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RADIATION DAMAGE OF BISMUTH GERMANATE CRYSTALS

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ABSTRACT

Recent CERN results on BGO radiation damage tests are presented, where the behaviour of different optical parameters like excitation, fluorescence and transmission spectra, is analysed as a function of photon irradiation at different wavelengths (from 1.88 eV to 1.33 MeV). Some attempts to cure damaged crystals, either by exposure to visible light or by annealing are also discussed. In the last section a qualitative model of the damage mechanism is described.

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1. INTRODUCTION

Bismuth Germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$:BGO) is going to be a very popular material in the High Energy Physics community for electromagnetic calorimetry. Among several advantages: high stopping power, large enough scintillation efficiency to use photodiode readout above a few MeV, very good energy resolution, etc. Some authors [1] also mentioned its relatively better resistance to radiation damage as compared to other shower detectors. As this point is crucial for the design of forward calorimeters for experiments around colliding machines, two groups, members of one of the LEP collaborations (CERN and Carnegie Mellon University) started systematic studies of radiation damage effects on BGO. Here CERN results are presented.

Crystals grown by Czochralski method at Crismatec (France) and Harshaw (Holland) have been tested. If not specified they are cut in parallelepipeds of $2 \times 2 \times 24 \text{ cm}^3$. One crystal $3 \times 3 \times 20 \text{ cm}^3$ grown by the Bridgman method in the Institute of Ceramics in Shanghai, was also studied. The crystals have all sides polished. Irradiations were made either at CERN with a 42 Curie cesium source, or at the Geneva Hôpital Cantonal with a 5800 Curie Cobalt source. In some cases the crystals were also exposed to the light from a Lambda Physik excimer pumped dye laser giving light pulses of about 10 mJ in 10 nsec from ultraviolet (308 nm) to more than 700 nm.

2. DAMAGE EFFECT AND RECOVERY TIME

Crystals are wrapped in white and aluminium paper and coupled to a 2" Philips XP 2262B phototube with an optical grease Rhodorsil B431 ($n = 1.5$) in a reproducible way (fig. 1). Light output given by a 5 μ Curie ^{22}Na radioactive source is first measured after a long stay (at least one week) in a dark room. Then the crystals receive 1000 rad in 7 minutes from the Hospital Cobalt source on their whole length (24 cm). After coupling to the PM the light output given by the sodium source is then measured as a function of time. Measurements are corrected for temperature variation ($- 1.6\%$ per $^{\circ}\text{C}$ for BGO scintillation) and PM stability is controlled with a NaI (Am) light pulser. Fig. 2 shows the result for two Crismatec crystals

(C7 and C16) and one crystal from Shanghai Institute of Ceramics. At least two time constants are visible with a transition regime of about 2 days. The short time constant corresponds to one to two days and the long one to about one month. It is also to be noticed that, although the initial damage is similar for the three crystals, the recovery is very different from crystal to crystal, and there is no direct relation with the initial crystal quality before irradiation: the Shanghai crystal was very clear and gave 9% more light with a ¹³⁷Cesium source than the Crismatec C16 which looked slightly yellowish, and 37% more light than the Crismatec C7 which was much more coloured.

All these results are in good agreement with those obtained by the Carnegie Mellon group [2]. The main difference is the very short time constant they observed (1 to 2 hours) which we cannot see because of the time we need between irradiation and the first measurement.

It must be said, that the way the measurements are done is very pessimistic because the effect is integrated over the whole length of the crystal. In colliding machines for instance, crystals are in general pointing to the vertex and if correctly shielded, their front face only sees the synchrotron radiation which at LEP will extend up to a few hundreds keV. In order to measure the penetration of the damage in these conditions, we have exposed the front face of one Crismatec crystal to 1400 Rad of ⁶⁰Cobalt (1.17 and 1.33 MeV gamma rays). The lateral transmission in the crystal was then measured with a low energy Argon laser beam (514 nm) and a photodiode as a function of the distance to the front face. The penetration of the damage is clearly seen in Fig. 3 and corresponds to about 3 cm. Nevertheless if a photomultiplier is coupled to the non damaged face, the light output decrease is of the order of 30% even for emitting points far from the damaged part of the crystal. This loss is due to the absorption of light rays emitted in a direction opposite to the PM and then back reflected by the end face.

