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The optical influence of Cr^{3+} and P^{5+} ions on the properties of doped $Bi_{12}SiO_{20}$

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The absorption coefficient of $Bi_{12}SiO_{20}$:Cr+P and $Bi_{12}SiO_{20}$:P single crystals is measured in the visible and far IR spectral regions. The influence of P^{5+} ions is determined in double doped sillenite. The energy level diagram of Cr^{3+} is produced. The Jahn-Teller effect is explained in the concrete crystals. The Racah parameters have been calculated also. The magnitude of the composite oscillations is determined in far IR region.

Key words: doped sillenites, Jahn-Teller effect, energy level diagram, composite oscillations.

INTRODUCTION

The sillenite-type $Bi_{12}SiO_{20}$ (BSO) crystals have applications in the dynamic holography, optical information processing, optical phase conjugation and real-time interferometry [1]. This is the reason of 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 optimization of the synthesis conditions of these materials. That is why the aim of the present work is to be presented the energy level diagram of Cr^{3+} in BSO:Cr+P and to be determined the composite oscillations in the crystals BSO:P and BSO:Cr+P.

EXPERIMENTAL

The investigated BSO crystals, either undoped or doped with Cr, P and co-doped with Cr+P were grown from stoichiometric melts $Bi_2O_3:SiO_2 = 6:1$ using the Czochralski method under conditions described in detail elsewhere [2]. High purity Bi_2O_3, SiO_2, Cr_2O_3 and P_2O_5 were used for syhthesis and doping. The concentration of P^{5+} is 1.6×10^{20} N/cm^{-1} in BSO:P and the concentration of this ion is 1.13×10^{20} N/cm^{-1} in BSO:Cr+P. The Cr^{3+} ions are inculcated on the co-doped crystal with the concentration 8.1×10^{16} N/cm^{-1}. The thickness of the samples is as follows: $d_{BSO:Cr+P} = 0.101$ cm, $d_{BSO:P} = 0.062$ cm.

The experimental set up for measurement of the absorption coefficient in the visible 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 measurements in the far IR region are performed by use of an IRAffinity-1Shimadzu Fourier Transform Infrared Spectrophotometer.

The absorption spectrum is measured in the spectral region 1.55–2.6 eV for BSO:Cr+P (Fig. 1a). The energetic level diagram of Cr^{3+} ion is presented in Fig. 2. The two-phonon absorption of BSO, BSO:P and BSO:Cr+P is shown in the spectral region 400–2000 cm^{-1} (Fig. 3a and 4a). The electron-vibrational interaction in far IR region of these crystals is measured in the spectral region 5000–6000 cm^{-1} (Fig. 3b and 4b).

RESULTS AND DISCUSSION

The absorption coefficient is calculated using the formula: $\alpha = (1/d)\ln(I_0/I)$, where I_0 is the intensity of the incident light, I is the intensity of the passing light and d is the sample thickness (Fig. 1a). The first derivative of the absorption coefficient at photon energy is calculated to be in the 1.5–2.6 eV spectral region (Fig. 1b). The $[d\alpha/d(h\nu)]$ determines only the number of electron transitions in a Cr^{3+} ion 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 $[d^2\alpha/d(h\nu)^2]$ (Fig. 1c).

