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## Low-temperature x-ray-induced optical properties of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ scintillators

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**Abstract.** Undoped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals exposed to a moderate dose (less than 15 krad) of x-ray irradiation at 12 K show a rapid decay in the x-ray-induced light emission intensity and very little increase in the optical absorption. The emission spectrum may be recovered by thermally storing the sample between 12 and 300 K, although the spectral distribution obtained depends on the storage temperature. The emission decay does not correspond to the light lost by increase in the optical absorption; the origin of this decay is attributed to the depopulation of pre-existing electronic traps of the material. Higher doses (6 Mrad or above) of x-ray irradiation at 12 K induce an isotropic EPR spectrum formed by a band centred at  $g = 2.0036$  and a half-width of 9 G; this signal has been attributed to the creation of trapped holes. On heating the sample to above 12 K after irradiation, broad intense optical absorption increases in the visible and ultraviolet regions; this optical absorption has been attributed to new hole-related centres (probably holes trapped in the oxygen sublattice). These centres are formed after the thermal release of the trapped holes initially induced by the x-rays. The defects induced by x-rays in undoped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals are unstable above 200 K but Mn impurities induce a stable colouration at room temperature. Fe and Cr impurities modify the colouration process at temperatures below 220 K but do not show stable x-ray-induced colouration at room temperature.

### 1. Introduction

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals are used as scintillators in high-energy photon (x-ray [1] and  $\gamma$ -ray [2]) and particle (neutron [3], electron [4] and positron [5]) detectors because of its room-temperature (RT) luminescence [1, 4, 6–9].

Several studies have reported a decrease in the RT luminescence yield during irradiation with the photons or particles to be measured [10–19]. This behaviour is a nuisance for accurate applications and its origin is still under discussion. Most of the studies [13, 16, 18, 19] indicate that the residual impurities are responsible for the increase of a broad optical absorption band in the visible and ultraviolet spectral regions; therefore the decrease in the luminescence intensity has been ascribed to the absorption of the emitted light in the optical absorption band induced by the photons or particles to be measured.

The shape of the optical absorption induced by irradiation at RT is nearly independent of the nature of the excitation [19] and does not depend markedly on the impurity incorporated in the crystal [13]. In some investigations the origin of the optical absorption has been ascribed to the presence of F centres [18] and, in others, holes trapped in cationic vacancies

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have been suggested [13], but evidence of the presence of vacancies in the lattice has not been offered.

Although in most applications  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  scintillators are used at RT, increased sensitivity may be obtained if the material is cooled to below RT [6]. On the other hand, operation below RT is required in some applications such as in the EUROBALL detector [20] or in atmospheric studies [21]; however, experimental information on the performance of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals at temperatures below RT is very scarce.

In this work we have studied for the first time to our knowledge the influence of the 12 K x-ray irradiation on the optical and paramagnetic properties of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . The nature of the defects formed and the origin of the luminescence yield decay observed at 12 K are discussed. Moreover the influence of some impurities (Fe, Mn and Cr) which have been reported to produce coloration at RT [13, 16, 18] has also been considered.

## 2. Experimental techniques

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals were grown by the Czochralski method in the crystal growth laboratories of the Universidad Autónoma de Madrid and in the Research Laboratory for Crystal Physics, Budapest. High-purity powders from Merck and Johnson Matthey were melted in platinum crucibles. Additional samples grown by Bridgman method were obtained from CERN, Geneva. The results reported later are independent of the origin of the samples. Doped samples were obtained using the Czochralski method by mixing and melting metal oxides with the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  powders. The impurity concentration in the crystal was determined by the plasma emission technique. The results obtained are  $[\text{Fe}] = 2 \times 10^{17}$  atoms  $\text{cm}^{-3}$ ,  $[\text{Mn}] = 9.3 \times 10^{17}$  atoms  $\text{cm}^{-3}$  and  $[\text{Cr}] = 43 \times 10^{17}$  atoms  $\text{cm}^{-3}$  for Fe-, Mn- and Cr-doped samples, respectively.

