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A REPORT ON RADIATION DAMAGE IN BARIUM FLUORIDE TO THE GEM COLLABORATION

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Craig L. Woody
Brookhaven National Laboratory

Abstract:

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A Report on Radiation Damage in Barium Fluoride to the GEM Collaboration

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Brookhaven National Laboratory

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1. Introduction

This report attempts to summarize the current status of what is know about radiation damage in barium fluoride crystals and how it relates to a high resolution electromagnetic calorimeter at the SSC. Although a concientious effort has been made to go back through the literature and include earlier measurements, the data contained in this report are surely not all inclusive. Unfortunately, there has been little work done on trying to understand the implications of radiation damage in crystals on the performance of a high resolution detector subjected to long term exposures of radiation. However, this is an extremely important issue if one is contemplating a large scale detector for the SSC, where it is known that the radiation levels will be high, and stringent requirements will be placed on precision and stability over many years.

This report is meant to be an objective summary of what is known, and *not* know, about radiation damage in BaF_2. The first section gives a brief summary of the scintillation properties of BaF_2. The following two sections summarizes some of the existing data on radiation damage. The next section attempts to identify some of the possible causes of radiation damage, and the last section discusses some possible steps which could be taken to further study and improve the radiation hardness of BaF_2. A brief discussion is also given on the requirements on radiation resistance for an SSC calorimeter. It is hoped that the information contained within this report will help clarify some of these issues and help to make future decisions on a more informed basis.

2. Summary of scintillation properties

Barium fluoride was discovered to be a fast inorgainic scintillator in 1982-1983 [1-3], having an emission at 220 nm with a very short decay time ($\sim$ 0.6 ns), and a second emission with a much longer decay time ($\sim$ 600 ns) at 310 nm. It has since be reported that the so-called fast component actually consists of three emission bands, one at $\sim$ 220 nm, another at $\sim$ 195 nm, and possibly another weak band at $\sim$ 175 nm [4-6]. Usually, only the 195 nm and 220 nm bands are useful for scintillation detectors, since the 175 nm band is very weak and usually cut off by the entrance window of most photomultiplier tubes. However, BaF_2 itself transmits well into the vacuum ultraviolet, with a band edge cutoff $\sim$ 120 nm (10.5 eV) [7-8], and extends well into the infrared to $\sim$ 14μm. Indeed, most of the initial interest in BaF_2 was as window material for use in UV and infrared optics.

The mechanism for the production of scintillation light in BaF_2 is believed to be due to an interband transition call a crossover transition [9-11], illustrated in Figure 1. It is also thought to be responsible for the luminescence observed in other inorganic crystals which are currently being investigated [12-14]. An electron with a minimum excitation energy of 18 eV is promoted from the core band (Ba^{2+}5p) to the conduction band (Ba^{2+}6s,5d), leaving a hole in the core band. This hole is immediately filled by a transition from the valence band ($2F^{-}$2p) to the core band, giving rise to the fast component emission. A spin orbit splitting of the core band produces transition energies of 5.5 eV and 7.5 eV, which are close to the experimentally observed emssions at 220 nm and 175 nm. The difference in energy between the valence band and the core band is less than the difference between the conduction band and the valence band, which implies that the emitted photon cannot be internally reabsorbed by the Auger process, and hence can escape the crystal as scintillation light. The remaining electron in the conduction band forms a metastable electron-hole state called a self trapped exciton, which radiatively annihilates producing the slow component luminsescence. The slow component can also be independently stimulated with lower excitation energy, effectively by photon absorption, throughout the fundamental absorption region. The crossover transition mechanism is consistent with a short decay time for the allowed (F^{-}2p) to (Ba^{2+}5p) transition, and the lack of thermal quenching, both of which have been verified experimentally.

3. Early radiation damage measurements

Early studies on the radiation hardness of BaF_2 optical windows showed conflicting results. A measurement by Messner and Smakula [15] of samples irradiated by 3 MeV electrons to a dose of 2 x 10^4 rad showed that a significant absorption band was induced in the region around 200 nm, along with minor absorption at $\sim$ 250 nm. Another measurement by Heath and Sacher [16] showed no change in transmission below 250 nm, and very little change above 250 nm, for samples exposured to 1-2 MeV electrons for doses up to 2 x 10^6 rad. Tzalmona and Pershan [17] used thermoluminescence and EPR (Elecron Paramagnetic Resonance) to study radiation damage in rare earth doped BaF_2. They found the damage they observed to be associated with impurity ions and interstitial fluorine atoms, which are related to defects in the crystal lattice.

After the discovery of the fast scintillation in BaF_2, Majewski and Anderson [18] studied the radiation damage in several small pieces of BaF_2 in an 800 GeV/c proton beam at Fermilab. Three thin, disk shaped crystals (two 38 mm dia. x 4 mm thick and one 22 mm dia. x 6 mm thick) obtained from Harshaw [19] were irradiated up to a dose of 1.3 x 10^7 rad. The change in transmission and light output was measured for only one of the samples. The light output measurements were carried out 7-8 weeks after the irradiation, and the transmission measurements were done four months later. As shown in Figure 2, they found essentially no change in transmission in the region of 190 nm to 240 nm, and only a slight change ($\sim$ 0.5% loss) from 240 nm to 300 nm. They compared the scintillation light output from the irradiated and unirradiation portion of the sample and reported no effect with an error they claimed to be $\sim$ 1%. Since their measurements were done long after the radiation exposure, they were clearly not sensitive to any short term damage effects which could have been affected by the long recovery period.

Later, Caffrey et.al. [20] exposed two cylindrical samples of BaF_2, one 1" dia. x 1" long and another 1" dia. x 2" long, to 1-2 MeV beta and gamma radiation from activated fuel rods from a reactor at the Idaho National Engineering Laboratory. Both samples were again obtained from Harshaw. Dose rates varied from $10^4 - 10^6$ rad/hr. The 1" sample showed a more or less uniform loss in transmission in the range 200-340 nm of $\sim$ 5% at a dose of 10^6 rad, and $\sim$ 8% at a dose of 10^8 rad. The 2" sample showed $\sim$ 5% loss at 200 nm and 15% loss at 300 nm for a dose of 10^8 rad. Their transmission curves are

shown in Figure 3. Significant natural recovery in the transmission of both samples was observed over a period of a few days to several months. They also observed a degradation in the energy resolution for ^{137}Cs gamma rays in the 1" sample from 16% FWHM to 21% FWHM, with a recovery to 17.1% after 3 days.

