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Optical spectra of doped $\text{Bi}_{12}\text{TiO}_{20}$ crystals

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Abstract. Single crystals of $\text{Bi}_{12}\text{TiO}_{20}$, both 'pure' and doped with various concentrations of V, W, Mo, Nd and Cr, have been studied. Absorption spectra in the energy range 2.0–2.8 eV have been obtained from classical reflection and transmission measurements. The constant-photocurrent method has also been employed in order to study absorption spectra in a wider energy range (1.3–2.8 eV). A well expressed absorption decrease at energies $h\nu > 2.2$ eV has been observed for $\text{Bi}_{12}\text{TiO}_{20}$: 0.056 wt% V and $\text{Bi}_{12}\text{TiO}_{20}$: 0.013 wt% Mo crystals. Also, a considerable absorption decrease has been measured at energies $h\nu < 2$ eV for $\text{Bi}_{12}\text{TiO}_{20}$: 0.056 wt% V and $\text{Bi}_{12}\text{TiO}_{20}$: 0.008 wt% W. The origin of some new absorption bands observed in doped $\text{Bi}_{12}\text{TiO}_{20}$ crystals as well as some differences in the effect of impurities on the optical absorption of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ crystals have been discussed.

1. Introduction

The non-linear photorefractive crystals with sillenite-type structure such as $\text{Bi}_{12}\text{GeO}_{20}$ (BGO), $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) and $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) have potential use in optical information processing, including spatial light modulators, optical computing, wave-front correction schemes and holographic information storage [1]. Among these materials, BTO crystals are the most interesting for applications because they have some advantages over BGO and BSO crystals including smaller optical activity, larger electro-optic coefficient, lower half-wave voltage and better sensitivity in the red spectral region [2–4].

The doping of BGO and BSO crystals with various impurities has been intensively studied for about 20 years. The results obtained show that different impurities change the crystals' properties in a different manner and to a different degree [5, 6]. Similar results have been obtained for the BTO crystals. It has been reported [7, 8] that small concentrations of V and Zn increase the photoconductivity and absorption in the blue–green region, while heavier doping strongly decreases them. So, it is an important task to study the influence of various impurities on the optical properties of BTO crystals.

In this paper the absorption of single BTO crystals, both 'pure' and doped with Mo, W, V, Nd and Cr, has been studied. Absorption spectra have been obtained from conventional transmission and reflection measurements as well as by using the constant-photocurrent method (CPM). The changes observed in the absorption spectra of the doped BTO crystals with respect to the absorption of 'pure' BTO crystals have been discussed.

2. Experimental details

BTO crystals were grown by the Czochralski method using a platinum crucible (5 cm in diameter and 6 cm in length) and a Kantal furnace in conjunction with a temperature control

system, which ensured a constant temperature (± 0.1 K) in the melt. Starting materials were Bi_2O_3 (purity, 99.999%) and TiO_2 (purity, 99.999%). They were mixed in a molar ratio 10:1. The melt was maintained for 48 h at a temperature of 10–15 K above the melting point. Crystals were pulled in air using (001)-oriented crystal seeds at a growth rate of 0.08–0.1 mm h^{-1} and a rotation rate of 15–20 rev min^{-1} . Then they were cooled slowly to room temperature at a rate of 20–30 K h^{-1} . Additional details on the BTO crystal growth technology have been described in [9]. Crystals up to 20 mm in diameter and 30 mm in length were grown. A darker core and typical interface facet morphology as already described by Tanguay *et al* [10] for BSO crystals were observed.

The doping metals were added to the melt as MoO_3 , WO_3 , Nd_2O_3 , V_2O_5 and Cr_2O_3 . The doping concentrations of the metals in the melt are presented in table 1. Inhomogeneous inclusions were monitored in the Mo- and V-doped crystals at doping concentrations of 0.066 wt% Mo and 0.112 wt% V. 'Pure' and W-doped as-grown BTO crystals were pale orange in colour but they turned to dark orange–brown after white-light illumination. A similar effect was observed for Mo- and Cr-doped crystals. They changed their colour to dark yellow–brown and dark brown. The colours of the V and Nd-doped crystals were pale yellow and dark yellow, respectively.