The samples were irradiated with polychromatic x-rays emitted by a Siemens x-ray generator (model Kristalloflex 2H) with a tungsten anode and a beryllium window. The low-energy x-rays emitted were filtered with a 2 mm aluminium plate ( $K\alpha$  line; 1559 eV). To induce defects in the samples the x-ray source was operated at 50 kV and 30 mA; under these conditions the x-ray output dose is estimated to be about 3 krad  $\text{min}^{-1}$ . To induce the luminescence reported later the x-ray source was operated at 30 kV and 20 mA; under these experimental conditions the x-ray output dose is estimated to be about 1.5 krad  $\text{min}^{-1}$ . In all our experiments the sample was 6 cm from the x-ray generator window.

Optical absorption measurements were performed at 12 K using a Varian spectrophotometer (model Cary 17). Electron paramagnetic resonance (EPR) experiments were performed at 90 K using a Varian spectrometer (model E-12), operated in the X band. Accurate values of the resonance magnetic fields and microwave frequencies were measured with a Bruker NMR gaussmeter (model ER035 M) and a Hewlett-Packard frequency meter (model 5342A), respectively.

Luminescence was excited at 12 K with the polychromatic emission of the x-ray generator mentioned above. The light emitted by the sample was analysed with a Bausch & Lomb high-intensity monochromator (20 nm passband); the selected light is recorded with an EMI photomultiplier (model 6256S). The emission spectra displayed below have been corrected for the spectral response of the equipment.

During the x-ray irradiation and optical measurements, the temperature of the sample was controlled with a closed-cycle He-gas Lake Shore-CTi cryostat which allows us to select any temperature in the range 12–300 K with a stability of  $\pm 2$  K. To perform EPR experiments, after irradiation at 12 K, the samples were transferred to a Varian cryostat (model E-257) operating in the 90–300 K temperature range.

### 3. Experimental results

#### 3.1. Undoped samples

Figure 1 shows the x-ray-induced luminescence of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals measured at 12 K. The intensity of the spectrum decreases quickly after irradiation for 4 min (the time spent to record the spectrum) and under our experimental conditions it reaches a steady spectral distribution after irradiation for 10 min. The spectrum observed after irradiation for 10 min corresponds well to those reported previously under ultraviolet light or x-ray excitation [6, 7].

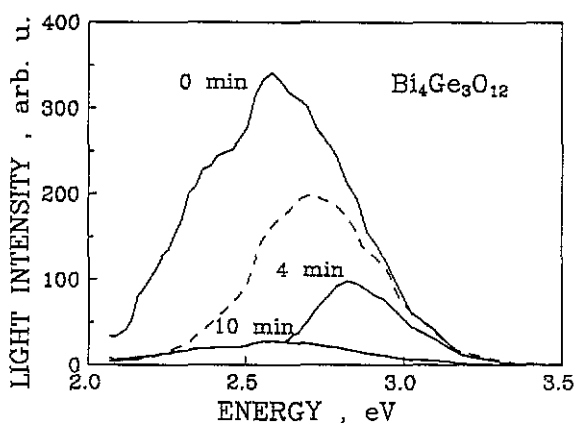


Figure 1. Evolution of the x-ray-induced emission of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals after short periods of x-ray irradiation at 30 kV and 20 mA (—). After the sample had been stored for 18 h at 12 K in darkness, partial recovery of the initial spectrum is observed (---).

It is worth noting at this point that the x-ray dose required to observe the decrease in the luminescence intensity is lower than 15 krad. Thus this effect and the defects responsible for it are not related to the coloration and paramagnetic centres reported later for longer x-ray irradiation times (x-ray dose, 6 Mrad or more).

If the sample is kept at 12 K in darkness for 18 h, the original spectral distribution is partially recovered, as can also be observed in figure 1 (broken curve).

