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Original Contribution

TETRAHEDRAL COMPLEX OF Cr^{3+} AND Cr^{4+} IONS IN $Bi_{12}SiO_{20}$

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ABSTRACT *Absorption measurement is taken in the visible spectral region (650 – 1300 nm). The dopants* Cr^{3+} *and* Cr^{4+} *ions occupy the tetrahedral sites in the crystal lattice of doped sillenite. The energy level structure of these ions in* $Bi_{12}SiO_{20}$*:Cr (BSO:Cr) are presented. The Dq-, B- and C-parameters of the crystal field theory for the* Cr^{3+} *and* Cr^{4+} *ions were obtained. The spin-coupling energy is also calculated for the chromium ions.*

KEY WORDS: *absorption spectrum, 3d transition metals, Racah parameters, energy of the spin pairing*

INTRODUCTION

Bismuth oxide compounds such as the sillenite-type $Bi_{12}MO_{20}$ (BMO, where M = Si, Ge, Ti) crystals are being extensively studied because of their potential applications including dynamic holography, optical information processing, optical phase conjugation and real-time interferometry [1–5]. The defect identification, including the dopant ions involved, their valence and local symmetry is essential because this information may guide the efforts for optimization of the synthesis conditions to obtain the intended material properties. In this paper, we present a detailed optical study of Cr^{3+} and Cr^{4+} ions which are in the tetrahedral coordination.

MATERIALS AND SAMPLES PREPARATION

$Bi_{12}SiO_{20}$ crystals belong to the sillenite family of materials with the space symmetry I23 with a body centered cubic unit cell (a = 10.102 Å), which contains 24 Bi^{3+} ions, 2 Si^{4+} ions and 40 O^{2-} ions (nominal valences). Two structural elements can be distinguished, the SiO_4 regular tetrahedron and the BiO_7 polyhedron [6]. The former exists at the corners and at the center of the cubic unit cell. In the BiO_7 polyhedron, each of the Bi^{3+} ions is surrounded by 7 oxygen atoms and is coordinated in a pseudo-octahedral configuration, in which the oxygen atom at one corner is replaced by two atoms at somewhat larger distance. BSO single crystals were grown in air by the Czochralski method from a melt containing a mixture of high purity (99.9999%) oxides including Bi_2O_3 and SiO_2 in a 6:1 molar ratio [7]. Platinum crucibles of 60 mm in diameter and 80 mm in height were used as containers. The crystals were grown in a <001> direction under conditions of low temperature gradient over the solution (5–7 ^{o}C/cm), at a growth rate of 0.7

mm/h and a rotation rate of 20 rpm. Fully facetted and optically homogeneous crystals of 35 mm in diameter and 50 mm in height were obtained. The starting chromium dopant was introduced into the melt solution in the form of the oxide Cr_2O_3. The analysis by atomic absorption spectrometry shows that they are present in the crystal at concentration of [Cr] = $4.9\text{x}10^{18}$ cm^{-3}. This corresponds to relative concentration [Cr]/[Si] = 0.25%.

EXPERIMENTAL RESULTS AND DISCUSSION

The electron paramagnetic resonance (EPR) identifies a chromium ion in the unusual Cr^{3+} valence replacing a substitutional Si^{4+} in tetrahedral oxygen coordination [8]. Evidence is found that the symmetry lowering from tetrahedral (T_d) to trigonal (C_{3v}) is not spontaneous, but induced by an associated defect. It has been previously reported that chromium in BSO and $Bi_{12}GeO_{20}$ (BGO) crystals occupies the tetrahedral metal M^{4+} sites in the oxidation states Cr^{5+} and Cr^{4+} and that both reduction under vacuum annealing and illumination pushes the balance toward Cr^{4+} [9–11]. The aim of this work is to explain the appearance of $3d^3$ transitions (Cr^{3+}) in the spectral region 650-900 nm and the observation of $3d^2$ transitions (Cr^{4+}) in the spectral region 900-1300 nm.

