diagrams with particular emphasis on doping with two different lanthanide ions
- proposal of a new method to determine the energy structure of matrices doped with any lanthanide ion using high-pressure spectroscopy,

It should be noted here that although the discussed papers provided a lot of information about the energy structure of lanthanide ion doped dielectric materials, they have also raised new questions that will (~~perhaps~~) **definitely** be answered in years to come.

At this point, it would be advisable to outline plans for the future, but instead I would like to pose the following questions, that I plan to answer in the near future:

- Will it be possible to determine the energy of ITEs by means of electrical-optical measurements?
- Will the high-pressure method allow to identify the types of traps that cause persistent luminescence?
- What is the lattice relaxation mostly dependent on and to what extent is it dependent on pressure?

...

d) Other scientific achievements

Since the beginning of doctoral studies in 2005, the applicant has conducted experiments in the Condensed Matter Spectroscopy Division under the supervision of professor Marek Grinberg. During this time, a research workshop has been developed to broaden the measurement possibilities. Nowadays, apart from the standard spectroscopy (a study of absorption, excitation and luminescence spectra and quantum yield), the range of available measurement techniques is extended to luminescence excitation, time-resolved luminescence, decay curves at varying temperatures and at high hydrostatic pressures obtained using the diamond anvil cell. It is worth noting that such measurement techniques are unique not only in Poland but also worldwide. This wide range of measurement capabilities allows for greater national and international cooperation, resulting in joint scientific projects listed in Appendix 4.

The scope of these projects included primarily the study of inorganic compounds in the form of crystals, powders, thin layers and glasses) such as oxides, nitrides, oxynitrides, fluorides, sulphides, oxysulphides and others, doped with the lanthanide and transition metal ions.

The research focused on the analysis of energetic structure of the dopants in the studied matrices and the energy transfer processes between the matrix and the luminescence centers.

The positions of the optically active ions in the crystalline hosts have been determined and the states between which the optical transitions occur as well as the main channels of nonradiative relaxation have been identified in the studied materials. The results of these studies have been presented at international conferences and described in a number of scientific publications, detailed in Appendix 4.

A number of papers published in 2008-2010 dealt with the study of selected fluoride materials doped with Eu^{2+} ions [31-33] and oxide materials doped with Pr^{3+} ions [28, 29]. The ITE model has been used for the analysis of the experimental results contained in these works. It explained both the linear and non-linear changes of the ITE state energy as a function of pressure. Non-linear behavior of ITE state energy is caused by pressure-induced mixing of this state with excited states of lanthanide dopant ($\text{Ln}^{\alpha+}$)*. The mixing of states is important in the case of Eu^{2+} ions, where the excited state is the $4f^65d^1$ configuration state. However, in the case of Pr^{3+} ions where the excited states belong the $4f^n$ configuration, the mixing of these states with the ITE state is negligible. This is due to the larger delocalisation of electrons occupying $4f^65d^1$ states in comparison with highly localized electrons in $4f^n$ configuration

states. The results of these studies have been summarized in [9] and [11] and in S. Mahlik's dissertation. [10]

In the papers [79-83], the luminescent properties of KMgF_3 and LiBaF_3 doped with Eu^{2+} ions at high hydrostatic pressures and variable temperatures were investigated. In these materials, emission in the form of narrow lines of about 360 nm associated with $f-f$ transitions is observed at atmospheric pressure instead of the typical $d-f$ Eu^{2+} transitions. At atmospheric pressure and at low temperatures, luminescence of $\text{LiBaF}_3:\text{Eu}^{2+}$ (where Eu^{2+} ions occupy Ba^{2+} sites) originates from $f-f$ and ITE emissions. With increasing pressure, these emissions are replaced by the $d-f$ emission. Such a phenomenon has not occurred in $\text{KMgF}_3:\text{Eu}^{2+}$, where the divalent Eu^{2+} occupies a monovalent K^+ ion site. In the paper [80] it has been found that the ITE does not exist in $\text{KMgF}_3:\text{Eu}^{2+}$, because the Eu^{3+} ground state is degenerated with the V.B. Additionally, the previously unknown luminescence has been demonstrated in the $\text{KMgF}_3:\text{Eu}^{2+}$, which appears at temperatures below 150 K and is only excited at wavelengths between 310 and 340 nm. This emission appears in the place of the Eu^{2+} $f-f$ transition and also consists of a series of narrow lines. It is related to the Eu^{2+} ion at strongly distorted centers. Such a center can be created when a twelfold coordinated Eu^{2+} ion is accompanied by one fluorine vacancy which captures one electron (the F center).