To study the thermal recovery of the x-ray-induced luminescence, we have performed the following experiment:

- (i) First the emission at 12 K was recorded under x-ray excitation.
- (ii) Then the sample was submitted to further irradiation at 12 K until a steady spectral distribution of the luminescence was reached.
- (iii) Later the sample was stored in darkness for 18 h at a given temperature and cooled to 12 K to record a new emission spectrum.

Before proceeding to store the sample at a new increasing temperature, step (ii) was repeated until a steady spectral distribution was again reached as a reference state. Figure 2 shows the results of this experiment. It may be observed that between 12 and 100 K a well defined emission appears at about 2.8 eV; at higher temperatures a shift in the emission to low energies is observed because of the contribution of a band at about 2.6 eV; this band does not appear after heating at RT but the former band still contributes.

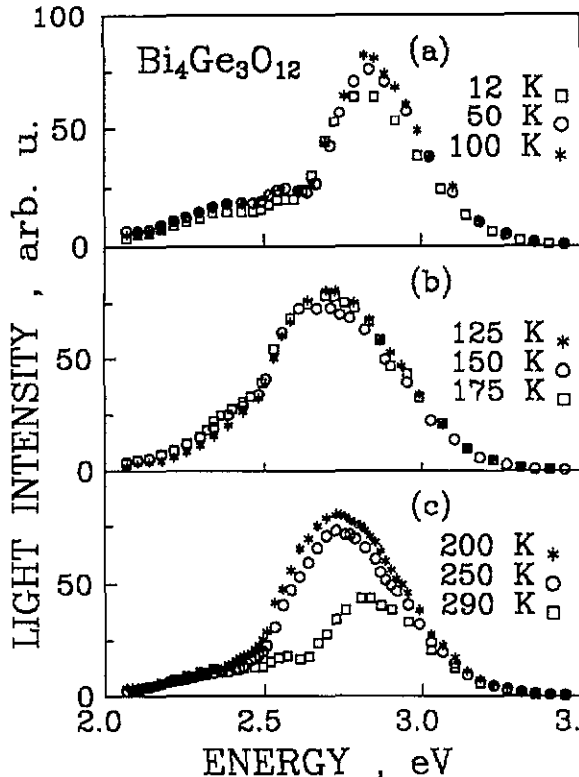


Figure 2. Thermal recovery of the short-time x-ray-induced luminescence of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals. The sample was stored for 18 h at each of the temperatures indicated in the figure; then it was cooled to 12 K to record the emission spectrum.

The contribution of the high-energy band to the emission spectrum at short times is observed even if the spectrum is recorded at 300 K.

For undoped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  we have not observed reliable changes in the optical absorption after irradiations on the time scale in which decay of the luminescence is observed. However, these changes have been observed after longer (and more intense) irradiations.

Figure 3 shows a comparison of the optical absorption spectra of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals before (full points) and after (full and broken curves) irradiation at 12 K with x-rays. It is worth noting that after irradiation a small (about  $5 \text{ cm}^{-1}$  at 3.5 eV) but reliable increase in the optical absorption is observed.

If the sample is heated for 10 min at increasing temperatures and cooled to 12 K in each temperature step to record the optical absorption spectrum, a large enhancement of the optical absorption is observed. The result of these experiments is included in figure 3. It is worth noting that no further x-ray irradiation was performed during this thermal treatment. The optical absorption which develops on increase in temperature is very broad and it is probably composed of several overlapping bands. In particular, after heating at 200 K the high-energy part of the spectrum decreases while the low-energy part increases. Above 200 K most of the x-ray-induced optical absorption disappears. A full recovery of the optical absorption was observed after heating at 400°C.

X-ray irradiation at 77 K produces a similar behaviour but the intensity of the optical absorption which develops on increase in the temperature is much lower.