3. IRRADIATION WITH PHOTONS AT DIFFERENT ENERGIES

In order to determine the activation energy of the damage centres, irradiations with photons at different wavelengths but with about the same energy density on the crystal were performed. The crystal (Crismatec 1 x 1 x 20 cm³) was first exposed to 175 Rad from the CERN 42 Curie ¹³⁷Cesium source corresponding to $6.6 \cdot 10^{11}$ gamma rays of 662 keV in 15 hours which means an energy density of 70 mJ/cm².

After almost full recovery, the same crystal was exposed to one shot of our excimer laser ($7.8 \cdot 10^{16}$ photons at 308 nm or 4.025 eV) corresponding to an energy density of 50 mJ/cm². The effect was similar to what was observed with the Cesium (Fig. 4). The fact that the damage looks slightly more important with the UV irradiation is probably caused by the non complete recovery after the Cesium irradiation.

Laser exposures to the same energy density but with green light at 514 nm (2.41 eV) and with red light at 660 nm (1.88 eV) did not produce any measurable effect. In the meantime irradiation with a nitrogen laser at 337 nm (3.68 eV) produced a strong damage.

These results suggest a threshold effect for radiation damage between 2.41 eV and 3.68 eV. On the other hand the fact that the damage depends on the total irradiation energy and not on the number of primary photons means that damage centres are produced by low energy photons at the end of the cascade, and confirms that their activation energy is rather low at a level of a few eV.

Finally, exposure to the daylight during only 6 minutes produced a 15% damage (certainly caused by the UV component of the daylight) which recovered in about one day (Fig. 4). This means that some precautions should be taken, when comparing light output from different crystals to check their quality.

4. EFFECT OF RADIATION ON SCINTILLATION EFFICIENCY OF BGO

In order to see if radiation damage affects scintillation efficiency of BGO, we have measured excitation and fluorescence spectra of crystals before and after irradiation. The set up is shown in Fig. 5-a. Two monochromators Jobin Yvon H20 were used in conjunction with a 150 W Xenon lamp and a Hamamatsu R446 photomultiplier. Excitation spectra were recorded by selecting a fluorescence line at 480 nm, and fluorescence spectra were excited at 300 nm. In these conditions, both excitation and fluorescence spectra look exactly the same in shape and intensity before and after irradiation (Fig. 5-b). This means that scintillation is not decreased by radiation when BGO is directly excited at maximum of excitation spectrum, but excitation with high energy gamma rays produced by radioactive sources could give different results, if some of these photons are trapped in the cascade process before they reach the BGO excitation energy. In order to check if there was such an effect, one crystal was strongly irradiated on half his length with an energy density of 2 J/cm² of UV light at 308 nm. The crystal was then mounted on the set up of Fig. 1 with the PM in position 2. Light output produced by a 30 μ Curie ⁶⁰ Cobalt source is shown in Fig. 6 as a function of the crystal position; no difference can be detected between the irradiated and the non irradiated part. The conclusion is then that BGO scintillation efficiency is not significantly modified by radiation damage.

5. EFFECT OF RADIATION DAMAGE ON LIGHT ABSORPTION

As scintillation is not modified, the only way to explain a light loss as high as 50% or even more (Fig. 2) is to suppose that scintillation light has been absorbed in the crystal on his way to the PM. Direct observation of the crystal after irradiation makes this conclusion obvious, as it shows a strong coloration grey, brownish or yellow which decreases with time when the crystal recovers.

In order to make more quantitative measurements, the transmission spectrum of crystals was measured before and after irradiation with a

Beckmann spectrophotometer schematically described in Fig. 7. For practical reasons the absorption was measured for 12 cm long crystals one from Harshaw of good quality and one from Crismatec of poor quality^(*). Transmission results before and after exposure to 1000 rad to the Cobalt source are shown in Fig. 8 and 9. Fig. 10 and 11 show the relative absorption increase with a strong effect at short wavelength, decreasing in the middle of the spectrum, and almost no damage in the red. This loss in the blue part of the spectrum explains why the crystal gets yellow or even brown after irradiation.

It must be said that the analysis of the transmission spectrum is a powerful way to detect medium quality crystals. Comparison of Fig. 8 and 9 shows even before irradiation a strong absorption band around 430 nm in the Crismatec crystal which does not exist in the Harshaw crystal. Also the behaviour after irradiation is quite different. The loss at any wavelength is about 3 times more important for the bad crystal. In addition to the bump at 500 nm in the relative transmission loss (Fig. 10 and 11), which is observed in both cases, there is another bump at 430 nm for the bad crystal, showing that the absorption band observed before irradiation, and probably related to some impurity in the BGO, is also a region of important sensitivity to radiation damage.

