THE COMPLEXES OF Co^{2+} IN $Bi_{12}SiO_{20}$ AND Co^{3+} IN $Bi_{12}TiO_{20}$

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ABSTRACT: We have investigated the absorption of the Co doped $Bi_{12}MO_{20}$ (M = Si, Ti) in the spectral region 12 092–18 149 cm^{-1}. The observed absorption band is due to the Co-impurity in the visible spectral region. This absorption band does not contain information about the exact energy position of the Co levels. Therefore, we have calculated the second derivative of absorption. It is established that Co^{2+} ions are surrounded by distorted tetrahedral coordination in $Bi_{12}SiO_{20}$ (BSO). The energy level structure of the Co^{2+} ion in BSO and this of Co^{3+} ion in $Bi_{12}TiO_{20}$ are also presented. We have calculated the crystal field parameter Dq and the Racah parameters B and C for Co^{2+} ion.

KEY WORDS: absorption spectrum, 3d transition metals, Jahn-Teller effect, spin-orbit interaction

INTRODUCTION

Sillenite-type $Bi_{12}SiO_{20}$ (BSO) pure and doped single crystals are widely used in optical devices, spatial-time light modulators and as holographic media [1,2]. BSO are cubic crystals, I23 space group symmetry, built up of $Si-O_4$ tetrahedrons and deformed $Bi-O_n$ polyhedrons [3], defined by some authors as $Bi-O_n$ (n = 7) - octahedrons [4] or as Bi-O-pseudo-octahedrons [5]. The chemical bonds Bi-O and Si-O in BSO are covalent [3]. After reported literature data most of doping ions in BSO are placed at metal position in $Si-O_4$-tetrahedron [6]. For Ru, Cu and Mn - ions there are data for occupation of both metal positions in tetrahedron (replacing Si) and in pseudooctahedron (replacing

Bi) [5,6,7]. Many studies on the optical absorption coefficient of doped with Al, P, Cr, Mn, Fe, Co, Ni, Cu, Se and Ru sillenites in the VIS spectral region have been reported so far and the effect of doping were discussed mainly in respect to possible oxidation states of doping ions, position of allowed electron transitions in the 1.5 – 2.2 eV region and the dependence of corresponding absorption coefficient on dopant concentration [5,7,8-16].

Nevertheless, until now there are no systematic complex investigations on doping effects on impurity levels in the band gap (1.5–2.2 eV). We attempt to present the effect of doping as well as to specify some of main parameters of the crystal field and the spin-orbit

interaction in the substructures of the sillenites.

MATERIALS AND SAMPLES PREPARATION

We investigated doped BSO and BTO crystals with Co. All the crystals were grown from stoichiometric melts $Bi_2O_3:SiO_2 = 6:1$ using the Czochralski method under conditions described in detail elsewhere [17,18]. High purity Bi_2O_3, SiO_2 and Co_3O_4 were used for synthesis and doping. The concentration of doping was determined by flame (Zeeman 3030) and electrical-thermal atomic (Varian 240) absorption spectrometry as well as by inductively coupled plasma atomic emission spectrometry (Jobin Yvon, ULTIMA 2).

EXPERIMENTAL RESULTS AND DISCUSSION

We measured absorption spectra of $Bi_{12}SiO_{20}:Co$ and $Bi_{12}TiO_{20}:Co$ in the spectral region 1.5-2.25 eV (Fig. 1a, Fig. 2a). It is seen that the cobalt number of the electron transitions in structure is complicated and its shape does not give information about the Co^{2+} and Co^{3+} ion. Therefore, the calculation of the first derivative of the absorption coefficient gives information about the number of the electron transitions in the investigated Co complexes (Fig. 1b, Fig. 2b). The exact energetic position of the electron transitions in the Co ion is determined by calculation of the second derivative of the absorption coefficient (Fig. 1c, Fig. 2c).