Figure 4 shows the EPR spectra taken at 90 K of a  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  sample irradiated at 12 K with x-rays. It should be noted that, because of the limited temperature range available with the cryostat used in the EPR technique, the spectrum labelled as 93 K corresponds to a sample heated after irradiation from 12 to 93 K. Thus according to figure 3 the state of the

sample is not equivalent to that obtained just after the irradiation at 12 K. The EPR spectrum observed is formed by a single line at  $g = 2.0036$  and a half-width  $\Gamma = 9$  G. This spectrum behaves nearly isotropically when the sample is rotated around the (001) axis of the crystal. On heating the sample above 173 K the intensity of this spectrum decays quickly.

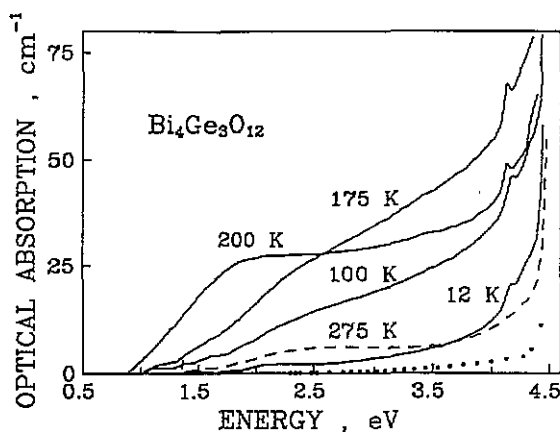


Figure 3. Optical absorption spectra of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals taken at 12 K, before irradiation ( $\bullet$ ) and after x-ray irradiation for 48 h at 12 K (50 kV and 30 mA) (—, ---). Different optical spectra are obtained after heating the sample for 10 min at the temperature noted on each curve.

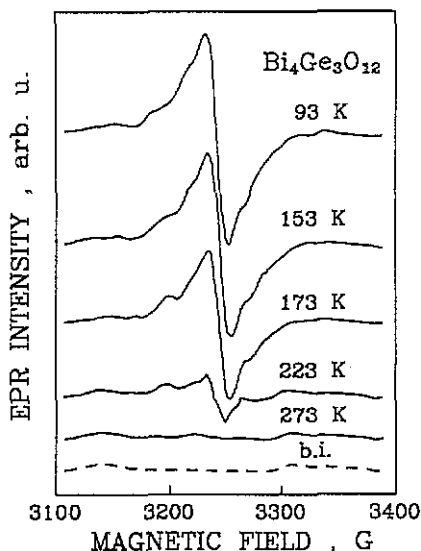


Figure 4. 90 K EPR spectra of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals obtained on a sample irradiated for 48 h (50 kV and 30 mA) at 12 K. The intensity of the spectra decreases after heating the sample for 10 min at the temperature noted on each curve. The 90 K EPR signal of the sample before irradiation is displayed (---, b.i.) for reference.

Figure 5 shows a comparison between the intensity of the EPR signal and the optical absorption at two representative wavelengths during a heat treatment from 12 K to RT. It is worth noting that for the temperature range where the optical absorption increases (12–200 K) the EPR signal decreases monotonically.

### 3.2. Doped samples

To analyse the influence of transition-metal impurities in the optical behaviour of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals after x-ray irradiation we have performed in Fe-, Mn- and Cr-doped samples similar experiments to those previously described for the high-dose irradiation regimen. Figure 6 shows the optical absorption of doped samples after 12 K x-ray irradiation and its evolution after heating the sample to increasing temperatures.

Fe-doped samples (figure 6(a)) show an optical behaviour rather similar to undoped samples; however, Mn- and Cr-doped crystals (figures 6(b) and 6(c), respectively) behave in a different way from undoped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . Mn-doped samples do not develop optical absorption during the thermal treatment; moreover the coloration induced is very stable even at RT (figure 6(b)); to remove this coloration the sample has to be heated to above 300 °C.