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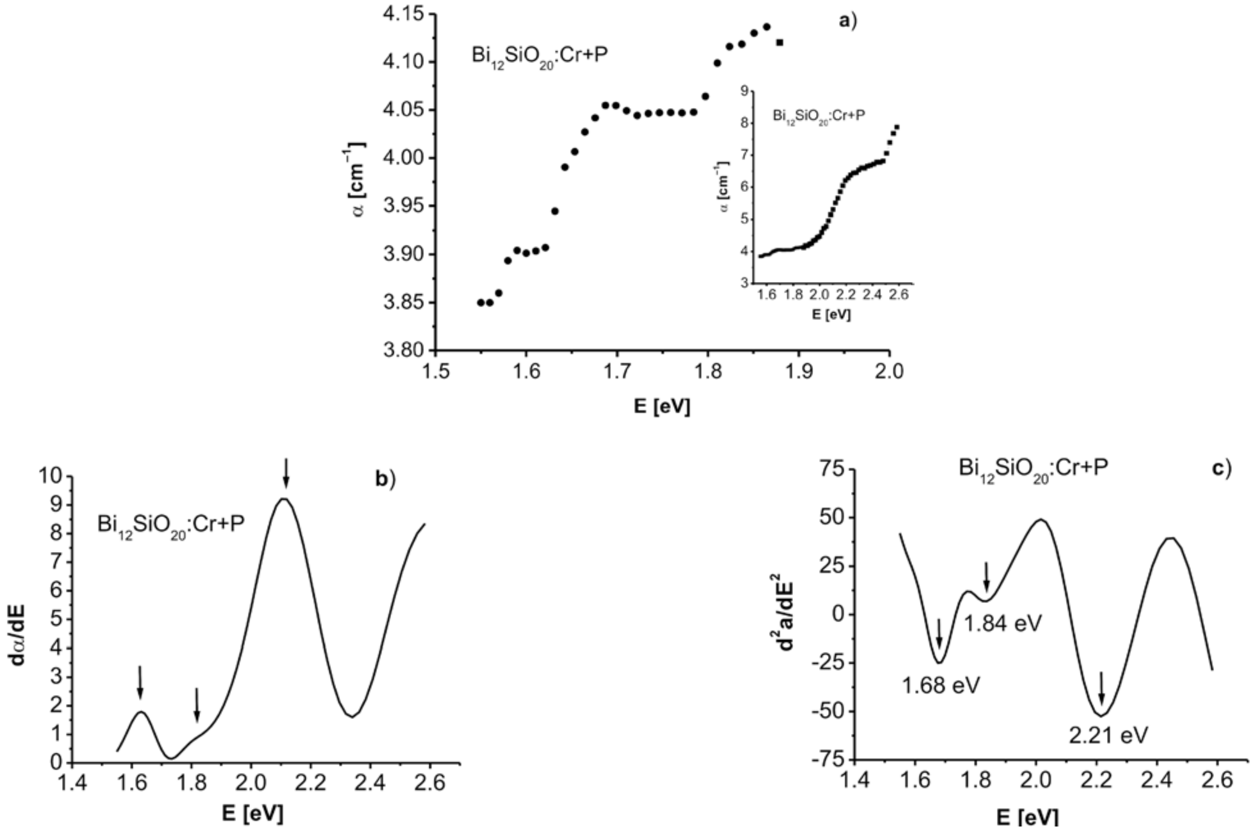
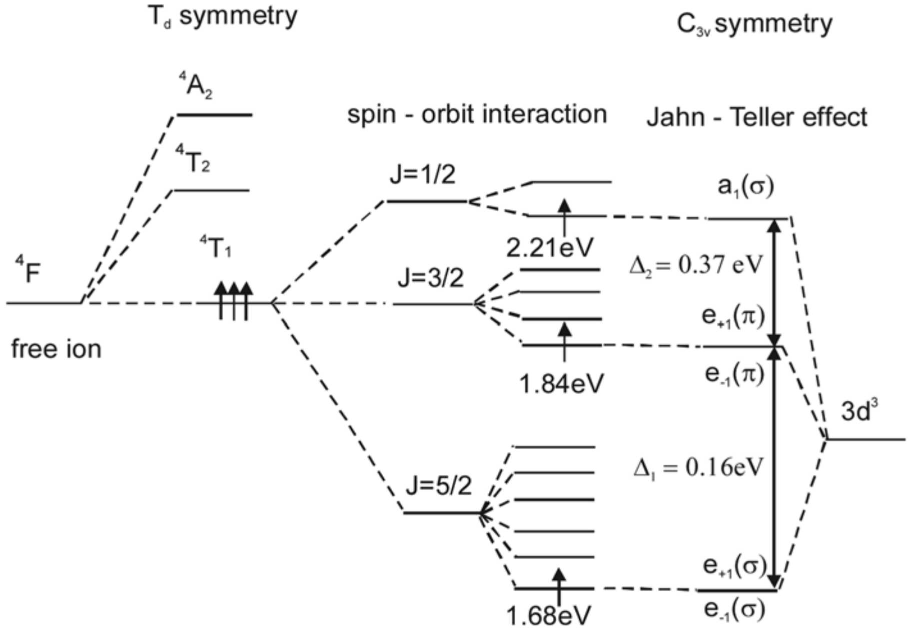