6. TRANSMISSION SPECTRUM RECOVERY

As irradiation seems to affect the light transmission in BGO in a way depending upon the wavelength, it is interesting to follow the recovery in transmission for different lines in the spectrum. Results are shown in Fig. 12 for the Crismatec $2 \times 2 \times 12 \text{ cm}^3$. Two time constants are visible with a transition zone, as in Fig. 2, but the recovery is faster at increasing wavelength. The behaviour of the short and the long time constants τ_S and τ_L is plotted as a function of the wavelength in Fig. 13 for two different crystals: Crismatec and Harshaw $2 \times 2 \times 12 \text{ cm}^3$. Although the quantitative effect is not the same for the two crystals, the general tendency is an important decrease of the time constants from blue to red.

(*) This test was made with the collaboration of G. Bobbink from Carnegie Mellon University.

This effect suggests the presence of several damage centres, each of them corresponding to an absorption at a given wavelength. Damage centres absorbing red light need probably less energy to recover than blue light absorbing centres.

7. CURING OF RADIATION DAMAGE

We have seen already that the excitation energy of radiation damage centres is probably low, of the order of a few eV. On the other hand the natural recovery of BGO with time suggests that the desexcitation energy from these metastable states is even smaller. In order to verify these ideas, we have exposed UV damaged crystals to visible light given either by a continuous wave He-Ne laser at 633 nm with an energy density of 5 mW/mm² or by a CW Argon laser at energy density of 4.25 mW/mm², 6.75 mW/mm² and 12 mW/mm². The transmission light was then measured as a function of time on a photodiode. Fig. 14 shows that the crystal recovers in all the cases, although the process is more efficient with green light than with red light. After a few minutes, some clear transparent channels are clearly visible in the crystal at the position of the laser beam pencils.

The recovery after 10 sec exposure behaves linearly with the Argon laser energy (Fig. 15). This implies that the recovery corresponds to a one photon process (a two photon process would have shown a quadratic dependence).

As the recovery was impressive at rather small energy (~ 2 eV given by the He-Ne laser), it was natural to check the influence of temperature at even smaller energy. A Crismatec crystal was strongly damaged with UV light. After a few days where light output from a Cesium source was measured as a function of time, the crystal was heated for two hours at 80° C and measured again at room temperature. The recovery of the crystal was more than 25%, where only 4% would have been expected without heating. The transmission through a UV damaged crystal was also measured as a function of time and temperature with a low energy Argon laser beam. Results are shown in Fig. 16. The initial recovering time constants are 4150 min at 25°C, 316 min at 40°C, 152 min at 60°C and 20 min at 80°C. This impressive improvement can be very important for practical curing in situ.

8. TENTATIVE MODEL OF RADIATION DAMAGE MECHANISM

We know that excitation energy for bismuth scintillation is of the order of 4 eV (~ 300 nm UV excitation). It has been shown by some authors [3,4] that excitation is not localized, but moves in the conduction band and can be trapped by some excitonic levels a few meV below the conduction band and in thermal equilibrium with it at room temperature (Fig. 17-a). Once a bismuth atom, or a more complex group containing bismuth like Bi^{3+} (GeO_4^{4-}) has been excited, part of its energy is dissipated in a non radiative way, mainly by a rearrangement of the atom positions in the crystal and phonon exchange, and only the remaining part produces the fluorescence, explaining the important Stokes shift between the excitation and the fluorescence spectrum.

Damaged centres have molecular orbitals corresponding to energy levels distributed between the valence and the conduction bands, with an important concentration around 3 eV above the valence band and responsible for the increase mainly in the blue. The desexcitation of these levels is non radiative (Fig. 17-b).

The question is to know the nature of the damaged centres. They can be excited states related either to the atoms of the network, or to some impurities. Our observation that the damage looks related to the crystal quality goes in the direction of some participation of the impurities even if the network itself is also involved.

Now the mechanism could be the displacement of an atom out of its equilibrium position, or the displacement of an electron, with the creation of an electron hole pair (a Frenkel pair) which can move almost freely in the crystal or be trapped in some sites. The very low excitation energy of the damage centres already mentioned in section 3 (between 2.41 eV and 3.68 eV) clearly favours the second solution.

