

Vanadium Characterization in BTO:V Sillenite Crystals

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Visible and Infrared Optical Absorption and Electron Paramagnetic Resonance (EPR) techniques have been used to characterize the intrinsic defects in sillenite type crystals: nominally pure $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) and doped with vanadium (BTO:V). Optical quality crystals, with the composition $\text{Bi}_{12.04\pm 0.08}\text{Ti}_{0.76\pm 0.07}\text{V}_{0.16\pm 0.02}\text{O}_{20}$, have been grown. Results obtained by these different techniques have shown unambiguously the 5+ valence state of the vanadium ion in BTO:V crystals. In pure BTO samples, the EPR and optical spectra show strong evidence of the presence of the intrinsic defect $\text{Bi}_M^{3+} + h_o^+$, which consists of a hole h^+ , mainly located on the oxygen neighbors of the tetrahedrally coordinated Bi^{3+} ion. After doping with vanadium, results have shown that the characteristic bands, associated to this hole defect center, disappear, suggesting its transformation in single Bi^{3+} . Anisotropy of the EPR spectra, at 20 K, is related to Fe^{3+} impurities.

Keywords: sillenite, photorefractive, defects, BTO

1. Introduction

Bismuth oxide compounds, with a $\text{Bi}_{12}\text{MO}_{20}$ chemical composition (where M = Ge, Si, or Ti), crystallize on the space group I23 (sillenite structure). They exhibit a number of interesting properties, including: piezoelectric, electro-optical, elasto-optical, optical activity and photoconductive properties. Specially interesting is the combination of the electro-optical and the photoconductivity properties, from which results the so-called photorefractive effect, consisting of a reversible light-induced change in refractive index¹. Due to these properties, sillenite crystals are useful for many advanced and promising applications, such as a reversible recording medium for real-time holography or for image processing applications^{2,3}.

Bismuth titanium oxide crystal, $\text{Bi}_{12}\text{TiO}_{20}$ (BTO), have some practical advantages relative to its isomorphous $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) and $\text{Bi}_{12}\text{GeO}_{20}$ (BGO), including lower optical activity, larger electro-optic coefficient and higher sensitivity to red light³. Depending on a good knowledge of the defects in these materials, a detailed understanding of the photorefractive behavior and, consequently, the optimization of its corresponding response, can result^{2,3}. In-

formation about the occurring microscopic process in the crystals and, eventually, materials with better properties, can be obtained by adding some impurities in the crystal composition.

Recently, few articles have been published about the optical properties of BTO:V crystals, with different amounts of vanadium impurity⁴⁻⁶. In particular, Volkov *et al.*⁶ have investigated the oxidation state of vanadium in BTO crystals, using optical absorption spectra, measured at room temperature, from 22000 to 1200 cm^{-1} and Electron Paramagnetic Resonance (EPR) measured in the range of 77 K to 300 K. They have concluded that the vanadium is present in 5+ valence state. However, Kool and Glasbeek⁷ have reported that the EPR spectra of V^{4+} in SrTiO_3 disappear above 35 K, therefore EPR measurements, below 35 K, are required to identify the oxidation state of vanadium ions in this material. Furthermore, it is well known from literature^{8,9} that the absorption bands near 750-800 cm^{-1} , in sillenite type crystals, are characteristic of the $(\text{VO}_4)^{-3}$ group. However, BTO crystals show low light transmission values for wave numbers lower than 1200 cm^{-1} , making necessary to employ more effective methods, in addition to the standard IR absorption tech-

niques, to characterize the $(\text{VO}_4)^{3-}$ absorption bands in BTO:V samples.

In this work, the growth process of an optical quality vanadium doped BTO crystal (BTO:V) and a more detailed study of the vanadium oxidation state, is reported. For optical characterization of the crystals, visible and infrared absorption were used. To investigate the ground state of the paramagnetic impurities, and the structure of the paramagnetic defects, which are responsible for the observed absorption bands, EPR measurements in the temperature range 20 - 300 K, were performed.

