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LETTER TO THE EDITOR

X-ray-induced defects in $Bi_{12}GeO_{20}$ single crystals

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Abstract. $Bi_{12}GeO_{20}$ single crystals irradiated at 12 K with x-rays exhibit a broad optical absorption from $\approx$ 0.5 eV to the optical absorption edge of the crystal. This optical absorption disappears on heating the sample above 150 K. Moreover, x-ray-irradiated samples also show an isotropic EPR spectrum formed by a band centred at $g = 2.0098$ and with a halfwidth of 35 G. Both experimental observations are attributed to the formation of holes trapped in regular oxygens of the lattice.

Single crystals of $Bi_{12}GeO_{20}$ (BGO) have attracted considerable attention because of their photorefractive capability [1]. Briefly, the photorefractive effect consists in the photoionization of donor centres present in the material, the transport of the carriers through the lattice and their later stabilization in trap centres.

The donor and trap centres in BGO seem to be intrinsic defects of the material [2, 3]; however, their nature still remains unclear in spite of the intense work performed. Therefore more basic work on the defects present in this material is required.

In $Bi_{12}SiO_{20}$ crystals (isomorphic to BGO) coloration has been reported after room temperature γ-irradiation [4], but a definitive model to account for the origin of the coloration was not proposed. In this work we present a study of the optical absorption induced by low-temperature (12 K) x-ray irradiation of BGO samples; additionally the presence of x-ray-induced electron paramagnetic resonance (EPR) signals is reported.

The present results increase knowledge about the defects observed in this material. Furthermore these results are expected also to be of interest in relation to the x-ray damage induced in $Bi_{12}GeO_{20}$, which produces a problem decrease in the luminescence yield of $Bi_{12}GeO_{20}$ scintillators used for high-energy photons and particle detection [5].

BGO single crystals were grown in air at the Crystal Growth Laboratory of the Universidad Autónoma of Madrid by the Czochralski technique. Bi_2O_3 and GeO_2 Puratronic Johnson–Matthey powders were used as starting materials.

Polychromatic x-ray irradiation was performed at 12 K using a Siemens generator, model Kristalloflex 2H operated at 50 kV and 30 mA. Soft x-rays were filtered through a 1 mm aluminium foil in order to produce a more homogeneous depth distribution of irradiation damage. Under our experimental conditions the irradiation dose was 3 ($\pm$1) krad min^{-1}.

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Optical absorption spectra were recorded at 12 K using a spectrometer in the X band with a field modulation frequency of 100 kHz. The temperature of the samples was controlled by means of a gas-flow temperature controller Varian E-257. Accurate values of the resonance magnetic fields and microwave frequencies were measured with a Bruker NMR gaussmeter (model ER 035 M) and a Hewlett–Packard frequency meter (model 5342A) respectively.

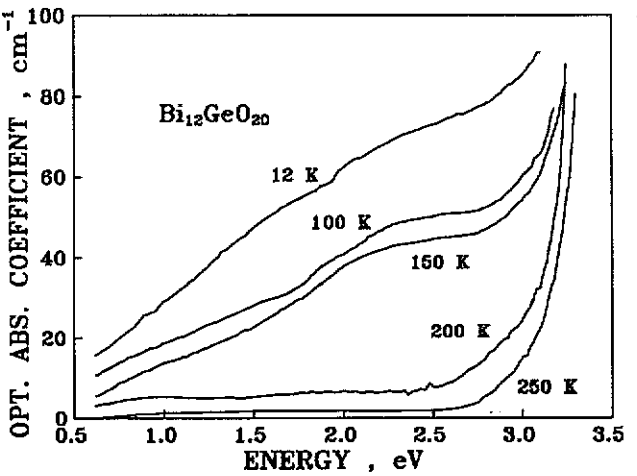

Figure 1. Optical absorption spectra taken at 12 K, of $Bi_{12}GeO_{20}$ single crystals after 10 h of x-ray irradiation at 12 K. Irradiation conditions, 50 kV and 30 mA. The numbers on the curves stand for the temperature at which the sample was kept during the 10 minutes taken to cool it back to 12 K to record the spectrum. The spectrum marked with 250 K is nearly equal to that observed before the x-ray irradiation. The curves have been shifted for clarity.