Murashita et.al. [21] carried out a series of tests on several small (20 x 10-12 x 1 mm^3) samples obtained from OKEN [22] and NKK [23] using ^{60}Co gamma rays, 2 MeV electrons and 12 GeV protons at KEK. Their data is shown in Figure 4. The samples from NKK exhibited a strong absorption band at $\sim$ 205 nm before irradiation, now know to be due to contamination from Pb^{2+} [24], and showed significant loss in transmission even at low doses ($\sim 10^2 - 10^3$ rad). The samples damaged heavily for doses of 1.2 x 10^7 rad, and showed natural recovery over a period of 4-5 months. Rapid recovery was observed with exposure to UV light from a mercury lamp for 1-12 hours. The OKEN samples, which did not exhibit any preirradiation absorption due to lead contamination, showed very little induced absorption even up to very high doses. A uniform loss in transmission of $\sim$ 5% was observed from 200 nm to 700 nm for a dose of 8.8 x 10^7 rad of electrons, and $\sim$ 15% for a dose of 8.8 x 10^8 rad. Although these samples were very thin, making it difficult to separate surface and volume effects, the authors claim that the optical attenuation of the OKEN sample was shortened by 14% due to an irradiation of 1 x 10^7 rad. This paper reports one of the most radiation resistant measurements of BaF_2, and also one of the least, and dramatically demonstrates how large sample to sample variations can be.

In another series of measurements carried out by Majewski and Bentley [25], a 1" dia. x 0.5" long sample from Harshaw was irradiated to a total dose of 2 x 10^7 rad using ^{60}Co at a rate of 8.6 x 10^4 rad/hr. After an initial dose of 1.15 x 10^7 rad, a 10% change in transmission was observed at 220 nm and $\sim$ 5% change at 500 nm, as shown in Figure 5. It was shown, however, that all of the loss in transmission could be recovered by repolishing the crystal, indicating that most of the damage had occurred at the surface. In fact, the transmission improved above its preirradiation level after polishing, indicating that the surface quality of the sample had not been good to begin with. It was theorized that some interaction had occurred between the crystal and the surrounding material (in this case, styrofoam) due to the irradiation which was related to the slightly hygroscopic nature of BaF_2 [26]. Increasing the dose to 2 x 10^7 rad resulted in a further small decrease

in transmission at shorter wavelengths, which was again almost completely recovered by repolishing. This study concluded that the good radiation hardness of BaF_2 was confirmed, but warned against the possible importance of surface effects and treatment.

Finally, a study was made on the radiation damage in doped BaF_2 crystals, which also included measurements on pure BaF_2 [27]. The motivation for studying doped crystals was that an earlier investigation showed that adding a small amount of lanthanum to the pure crystal suppressed slow component scintillation light without reducing the fast component, thus enhancing its high rate capabilities. [28]. The samples used for the radiation damage measurements were quite small (10 x 10 x 2 mm^3), making it difficult to draw any conclusions about the attenuation lengths in larger samples. It was found that the pure BaF_2 sample showed no significant induced absorption in the region around 220 nm up to a dose of 10^6 rad, although some induced absorption was observed in the region $\sim$ 550 nm. The transmission spectra were measured *during* as well as after irradiation, as shown in Figure 6. The doped samples, to which 0.1-5.0 % of various rare earth elements were added, in general showed complex absorption sepctra throughout the visible and UV regions before irradiation, resulting in significant loss of the fast component scintillation light. Only two dopants, lanthanum and thulium, had no major absorption bands in the region of the fast component. Upon irradiation, the lanthanum doped samples showed no significant transmission loss up to 10^6 rad in the short wavelength region, but exhibited a strong absorption band $\sim$ 500 nm. The 500 nm absorption band decayed away quickly after a few hours, and was completely gone after about one week. The thulium doped samples damaged heavily in the short wavelength region, implying a severe loss in fast component light output. The transmission curves for the lanthanum and thulium doped samples are shown in Figure 7. The conclusion of this study was that lanthanum doping of BaF_2 up to the $\sim$ 1% level provided some slow component suppresion and did not adversely affect the radiation hardness of the pure material.

In general, these early studies concluded that BaF_2 is indeed rather radiation hard, certainly more so than any other inorganic scintillator known at the time. However, only a limited number of small samples were measured under a variety of conditions, and large sample to sample variations were observed The results ranged from very good radiation resistance to very poor. However, in many cases, only the change in optical transmission

was measured before and after irradiation, and no determination was made of the change in scintillation light output. Virtually all of the studies were carried out at dose rates which are much higher that would be expected at the SSC. No attempt was made in any of the studies to correlate the effects of radiation damage to the purity of the crystals or the conditions under which they were grown. In that sense, one could say that the true intrinsic radiation hardness of BaF_2 has not yet been measured, and only that the preliminary measurements look encouraging.

4. Recent radiation damage measurements

With the recent interest in BaF_2 for the SSC, a number of groups have begun to carry out more detailed studies of radiation damage in BaF_2 crystals. Measurements have been made by the CalTech, BNL and Carnegie Mellon groups within the GEM collaboration, as well as other groups in Japan and in the Soviet Union. Many of these results have been presented to the collaboration already and are given in various reports [29-31]. A breif summary of those results will be given here.

Measurements have been carried out at CalTech using ^{60}Co radiation up to 2 x 10^7 rad, and with neutrons at the UC Irvine reactor up to 10^{14} n/cm^2. Figure 8 shows the loss in transmission in two 1" dia. x 1" long samples after irradiation with gammas and neutrons, and the recovery induced by heating the crystals to 500^oC for 3 hours. Several effects are apparant from these data. First, saturation in the transmission loss occurs above 3 x 10^3 rad, with no further decrease in transmission up to 2 x 10^7 rad. This is an important observation, since it typical of the type of damage caused by impurities or defects, rather than intrinsic damage to the crystal lattice. This effect is discussed in section 5 below. Second, there is no observed difference between the damage caused by neutrons and that caused by gammas. This shows that the damage is independent of the type of radiation, implying that the amount of damage is determined only by the number of potential absorption centers within the crystal. Finally, the loss in transmission is recovered by heating, which indicates that the absorption is caused by charges held in shallow traps which can be thermally liberated.

Similar effects of saturation and annealing in the UV transmission have been observed by other groups. In a study described in [32] several 1" dia. x 1 " long samples were exposed to ^{60}Co up to 4.7 x 10^6 rad at a dose rate of 3.4 x 10^4 rad/hr. The different samples showed varying amounts of induced absorption, but all showed a similar saturation behavior. Figure 9 shows the change in transmission of three of the samples as a function of dose. The change in the region of the fast component was typically very small ($\sim$ few percent). The absorption at longer wavelengths increased up to 10^4 rad and then leveled off. In this study, the light output was also measured in the same samples and was found to decrease by $\sim$ 30% for a dose of 10^4 rad, and then also leveled off. Similar effects were seen for both the fast component and the total light output (fast plus slow), as shown in Figure 10. The saturation in transmission and light output occurred at the same dose, but the amount of light loss could not be explained by the small loss in transmission. This leads to the question of whether the scintillation light output (i.e., the *scintillation efficiency*) is also decreasing, or whether the apparant loss in light output can be explained by other effects such as multiple reflections or changes at the surface of the crystal. A change in scintillation efficiency would have to effect both the fast and slow components in a similar way in order to explain the data in Figure 10.