2. Crystal Growth

The crystals growth experiments were made by pulling technique, using a resistive heating furnace, equipped with a 808 Eurotherm microprocessor-based digital temperature controller unit, attached to a Pt-Pt10%Rh thermocouple¹⁰. The temperature fluctuations were typically lower than 0.2 °C, as measured near the crucible. An axial temperature gradient above the melt, about 30 °C/cm, was measured with a platinum thermocouple attached to the seed holder. High purity platinum cylindrical crucibles, with 35 x 35 mm approximated dimensions, were used.

Because bismuth titanium oxide melts incongruently, single crystals of BTO:V have been grown from high temperature nonstoichiometric solutions, with excess of Bi_2O_3 solvent. The starting batch melt was prepared by thoroughly mixing of appropriate amounts of bismuth oxide (Johnson Matthey, 99.9995%), titanium oxide (Johnson Matthey, 99.995%) and vanadium oxide (Merck, extra pure), followed by its melting, at temperatures in the range of 900 °C to 950 °C, during periods of time varying from 12 to 24 h. All runs have been carried out in air. BTO seeds oriented along the [001] direction, held in a pure platinum seed holder, have been used to initiate the crystal growth. Pulling rates in the range of 0.1 to 0.2 mm/h, and rotation rate of 30 rpm were used. After growth, the crystals were annealed at 750 °C, in an appropriate furnace in order to reduce thermal stresses.

Starting compositions of $10\text{Bi}_2\text{O}_3:(1-x)\text{TiO}_2:x/2\text{V}_2\text{O}_5$, where $x = 0.10, 0.13, 0.15$ and 0.25 , were used. For $x = 0.25$ no single crystal was obtained, but a polycrystalline material was withdrawn from the crucible. For another values of x single crystals were obtained. All the grown crystals presented in their structure many defects such as inclusions, cracks and high mechanical fragility, only the crystal with $x = 0.10$ presented optical quality. Intense stress induced birefringence can be seen in these samples by analysis in an optical microscope, equipped with crossed polarizers. The probable origin of these defects is the constitutional supercooling which arises because of the high segregation coefficient of vanadium in this system. This is corroborated by the cellular structure that can be seen at the end face of the crystals. The composition of the grown

crystal with $x = 0.10$ in the melt, was measured by Wavelength Disperse Spectroscopy (WDS), in a digital scanning electron microscope. Its chemical formula can be written as $\text{Bi}_{12.04\pm 0.08}\text{Ti}_{0.76\pm 0.07}\text{V}_{0.16\pm 0.02}\text{O}_{20}$, where the oxygen content was obtained by stoichiometric calculations. From these results, the effective segregation coefficient for vanadium in BTO was calculated as $k_{\text{eff}} = 1.6 \pm 0.2$. Pictures of as-grown BTO:V crystals are shown in Fig. 1. The first two crystals in the left side were grown from $x = 0.10$ in the melt, and the others from $x = 0.15$. Structural defects can be seen in the two crystals at right side.

3. Experimental Techniques

All measurements in BTO:V were performed with samples obtained from crystals grown of the melt composition $x = 0.10$. The nominally pure BTO samples were obtained from the single crystals grown as described before. The samples used for optical absorption were cut and carefully polished, with thickness ranging from 160 to 800 μm . Samples for photoacoustic measurements were used as a very fine powder obtained from the crystals. For EPR measurements, X-ray oriented samples, with cross section of 2 x 2 mm, were used.

All optical measurements were performed at room temperature. Optical absorption in the visible region was measured with a Cary 17 spectrophotometer. At the infrared region a Nicolet spectrophotometer (model 850) was used to measure the optical transmission in the high energy range, where the samples have a high transmission coefficient. At the lowest energy range, below 1000 cm^{-1} , photoacoustic technique was used.

