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Absorption structure of Rh^{4+} in doped $Bi_{12}TiO_{20}$ **P. Petkova¹ and K. Boubaker²**¹*Shumen University “Konstantin Preslavsky”,
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Abstract: *The absorption coefficient of $Bi_{12}TiO_{20}:Rh$ single crystals is measured in the spectral region 600-950 nm. The oscillator strength f and the transition moment of the impurity band Q are calculated in the near infrared spectral region. The effective mass of doped single crystal has been determined also.*

Keywords: *doped sillenite, oscillator strength, transition moment of the impurity band, effective mass.*

Introduction

$Bi_{12}TiO_{20}$ (BTO) are known as sillenite type photorefractive crystals and these materials represent the best inorganic materials for real-time image processing applications [1]. Therefore their good photoconductivity and high charge carrier mobility, they are used in dynamic information processing, interferometry and optical metrology [2].

The ability to combine doped BTO crystals with liquid crystals into an organic-inorganic hybrid structure is an attractive and it opens new possibilities to design future nonlinear optical devices for real-time image processing and display technology [3,4]. For that reason, the response time and photosensitivity have been improved in the near infrared spectral range (NIR) for the investigated samples [5]. The authors of [6] report that rhodium is an excellent dopant in BTO which significantly improves the photosensitivity as well as the response speed during holographic recording in the NIR.

Materials and Methods

Rh-doped BTO crystals were grown by the top seeded solution growth method [7]. The growth process was conducted at an atmosphere of 85% air and 15% Ar. Rhodium was introduced into the melt solution as RhO_2 and the Rh concentration of $5.2 \times 10^{18} \text{ cm}^{-3}$ in the grown crystals was determined by atomic absorption spectroscopy.

The optically polished crystal plate ($d = 0.5 \text{ mm}$) was prepared for the absorption measurements.

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 is calculated using the formula:

$$\alpha = (1/d) \ln(I_0/I), \quad (1)$$

where I_0 is the intensity of the incident light, I is the intensity of the passing light and d is the sample thickness.

Results and Discussion

The absorption coefficient of the investigated sample has been measured to be between 600 and 950 nm (Fig.1a). The first derivative of the absorption coefficient at photon energy is calculated to be in the investigated spectral region. The $[d\alpha/d(h\nu)]$ determines only the number of electron transitions in a Rh^{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 $[d^2\alpha/d(h\nu)^2]$. The three electron transitions in Rh^{4+} are realized respectively at 698 nm ($14\,327 \text{ cm}^{-1}$), 781 nm ($12\,804 \text{ cm}^{-1}$) and 824 nm ($12\,136 \text{ cm}^{-1}$) (Fig. 1c).

The strength of the three-dimensional harmonic oscillator determines from the ratio of the real intensity and the intensity of the radiation of the electron. $f = 1$ for such "ideal electron". The transitions of the oscillator classify by the strength f and this connects the theory with the experiment. $f = 1$ for the allowed transition; for single symmetric band (table 1):

$$f = 4.32 \cdot 10^{-9} \int_{\lambda_1}^{\lambda_2} \alpha(\lambda) d\lambda \quad (3), \text{ where } \alpha(\lambda) \text{ not depends on the concentration of the solutions [8].}$$

The next equation $Q = \sqrt{\frac{f}{v \cdot 1,096 \cdot 10^{11}}} \quad (4)$ explains the connection between the oscillator strength f and the transition moment of the impurity band Q , where v is the frequency of the band centre.

$f_0 = f/[1 + \exp(-\theta/T)] \quad (5)$, where θ is the frequency of the total asymmetric vibration and $T = 300 \text{ K}$. The frequency of the vibration ω of the complexes is connected with θ by the equality $\omega = \theta/1.44 \text{ [cm}^{-1}]$ ($\omega = 2\pi c/\lambda$, $c = 3 \cdot 10^8 \text{ m/s}$).

The value of oscillator strength for BTO:Rh is $0.7038 \cdot 10^{-5}$ and this means that the electron transitions in rhodium are allowed without some coupling [8]. Therefore $Q = 0.1131 \cdot 10^{-10}$, $\theta = 4.5206 \cdot 10^{-4} \text{ s}^{-1}$ and $f_0 = f$ in our case.