To study this, a measurement was made of the scintillation emission spectrum of another sample *during* irradiation, the results of which are shown in Figure 11a. In this sample, neither the shape nor the intensity of the emission spectrum changed during irradiation. However, the transmission spectrum did change, as shown in Figure 11b, and a 30% decrease in light output was observed. These apparantly conflicting results could be due to a dose rate effect caused by the large amount of ionization produced in the crystal during irradiation, giving a higher scintillation light yield during irradiation than after, or it could be due to increased effects of radiation damage at the surface causing changes in the light collection efficiency. The full explaination of these results clearly requires additional study.

A similar effect was seen by Muramaki et.al. [33], in which the change in attenuation length and scintillation light output was measured in several small samples (30 x 40 x 5 mm^3) supplied by OKEN. Measurements were made at several dose rates ranging from 6 x 10^4 rad/hr to 8 x 10^5 rad/hr. As shown in Figure 12, they observe a relatively small

change in transmission in their samples ($\sim$ 10% at 210 nm for a dose of 10^7 rad), but a disproportionately larger change in light output ($\sim$ 50%). A deterioration of $\sim$ 20% in the energy resolution, measured with ^{137}Cs gamma rays, was also observed after irradiation. Most of the loss in transmission and light output occured at $\lesssim 10^6$ rad, with little additional change between 10^6 and 10^7 rad. They use a Monte Carlo program to compute the amount of loss in light output expected from the increased absorption due to irradiation. They also concluded that the induced absorption alone is not enough to explain the decrease in light yield, and infer an additional loss in scintillation efficiency of $\sim$ 20%.

It should be noted that some recent measurements made by the group at Carnegie-Mellon [30] on the light output of BaF_2 after irradiation indicated that very little loss in light output ($\sim$ 3-6 %) occured for small samples (2 x 2 x 3 cm^3) which were given a dose of 1.3 x 10^5 rad of ^{60}Co radiation.

Recovery was also measured for several samples in ref. [32] which showed very little natural recovery in either transmision or light output with time, but essentially complete recovery in both with exposure to UV light. It was noted that the recovery with UV light could be halted and resumed without affecting the recovery process. Nearly complete recovery in transmission, light yield and energy resolution was also observed in ref. [33] after 22 hours exposure to sunlight.

In the study in ref. [32], two large, 25 cm long crystals were irradiated with ^{60}Co gamma rays and measurements made on their change in transmission and light output. One crystal was grown at the Beijing Glass Research Institute (BGRI) and was cut and polished at the Shanghai Institute if Ceramics (SIC). The other sample was produced by Merck at their Korth facility in Keil, Germany [34]. The results are shown in Figure 13. A significant change in transmission is observed after only 10^3 rad, and much larger amount after 10^4 rad. The structure of the absorption bands is quite different in the two samples, but the amount of induced absorption is approximately the same. This implies that the absorption may be caused by *different* impurities which are present at approximately the same level in the two samples. The light output decreased by $\sim$ 30-40% in both samples after 10^3 rad and showed a nonuniformity in light loss across the length of the crystal. This again indicates the presence of impurities which would tend to collect at one end of the ingot during growth, as discussed in section 5 below.

Measurements by He et.al at IHEP Beijing also showed saturation and recovery in crystals grown at BGIR. In addition, it was shown that crystals could be "cycled", in which samples were exposured to 10^6 rad of gamma radiation, reaching a saturation level in their loss in transmission, and were then recovered by exposure to sunlight. A subsequent exposure to radiation produced the same saturation level, followed by a second recovery. Three such cycles were carried out without permanent damage to the crystal.

In a study carried out at CERN [35] a 2 x 2 x 5 cm^3 sample of BaF_2 was irradiated with ^{60}Co gamma rays to a dose of 5 x 10^7 rad. Only a small, almost uniform change in transmission was observed in the wavelength range from 200-350 nm, and no effect was seen on the scintillation. The transmismission spectrum is shown in Figure 14. The sample was then further irradiated to 1.7 x 10^8 rad by placing the sample close to the primary proton beam at the CERN SPS. After this dose, the crystal became blue and lost half of its transmission below 230 nm.

Studies have also been made on radiation effects in BaF_2 crystals grown in the Soviet Union [36]. Samples $\sim$ 5 cm long produced near Leningrad [37] were irradiated with ^{60}Co at a rate of 7.8 x 10^4 rad/hr. The possiblty of surface deterioration was noted as in [25], and the samples were irradiated in sealed, glass containers to exclude the influence of moisture during irradiation. Nevertheless, the optical attenuation length at 220 nm decreased from 86 cm to $\sim$ 32 cm after a dose of 10^6 rad, as shown in Figure 15. This loss was attributed mainly to impurities in the samples. Almost full recovery in the transmission was observed after exposure to UV light from $\sim$ 10 minutes to several hours, depending on the intensity of the light source.

In the study carried out in [32], a strong phosphorescense, or afterglow, was observed in all of the irradiated samples. This phosphorescense has been observed in other samples, but appears to a vary significantly from crystal to crystal [38]. Phosphorescense is not an uncommon phenomenon in scintillating crystals and has been observed in several other materials [39]. The phosphorescense in BaF_2 can characterized by one component with a very short decay time ($\sim$ 10 seconds), and a second component with a much longer decay time which can persist for weeks or even months. Decay curves for the phosphorescense measured after several doses of ^{60}Co radiation, are shown in Figure 16. The emission spectrum, given in Figure 17, shows that the phosphorescense occurs at nearly the same

wavelength ($\sim$ 330 nm) as the slow component scintillation emission. This is fortuitous, since it should therefore be essentially undetectable by the solar blind readout envisioned for the BaF_2 calorimeter unless the intensity is extremely high. It does, however, cause a severe background problem with a non-solar blind readout. Another interesting property of the phosphorescense is its reactivation by exposure to roomlight. Figure 18 shows the phosphorescense activation and decay measured in a sample which was given two short exposures to roomlight. The activity is seen to die away after the first exposure and then reappear with greater intensity after the second, longer exposure. However, after a sufficiently long exposure to sunlight, the phosphorescence dies away completely.

It was noted in ref. [32] that the amount of phosphorescence activity seemed to saturate at about the same dose level at which saturation was observed in the induced absorption and loss in light output. Also, the recovery in transmission and light output, and the cessation of the phosphorescence with UV light, tend to imply that all three radiation induced effects are related. In particular, the phosphorescence is typical of what is observed in other materials where charges, which are liberated during irradiation, become trapped on sites within the crystal, perhaps impurities or defects, and require a minimum energy of a few eV to be released. Once released, either by raising the temperature or supplying external light, the charges are free to recombine on luminescent centers, giving rise to the phosphorescence. Once all of the trapped charges have been released, no further phosphorescence occurs. This results again supports the notion that the radiation effects are related to either impurities or defects, and are not necessarily related to the intrinsic radiation hardness of the pure crystal.