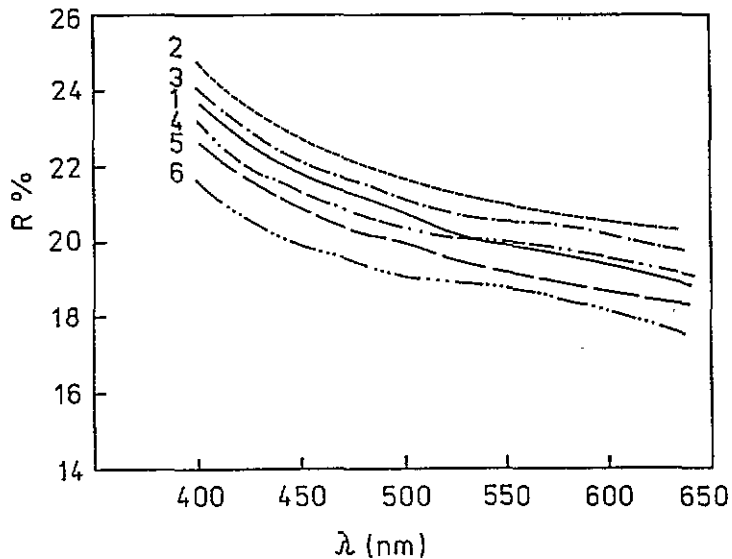


Figure 1. Reflectivity R versus wavelength λ of BTO crystals both 'pure' (curve 1) and doped with 0.043 wt% Nd (curve 2), 0.007 wt% Cr (curve 3), 0.013 wt% Mo (curve 4), 0.008 wt% W (curve 5) and 0.056 wt% V (curve 6).

Optical measurements were carried out on samples cut perpendicular to the growth axis (001). An identical polishing procedure without chemical etching was performed for all the samples. Transmission and reflection spectra were measured on a Perkin–Elmer 330 double-beam spectrophotometer. Parallel plates with a thickness of 0.3–2 mm and 5 mm were used for transmission and reflection measurements, respectively. A fit in the 550–600 nm range has been made between the reflection spectrum of 'pure' BTO obtained here and that calculated from the spectral dependence of the refractive index $n(h\nu)$ reported in [11]. Constant-photocurrent measurements were performed using monochromatic light

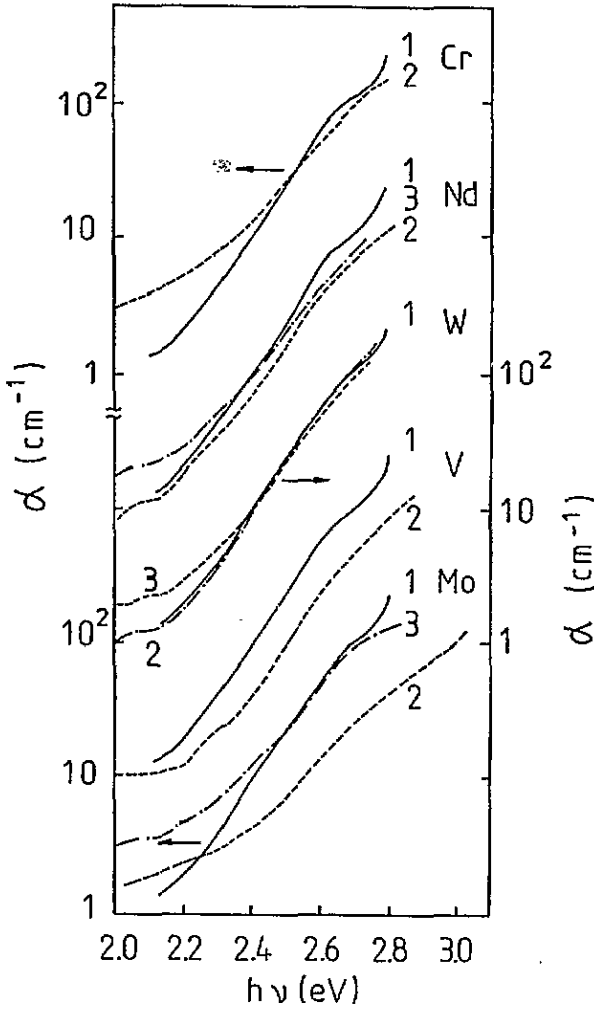


Figure 2. Absorption coefficient α versus energy of 'pure' BTO crystals (curve 1) and BTO crystals doped with different metals at low doping concentration (curve 2) and high doping concentrations (curve 3). All doping concentrations are given in table 1. For clarity the spectra of crystals doped with each of the metals are translated upwards by one order of magnitude with respect to the previous spectrum. The α scales are designated for the Mo, W- and Cr-doped crystals.