Fig. 1. The absorption coefficient (a), the calculated first derivative of α(E) (b) and the second derivative of absorption coefficient (c) for BSO:Cr+P in the spectral region 1.55–2.6 eV

The d-orbital e_g is split of $e_{\pm 2}(\delta)$ and the d-orbital t_{2g} is split of the two orbitals $e_{\pm 1}(\pi)$ and $a_1(\sigma)$, when the symmetry changes from T_d to C_{3v} [3] (Fig. 2). The transformation of the symmetry due to the Jahn-Teller effect. The radial parameters Ds and Dt are conditioned by the potential $V_{tetr.}$ [4]. In the case of C_{3v} symmetry the distance between $e_{+2}(\delta)$ and $e_{-1}(\pi)$ is $\Delta_1 = 3Ds - 5Dt = 129\ cm^{-1} = 0.16\ eV$. This is the distance between the first and the second electronic transition in the Cr^{3+} ion (Fig. 2). The distance between $e_{+1}(\pi)$ and $a_1(\sigma)$ is $\Delta_2 = Ds + 10Dt = 299\ cm^{-1} = 0.37\ eV$. This is the distance between the second and the third 3d-electronic transition in the chromium (Fig. 2). The values of these two parameters are calculated by our experiment. Thus the values of the parameters Dt and Ds are as follow 21.94 and 79.6. McClure [5] has determined the next parameters $\delta\sigma = \sigma_z - \sigma_{xy} = -1.5Ds - 1.88Dt$ and $\delta\pi = \pi_z - \pi_{xy} = 1.5Ds + 2.5Dt$. The values of these two parameters for the complex $[CrO_4]^{6-}$ are $\delta\sigma = -161$ and $\delta\pi = -65$ and they can be considered as indirect indicators for the antibonding properties of σ- and π- ligands. The literature [6] informs us of the Nephelauxetic parameter β = B (complex)/B (free ion). If the value of β is in the interval 0.54–0.81, it manifests the metal ligand σ bond. The calculation of this parameter for BSO:Cr+P ($\beta = 0.4$) shows that the metal ligand π bond is done. The spin-orbit interaction splits the state $^4T_1$ (^4F) of one sextet (J = 5/2), one quartet (J = 3/2) and one doublet (J = 1/2) (Fig. 2).

The high-frequency part of the spectrum of the two-phonon absorption (Fig. 3 and 4) is given by the phonons related to vibrations of $[SiO_4]$ and $[PO_4]^{3-}$ complexes. The frequency of the two-phonon transition is equal to the sum or the difference of the frequencies ω_i and ω_j of the fundamental oscillations [7]. The oscillations of the crystal lattice are due to oscillations of $[MO_4]$. The tetrahedrons are surrounded by heavy Bi atoms and this is the reason for the absence of absorption structure displacements. That is why Cr does not shift the position of the absorption maxima at 1616 cm^{-1}, 1662 cm^{-1}, 1868 cm^{-1} and 1934 cm^{-1}. The Cr^{3+} ions make the absorption maxima at 1616 cm^{-1} and 1662 cm^{-1} more intensive and the phosphorus removes completely these two maxima in this spectral region. The doping of the crystal lattice with P^{5+} ions leads to the observation of the maxima at 1868 cm^{-1} (965 + 903) and at 1934 cm^{-1} (967 × 2). The Cr^{3+} ions make these two maxima only more intensive. The next two maxima at 1361 cm^{-1} (680.5 × 2) and 1397 cm^{-1} (679 + 718) are due only to the influence

Fig. 2. The energetic level diagram of Cr^{3+} ion



of the phosphorus in the crystal lattice. The first of them consists of the overtone ($T_M \times 2$) and the second one consists of the composite oscillations ($T_M + A_M$). The absorption maximum at 1260 cm^{-1} (668 + 603) consists of the composite oscillations (T_M + F). The phosphorus completely removes this maximum (Fig. 3a) and the chromium makes the same maximum more intensive (Fig. 4a). The