The optical absorption spectrum of Cr-doped samples before x-ray irradiation shows several absorption bands similar to those observed in Cr-doped  $\text{Bi}_{12}\text{GeO}_{20}$  single crystals

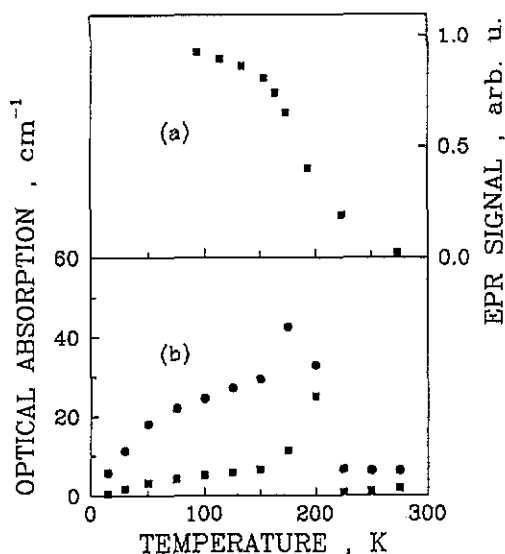


Figure 5. (a) Thermal evolution of the 90 K EPR intensity of a  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  sample irradiated at 12 K for 48 h (50 kV and 30 mA). (b) Thermal evolution of the 12 K optical absorption of a  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  sample irradiated at 12 K for 48 h (50 kV and 30 mA):  $\bullet$ ,  $\hbar\omega = 3.5$  eV;  $\blacksquare$ ,  $\hbar\omega = 1.8$  eV.

[22]; these bands arise from crystal-field transitions of  $\text{Cr}^{4+}$  ions [23, 24]. The x-ray irradiation induces an increase in background absorption similar to that observed in undoped samples; however, the intensity of this background (before heating above 12 K) is about one order of magnitude larger than in undoped samples.

Moreover in Cr-doped samples an EPR signal at  $g = 2.0072$  is observed after x-ray irradiation at 12 K. Figure 7(a) shows the appearance of the signal after removal of the background EPR spectrum corresponding to  $\text{Cr}^{4+}$  ions in tetrahedral sites [23]. The intensity of this EPR signal increases on heating from 90 to 175 K (see figure 7(b)); above this temperature the intensity of the EPR spectrum decays.

It has to be mentioned that in Fe- or Mn-doped samples we have not observed x-ray-induced EPR signals similar to that reported above for Cr-doped samples. In Fe-doped samples this may be due to the low concentration of Fe available, and in the Mn-doped samples if the same new EPR signal is created during irradiation its detection is difficult because of the overlap with the very intense EPR spectrum of  $\text{Mn}^{2+}$  ions.

#### 4. Discussion

A remarkable result included in figure 3 is that the optical absorption of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals after x-ray irradiation at 12 K increases only a very little. This behaviour is different from that observed for  $\text{Bi}_{12}\text{GeO}_{20}$  crystals [25]. In the latter oxide, after similar irradiation conditions, broad optical absorption bands have been observed; moreover on increase in the temperature of the sample to RT the intensity of the optical absorption decreases monotonically [25].

On increase in the temperature of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals to above 12 K, optical absorption appears, which is similar to that previously observed for  $\text{Bi}_{12}\text{GeO}_{20}$  [24]. This behaviour suggests that the electronic excitation induced in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  at 12 K by the incident x-rays is stored in a defect which does not contribute to the optical absorption. On heating above 12 K this defect becomes unstable and the electronic excitation migrates to new centres.

The evolution of the intensities of the EPR signal and optical absorption shown in figure 5 further supports the hypothesis above. Up to 200 K, the decrease in the EPR signal