The effective mass of electrons of doping elements can be calculated by the next formula:

$$m^* = \hbar^2 / (d^2E/dk^2), \quad (6)$$

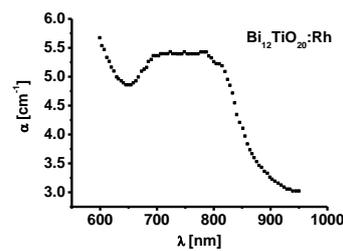
where $\hbar = h/2\pi$ (h is Planck constant) and $k = \alpha\lambda/4\pi$. The different values of effective mass for Rh doped BTO are presented on Fig. 2 in the spectral region 600-950 nm. The values of m^* of rhodium electrons vary between $9.28 \cdot 10^{-28}$ to $1.6 \cdot 10^{-30} \text{ kg}$.

The calculation of the cross-section of the impurity absorption is very important, when we search the answer of question how the radiation is absorbed by the impurity ions in the crystals [9].

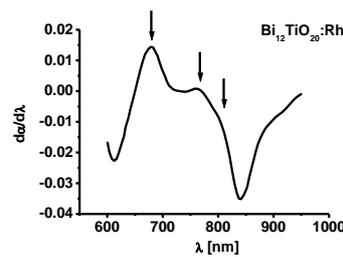
The total cross-section σ_a of the impurity absorption is defined by the integration within the absorption band of the impurity ions

$$\sigma_a = (1/N) \int \alpha(\lambda) d\lambda, \quad (7)$$

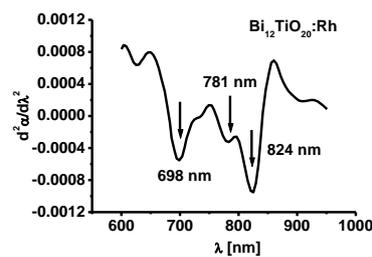
where N is the number of the impurity ions in the unit volume, $\alpha(\lambda)$ is the impurity absorption coefficient typical of an energetic interval from λ_1 to λ_2 .



a)



b)



c)

Figure 1a) Absorption spectra of $\text{Bi}_{12}\text{TiO}_{20}:\text{Rh}$ in the spectral region 600-950 nm; b) The calculated first derivative of $\alpha(\lambda)$ in the same spectral region; c) The calculated second derivative of $\alpha(\lambda)$ there.

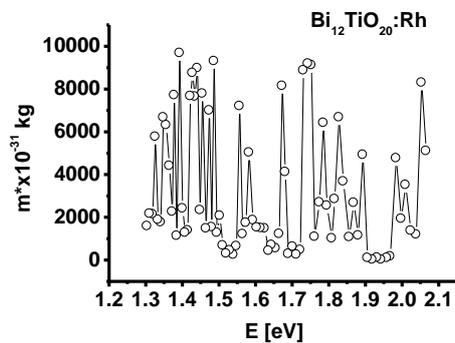


Figure 2 Effective mass m^* of ions Rh^{4+} ions in $Bi_{12}TiO_{20}$.

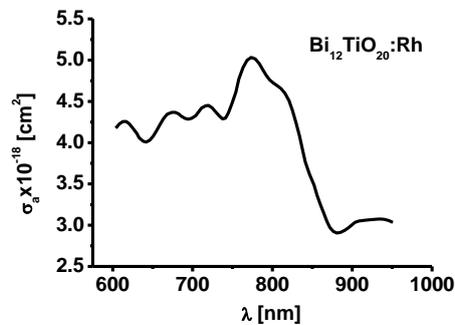


Figure 3 The total impurity cross-section σ_a of $Bi_{12}TiO_{20}:Rh$.

Conclusions

The electron transitions in rhodium are allowed and this is very good reason for the investigation of photochromic effect of doped bismuth titanate. The effective mass of electrons of Rh^{4+} ions is calculated, which will help for the future investigation of conductivity of BTO:Rh. The total cross-section of rhodium ions has values from $2.75 \times 10^{-18} \text{ cm}^2$ to $5.25 \times 10^{-18} \text{ cm}^2$, which means that these ions influence considerably on the optical properties of doped BTO.

Acknowledgements

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