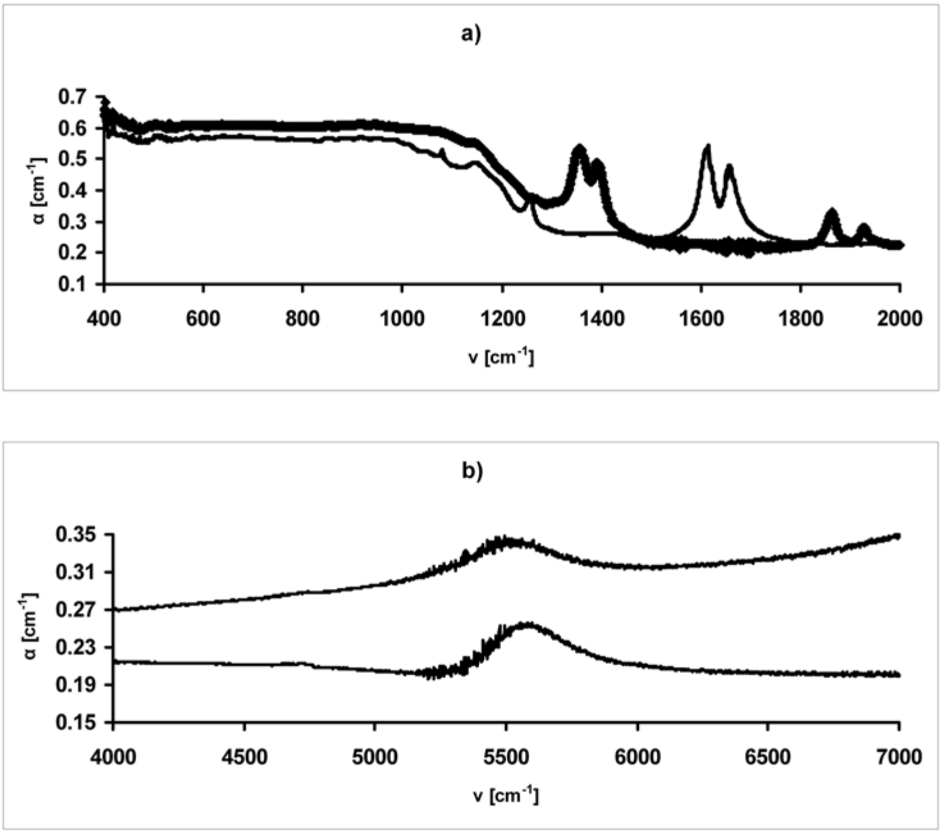


Fig. 3. a) Two-phonon absorption of BSO and BSO:P in the spectral region 400–2000 cm^{-1}; b) electron-vibrational interaction in far IR region of these crystals in the spectral region 5000–6000 cm^{-1}