5. Potential causes of radiation damage

The identification of specific causes of radiation damage in any material is an extremely difficult problem. This because radiation damage is an inherently complex process and is often dependent on a number of different factors. It is important, however, to distinguish between radiation damage which is intrinsic to the material of interest, and damage caused by various type of inhomogenities, such as impurities or defects. This is critical because, if the observed radiation damage is due to inhomogenities, then various steps can be taken

to improve the radiation hardness to the intrinsic level of the host material. However, it is also sometimes possible to improve the intrinsic radiation hardness by introducing inhomogenities into the host, as was done in the case of BGO [40]. In either case, it is a complicated process to idenitfy and understand the effects of inhomogenities in the host, which requires careful study.

In the case of BaF_2, there are several indications that the radiation damage observed so far is due to either impurities or defects. One is the saturation effect observed in both the loss in transmission and light output with increasing dose. Saturation would be expected to occur if there are a finite number of either impurities or defects which act as sites for color center formation. Once these traps are filled with charges liberated by the radiation, no further damage occurs. These color centers also exhibit well defined absorption bands, which are characteristic of particular impurities in the crystal. A specific case of this is the 205 nm absorption band due to Pb^{2+} which has been correlated with poor radiation hardness.

The recovery observed in the transmission, light output, and the elimination of the phosphorescence by heating or exposure to UV light, also supports the supposition that the damage is caused by inhomogenities. Charges produced during irradiation are caught in traps at impurity or defect sites and are released by supplying external energy. Since recovery occurs at fairly low temperatures and with UV light, these traps must be rather shallow ($\lesssim$ few eV). The fact that nearly full recovery occurs, and that the damage can be cycled over several exposures, shows that no permanent damage is produced in the lattice, and that the intrinsic radition hardness of the pure material may be quite good.

It is nevertheless difficult to identify *what* impurities are responsible for the observed damage, or whether the damage is related to defects in the lattice. It is likely that the damage could be caused by more than one impurity, and that much of the sample to sample variation observed in previous measurements is related to different amounts of impurities in different samples. Although it is unknown at this time exactly what impurities are likely to cause radiation damage, and at what levels they can be tolerated in the final crystal, work has already begun on indentifying the possible causes of damage due to impurities which could be introduced from the raw material, or during growth. This effort is being carried out by SIC and BGRI, and by Merck at their facilities at Korth in Germany and

Optovac [41] in the U.S.. Some recent progress in trying to understand the causes of radiation damage in BaF_2 was reported by SIC, BGRI and several Chinese university groups at the Precision Electromagnetic Calorimeter Workshop held in Shanghai, China in May and June of this year. Their results are given in several contributions to that conference [42-44] and are also summarized in ref. [30].

In one of these studies, samples were taken at various places from a 30 cm ingot grown at SIC. It was found that the amount of damage increased for samples taken near the top of the ingot, as shown in Figure 19. This result is consistent with the non-uniformity in the amount of damage from one end of the crystal to the other shown in Figure 13. The reason for this non-uniformity can be understood from the method of growth. The crystals were grown by the Bridgman-Stockbarger method in which the raw, purified powder is placed in a crucible (usually graphite), which is then placed inside an vacuum oven, as illustrated in Figure 20.. The oven has a temperature gradient which varies from above the melting point (1280^oC) at the top to below the melting point at the bottom. The crucible is lowered through the temperature gradient at a prescribed rate, which causes the crystal to solidify starting at the bottom of the crucible. Impurities are forced to the top of the melt by zone refining and collect at the solid-liquid interface. These impurities also diffuse as the crystal grows, creating a band of imputities at the top of the ingot. In order to obtain long finished crystals, it is necesary to retain part of the crystal which may contain these impurities. Also, because BaF_2 is slightly hygroscopic, a large amount of moisture is adsorbed onto the surface of the raw powder, and so-called scavanger is added to remove the oxygen from the melt. In the case of BaF_2, the scavanger is usually PbF_2. The PbF_2 reacts with oxygen to form PbO, which has a low vapor and is pumped away during growth. However, if too much PbF_2 is added, or if the crystal is cooled too quickly, either lead or oxygen can be trapped at the bottom of the ingot.

It is likely that only *certain* impurities are critical in causing radiation damage, and others could be quite innocuous. Certain elements are chemically very similar to either barium or fluorine and can be present in the crystal in fairly large amounts. Trace analyses have been done on BaF_2 raw material at both BGRI and at Merck and have shown very different levels for different impurities. An example of such an analysis done on Merck Optipur BaF_2 material is shown in Table I. Many cationic impurities, which are relatively

easy to detect and eliminate, are present at the less than 1 ppm level, while others, such as strontium and calcium, which are chemically similar to barium, are present at a much higher level. Rare earth elements can usually be identified in the finished crystal by their characteristic absorption spectra. Spectra on some of the rare earth elements in a BaF_2 host are given in ref. [27]. An absorption peak at $\sim$ 290 nm, which is often observed as a few percent dip in transmission in crystals grown at SIC and BGRI, is probably due to cerium contamination at the level of a few ppm. Cerium is a rare earth impurity of considerable interest, since it has long been known that it can change the luminescence properties of BaF_2 [45-46], and can also improve the radiation hardness of some materials, such as glasses [47]. The effect of cerium in BaF_2 was discussed detail at the Shanghai Workshop and it was concluded that cerium doping did not improve the radiation hardness of BaF_2. As mentioned above, the effect of other rare earths were also studied in ref. [27], and it was shown that lanthanum did not seriously affect the transmission of BaF_2 in the region of the scintillation emissions after irradiation, although a pronounced absorption band was produced in the visible. Thulium, however, did produce strong absorption in the UV region. SIC also showed that europium did not improve the radiation hardness of BaF_2, incontrast to its effect on BGO, nor did doping with iron or cobalt.

As indicated in Table I, some impurities, such as oxygen, nitrogen and carbon are not tested for. Oxygen is especially difficult to detect in fluoride crystals due to its chemical similarity to fluorine. It is clear, however, that oxygen could easily be present in significant quantities in crystals grown by the Bridgman-Stockbarger method for the reasons given above. SIC has correlated the absorption in the 190-250 nm region with the level of oxygen content in unirradiated crystals. An indication of this is given in Figure 21 from ref. [42], showing the absorption spectra for two BaF_2 samples, one deliberately produced with a high oxygen content and the other without. It is believed that this absorption is caused by lone O^{2-} ions or $O^{2-} - O^{2-}$ pairs. Measurements of the transmission of crystals in the infrared show no evidence of the very sharp absorption peak at 3630 cm^{-1} which is characteristic of OH^-. Diffraction studies with an electron beam also verifed the presence of dissolved oxygen. Figure 22 shows a diffraction pattern taken just after starting an electron irradiation which exhibits a very symmetric pattern, indicating a low density of dislocations. After a few minutes of irradaition, diffraction rings appear which have been

identified as BaO. It is presumed that this is the result of oxygen atoms or molecules being transformed into oxygen ions during irradiation which then displace a fluorine atom at a lattice site. In addition to forming BaO, oxygen can also form $O^{2-} - F^{+}$ dipoles. During irradiation, these dipoles can decompose, increasing the concentration of O^{2-} ions, thus increasing the absorption in the 190-250 nm region, as well as providing free F^{+} ions which can trap electrons to form F-centers. Exposure to UV light after irradiation can free electrons from their F-center traps, allowing the fluorine ions to recombine with the O^{2-} ions, reforming the dipoles and producing reovery.