Figure 1 shows the optical absorption observed after the x-ray irradiation (12 K curve). A broad spectrum covering the visible and near-infrared regions was observed.

After the x-ray irradiation the sample was heated for 10 minutes at increasing temperatures between 12 and 300 K; after each heating step the sample was cooled to 12 K to record the optical absorption (hereafter we will refer to this treatment as thermal bleaching). The results obtained are included in figure 1.

It may be observed that most of the x-ray-induced coloration disappears on heating above 150 K. The spectrum observed after heating at 250 K is nearly equivalent to that corresponding to the sample before irradiation. The ony difference is a small increase (≈ 2 cm^{-1}) in the visible. This increase is probably related to the presence of a small concentration of uncontrolled impurities.

Figure 2 shows the EPR spectrum observed after the x-ray irradiation at 12 K and the transfer of the sample to the cryostat of the EPR spectrometer (at ≈ 93 K). The EPR signal observed at 93 K is formed by a broad central line at $g = 2.0098$ with halfwidth $\Gamma = 35$ G, and some minor structured spectrum overlapping with it. When the sample is rotated, the central line behaves isotropically.

We have studied the behaviour of the EPR spectrum during a thermal bleaching treatment similar to that described previously for the optical measurements. The evolution of the EPR spectrum is shown in figure 2. When the sample is heated above 150 K, the intensity of the EPR signal at $g = 2.0098$ decreases and a new isotropic

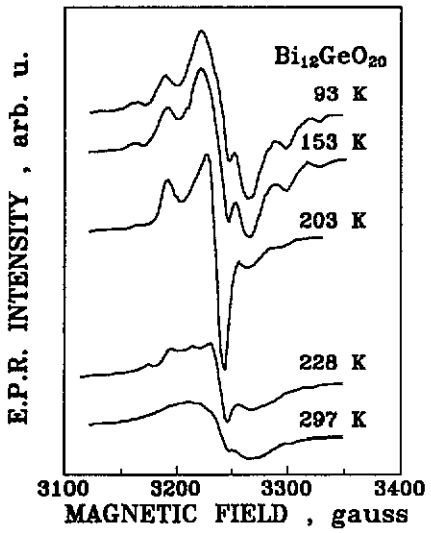

Figure 2. Electron paramagnetic resonance spectra observed in $Bi_{12}GeO_{20}$ single crystals after 10 h of x-ray irradiation at 12 K. Irradiation conditions, 50 kV and 30 mA. The numbers on the curves stand for the temperature at which the sample was kept during the 10 minutes taken to cool it back to 93 K to record the EPR spectrum.

EPR band grows with $g = 2.0060$ and a halfwidth $\Gamma = 15$ G. The intensity of the new EPR signal decreases on heating above 200 K.

EPR lines with a g-value higher than that corresponding to the free electron have often been associated in oxides with a hole trapped in the oxygen sublattice [6]. This defect, usually called a small polaron, also gives rise to broad optical absorption bands associated with the light-induced mobility of the hole between equivalent oxygens of the centre [6, 7].

We propose that the x-ray irradiation of BGO single crystals produces holes that are self-trapped in the oxygens of the BGO lattice. These centres are responsible for the optical absorption observed in figure 1 immediately after the x-ray irradiation.

The thermal bleaching from 12 to 100 K induces a decrease in the intensity of the optical absorption. However, the shape of the bands does not change; therefore after the thermal bleaching at 100 K the same kind of defects are expected still to be present in the sample, and the EPR spectrum observed in figure 2 at 93 K may be associated with the hole trapped in the oxygens of the lattice.

BGO crysals have a cubic structure called sillenite [8]. In this lattice Ge^{4+} is coordinated with a tetrahedron of oxygens while Bi^{3+} is coordinated with seven oxygens forming a pseudo-octahedron. This fact may explain the broad appearance of the optical absorption, because both centres are likely to contribute to the optical absorption observed after the x-ray irradiation at 12 K.