(with a 4 nm spectral width) obtained from a diffraction grating monochromator MDR 2. The specimens were about 1 mm thick and provided with gold-sputtered planar contacts spaced about 1 mm. They were illuminated with chopped light (2 Hz) and the photocurrent, measured with a selective Unipan 232 nanovoltmeter, was kept constant by varying the lamp supply voltage. The absolute $\alpha(h\nu)$ -values were determined by fitting the CPM spectra with $\alpha(h\nu)$ spectra obtained from the optical measurements. Similarly to the case of BSO crystals [12] the quantum efficiency was accepted to be $\beta \approx 1$.

3. Results and discussion

3.1. Optical measurements

The dependences of the absorption coefficient of 'pure' and doped BTO crystals have been calculated using the relation [13]

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (1)$$

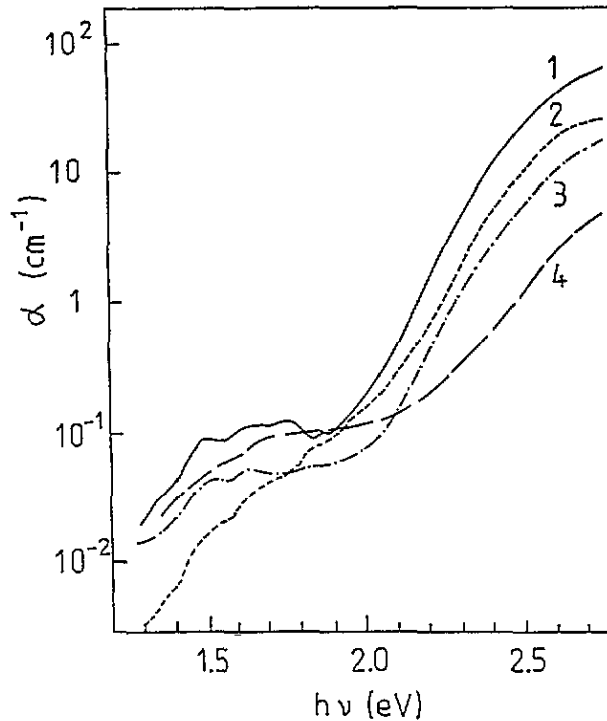


Figure 3. CPM absorption spectra of 'pure' BTO crystals (curve 1), BTO:0.056 wt% V (curve 2), 'pure' BSO crystals (curve 3) and BSO:0.028 wt% V (curve 4).

where d is the sample thickness and the R -values have been taken from the spectra presented in figure 1. $\alpha(h\nu)$ spectra in the 2–2.8 eV region of 'pure' BTO crystals and of BTO crystals doped with different impurities are shown in figure 2. The spectrum of 'pure' BTO is in good coincidence with those reported by other workers [7, 14, 15]. As has been mentioned above, a diverse influence of the different impurities on the 'shoulder' absorption has been observed for BSO and BGO crystals. Our results confirm these observations. Figure 2 shows that V and Mo incorporated in appropriate concentrations strongly decrease the absorption coefficient at energies higher than 2.3 eV. On the other hand, W, Nd and Cr induce only a slight 'bleaching' in the 2.6–2.8 eV region. A comparison with the results obtained for BSO: V and BSO: Cr crystals [16] shows that the effect of V on the BTO 'shoulder' absorption is similar to that for BSO crystals. However, the Cr doping of BTO crystals does not cause the strong absorption increase in the 'shoulder' observed for BSO crystals. Skorikov *et al* [7, 8] have also observed a 'bleaching' in the 'shoulder' region induced by V and Zn doping. They have connected this effect with the decrease in the defects responsible for this absorption.

We consider [16] that the main defects absorbing in the 'shoulder' region in BMO crystals ($M \equiv \text{Ge, Si, or Ti}$) are Bi atoms situated in tetrahedral M positions. They are compensated acceptors negatively charged in the dark. The 'bleaching' is a result of a decrease in the concentration of these centres since some of the M positions are occupied by impurity atoms instead of Bi atoms. According to this model, one can conclude that most probably V and Mo impurity atoms occupy Ti^{4+} tetrahedral positions in BTO crystals while W, Nd and Cr occupy other positions. Additional studies similar to those performed on BSO crystals [16] will give the possibility of defining more precisely the positions of the impurity atoms in BTO crystals.