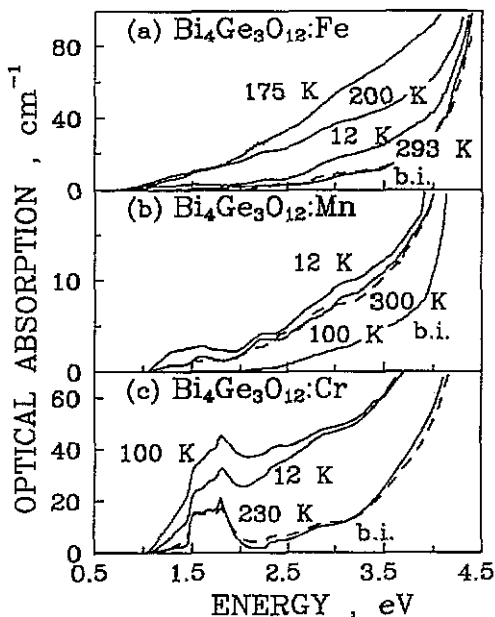


Figure 6. Optical absorption spectra at 12 K of (a) Fe-doped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  samples irradiated for 18 h at 12 K ( $[\text{Fe}] = 2 \times 10^{17}$  atoms  $\text{cm}^{-3}$ ), (b) Mn-doped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  samples irradiated for 18 h at 12 K ( $[\text{Mn}] = 9.3 \times 10^{17}$  atoms  $\text{cm}^{-3}$ ) and (c) Cr-doped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  samples irradiated for 18 h at 12 K ( $[\text{Cr}] = 43 \times 10^{17}$  atoms  $\text{cm}^{-3}$ ): b.i., spectra before irradiation; ---, spectra after heating close to rt.

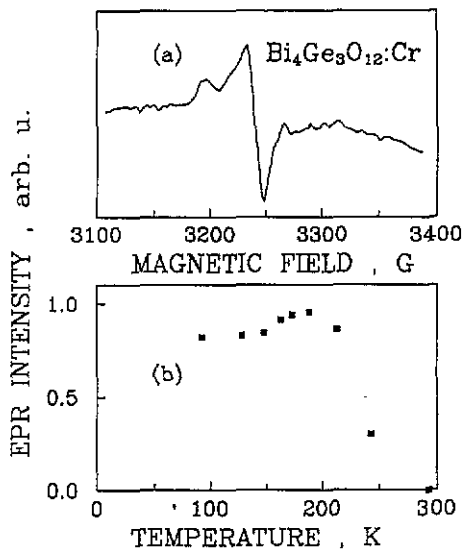


Figure 7. (a) EPR signal observed at 90 K for a  $\text{Bi}_4\text{Ge}_3\text{O}_{12}:\text{Cr}$  crystal after x-ray irradiation for 18 h at 12 K. The spectrum shown corresponds to a sample heated to 175 K after the x-ray irradiation. (b) Evolution of the intensity of the EPR signal shown in (a) on heat treatment at increasing temperatures.

correlates with an increase in the optical absorption. Above 200 K both defects are unstable and disappear. Thus the x-ray irradiation at 12 K creates a paramagnetic defect. When this defect is thermally unstable above 12 K, new centres with strong optical absorption appear. The thermal instability of the original defect is probably related to the increase in defect mobility previously observed above 30 K [26].

Figure 4 shows the EPR signal observed for  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals after x-ray irradiation at a low temperature (12 K). The value of the  $g$ -factor obtained is larger than that corresponding to the free electron,  $g_e$ . In other oxides, EPR signals with  $g > g_e$  have been typically attributed to trapped holes [27]. Holes trapped in the oxygen sublattice (usually denoted 'small-polaron' centres) have been observed in several oxides [28, 29] and typically exhibit intense broad optical absorption bands.

In figure 5 it has been shown that the EPR signal intensity decreases when the optical absorption increases. Thus the centre responsible for the EPR does not correspond to a hole trapped on oxygen ions. The most likely possibility is a hole trapped in the cation sublattice or in cationic vacancies. A hole trapped on Bi ions is ruled out by the lack of hyperfine splitting (the nuclear spin of bismuth is  $\frac{9}{2}$  with 100% natural abundance). A hole trapped on Ge ions (hyperfine splitting of the EPR would be very weak because there is only 7.7% of Ge isotopes with a nuclear spin different from zero) or in cation vacancies are more plausible possibilities.