The optical absorption of small polarons is made up of two components for light parallel ($\parallel$) and perpendicular ($\perp$) to the optical axis of the defect. Moreover, the relative position and intensity of the components is different for polarons in octahedral or tetrahedral coordination. The following expressions describe the shape of the optical absorption components for small polarons in octahedral coordination [9]

$$
\begin{aligned}
I_{\parallel} &= I_0(W/\pi)^{1/2}\exp[-W(\hbar\omega - 2E_{JT} - 2J)^2] \\
I_{\perp} &= I_0(W/\pi)^{1/2}\exp[-W(\hbar\omega - 2E_{JT})^2] \\
W^{-1} &= 4E_{JT}\hbar\omega_0 \coth(\hbar\omega_0/2kT)
\end{aligned} \tag{1}
$$

and in tetrahedral coordination [7]

$$
\begin{aligned}
I_{\parallel} &= 4I_0(W/\pi)^{1/2}\exp[-W(\hbar\omega - (8/3)E_{JT} + 2J)^2] \\
I_{\perp} &= I_0(W/\pi)^{1/2}\exp[-W(\hbar\omega - (8/3)E_{JT} - J)^2] \\
W^{-1} &= (16/3)E_{JT}\hbar\omega_0 \coth(\hbar\omega_0/2kT)
\end{aligned} \tag{2}
$$

where $\hbar\omega$ is the photon energy, E_{JT} is the Jahn–Teller energy, J is the resonance integral, k is Boltzmann's constant, T is the temperature and $\hbar\omega_0$ is the energy of the phonon coupled to the polaron.

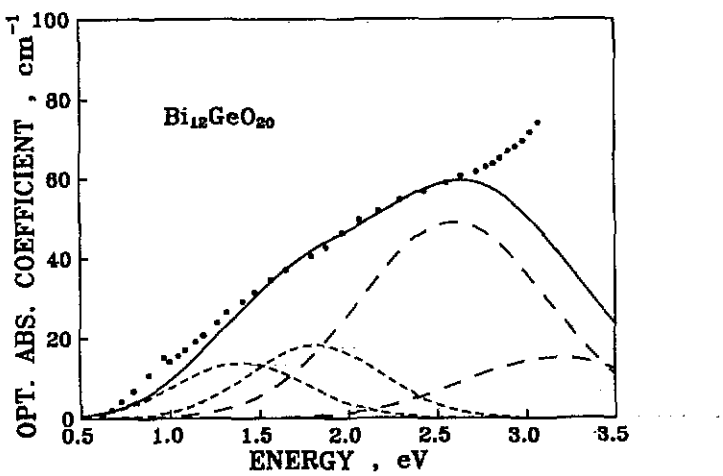

Figure 3. Fit of the experimental optical absorption (points) observed after the x-ray irradiation at 12 K. The dashed lines are the components ($I\hbar\omega$) obtained assuming the following values for the parameters: octahedrally coordinated polaron (short-dashed lines), $I = 9.7\ \mathrm{cm}^{-1}$, $\hbar\omega_0 = 0.11$ eV, $E_{JT} = 0.65$ eV, $J = 0.22$ eV; tetrahedrally coordinated polaron (long-dashed lines), $I_0 = 6.5\ \mathrm{cm}^{-1}$, $\hbar\omega_0 = 0.10$ eV, $E_{JT} = 1.08$ eV, $J = 0.20$ eV. The solid line is the convolution of the four components.

Figure 3 shows a fit of the optical absorption observed after the x-ray irradiation at 12 K using equations (1) and (2). In spite of the uncertainty in the selection of the eight free parameters, the fit qualitatively agrees with the assumption that both coordinations contribute to the optical absorption observed; otherwise more narrow optical absorption bands should appear.

The weak EPR spectrum overlapping the central one is probably related to the presence of uncontrolled impurities.

Above 150 K the x-ray-induced optical absorption decreases as well as the EPR signal with $g = 2.0098$. This behaviour is attributed to the thermal instability of the holes trapped in the regular oxygens of the lattice. In figure 2 a narrow interval of

bleaching temperatures (150–200 K) was observed where a new EPR signal appears; this behaviour is probably related to the trapping of the hole in other lattice defects or uncontrolled impurities.

The x-ray irradiation of BGO single crystals produces a characteristic coloration of the samples; moreover an isotropic EPR signal appears. It has been suggested that both phenomena are due to holes trapped in regular oxygens of the lattice. These holes are released at temperatures higher than 150 K when the coloration and the EPR spectrum disappears.

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