Jahn-Teller Effect And Spin-Orbit Interaction In Bi$_{12}$SiO$_{20}$:Ru

P Petkova
Shumen University “Konstantin Preslavsky”, 115 Universitetska street, 9712 Shumen, Bulgaria
E-mail: Petya232@abv.bg

Abstract. The investigation of the optical properties of doped cubic crystals with the apparatus of molecular quantum mechanics is very important for their application in practice. This is the reason for the analysis of the experimental results of the Ru$^{4+}$ and Ru$^{5+}$ octahedral complex in the crystal lattice of doped Bi$_{12}$SiO$_{20}$. This paper makes a comparison between the manifestation of the Jahn-Teller effect and the spin-orbit interaction in the visible spectral region where the absorption structure of ruthenium is observed. In this work, the calculations are connected with the determination of Racah’s parameters of the crystal field. The spin-orbit interaction and the exchange interaction are also analyzed.

1. Introduction
The sillenite-type Bi$_{12}$SiO$_{20}$ (BSO) crystals display optical activity and a strong photochromic effect. They are applied in dynamic holography, optical information processing, optical phase conjugation and real-time interferometry [1, 2]. This is the reason for the investigation of their optical properties.

The determination of the valence and the local symmetry of the involved dopants in the crystal structure is very important for the optimization of the synthesis conditions of these materials. That is why the aim of the present work is to present the energy level diagram of Ru$^{4+}$ and Ru$^{5+}$ in BSO:Ru.

2. Experimental Details
The crystals were prepared from a stoichiometric solution using the Czochralski method. The purity of the starting oxides used was 99.9999% for Bi$_2$O$_3$ and SiO$_2$. The structure of the sillenite is the final result from Si$^{4+}$ tetrahedrons and Bi$^{3+}$ octahedrons. The dopant was placed in the melt solution in the form of the oxide RuO$_2$. The concentration of the ruthenium ions in the crystal lattice was Ru – 3.23x10$^{20}$ cm$^{-3}$. The maximum ruthenium concentration in the melt was established by several experiments which determined the optically homogeneous doped crystals without other phase inclusions. The diameter of the synthesized crystals was 30-45 mm and their length was 70-100 mm.

The experimental set up for the measurement of the absorption coefficient in the visible region consisted of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector. The investigation was carried out with an untreated sample that has been illuminated with UV light for 30 min.
3. Results and Discussion

The absorption coefficient is calculated using the formula: \( \alpha = \frac{1}{d} \ln \left( \frac{I_0}{I} \right) \), where \( I_0 \) is the intensity of the incident light, \( I \) is the intensity of the passing light and \( d \) is the sample thickness. The absorption spectrum of the untreated and illuminated crystals is measured in the spectral region 1.6-1.8 eV (figures 1, 2). A well pronounced curvature can be observed around 1.70 eV when BSO:Ru is untreated (figure 1). This curvature is missing in the illuminated state of the crystal (figure 2). In order to explain this difference, the first derivative of the absorption coefficient must be calculated. \( \frac{d\alpha}{dE} \) provides information only for the number of 4d electron transitions in the Ru ion. So the second derivative of the absorption coefficient must be calculated. Thus information for the exact energetic position of 4d electron transitions is derived. It is seen that the number of the electron transitions in Ru\(^{4+}\) is two when the crystal is untreated (figure 1). The energy of these two electron transitions is as follows: 1.66 eV and 1.74 eV. The number of the electron transitions is three when the sample is illuminated and the valence of the ruthenium ion is 5+ (figure 2). This fact is connected with the colour changing of the crystal. The maximum around 1.73 eV in the first derivative of \( \alpha(E) \) consists of two overlapping transitions (1.71 eV and 1.75 eV) in the second derivative of the absorption coefficient (figure 2). The energetic diagram of the 4d electron transitions in Ru\(^{4+}\) is presented in figure 3. The investigation of Bi\(_{12}\)SiO\(_{20}\)-Ru by Magnetic Circular Dichroism (MCD) proves that Ru\(^{4+}\) is inculcated in the Bi\(^{3+}\) octahedrons in the crystal lattice [3]. The symmetry of the octahedral complex changes to the tetragonal symmetry \( D_{4h} \), because the ruthenium ions have smaller ionic radius than Bi\(^{3+}\). The final result is expressed in the octahedral extension and it concludes in the appearance of the static Jahn-Teller effect in the basic energy level. The value of the crystal field parameter \( D_q \) is 14760 cm\(^{-1}\) for the Ru\(^{4+}\) ion. When there is more than one electron in an atom, there is certain electrostatic repulsion between those electrons. The strength of the repulsion varies from one atom to another depending upon the number and spin of the electrons and the orbitals they occupy. The total repulsion can be expressed in terms of the two parameters \( B \) and \( C \) which are known as the Racah parameters. The Racah parameters for the chromium are as follows: \( B = 1476 \) cm\(^{-1}\) and \( C = 6642 \) cm\(^{-1}\). The literature [4] informs of the Nephelauxetic parameter \( \beta = B \) (complex)/B (free ion). If the value of \( \beta \) is in the interval 0.54-0.81, it manifests the metal ligand \( \sigma \) bond. The calculation of this parameter for BSO:Ru (\( \beta = 1.43 \)) shows that the metal ligand \( \pi \) bond is present. The tetragonal distortion of the octahedral complex has full potential \( V(D_{4h}) = V_{Oh} + V_{D4h} \). If the matrix elements are known, the value of the parameter \( D_q \) and the radial parameters \( D_s \) and \( D_t \) will be known. The parameter \( D_t \) determines the difference between the equatorial and the axial center: \( D_t = \frac{4}{7}[D_q(xy) - D_q(z)] \). If the approximation of the theory of the ligand field is applied, then \( D_q \sim \frac{1}{t^2} \), where \( t = 0.1466 \) cm\(^{-1}\) is the length of the bond M-O. Hence, \( r(xy) / r(z) = \frac{D_q(z)}{D_q(xy)} \cdot \frac{1}{6} = 0.895 \). For the complex under investigation, \( D_q(x) = 0.0049 \) cm\(^{-1}\) and \( D_q(xy) = 0.0095 \) cm\(^{-1}\). The value of \( D_t \) is 0.0026 cm\(^{-1}\). The parameter \( D_s = 0.014 \) cm\(^{-1}\) is defined by the equation \( \Delta_3 = D_s + 10D_t \) (Figure 3). The symmetry of the complex is such that \( e_g \) and \( t_{2g} \) orbitals of the metal correspond only to \( \pi - \text{anti-connecting and } \pi - \text{anti-connecting orbitals} \) [5]. The parameters \( \delta \sigma \) and \( \delta \pi \) are determined as follows: \( \delta \sigma = \sigma_z - \sigma_x = -(12/8)D_s - (15/8)D_t, \delta \pi = \pi_z - \pi_x = -(3/2)D_s + (5/2)D_t \). The parameters \( \sigma \) and \( \pi \) are indirect indicators for the \( \sigma - \text{anti-connecting and } \pi - \text{anti-connecting properties of the ligands} \). Finally, \( \delta \sigma = -0.0161 \) cm\(^{-1}\) and \( \delta \pi = 0.0275 \) cm\(^{-1}\). The electron transitions in Ru\(^{4+}\) realize from the basic state \( ^3A_{2g} \) (F) to the first excited state \( ^1T_{2g} \) (F) (figure 3). These three electrons are situated on the \( d_{xz}, d_{xy} \) and \( d_{z^2} \) respectively.