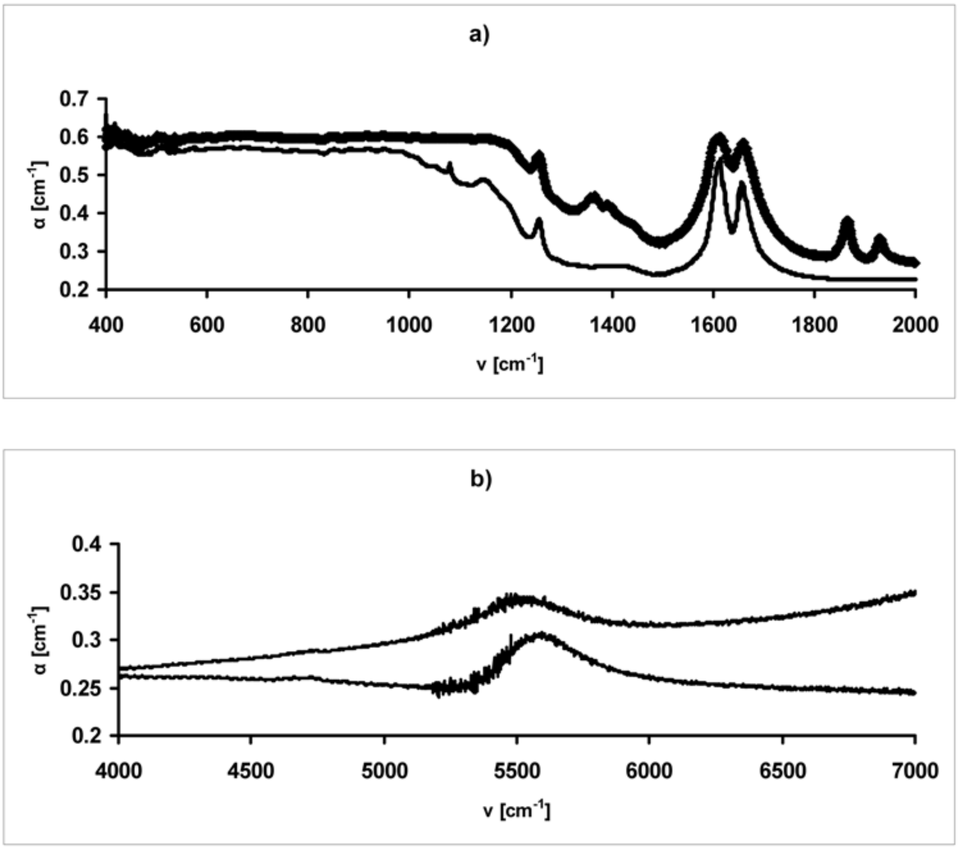


Fig. 4. a) Two-phonon absorption of BSO and BSO:Cr+P in the spectral region 400–2000 cm^{-1}; b) electron-vibrational interaction in far IR region of these crystals in the spectral region 5000–6000 cm^{-1}.

maxima at 5508 cm^{-1} (Fig. 3b and 4b) is determined by the two-phonon transition that is caused by [SiO_4] oscillations. The chromium and phosphorus shifts this maximum to the larger frequencies and the values of the absorption coefficient are lower there.

We can observe direct and indirect mechanism of excitation of the two-phononic transitions. The first of them is determined by the optical anharmonicity and the second one is determined by the mechanical anharmonicity [8]. In the first case, the crystal changes its state when the photon passes through it. This state of the crystal differs from its initial state with the energy equal to twice the energy of the photon. The two-phonon excitation for the molecule MO_4 is due to an anharmonicity and it consists of an overtone and a composite tone. The absorption maximum at 1616 cm^{-1} (827 + 789) consists of the composite oscillations ($T_M + A_M$) (Fig. 3a and 4a). The second absorption maximum at 1662 cm^{-1} (831×2) consists of the overtone oscillation (T_M×2) (Fig. 3a and 4a). The presence of phosphorus leads to the disappearance of these two maxima and the presence of chromium leads to increased intensity of these maxima.

CONCLUSIONS

1. The calculations of the first and the second derivative of α(E) give three electron transitions in Cr^{3+} ions which are inculcated on the tetrahedral complexes.

2. The strong Jahn-Teller effect manifests and the tetrahedral complexes are distorted. The new symmetry of these complexes is C_{3v}.

3. The parameters D_s and D_t are determined. This is important, because we can conclude that the π-bond is stronger than the σ-bond in the tetrahedral complexes. This fact is due to the presence of the P^{5+} ions in the doped and co-doped crystals.

4. The P^{5+} ions have strong influence on the two-phononic transitions in the far IR region for BSO:P and BSO:Cr+P.

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ОПТИЧНО ВЛИЯНИЕ НА ЙОНИТЕ Cr^{3+} И P^{5+} ВЪРХУ СВОЙСТВАТА НА ЛЕГИРАНИ КРИСТАЛИ ОТ $Bi_{12}SiO_{20}$

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(Резюме)

Измерен е коефициентът на поглъщане на единични кристали от $Bi_{12}SiO_{20}$, легирани с фосфор и двойно легирани с хром и фосфор във видимата и в далечната ИЧ област. Определено е влиянието на йоните P^{5+} в двойно легирания силенит. Представена е енергетичната диаграма на нивата на йона Cr^{3+}. Обяснен е ефектът на Ян-Телер в конкретните кристали. Изчислени са също и параметрите на Рака. Определен е директният и индиректният механизъм на двуфононното поглъщане в далечната ИЧ област.