The experimental set up for measurement of the absorption coefficient in the visible and near IR region consists 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 absorption coefficient of the investigated samples has been measured to be between 650 and 1300 nm (Figs.1a and 2a). The first derivative of the absorption coefficient at photon energy is calculated to be in the 680-1300 nm spectral region. The $[d\alpha/d(h\nu)]$ determines only the number of electron transitions in a Cr^{3+} and Cr^{4+} ions and it does not give an exact information about the energy position of these transitions. This is the reason for the calculation of the second derivative of the absorption coefficient $[d^2\alpha/d(h\nu)^2]$.

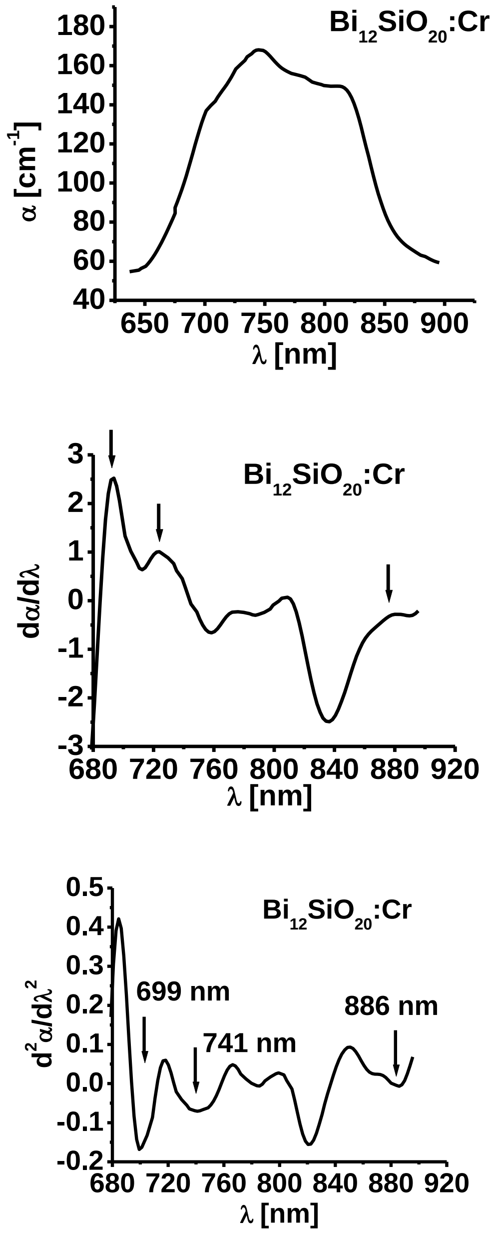

Figure 1 a) Absorption spectrum of $Bi_{12}SiO_{20}$:Cr^{3+} in the spectral region 650 – 900 nm; b) first derivative of absorption coefficient; c) second derivative of absorption coefficient.