For EPR measurements, a home built CW spectrometer, operating at X-band, with field modulation frequency of 85 kHz, was used. For allowing comparison among samples spectra, intensities were measured by normalization with the spectrum of a standard ruby sample ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$),

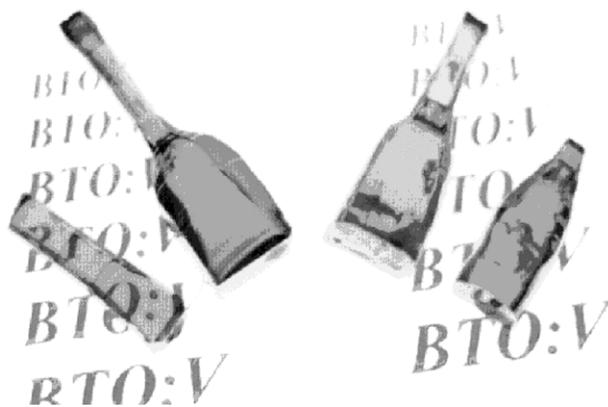


Figure 1. Some as-grown BTO:V crystals. The first two crystals in the left side were grown from composition $x = 0.10$ in the melt, and the others from $x = 0.15$. Structural defects can be seen in the two crystals at right side.

placed inside the microwave cavity and kept at room temperature. A very precise Gaussmeter (Sentec, model 1101) and a Frequency Counter (Hewlett Packard, model 5352B) were used, respectively, for accurate measurements of the magnetic field and microwave frequency values. With this facility, and because of the high stability of the magnet power supply and microwave frequency, the g-values can be measured with an absolute accuracy of ± 0.0001 . A "Helitran" type gas-flow temperature controller have provided temperature control set with ± 1 K precision, within the range of 20 to 300 K.

4. Results and Discussion

4.1. Optical absorption spectra

In the visible region there is only one perceptible change in the absorption spectra of BTO:V, in comparison to that of the nominally pure BTO, which is the broad absorption shoulder, at the photon energy range of 2.3 to 3.0 eV, typical for crystals of the sillenite type¹¹, but absent in the spectra of the vanadium doped samples. This absorption is associated with the intrinsic defect ($Bi_M^{3+} + h_o^+$), due to an improper occupation of the tetrahedrally coordinated M site, of an Bi^{3+} coupled with a hole, h^+ , in the surrounding oxygen tetrahedron¹¹. It is known that the absorption shoulder is absent in crystals with 3+ (e.g. Ga and Al) or 5+ (e.g. P) doping ion valences^{11,12}. This has been explained, by assuming a transformation of the absorption center ($Bi_M^{3+} + h_o^+$) to Bi_M^{5+} , with the first type of dopants and, to Bi_M^{3+} with the second type of dopants^{12,13}. According to this model, it is expected that the vanadium ion in BTO:V samples, studied here, are to be most probably in the oxidation state 3+ or 5+. Measurements of the FT-IR transmission spectra of BTO and BTO:V, in the range 400 - 6000 cm^{-1} , have shown only one perceptible change: the appearance of a doublet with maximum absorption at 1528 and 1559 cm^{-1} . This is in accordance with Volkov *et al.*⁶ which have related this effect to two-phonon transitions, which are associated to the $(VO_4)^{3-}$ group in the M site of the crystal structure. As above-mentioned, BTO crystals have very low light transmission values for wave numbers lower than 1200 cm^{-1} . To get a better definition of this spectral region, the IR spectra were obtained using photoacoustic techniques. The photoacoustic spectra, between 400 to 1000 cm^{-1} , are shown in Fig. 2. A clear absorption band centered at 767 cm^{-1} , observed only in the doped sample BTO:V, is a characteristic band of the $(VO_4)^{3-}$ group in sillenite type structures^{8,9}. This fact is an indication that the oxidation state of vanadium, in this material, is 5+. The remainder spectral region showed no difference between BTO and BTO:V samples.