The increase in the optical absorption of undoped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals observed after the 12 K x-ray irradiation is about  $3 \text{ cm}^{-1}$  at 2.6 eV (the energy of the luminescence emission maximum). To reach this increase, irradiation for 48 h was required. This small enhancement in the optical absorption may not explain the strong decrease in the x-ray-induced emission intensity shown in figure 1. Moreover this decrease takes place on a time scale one order of magnitude shorter than the enhancement in the optical absorption; therefore the two phenomena are not related.

The x-ray-induced emission recovers after thermal treatments in darkness (see figure 2); this suggests that the light emitted at short irradiation times arises from the excitation of pre-existing traps that become depopulated by the x-ray irradiation. When these traps have been emptied, steady emission is reached. Longer irradiations decrease the intensity of this steady emission only slowly; this latter behaviour is related to the increase in the optical absorption induced by the x-rays. This two-step behaviour has also been observed in the RT emission of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  scintillators excited with  $\gamma$ -rays [11, 12] but previously it was merely attributed to the increase in the optical absorption.

The nature of the pre-existing traps may not be definitively ascertained with the present knowledge of native defects in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals, but their presence is further supported by the photoconductivity excited with ultraviolet light [30].

It has to be noted that this transient behaviour of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  scintillators (present even for irradiation at RT) should be carefully considered in relation to the linearity of the device and to the spectral matching of the photodetector attached to the scintillator crystal.

(i) If the flux of particles or photons to be measured modifies the population density of the traps, the linearity of the detector may not be preserved; in this case, previous irradiation to reach steady-state emission could improve the device linearity although a lower sensitivity would be the penalty.

(ii) The spectral distribution of this transient emission changes with change in the storage temperature; this had to be considered in relation to the spectral response of the photodetector attached to the scintillator.

We have shown above that, as long as the temperature of the sample is kept at 12 K, the optical absorption induced by the incident x-rays is rather low. This behaviour changes significantly as a result of the presence of certain impurities.

According to figure 6 the presence of Mn induces an increase in the coloration at 12 K with respect to that of the undoped material. This behaviour is probably related to the ability of Mn ions to trap electrons or holes; this allows at RT the presence of stable holes responsible for the optical absorption bands. In fact a marked decrease in the concentration of  $\text{Mn}^{2+}$  ions has been observed under ultraviolet light irradiation [31].

Cr impurities also induce an enhancement in the optical absorption at 12 K. This optical absorption is probably related to holes trapped at oxygen ions close to  $\text{Cr}^{4+}$  ions replacing Ge host cations [23, 24]. These centres should have optical properties only slightly different from those polarons self-trapped in regular oxygen ions. We propose that the EPR signal observed in figure 7(a) corresponds to Cr-perturbed polarons. According to figure 7(b) the concentration of these centres increases for temperatures up to 175 K and decreases for higher temperatures according to the evolution of the optical absorption displayed in figure 6(c).

The relatively small influence of Fe impurities in our sample is probably due to the low Fe concentration in comparison with the other impurities considered in this work; however, Fe should also enhance the x-ray-induced optical absorption as was observed under electron,  $\gamma$ -ray and ultraviolet light excitation [19, 31].

## 5. Conclusions

Short-time low-temperature (12 K) x-ray irradiation of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  scintillators induces a decrease in the intensity of the emitted light. This phenomenon has been attributed to the depopulation of thermally filled pre-existing trap levels related to native defects of the material. Higher doses of incident x-rays at 12 K create trapped holes (probably in the cation sublattice or in cation vacancies).

On increase in the temperature of the sample after irradiation these trapped holes become unstable and transfer the electronic excitation to the oxygen sublattice. This produces an increase in the optical absorption of the sample stable up to about 200 K.

The presence of some impurities (in particular Mn) in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals allows trapped holes to become stable, even at room temperature; this is probably due to the ability of transition-metal impurities to trap electrons. Moreover, holes may be also trapped in Cr-perturbed polarons; these centres have optical absorption close to that observed for self-trapped polarons.

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