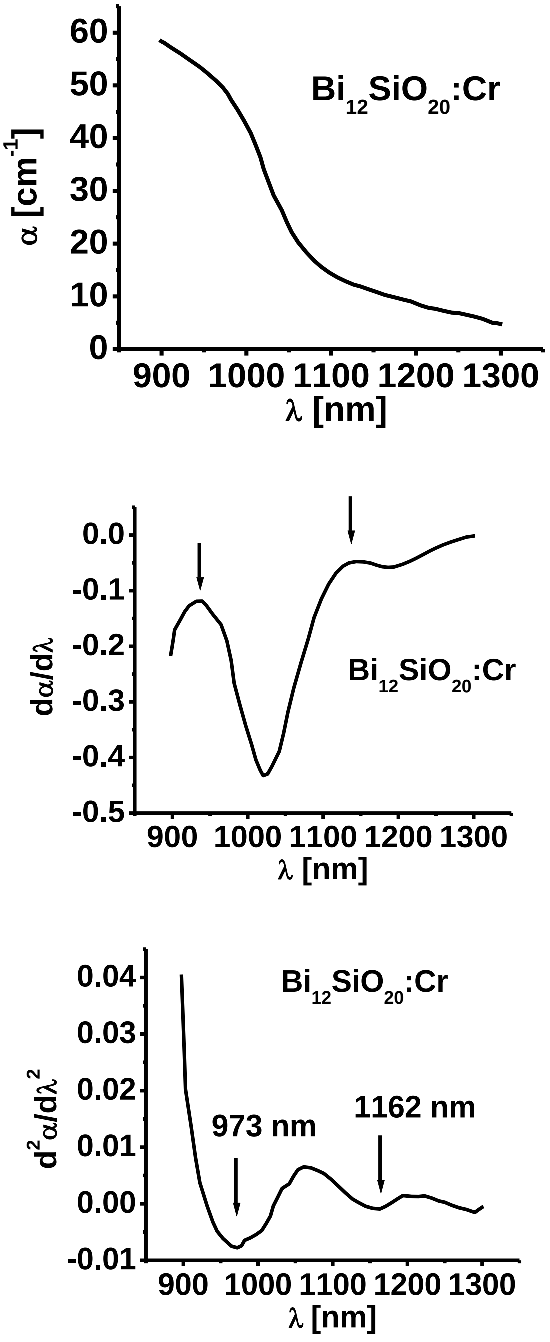

Figure 2 a) Absorption spectrum of $Bi_{12}SiO_{20}:Cr^{4+}$ in the spectral region 900 – 1300 nm; b) first derivative of absorption coefficient; c) second derivative of absorption coefficient.

The absorption coefficient is calculated using the formula: (1) $\alpha = (1/d)\ln(I_0/I)$,

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 components of the Cr^{3+} structure that are connected with the electron transitions are ${}^4A_2({}^4T_1({}^4F)) \rightarrow {}^2E({}^2G)$ (1.4 eV), ${}^4A_2({}^4T_1({}^4F)) \rightarrow {}^4A_1({}^4T_2({}^4F))$ (1.67 eV) and ${}^4A_2({}^4T_1({}^4F)) \rightarrow {}^2E({}^2T_1({}^2G))$ (1.77 eV) (Fig. 3). The absorption structure of Cr^{4+} includes the next two electron transitions ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{2g}({}^3F)$ (1.07 and 1.27 eV) (Fig. 4). The crystal field parameter D_q and the Racah parameters *B* and *C* are calculated for Cr^{3+} and Cr^{4+}. The values of *B* are 910 cm^{-1} and 944 cm^{-1}. The values of the parameter *C* are 4213 cm^{-1} and 4446 cm^{-1}. The values of the crystal field parameter D_q are 1365 cm^{-1} and 944 cm^{-1}.

If the electron transitions are realized between the basic and the closest low energy excited states, then they are connected with the manifestation of the dynamical Jahn-Teller effect (Fig. 3). This effect is manifested as the deformation of the chromium tetrahedron and the T_d symmetry transforms into the C_{3v} symmetry. The ionic radii of Si^{4+}, Cr^{3+} and Cr^{4+} are as follows 40 Å, 75.5 Å and 69 Å. Thus it can be observed the tetrahedral distention. The final result is expressed by the great influence of the Jahn-Teller effect on the energy values of the observed impurity absorption bands (Fig. 3) and the chromium complex becomes stable under the influence of the spin-orbit interaction.

After the spin-orbit interaction the total angular momentum J becomes equal to 1/2 and 3/2. The EPR of chromium doped $Bi_{12}SiO_{20}$ gives information that the total spin angular momentum S is 3/2 [8]. In this connection, they are two possibilities for the total orbital angular momentum L = 0 and L = 1. The case when L = 1 is very interesting, because the orbital quantum number l = ±1. The ligand gives one electron to the metal ion when the charge transfer is observed [12]. This electron becomes indistinguishable from the other electrons of the metal ion. Thus we can change the value of the exchange energy and it can increase or decrease. Thereby the spin-coupling energy (SCE) corrects. This energy is presented by the formula:

(2) $E_{SCE} = P[3/4q - [3q(q-1)]/(16l+4) - S(S+1)]$,

where P is a parameter of spin coupling and it depends on the parameters B and C and q is the number of the electrons of the metal ion. When the charge transfer from ligand to the metal ion is observed, the parameter P is calculated using the formula:

(3) $P = 7/6[(5/6)B+C]$.