The following scheme can then be proposed. A few eV are needed to create a Frenkel pair from an atom in the BGO which is probably very often an impurity atom or a group of atoms in which an impurity is present. The molecular orbitals are then rearranged in such a way that some energy levels

appear between the valence and the conduction bands, mainly around 3 eV above the valence band. This Frenkel pair is in a very unstable state and only about 30 meV (the thermal energy corresponding to 60°C) are necessary to destroy it. (Fig. 17-c). The different recovery time constants could correspond to Frenkel pairs trapped in different BGO sites at slightly different energies.

9. CONCLUSIONS

Although less sensitive than other materials frequently used in calorimetry like lead glass or Sodium Iodide, BGO suffers from radiation damage and can lose more than 50% in light output, after an exposure to 1000 Rad ⁶⁰ Cobalt, mainly because of an increase of absorption in the blue part of the spectrum. On the other hand, excitation energy for the damage centres looks very low (between 2.41 and 3.68 eV) and the energy for recovering much lower (about 30 meV), so that rather simple solutions can be envisaged for in situ treatment of damaged crystals. In addition some efforts to improve the crystal quality by reducing the impurity contents should enhance the BGO resistivity to radiation damage.

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FIGURE CAPTIONS

- Fig. 1 Experimental set-up to measure the light output, the resolution and the crystal uniformity. Excitation is produced either by a radioactive source or by a nitrogen laser.
- Fig. 2 Recovery as a function of time of two crystals from Crismatec ($2 \times 2 \times 24 \text{ cm}^3$)(C7 and C16) and one crystal from the Shanghai Institute of Ceramics ($3 \times 3 \times 20 \text{ cm}^3$)(S4) after a strong irradiation of 1000 rad ^{60}Co in 7 minutes.
- Fig. 3 Lateral transmission of a crystal, the front face of which was exposed to 1400 Rad ^{60}Co .
- Fig. 4 Recovery of one Crismatec crystal ($1 \times 1 \times 20 \text{ cm}^3$) after exposure to 70 mJ/cm^2 ^{137}Cs , 50 mJ/cm^2 UV light (308 nm) and 6 minutes of daylight.
- Fig. 5(a) Experimental set-up of the spectrofluorometer to measure excitation and fluorescence spectra.
- Fig. 5(b) Excitation and fluorescence spectra of one Crismatec crystal before and after a strong UV irradiation.
- Fig. 6 Scintillation efficiency of a crystal irradiated on half its length as a function of the position in the crystal.
- Fig. 7 Schematic view of the Beckmann spectrophotometer.
- Fig. 8 Transmission spectrum of a Harshaw crystal ($2 \times 2 \times 12 \text{ cm}^3$) before and after irradiation to 1000 Rad ^{60}Co .
- Fig. 9 Transmission spectrum of a Crismatec ($2 \times 2 \times 12 \text{ cm}^3$) before and after irradiation to 1000 Rad ^{60}Co .
- Fig. 10 Transmission loss as a function of the wavelength for the Harshaw crystal before and after irradiation to 1000 Rad ^{60}Co .

- Fig. 11 Transmission loss as a function of the wavelength for the Crismatec crystal before and after irradiation to 1000 Rad ^{60}Co .
- Fig. 12 Transmission recovery of the Crismatec $2 \times 2 \times 12 \text{ cm}^3$ crystal at different wavelengths.
- Fig. 13 Transmission recovery time constants as a function of the wavelength for two crystals $2 \times 2 \times 12 \text{ cm}^3$, one from Harshaw, one from Crismatec.
- Fig. 14 Transmission recovery of a crystal when exposed to 5 mW/mm^2 He-Ne laser light and 4.25, 6.75 and 12 mW/mm^2 Argon laser light.
- Fig. 15 Transmission recovery in the first 10 sec as a function of the Argon laser energy.
- Fig. 16 Transmission recovery at 514 nm of a UV damaged Crismatec crystal $2 \times 2 \times 24 \text{ cm}^3$ at $T = 25^\circ, 40^\circ, 60^\circ$ and 80°C .
- Fig. 17(a) Currently accepted model of BGO excitation and emission mechanisms.
- Fig. 17(b) Proposed modification of the previous model in case of radiation damage.
- Fig. 17(c) Energy levels of a metastable damaged centre.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5a

λ (nm)

FIG. 5b

FIG. 6
Position in crystal (cm)

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12
t (hour)

FIG. 13

FIG. 14

FIG. 15

FIG. 16

ENERGY DIAGRAM OF A DAMAGED CENTER

FIG. 17