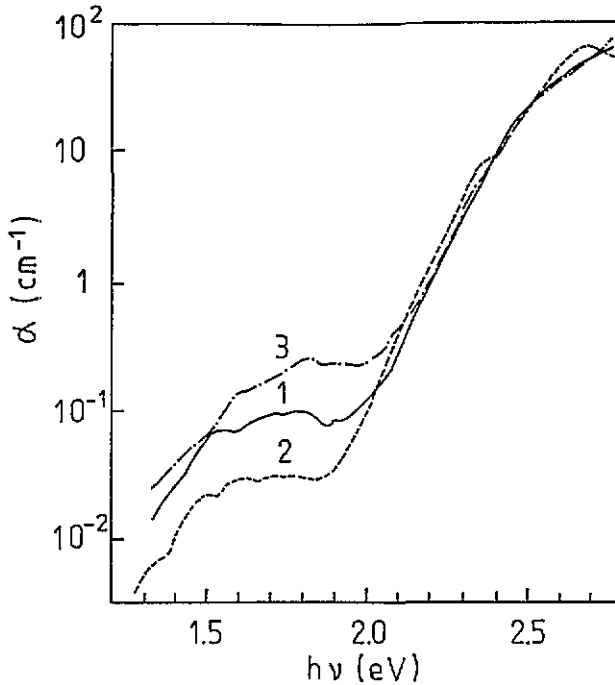


Figure 4. CPM absorption spectra of 'pure' BTO (curve 1), and BTO:W crystals doped with 0.008 wt% W (curve 2) and 0.08 wt% W (curve 3).

Some changes in α , arising as a result of the doping, can also be seen at lower energies in figure 2. They have been studied in more detail using CPM measurements and will be discussed below.

3.2. Constant-photocurrent method measurements

The CPM has already been applied in order to investigate deep levels in single-crystal semi-insulating GaAs [17] as well as to study low-energy absorption in BSO crystals, both 'pure' and doped with transition metals [16]. It is based on the connection between the sample absorption α and the photocurrent I_p flowing through the sample volume. When the steady-state concentration of the photogenerated carriers is kept constant during the change in the photon energy and on the assumption that there is no spectral dependence of the photogenerated carrier mobility, the spectral dependence of the low-energy absorption coefficient is given by [18]

$$\alpha(h\nu) = \text{constant}/F(h\nu) \quad (2)$$

where F is the intensity of the illumination. Figures 3–7 present CPM spectra obtained for 'pure' BTO crystals and for BTO crystals doped with different impurity concentrations. A comparison with the CPM spectra of 'pure' BSO and of BSO doped with V (figure 3) and Cr (figure 7) is made in order to demonstrate some differences in the effect of the impurities on the BTO and BSO absorption.

Three absorption bands at about 1.5, 1.65 and 1.8 eV can be distinguished in the low-energy absorption region ($h\nu < 2$ eV) of 'pure' BTO crystals. Peaks at 1.6, 1.8, 2.5, 2.8 and

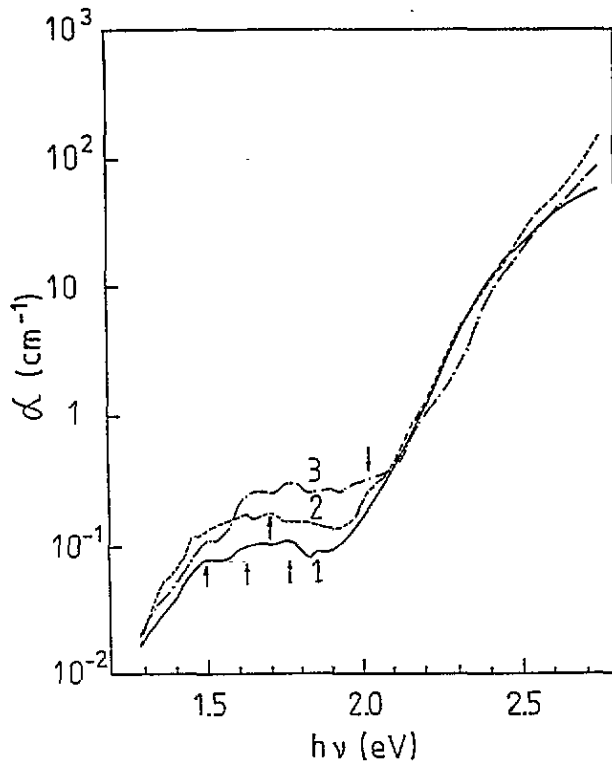


Figure 5. CPM absorption spectra of 'pure' BTO (curve 1) and BTO:Nd crystals doped with 0.043 wt% Nd (curve 2) and 0.085 wt% Nd (curve 3).