The final result is that E_{SCE} = 13 920 cm^{-1} for Cr^{3+} ion and E_{SCE} = 6410 cm^{-1} for Cr^{4+}.

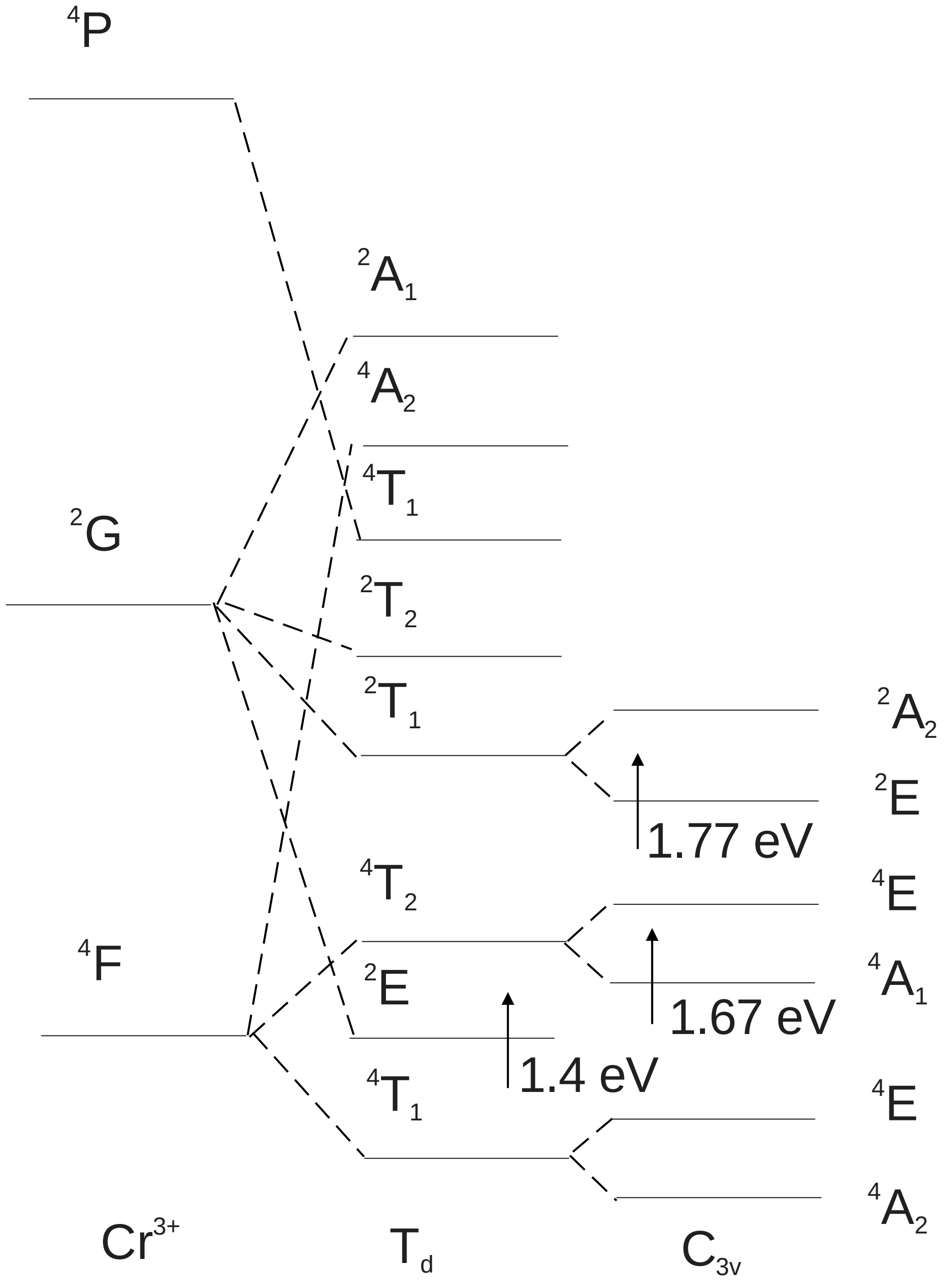

Figure 3 Energetic diagram of Cr^{3+} ion in C_{3v} symmetry.

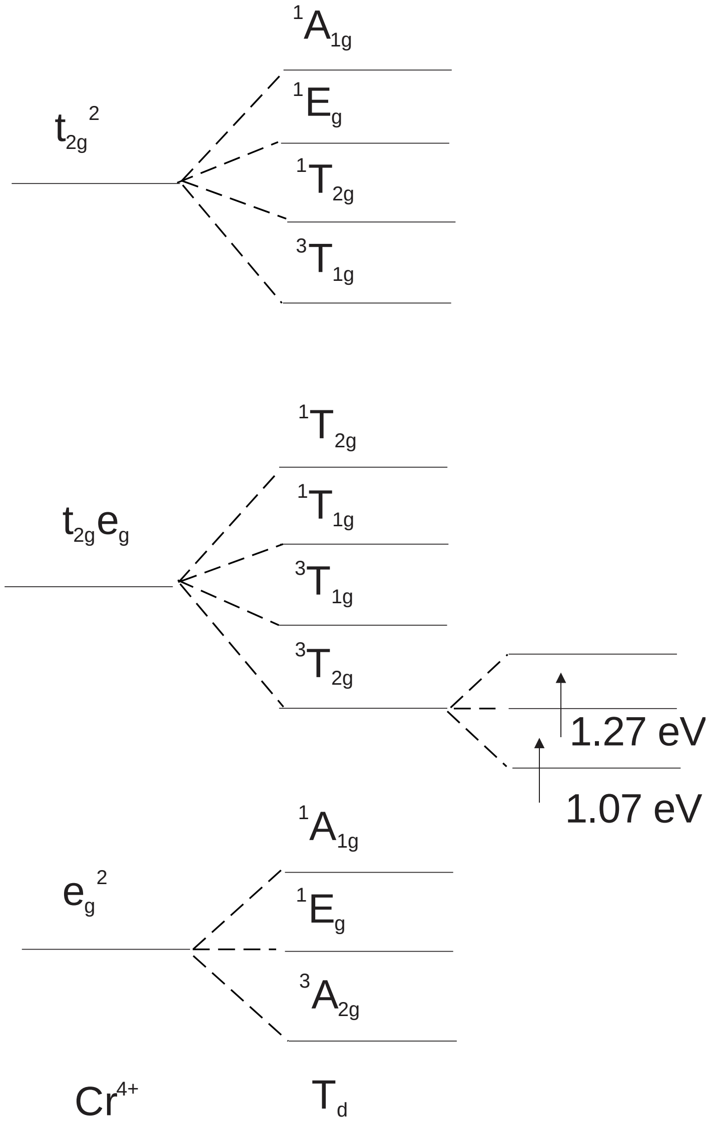

Figure 4 Energetic diagram of Cr^{4+} ion in T_d symmetry.

CONCLUSIONS

In this work, the interesting fact is that the impurity absorption structure in the visible spectral region is a combination between the structure of Cr^{3+} and Cr^{4+} ions.

The tetrahedral complex of Cr^{3+} manifests stronger Jahn-Teller effect and the tetrahedral complex of Cr^{4+} appears stronger spin-orbit interaction.

The charge transfer for $O^{2-} \rightarrow Cr^{3+}$ is realized at bigger spin-coupling energy in comparison with the value of the spin-coupling energy for $O^{2-} \rightarrow Cr^{4+}$.

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