The task under study in [84-86] was the determination of the energy structure of systems in which optically active ions Eu^{2+} and Eu^{3+} exist simultaneously. The possibility of simultaneous existence of stable Eu ions in the 2+ and 3+ states in one lattice is discussed in relation to the energy of charge compensation defects, with particular emphasis on the position of the Fermi level in such systems. The works highlighted the possibility of short-range and long-range compensation as well as the effects that cause of such compensations. The obtained results showed the general rule that Fermi energy depends on thermal processing of the given material and on doping with lanthanide ions as well as on the concentration of natural defects such as cationic vacancies. Therefore, Fermi energy from undoped material can not be considered a parameter that determines the charge state of Eu ions.

Another group of test materials were nitrides and oxide-nitrides doped with Ce^{3+} and Eu^{2+} ions. [87-92] These groups of materials are particularly promising as phosphors for use in white light emitting diodes (w-LEDs) due to the efficient broadband absorption in the blue light range and luminescence in the spectral range from blue to red.

In all examined materials, the positions of optically active ions in the crystal lattice were determined and the states between which the radiative transitions occur as well as the main channels of non-radiative relaxation were identified.

In papers [87-91] it was shown that non-radiative transitions responsible for temperature-quenching luminescence of lanthanide ions occur through electron transitions from the excited ions of the dopant into the C.B. (mainly formed by the lattice ions) or into the ITE exciton states.

The dependence of luminescence quenching on the temperature allowed to determine the activation energy, with the aid of which then the energies of the ground states of the dopant ions in the band structure were determined. In addition, it has been shown that materials in which ions were located in the empty channels of the host (AlN and β -SiAlON) are characterized by the smallest pressure shifts of the emission bands and the lowest values of the lattice relaxation energy. This in the case of β -SiAlON resulted in luminescence spectra consisting of a series of narrow lines for Eu^{2+} at low temperature. [92]

In the case of a series of $(\text{Sr}_{0.98-x}\text{Ba}_x\text{Eu}_{0.02})\text{Si}_2\text{O}_2\text{N}_2$ materials, a relationship between the chemical (expressed by the Sr to Ba ratio) and the mechanical (pressure-induced) effect of the crystal compression leading to phase transitions was demonstrated. A phase transition diagram has been developed, which shows that the value of the pressure at which the phase transition occurs decreases linearly with the increase in Ba^{2+} concentration in the tested series of materials. [90] In the paper [90], the effect of the second coordination zone on affect the spectroscopic properties of Eu^{2+} ions has been discussed. In particular, it has highlighted a situation in which the cations form linear chains.

In this kind of linear chain of positive ions, the 5d orbitals of the Eu^{2+} ion are spatially oriented towards the positive ions chain and extend partly beyond the first coordination zone. The effect of this delocalization is the expansion of the bandwidth of emission and increase of the Stokes shift.

The papers [74, 75, 93-95] present the potential applications of oxide and fluoride materials doped with Mn^{4+} ions as red phosphors for the w-LEDs. In order to describe the spectroscopic properties of Mn^{4+} ions, an extended crystal field model, with particular emphasis on the influence of the spin-orbit interaction, has been used. The impact of the local environment around the Mn^{4+} ions on the intensity of the zero-phonon line has also been determined in the works. Regarding the applications, the contribution of the zero-phonon line to the spectrum should be substantial.

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