3.0 eV have been observed in the photoconductivity of 'pure' BTO crystals [15]. Two of them (1.6 and 1.8 eV) coincide quite well with our results. In [15] the peak at about 1.5 eV was not observed.

Some general conclusions can be drawn from the absorption spectra presented in figures 3–7.

(1) One can see that the absorption coefficient α for BTO crystals is considerably higher than α for BSO crystals in the whole energy region studied. This result confirms the fact that the concentration of own defects in BTO crystals is much higher than in BSO crystals [1].

(2) As has been reported [16], the doping of BSO crystals increases the low-energy absorption (figure 3 and 7). In contrast with this, the doping of BTO crystals with V (figure 3) and W (figure 4) decreases low-energy absorption. Kolosov *et al* [19] have also reported such an α decrease in BTO crystals doped with V and Nd without any discussion of this effect. The α decrease obtained as a result of the BTO doping can be connected with a decrease in the concentration of own defects. This suggestion has been supported by the results of photosensitivity measurements in different specimens. As can be seen from figures 3 and 4, the doping with a small W concentration and even with a large V concentration leads to a considerable low-absorption decrease. At the same time (table 1) the photocurrent through the BTO:W sample (under illumination with $\lambda = 600$ nm) is greater than I_p through 'pure' BTO (for the same sample geometry). This I_p increase can be related to a decrease in the concentration of some own defect centres playing the role of fast recombination centres

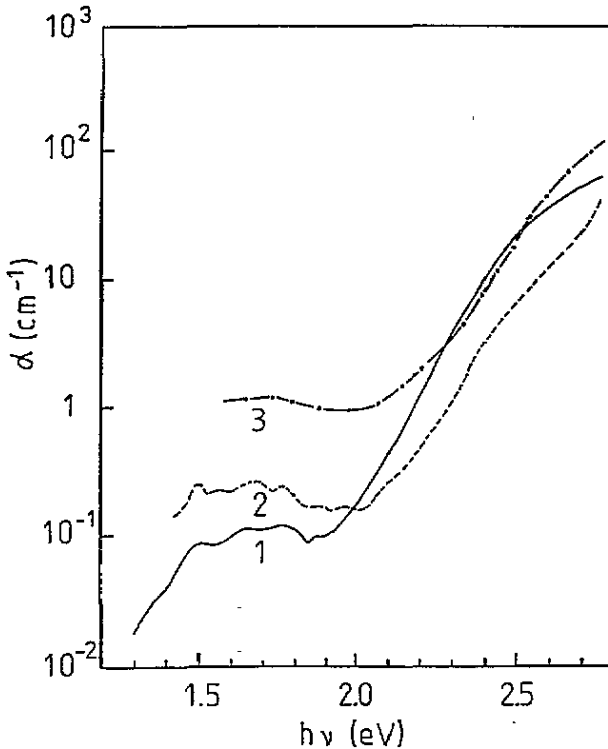


Figure 6. CPM absorption spectra of 'pure' BTO (curve 1) and BTO:Mo crystals doped with 0.013 wt% Mo (curve 2) and 0.033 wt% Mo (curve 3).

[13]. The situation is similar in BTO:V crystals, where the photocurrent keeps its high value although the V concentration is quite high.

(3) As in BSO crystals the higher doping concentration in BTO crystals increases the low-energy absorption (figures 4–7). However, some differences have to be emphasized. One can see from figures 3 and 7 that the same Cr concentration or an even higher V concentration in BTO crystals leads to a considerably smaller α -value in the low-energy region than in BSO crystals. Indeed, BTO:Cr crystals do not show the reddish colour typical for BSO:Cr crystals. The difference is probably connected with the existence of a large number of defects (approximately 10% Ti vacancies as well as strong deformation of the 'ideal' sillenite structure [20]) in BTO crystals because the Ti atoms occupying the tetrahedral positions are too large.

A further examination of the low-absorption part of the spectra in figures 3–7 shows the following.

(1) Although the doping of BTO crystals with V strongly decreases α , the same three absorption bands as in 'pure' BTO are pronounced (figure 3) but the different absorption bands decrease to different degrees. The band at 1.5 eV decreases most strongly.