In this section we describe our crystal-field model for the Co^{2+} center in $Bi_{12}SiO_{20}$. This model includes a full treatment of the C_{3v} crystal field which acts upon the Co^{2+} ion. The Co^{2+} impurity in BSO has the d^7 configuration, which we treat as a three-hole configuration. The crystal-field potential consists of the field of T_d symmetry. This means that the tetrahedral coordination about the Co^{2+} ion has four oxygen ions. The tetrahedral crystal field splits the one-hole d states so that the
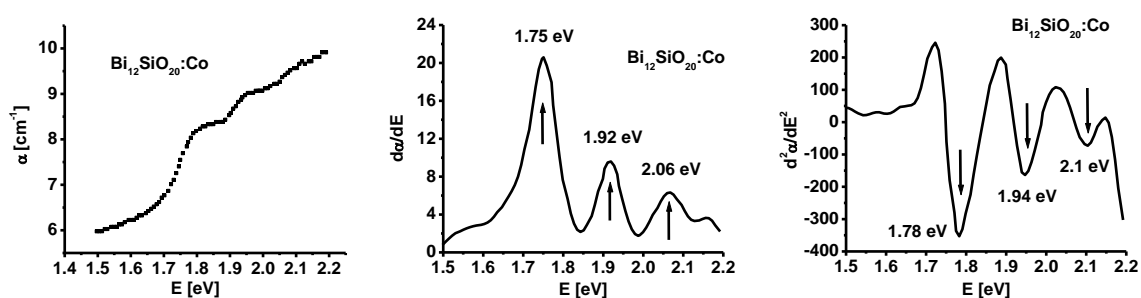

Figure 1 a) Absorption spectrum of $Bi_{12}SiO_{20}:Co^{2+}$ in the spectral region 1.5-2.2 eV; b) first derivative of absorption coefficient; c) second derivative of absorption coefficient.

Figure 2 a) Absorption spectrum of $Bi_{12}TiO_{20}:Co^{2+}$ in the spectral region 1.55 – 2.25 eV; b) first derivative of absorption coefficient; c) second derivative of absorption coefficient.
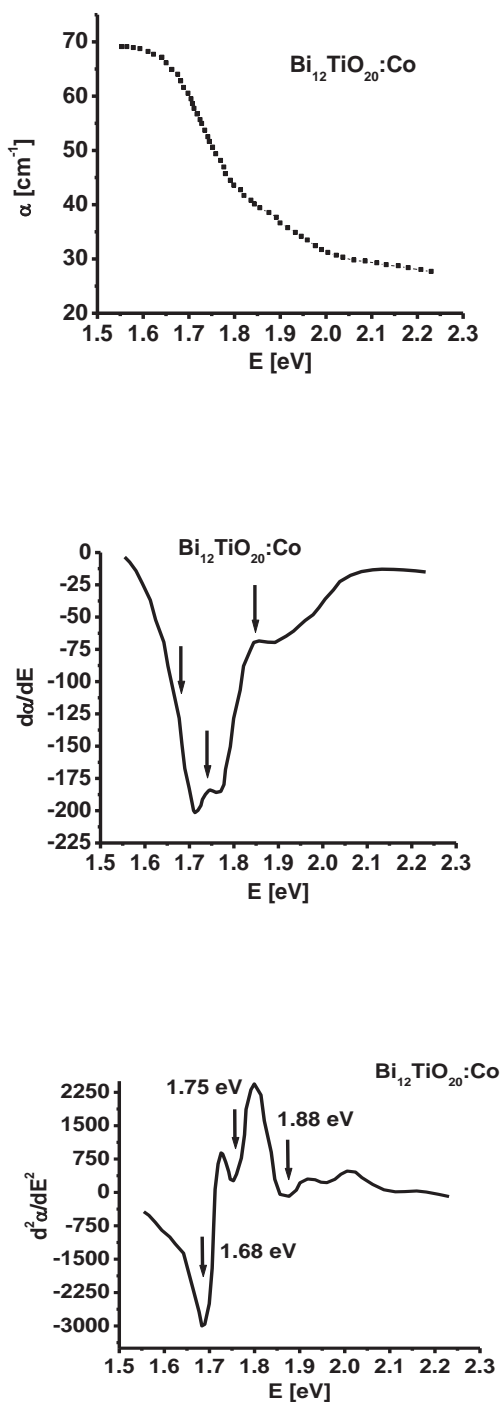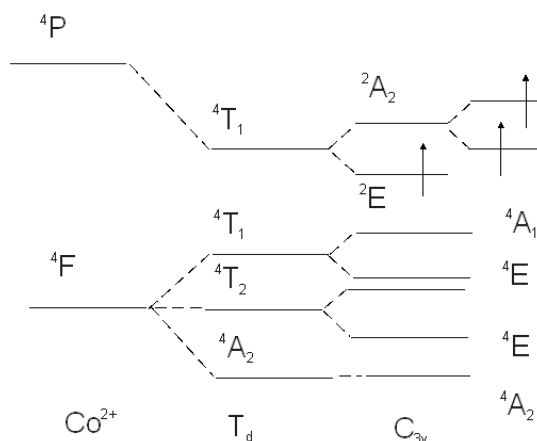
Figure 3 Energetic diagram of Co^{2+} ion in C_{3v} symmetry.