4.2. EPR spectra

EPR measurements have been performed in the temperature range of 20 K to 300 K. The results obtained for BTO and BTO:V samples, at 20 K, are shown in Fig. 3. At room temperature, the EPR spectra of the nominally pure BTO samples have shown only one intense and highly isotropic lorentzian line, with $g = 2.0061$ and peak to peak width of about 95 gauss. In contrast with what has been reported before^{6,14}, no other bands, arising from paramagnetic impurities ions such as iron, chromium or manganese, were observed at room temperature. The well defined room temperature EPR band, observed in here, is not expected to come from those ions; it is most likely to come from an effective spin 1/2, such as an electron or a hole center, without hyperfine interactions. The fact that the measured g-value is slightly greater than the free electron value (2.0023) is an indication that this spectrum is due to a hole center. A similar spectrum was reported by Baquedano *et al.*¹⁴ for BSO crystal. Their results, and the optically detected magnetic resonance investigations conducted by Reyher *et al.*¹⁵, have showed that the paramagnetic center responsible for this spectrum, in nominally pure sillenite crystals, is due to the intrinsic defect ($Bi_M^{3+} + h_o^+$). Accentuated changes in the EPR spectra of pure BTO samples, at 20 K, relative to the room temperature data, can be observed in Figs. 3a and 3b. In addition to a reduction in the line width (from 95 to 50 gauss), the line becomes anisotropic. If the magnetic field is applied parallel to the [100] direction, resolved structures can be clearly seen, showing satellites on each side of the main absorption line. The intensities of the satellite lines decrease with increasing temperature, but remain resolved up to 150 K. Above 150 K their intensities are very low and the resulting line is isotropic. Similar spectra have been observed for BSO¹⁶ and BGO¹⁷ single crystals, doped with iron. The associated defect is attributed to Fe^{3+} ions, located in tetrahedral

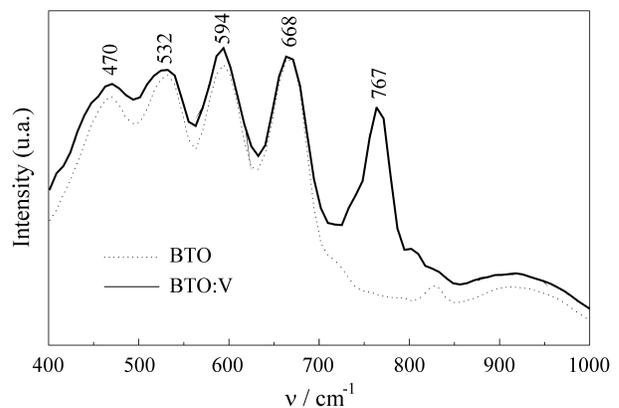


Figure 2. Photoacoustic spectra between 400 to 1000 cm^{-1} of BTO and BTO:V samples. The absorption band centered at 767 cm^{-1} is characteristic of the $(VO_4)^{3-}$ group in sillenite type crystals and the remainder are related to Bi-O modes.

positions at the Si or Ge sites. Due to the high symmetry at the iron site, the resulting triplet structure repeats when the magnetic field is rotated 90° in the [100] plane, as were observed in this study. According to this argument, the spectrum of the pure BTO sample, at 20 K, can be interpreted as a superposition of the anisotropic spectrum of Fe^{3+} impurities, located at high symmetry sites, with an isotropic line produced by the presence of the hole centers. EPR spectra of the vanadium doped sample are shown in Figs. 3c and 3d, where it can be seen no evidence of the hyperfine splitting, usually consisting of 8 absorption peaks (nuclear spin $I = 7/2$), characteristic of the paramagnetic vanadium spectrum. Based on this fact, it could be concluded that the vanadium in BTO:V crystals is in a diamagnetic state, so its valence state must be $5+$. This in accordance with previous works^{8,9}. Another interesting feature in the spectrum of the BTO:V sample, when compared to pure BTO, is a great reduction in line intensity, as it can be seen in Figs. 3c and 3d. After doping, it is apparent the complete disappearance of the absorption band associated to the hole center. The paramagnetic center, responsible for the weak and almost isotropic absorption band observed in BTO:V has not been identified. With increasing temperature, the BTO:V spectrum gets weaker and, within the sensitivity of