Although much attention has been given to the presence of impurities, similar effects of color center formation can be caused by defects. Defects can be produced during the the growth and annealing process if the conditions for single crystal formation are not achieved, which is usually the case. Flourine atoms at interstital lattice sites could be a common result of defect formation. Internal stress is built up inside the crystal as it grows due to its high coefficient of thermal expansion, poor thermal conductivity and the large thermal gradient inside the oven. Crystals are cooled slowly during the annealing stage to relieve this stress, but the relaxation can be incomplete depending on the details of how slowly and at what temperature the crystal is annealed. An indication of residual strain can be seen by observing the strain birefringence produced when samples are illuminated with polarized light. A clear indication of such strain has been observed in many samples. Other types of defects can appear as small bubbles, scattering centers or polycrystalline regions which give rise to further inhomogenities. It is not clear how much these types of imperfections contribute to a crystals suseptibility to radiation, but it should certainly be considered as a possible source of damage.

Finally, great deal of work has also been done on the study on radiaton damage in other fluoride crystals, mainly in connection with their use for excimer lasers. This work has focused mainly on MgF_2 and CaF_2, but also includes BaF_2 and SrF_2. It was found in the case of CaF_2 that oxygen and hydroxyl ions produce absorption in the $\sim$ 200 nm wavelength region, similarily as in BaF_2, and resulted in increased sensitivity to radiation damage [48]. The presence of yttrium was also associated with a decrease the radiation hardness of CaF_2 [49]. Crystals doped with sodium (NaF) showed a similar effect to yttrium doped samples [50], where it is believed that oxygen contamination was enhanced

by the addition of the dopant. Additional information on color center formation and radiation effects in these materials can be found in refs. [51-54]. There has also been a great deal of interest in CeF_3 as a fast scintillator for high energy physics applications [55-56]. This material is currently being devloped by Optovac in collaboration with the Crystal Clear Collaboration at CERN [57]. Initial results on the radiation resistance of CeF_3 look quite promising, with little change in transmission observed in small samples up to doses of 10^7 rad. Finally, Optovac has also been developing PbF_2, a high density Cherenkov material, for electromagnetic calorimeter applications. In the process of producing high purity crystals up to 20 radiation lengths long, the radiation resistance of PbF_2 was greatly improved [58]. It is expected that a similar result could be achieved with BaF_2.

6. Improving radiation resistance

From the discussion given above, it is clear that a number of radiation effects are seen in BaF_2 crystals which could affect the performance of a high resolution electromagnetic calorimeter at the SSC. It is therefore important to define what these effects are, and what steps can be taken to either reduce or eliminate them. This will require a thorough, *systematic* study of the effects of damage, and close coordination of the results with the manufacturers of the crystals who are striving to improve them. It is also important to specify what the expected radiation levels will be for the calorimeter at the SSC, and what requirements will be placed on it in terms of stability. These parameters have not yet been completely specified, but a brief discussion of some of these items are given below.

Based on the present information, it would appear that in general, reducing the number of impurities would reduce the number of possible sources of damage. It should be noted that no special effort has yet been made to specifically reduce the level of impurities in BaF_2 in order to improve its radiation hardness. The higher levels of purity which have been achieved have been mainly to increase the UV transmisison and light yield of larger crystals. In principle, it is possible to reduce a wide variety of impurities by extensive purification of the raw material. Although this may be possible in principle, it may be difficult or expensive to do in practice when a large number of crystals are required. Another process, which has been used successfully by Optovac to improve the purity and radiation hardness

of PbF_2, is sublimination of the raw material before growth. This technique could be more easily adapted to large scale production. However, identifying which impurities are critical in producing radiation damage would be a major advantage. A variety of chemical analyses can be performed on the material at various stages of processing, starting with the raw material, up through the finished product, which could shed light on which impurities are present and how they enter the final crystal. Much of the current work has focused on measurements of the UV transmission in the range from 200-800 nm. Although this is a convienent range for many types of spectrophotometers, measuring the transmission outside this range, such as in the VUV or infrared region, should not be overlooked in searching for absorption bands due to impurities. However, many more sophistocated techniques of chemical analysis can also be used. Some of these include ICP (Inductively Coupled Plasma Atomic Emission Spectroscopy), RNAA (Radiochemical Neutron Activation Analysis), SIMS (Secondary Emission Spectroscopy), GDMS (Glow Discharge Mass Spectroscopy), ESR (Electron Spin Resonance Spectroscopy) and SIRIS (Sputter Initiated Resonance Ionization Spectroscopy).

Additional improvements in crystal purity could be made through changes in the growth conditions. This may involve changes in the operating conditions of the furnaces, such as temperature and pressure, as well as changes in the types of materials used crucibles, heaters, etc. Techniques also exist for processing the raw material with a reactive gas, such as HF, which can interact with impurities and be later carried away. The use of different scavanger agents, other than PbF_2, and improved tehniques for removing oxygen, can also be explored.

The process of annealing should also be carefully studied and related to the number of defects in the crystal. Given that many samples tested so far have exhibited considerable residual stress, an attempt should be made to produce samples with reduced stress and study its effect on radiation hardness. This could be done by making relatively simple changes in the parameters currently being used for annealing. The number of defects in the samples could be infered from analysis of the strain birefringence, or related to inhomogenities in the refractive index, which could be determined by interferometry.

The radiation levels expected at the SSC have been described in detail in several reports [59-60]. There it is stated that the maximum source of radiation damage in an

electromagnetic calorimeter will be due to the flux of incident photons, arising mainly from π^o decays, and will occur at a point inside the calorimeter where the electromagnetic shower reaches its maximum intensity ($\sim$ 5 radiation lengths). The photon dose at shower maximum, taken from [59], is given in Figure 23. This vertical axis in this figure has been corrected *downward* by a factor of 1/3, as was given in a later erratum. The dose can be parameterized as:

$$D = \frac{A}{R^2 sin^{2+\alpha}\theta}$$

where R is the distance from intersection point in meters, θ is the polar angle measured from the axis of the crossing beams, $\alpha = 0.93$ for photons, and A = 1.24 x 10^4 rad/year. At a given distance, the dose is minimum at $\theta = 90^o$ and increases rapidly at smaller angles. The proposed coverage of the BaF_2 calorimeter is $|\eta| \leq 1.32$ at a distance of 75 cm for the barrel, and $1.32 \leq \eta \leq 2.5$ at a distance of $\pm$ 164 cm for the two endcaps. This implies a dose ranging from 2.2 x 10^4 rad/year to 2.8 x 10^4 rad/year for the barrel, and from 2.8 x 10^4 to 1.0 x 10^6 for the endcaps. While it is obvious that the highest dose will occur in the forward region of the endcaps, the dose received by the main portion of the calorimeter will be significantly less. This also raises an important issue of *dose rate*. The rate of dose at the SSC is significantly lower than the rate at which virtually all radiation damage measurements so far have been carried out. This could be an important point, since the processes which cause radiation damage and those which result in recovery are driven by the kinetics of these reactions and are constantly tending towards equilibrium. When the relative rates of these processes are very different, as in the case of high dose rates, this equilbium may not be reached. This could lead to very different results when the measurements are performed at lower dose rates. It is, therefore, important to determine the effects of radiation damage at the dose rates which will actually be present at the SSC.