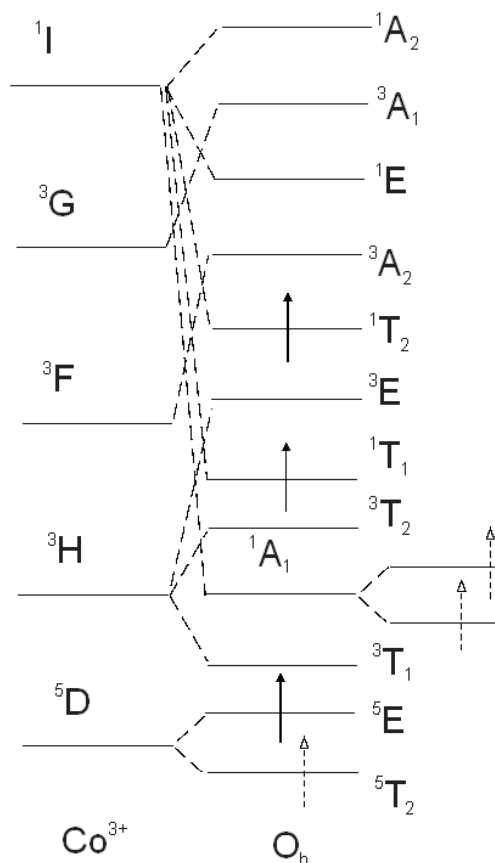Figure 4 Energetic diagram of Co^{3+} ion in O_h symmetry.

t_2-symmetry holes are lower in energy than the e-symmetry holes by an amount 10Dq. The partial removal of the fivefold degeneracy of the d states splits the ^4F term into three manifolds: $^4A_2$, $^4T_2$ and $^4T_1(^4F)$. The ^4P term spans the manifold $^4T_1(^4P)$. These splittings are shown in Fig. 3. The Jahn-Teller effect manifests as distortion of the tetrahedron and the

final result is the lower symmetry C_{3v} (Fig. 3). The bond between the Co^{2+} ion and the surrounding ligands is covalent. This covalency reduces the positive charge of the metal ion as a result of the inductive effect of ligands [19]. The reduction of the positive charge of the Co ion leads to an increase in the radial extension of the d-orbitals.

Thus the electron-electron repulsions weaken and the energy of the state ^4P decreases. The influence of the covalency leads to the reduction of the difference in the energies between the states ^4F and ^4P in the Co complex. This difference is less in comparison with the difference in the same energies of the gaseous ion. The lowering of the level ^4P determines the magnitude of the covalency. This effect is famous as Nephelauxetic. Sometimes it is expressed by the parameter $\beta_0 = [(B - B')/B].100$, where B is the Racah parameter for the free ion and $B' = 650$ cm^{-1} [20] is the same parameter for the complex. β_0 shows the percentage of the energetic decrease of the state ^4P for Co^{2+}. The calculations show that $\beta_0 = 28\%$. This means that the Jahn–Teller effect is stronger. The equation $Dq^2 = (18B^2 + 3B)/8$ is the result of the transformation of the matrix of the energies $^4T_1(^4F)$ and $^4T_1(^4P)$. The value of the crystal field parameter Dq is 975 cm^{-1}. The other Racah parameter C is equal to 2925 cm^{-1}.

The literature [21] informs us of the Nephelauxetic parameter $\beta = B(\text{complex})/B(\text{free ion})$. If the value of β is in the interval 0.54–0.81, it manifests the metal ligand σ bond. In the case of Co doped BSO the ligand bond is σ, because $\beta = 0.72$.

