The behaviour of osmium ions in the tetrahedral oxygen coordination

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In this work, the absorption spectrum of $Bi_{12}SiO_{20}$:Os is investigated. The crystal changes its state from the untreated to the illuminated. The experiment is conducted at the room temperature in the spectral region 1.6–2.2 eV. The energetic diagram of the electron transitions in Os^{5+} is presented. The Schrödinger equation is solved for the Os^{5+} ions which are chemically bonded with the oxygen ions.

Key words: Schrödinger equation, doped sillenites, transition metal ions.

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 Os^{5+} in BSO:Os.

EXPERIMENTAL

The crystals were prepared from a stoichiometric solution using the Czochralski method. The purity of the starting oxides used was 99.9999% for Bi_2O_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 OsO_4. The concentration of the ruthenium ions in the crystal lattice was Os – 6.33×10^{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 lenght 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.

RESULTS AND DISCUSSION

The absorption coefficient of the investigated samples has been measured to be between 564 and 775 nm (Figs.1a and 2a). The first derivative of the absorption coefficient at photon energy is calculated to be in the 564–775 nm spectral region. The $[d\alpha/d(h\nu)]$ determines only the number of electron transitions in a Os^{5+} ions and it does not give an exact information about the energy position of these transitions (Figs.1b and 2b). This is the reason for the calculation of the second derivative of the absorption coefficient $[d^2\alpha/d(h\nu)^2]$ (Figs.1c and 2c). 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 Os^{5+} structure that are connected with the electron transitions are $^4T_{1g}(^4F) \rightarrow ^4T_{2g}(^4F)$ (Fig. 3). Our assumption is that Os^{5+} replaces Si^{4+} in the silicon tetrahedrons. The ionic radius of Os^{5+} ion is 0.575 Å and the ionic radius of Si^{4+} ion is 0.40 Å. Thus the oxygen tetrahedrons are shortened along z axis and Jahn-Teller effect is bigger than the

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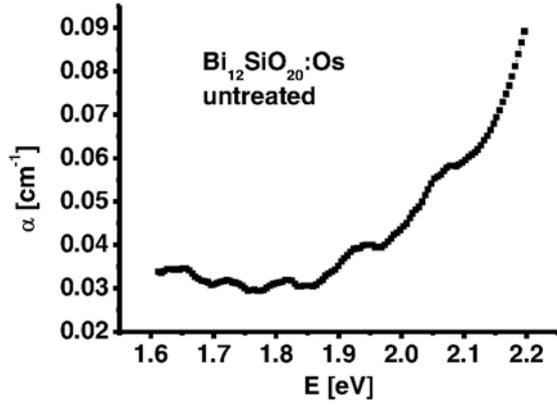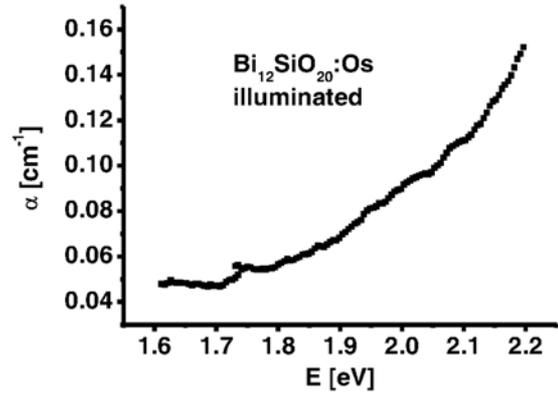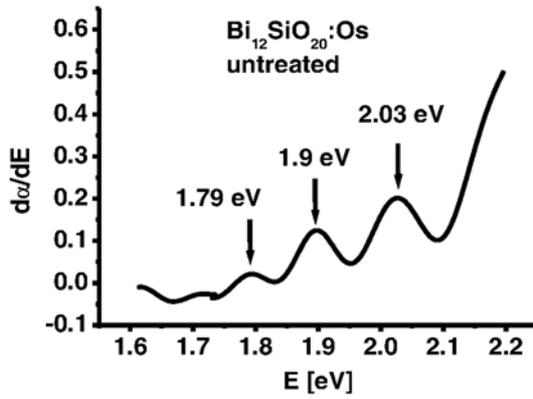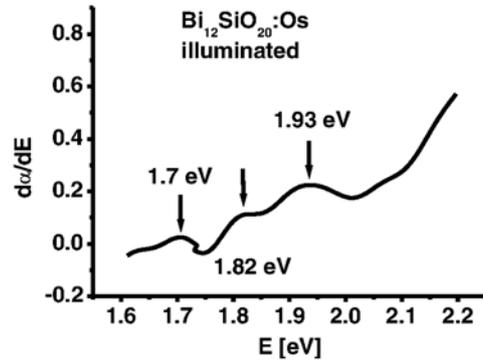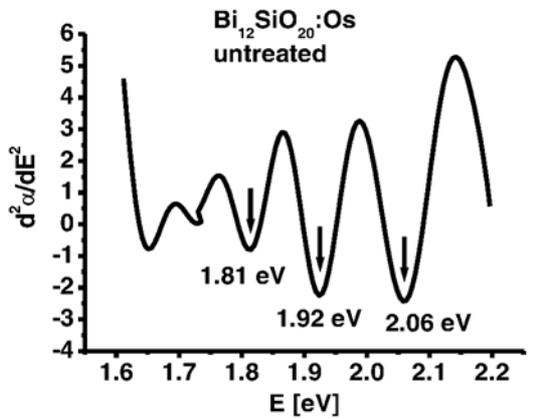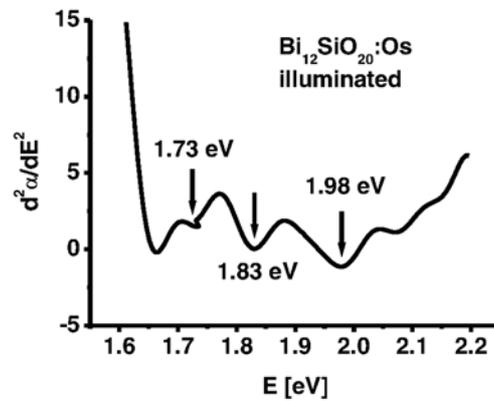
Fig. 1. a) The absorption coefficient $\alpha(E)$, b) first derivative $d\alpha/dE$ and c) second derivative $d^2\alpha/dE^2$ for the untreated $Bi_{12}SiO_{20}$:Os