Another important question is what level of dose can be tolerated with an acceptable change in response of the calorimeter. The answer is intimately connected with the question of calibration. A scheme for precise calibration of individual elements of the detector will have to be an integral part of the calorimeter system. This will anyway be required in order to achieve the desired resolution of $2\%/\sqrt{E} \oplus 0.5\%$ and maintain this level of precision throughout the experiment. Due to the high initial light output of BaF_2 when coupled to

a solar blind photocathode ($\gtrsim$ 50 photoelectrons per MeV), the photostatistics term in the energy resolution is quite small ($\sim 0.4\%/\sqrt{E}$). Consequently, a substantial decrease light yield can be tolerated without seriously affecting the statistical term in the resolution. However, it nonuniformities in the changes in the light output could affect the overall constant term, and the effect of this would have to be carefully monitored. It is important, however, to bear in mind that the detector need not remain absolutely stable over time, but only that the changes remain within acceptable limits and can be corrected for. Finally, the effect of saturation and the lack of natural recovery are advantageous, since, in the absence of totally radiation resistant crystals, one could contemplate preirradiation of the crystal volume and operating the detector around this more stable operating point.

7. Conclusions

In conclusion, it is apparant that much *is* known about the radiation effects in BaF_2, although many uncertainties still remain. The earlier measurements showed that, on the basis of a few small samples, BaF_2 did not exhibit any serious damage up to rather high levels of radiation dose. Unfortuantely, these measurements were not conclusive, since many of them were carried out under widely different, and often uncontrolled, conditions. Large sample to sample variations were observed, and many studies measured only the change in transmission and not the change in scintillation light output. More recent studies have concentrated on measuring parameters, such as light output, which are of more interest for calorimeter applications. Additional effects, such as the radiation induced phosphorescence, have only recently been observed. The study of radiation damage in large crystals has only just begun, and it appears that the effects in large crystals are worse than would be infered from the best results with smaller samples.

The evidence presented here indicates that the radiation effects observed so far are most likely caused by either impurities or defects, and that the intrinsic radiation hardness of pure BaF_2 may be quite good. The role of impurities and defects on the radiation damage is slowly beginning to emerge. Some impurities, such as rare earths and certain cationic impurities, have already been identified as potential causes of increased radiation suseptibility. It is known what steps could be taken to reduce the level of these types of

impurities. Other contaminants, such as oxygen, are more difficult to detect and eliminate. A better understanding is required to determine what level of oxygen contamination can be tolerated while maintaining good radiation hardness in the final crystals. It is also known that defects are present in many of the samples tested, and it may be impossible to eliminate the presence of defects completely. Again, it is therefore important to not only strive to reduce the number of defects, but also determine what level of defects is acceptable.

Although a considerable amount of work has already been done, it is clear that much more effort is required to fully understand the effects of radiation damage in BaF_2 if one is to consider its large scale use for calorimetry at the SSC. The requirements for a high precision electromagnetic calorimeter demand high stability in a strong radiation field over many years of operation. The question of changes with radiation dose are intimately related to those of calibration and monitoring. This will require a careful study of all radiation effects in crystals of the type which will be used in the actual calorimeter, and a coordiation of these results with the requirements of the final detector.

8. Acknowledgement

I would like to thank Rob Sparrow from Optovac, Inc. for many useful and informative discussions on the subjects of crystal growth and radiation damage in fluoride crystals which contributed greatly to the information contained in this report.

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Table I Trace element analysis of Merck Optipur BaF_2 raw material. Conversion to ppm by weight is given by $\mathbf{ppm}_{weight} = \mathbf{ppm}_{atomic}$ x A x N / M, where A = atomic number of impurity, N = number of atoms in the host (3 for BaF_2), and M = Molecular weight of the matrix (175 for BaF_2).

BaF_2	MW	175.34
	SG	4.89
	Mp	1368°C
	Bp	2272°C

Melt grown; crystal fragments.

Mass-Spectrographic Analysis

Uranium	U	< .01
Thorium	Th	< .01
Bismuth	Bi	< .01
Lead	Pb	< .02
Thallium	Tl	< .01
Mercury	Hg	< .03
Gold	Au	< .03
Platinum	Pt	< .03
Iridium	Ir	< .02
Osmium	Os	< .02
Rhenium	Re	< .02
Tungsten	W	< .1
Tantalum	Ta	< .1
Hafnium	Hf	< .1
Lutetium	Lu	< .1
Ytterbium	Yb	< .4
Thulium	Tm	< .01
Erbium	Er	< .03
Holmium	Ho	< .01
Dysprosium	Dy	< .4
Terbium	Tb	< .1
Gadolinium	Gd	-
Europium	Eu	< .6
Samarium	Sm	< .04
Neodymium	Nd	< .04
Praseodymium	Pr	< .1
Cerium	Ce	< .1
Lanthanum	La	< 1
Barium	Ba	Base
Caesium	Cs	< .01
Iodine	I	< .01
Tellurium	Te	< .3
Antimony	Sb	< .06
Tin	Sn	< .1
Indium	In	< .01
Cadmium	Cd	< .03
Silver	Ag	< .02
Palladium	Pd	< .05
Rhodium	Rh	< .01
Ruthenium	Ru	< .02
Molybdenum	Mo	< .03
Niobium	Nb	< .01
Zirconium	Zr	3
Yttrium	Y	< .1
Strontium	Sr	30
Rubidium	Rb	< .01
Bromine	Br	0.6
Selenium	Se	< .02
Arsenic	As	.3
Germanium	Ge	< .03
Gallium	Ga	< .03
Zinc	Zn	.02
Copper	Cu	.01
Nickel	Ni	< .03
Cobalt	Co	< .1
Iron	Fe	.3
Manganese	Mn	< 0.01
Chromium	Cr	< .01
Vanadium	V	< .01
Titanium	Ti	< .01
Scandium	Sc	< 1
Calcium	Ca	10
Potassium	K	.3
Chlorine	Cl	3
Sulphur	S	3
Phosphorus	P	1
Silicon	Si	3
Aluminium	Al	1
Magnesium	Mg	< .01
Sodium	Na	< .01
Fluorine	F	Base
Oxygen	O	-
Nitrogen	N	-
Carbon	C	-
Boron	B	.03
Beryllium	Be	< .01
Lithium	Li	< .01

Harmful

All figures are quoted in ppm atomic

Harmful by inhalation and if swallowed.
Avoid contact with skin and eyes.

The sale of materials described in this data sheet will be covered by the General Conditions of Sale of BDH Limited, a copy of which is available on request.