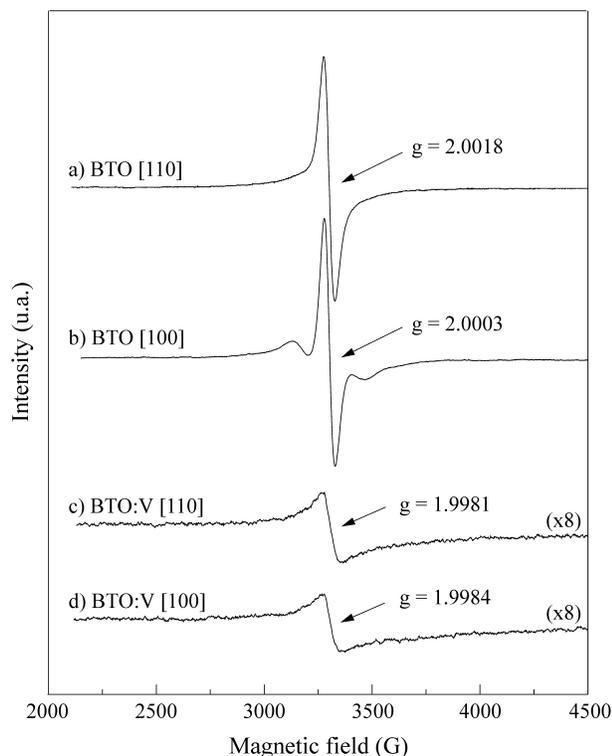


Figure 3. EPR spectra of BTO and BTO:V samples. Measurements were taken at 20 K, with the magnetic field oriented parallel to [110] and [100] directions. G-values were measured at the zero crossing point of the lines. Accuracy on the g-values is limited by baseline position error, and estimated to be ± 0.0005 .

the equipment, it can be hardly seen at room temperature. Furthermore, the line shape observed in BTO:V sample is complex, having a relatively narrow band on top of a broad background signal. The disappearance of the isotropic absorption line, caused by vanadium doping, can be interpreted by the same mechanism which is responsible for the absorption shoulder disappearance in the visible spectrum: the partial transformation of the paramagnetic center ($\text{Bi}_M^{3+} + h_o^+$) in Bi_M^{3+} or Bi_M^{5+} . The anisotropic lines observed in the pure sample, at 20 K, which are assigned to Fe^{3+} impurities, do not appear in the spectrum of the doped samples. However, an isotropic EPR line, with $g \approx 4.3$ (not shown in Figs. 3c and 3d) was observed in the BTO:V spectrum at 20 K, indicating that the Fe^{3+} impurity is, in this case, located at a low symmetry site. Iron has a lower segregation coefficient, compared to vanadium so, it is reasonable to expect that the high symmetry sites will be occupied by vanadium ions. The traditional explanation for the occurrence of the $g \approx 4.3$ line suggests that it is due to Fe^{3+} ions with rather large crystal field splittings¹⁸⁻²⁰. In a weak magnetic field and for the extreme case of rhombic symmetry, where the ratio between the zero-field splitting parameters is $E/D = 1/3$, an intense, isotropic and sharp absorption line is expected with $g = 30/7 = 4.28$. Small departures from the extreme rhombic condition will manifest themselves in three distinct g-values with average of about 4.3. This may lead to a broadening or can be seen in the structure often observed on the $g = 4.3$ feature.

5. Conclusions

An important defect in sillenite crystals, such as BTO, has been identified by Optical Absorption and EPR results, and it consists of an Bi^{3+} ion associated with a hole. The disappearance of this defect, after doping with vanadium, observed by optical and magnetic techniques, can be explained by previous models. Results, in here, allowed to conclude, unequivocally, that the valence state of vanadium ions in BTO crystals is $5+$.

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