Fig. 2. a) The absorption coefficient $\alpha(E)$, b) first derivative $d\alpha/dE$ and c) second derivative $d^2\alpha/dE^2$ for the illuminated $Bi_{12}SiO_{20}$:Os

spin-orbit interaction there. If the Os^{5+} ion is caught by a one-dimensional hole than its potential can be described as: 1) V = 0, a≤x≤b (a, b are the borders of the hole) and 2) V = ∞ in the other cases. In the first case the Schrödinger equation has the following form: (2) $E\psi(x) = -(\hbar^2/2m)*(d^2\psi/dx^2)$ [3]. If $k = (2mE)/\hbar^2$ after some transformations we will find that (3) $(d^2\psi/dx^2) + k^2\psi = 0$. The solution of the last equation is (4) $\psi(x) = A\sin(kx) + B\cos(kx)$. The

constants A and B are determined by normalizing the wavefunction i.e.

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = 1.$$

In our situation $A = \sqrt{(2/a)}$ and $B = \sqrt{(2/b)}$. When $\psi(a) = 0$ than $ka = n\pi$ and $kb = (2n+1)\pi$. Thus $k = [(n+1)\pi]/(b-a)$, n = 1, 2, … Therefore the final
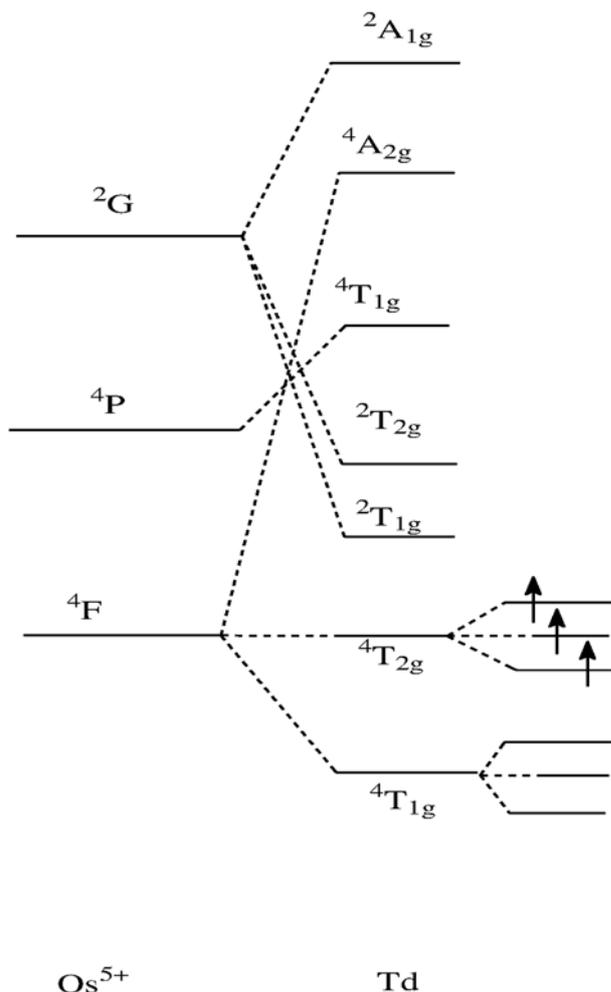
Fig. 3. The energetic diagram of Os^{5+} ion in the tetrahedral symmetry

form of the solution (4) is $\psi(x) = A\sin\{[(n+1)\pi]/(b-a)\} + B\cos\{[(n+1)\pi]/(b-a)\}$. When the Os^{5+} ion is caught by a one-dimensional hole than its wavefunction is $\psi(x) = 0.0592*\sin\{[(2+1)\pi]/(775-564)\} + 0.51*\cos\{[(n+1)\pi]/(b-a)\}$ or in the end $\psi(x) =$

$0.0592*\sin(0.0446x) + 0.51*\cos(0.0446x)$. This is the way to calculate $\psi(x)$ at each minimum on the Figs. 1c and 2c. The values of the wavefunction are respectively $\psi_3(2.06) = 0.4817$; $\psi_2(1.92) = 0.4754$; $\psi_1(1.81) = 0.4693$ for the untreated BSO:Os and $\psi_3(1.98) = 0.4783$; $\psi_2(1.83) = 0.4704$; $\psi_1(1.73) = 0.464$ for the illuminated doped sample. The energy of the basic state of Os^{5+} ion is $E_1 = (\pi^2*\hbar^2)/[2m(b-a)^2]$ and the energy of the first excited state is $E_2 = [2^2*(\pi^2*\hbar^2)]/[2m(b-a)^2]$. The difference between these two energies is $\Delta E = 8.7$ cm^{-1}. The distance between the energy levels $^4T_{1g}(^4F)$ and $^4T_{2g}(^4F)$ is the same (Fig. 3).

CONCLUSIONS

The illumination with UV light leads to the shifting of the energy position of the electron transitions to the bigger wavelengths.

Jahn-Teller effect is bigger than the spin-orbit interaction in the oxygen tetrahedrons.

The Schrödinger equation is solved in the spectral region of the osmium absorption structure.

The values of $\psi(x)$ decrease with the increasing of the wavelength in the spectral region of the Os^{5+} structure.

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ПОВЕДЕНИЕ НА ОСМИЕВИ ЙОНИ В ТЕТРАЕДРИЧНО КИСЛОРОДНО ОБКРЪЖЕНИЕ

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(Резюме)

В тази работа е изследван спектъра на поглъщане на $Bi_{12}SiO_{20}$:Os. Състоянието на кристала се променя от нетретирано в осветено. Експериментът е проведен при стайна температура в спектралната област 1.6–2.2 eV. Представена е енергетичната диаграма на електронните преходи в Os^{5+}. Решено е уравнението на Шрьодингер за йоните Os^{5+}, които са химически свързани с обкръжаващите ги кислородни йони. Облъчването с ултравиолетова светлина води до отместване на енергетичното положение на преходите на електроните към по-големите дължини на вълната. Ефектът на Ян-Телер е по-голям в сравнение със спин-орбиталното взаимодействие в кислородните тетраедри. Стойностите на $\psi(x)$ намаляват с нарастване на дължината на вълната в спектралната област на абсорбционната структура на Os^{5+}.