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June 1989

Cross luminescence :
- Most of the alkali-earth halide binary compounds
- Fast UV
- Temperature independant
- Optical structure not much modified *by addition of a third heavy component*

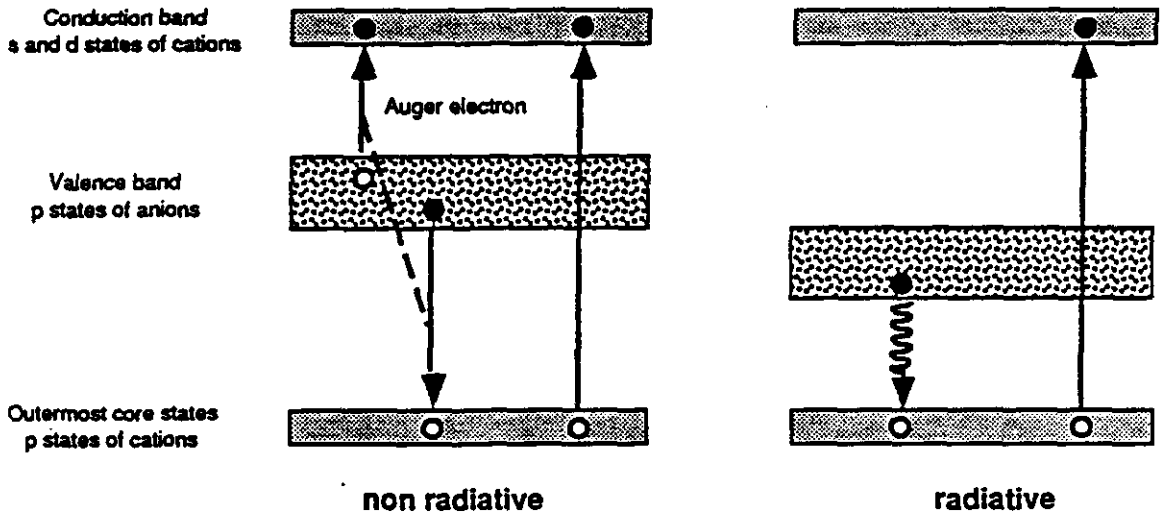


Fig.1a The cross luminescent mechanism responsible for emission of the fast UV light in BaF_2 . The radiative transition (right) competes with a non-radiative transition resulting in Auger emission (left). (from ref.[30])

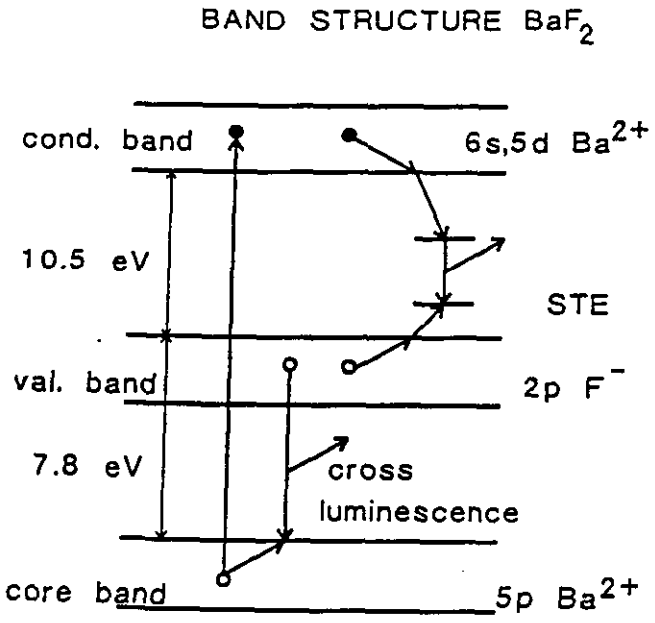


Fig.1b The band structure of BaF_2 and the scintillation mechanisms. (from ref.[12])

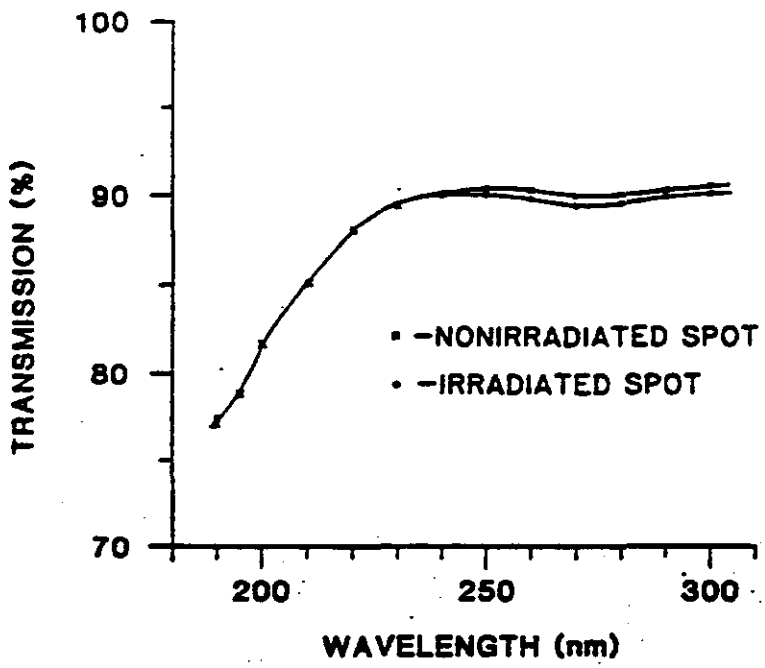


Fig.2 Transmission curves measured in the center of the irradiated spot and in the nonirradiated region of the crystal #3.

(from ref.[18])

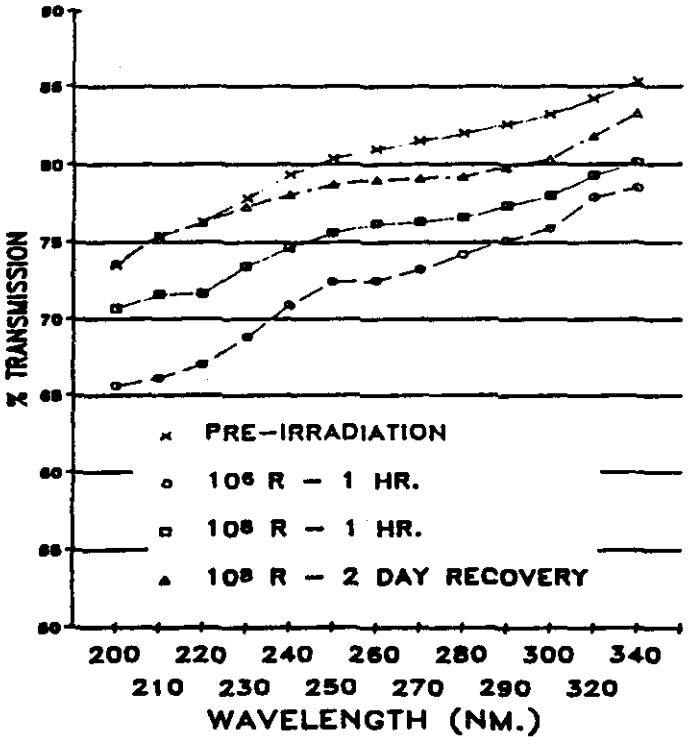


Fig.3a Plot of optical transmission for 1" x 1" BaF_2 crystal for total integrated dose up to 8 x 10^7 R and recovery after 2 days.