The spin-orbit parameters for the examined Co tetrahedrons are as follow: S = 3/2, J = 1/2; 3/2 and L = 0; 1. The contribution of the spin-orbit interaction in the energy of each level is expressed as $E = (1/2)\lambda[J(J+1) - L(L+1) - S(S+1)]$ [10]. Therefore, $E_{J=3/2,L=0} = 89$ cm^{-1} and $E_{J=1/2,L=1} = 445$ cm^{-1} for the Co complex in $Bi_{12}SiO_{20}$. The difference between the energies of two neighbouring states arising due to the spin-orbit interaction is determined by the expression $\Delta E_{J,J+1} = \lambda(J + 1)$ [22]. Thus $\Delta E_{1/2,3/2} = 267$ cm^{-1} and $M_S = 3/2$, $M_L = 0, \pm 1$.

It is shown in the literature that when the Co^{3+} ion is in the octahedral coordination they are three absorption bands $^5T_2 \rightarrow {}^5E$ (11 000-14 000 cm^{-1}), $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ (14 000-36000 cm^{-1}) [23]. In our case, they are three absorption bands which are connected with three electron transitions in Co^{3+} (Fig. 4).

CONCLUSIONS

In this work, the interesting fact is that the impurity absorption structure in the visible spectral region for $Bi_{12}SiO_{20}$ is characteristic for Co^{2+} and this for $Bi_{12}TiO_{20}$ is characteristic for Co^{3+}. The Co^{2+} ions are in the tetrahedral coordination and the Co^{3+} ions in the octahedral coordination. The Jahn-Teller effect is stronger than the spin-orbit interaction in the tetrahedral cobalt complex.

REFERENCES

[1] Gunter P and Huignard J 2006 *Photorefractive materials and their applications.* Part 1, New York, Springer Science+Buisness Media

[2] Gunter P and Huignard J 2007 *Photorefractive materials and their applications.* Part 2 and 3, New York, Springer Science+Buisness Media

[3] Mihailova B, Gospodinov M and Konstantinov L 1999 *J. Phys. Chem. Solids* 60 1821

[4] Marinova V, Veleva M and Petrova D 2001 *JAP* 89 2686

[5] Ramaz F, Rakitina L, Gospodinov M and Briat B 2005 *Opt. Mat.* 27 1547

[6] Kargin Y, Burkov V, Maryin A and Egorysheva A 2005 Alphabet, Moscow 180 (in Russian)

[7] Marquet H, Tapiero M, Merle J, Zielinger J and Launay J 1998 *Opt. Mater.* 11 53

[8] Nechitailov A, Krasinkova M, Mokrushina E, Petrov A, Kartenko N and Prokofiev V 2000 *JNORG* 36 820

[9] Egorisheva A, Burkov V, Kargin Y, Vasiliev A, Volkov V and Skorikov V 2001 *JNORG* 37 817

[10] Egorisheva A 2005 *JNORG* 50 407

[11] Marinova V, Lin S, Hsieh M, Liu R and Hsu K 2009 *Photorefractive Matt, Effects, and Devices PR'09* P1-39

[12] Egorisheva A, Volkov V, Coya C and Zaldo C 1998 *Phys. Stat. Sol.* B 207 283

[13] Potera P and Pircuch A 2007 *Physica* B 387 392

[14] Kovacs L, Capelli R and Gospodinov M 2008 *Vib. Spec.* 46 69

[15] Zmija J and Malchowski M 2008 *Arh. Mat. Sci. Eng.* 33 101

[16] Ahmad I, Marinova V and Goovaerts E 2009 *Photorefractive Matt, Effects, and Devices PR'09* P1-38

[17] Gospodinov M and Doshkova D 1994 *Cryst. Res. Technol.* 29 603

[18] Petrova D, Gospodinov M and Sveshtarov P 1995 *Mat. Res. Bull.* 30 1201

[19] Drago R 1981 *Physical Methods in Chemistry*, University of Illinois, Urbana

[20] Egorisheva A Burkov V Kargin Yu Volkov V 1995 Neorg. Mater. 31 1087-1093

[21] Chandra S, Gupta L 2005 *Spectrochimica Acta Part A* 62 1125–1130

[22] Ballhausen C J 1964 *Introduction to Ligand Field Theory*, New York, Mc Graw – Hill Book Company, Inc.

[23] Burkov V Egorisheva A Kargin Yu 2003 Zhurnal Neorg. Himii 48 620-638