(2) The doping with W and Nd preserves the $\alpha(h\nu)$ shape similar to that of 'pure' BTO. However, the absorption at 1.5 eV is again smaller than at 1.65 and 1.8 eV for the higher dopant concentrations. On the other hand the absorption band at about 1.6 eV is more pronounced (figures 4 and 5, curves 3). Moreover, two new absorption bands appear in the BTO:Nd spectra (figure 5) at $h\nu = 2.04$ eV (curves 2 and 3) and 1.7 eV (curve 2).

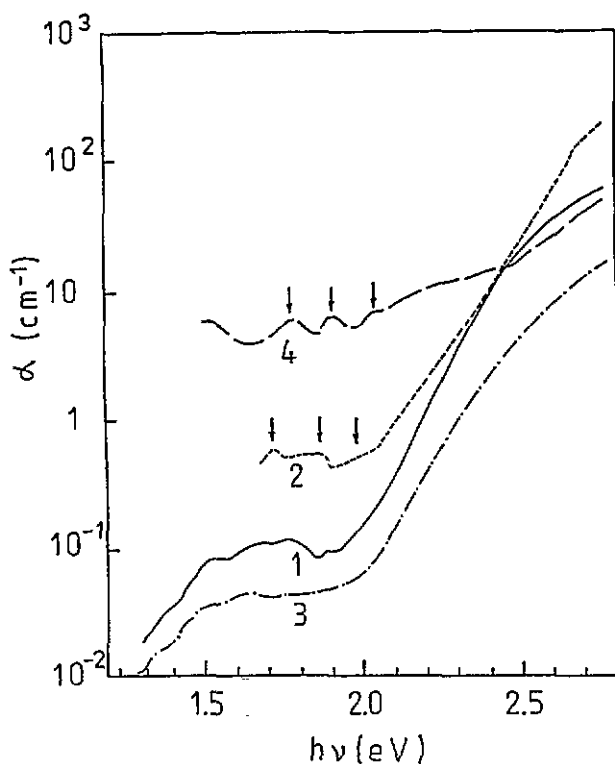


Figure 7. CPM absorption spectra of 'pure' BTO crystals (curve 1), BTO:0.007 wt% Cr (curve 2), 'pure' BSO crystals (curve 3) and BSO:0.007 wt% Cr (curve 4).

Table 1. Dopant concentrations and photoconductivities of BTO crystals investigated.

Kind of impurity	Impurity concentration in the melt (wt%)	Photocurrent I_p (arbitrary units)
'Pure'		2900
Mo	0.013	70
	0.033	17
W	0.008	7500
	0.08	420
Nd	0.043	170
	0.085	360
V	0.056	1400
Cr	0.007	21

These energy positions are very close to those of the new absorption bands observed in BSO:Nd (0.65 at% Nd) which are at $h\nu = 2.09$ eV and $h\nu = 1.67$ eV [21]. As known [21], absorption and emission of Nd^{3+} ions do not depend on the kind of the media in which they are incorporated since the absorption occurs into the 4f shell screened by the $5s^2$ and $5p^6$ fully occupied shells. Hence both new bands observed in BTO crystals are most probably due to the Nd^{3+} ions incorporated.

(3) The absorption spectra of BTO:Cr and BTO:Mo crystals demonstrate a number of absorption bands in the low-energy region. Three weak bands at about 1.7, 1.85 and 1.95 eV can be seen in figure 7 (curve 2). Similar bands have also been observed in BSO:Cr crystals (figure 7, curve 4) but all of them were slightly shifted to higher energies (by about 0.05–0.1 eV). In both kinds of crystal these bands are probably due to Cr ions (Cr^{2+} and/or Cr^{3+} [22]). The small difference in the band positions observed for BSO:Cr and BTO:Cr crystals is possibly due to small differences in their crystal lattices because of the different sizes of Si and Ti atoms. Concerning BTO:Mo crystals the origins of the absorption bands observed at energies lower than 2.1 eV still remain unclear.

4. Conclusion

Diverse changes in the absorption of BTO crystals doped with different metals have been observed, similarly to those reported for BSO and BGO crystals. However, contrary to BSO crystals it has been established that high impurity concentrations induce in BTO crystals a relatively small absorption increase. This difference has been related to the existence of a higher defect concentration in BTO crystals.

Acknowledgment

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