This paper discusses the electronic structure of 3d valence electrons of Co which is embedded in a metallic glass host. It is convenient to introduce the exchange interaction \( J(dd) \) here, describing the intrashell exchange attraction between parallel spins [6]: \( J(dd) = 1/14(\delta^2 + F^2) \) and the additional parameter describing the angular part of the multiplet splitting is \( C(dd) = 1/14(9/7F^2 - 5/7F^0) \). J and C are especially useful when describing the lowest state of an \( \Gamma \) multiplet. For d electrons \( l = 2 \). According to Hund’s rule, this is always the state with the highest possible spin quantum number. In the case under investigation, the values of \( J(dd) \) and \( C(dd) \) are as follows: 14 465 cm\(^{-1}\) and 6642 cm\(^{-1}\). The next equations are fulfilled for the glass systems under investigation \( F^2 = 49F_2 \) and \( F_4 = 441F_4 \).
where $F_2$ and $F_4$ are the Condon–Shortley parameters. The integral of the exchange interaction $K(z^2,xy) = 4B + C = 12546 \text{ cm}^{-1}$. This exchange interaction is realized between the orbitals $d_{z^2}$ and $d_{xy}$. The orbital $d_{xy}$ has very important role, because when the crystal is illuminated one electron is situated on this orbital. In the opposite case, when the sample is untreated, the $d_{xy}$ orbital is empty (figure 3).

![Figure 1](image-url)

**Figure 1.** The absorption coefficient $\alpha(E)$, first derivative $d\alpha/dE$ and second derivative $d^2\alpha/dE^2$ for the untreated $\text{Bi}_{12}\text{SiO}_{20}:\text{Ru}$. 
Figure 2. The absorption coefficient $\alpha(E)$, first derivative $d\alpha/dE$ and second derivative $d^2\alpha/dE^2$ for the illuminated $\text{Bi}_{12}\text{SiO}_{20}:\text{Ru}$. 
Figure 3. Energetic diagram of the 4d electron transitions in Ru$^{5+}$.

Conclusions
The illumination with UV light of the crystal Bi$_{12}$SiO$_{20}$:Ru clearly shows that Ru$^{4+} + e^- \rightarrow$ Ru$^{5+}$ in the visible spectral region. This is very important for its application in practice as holographic information storage. The metal ligand bond in BSO:Ru is $\pi$, which means that Ru ions defy very big dynamic disorder in the crystal lattice. The intrashell exchange attraction between parallel spins is stronger than the angular part of the multiplet splitting in the case of Ru$^{5+}$ ions.

References
[1] Raciukaitis G Gavryushin V Kubertavicius V Puzonas G 1993 Jpn. J. Appl. Phys. 32 645
[2] Marinova V Veleva M Petrova D Kourmoulis I M Papazoglou D G Apostolidis A G Vanidhis E D Deliolanis N C 2001 Journal of Applied Physics 89 2686-2689
[3] Ramaz F Rakitina L Gospodinov M and Briat B 2005 Optical Materials 27 1547-1559
[4] Chandra S Gupta L 2005 Spectrochimica Acta Part A 62 1125
[5] Mc Clure D S Advances in the Chemistry of Coordination compounds 1961 New York Macmillan 498
[6] van der Marel D Sawatzky G A 1988 Physical Review B 37 10674–10684