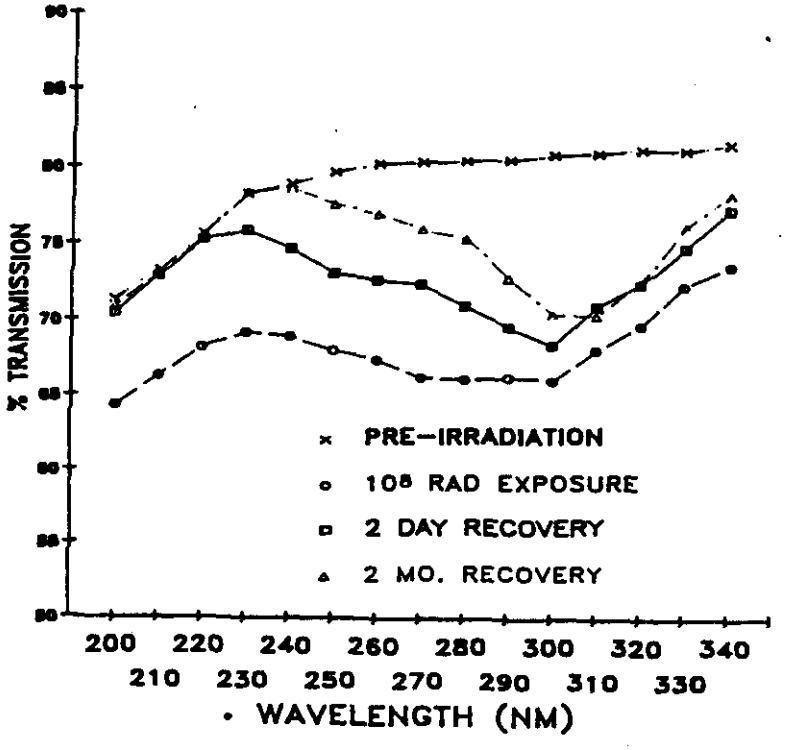
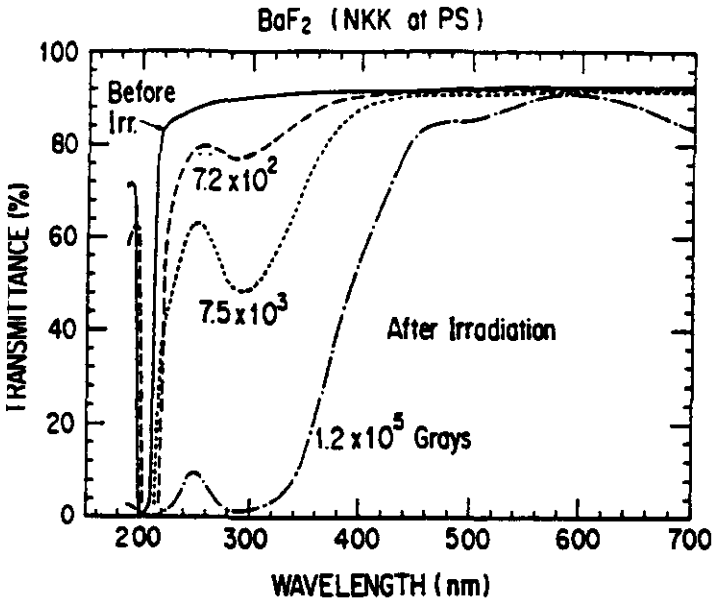
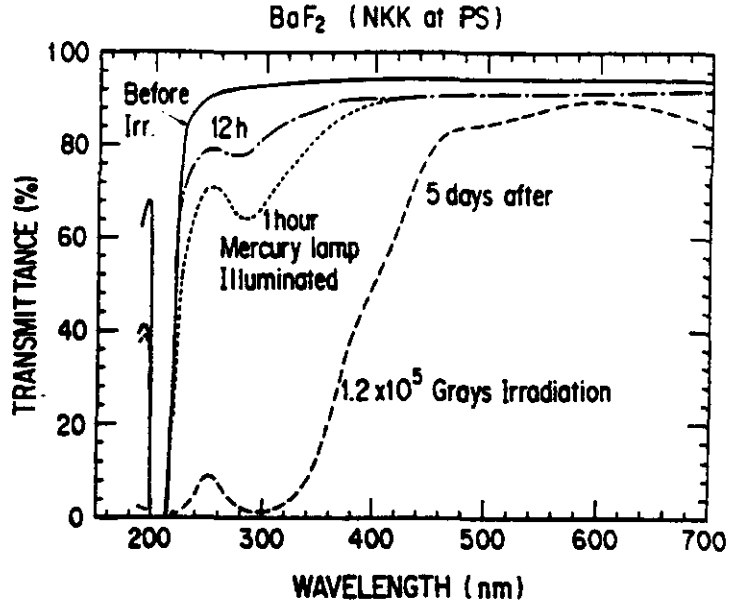


Fig.3b Optical transmission for 2" BaF_2. Data are shown before irradiation, after 8 x 10^7 R, and recovery up to 2 months. Long term damage is seen in the 300 nm, region.

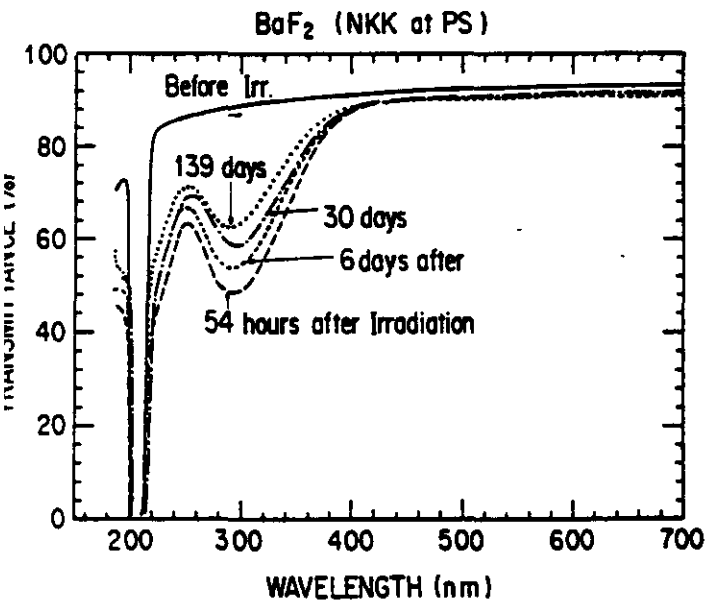
(from ref.[20])



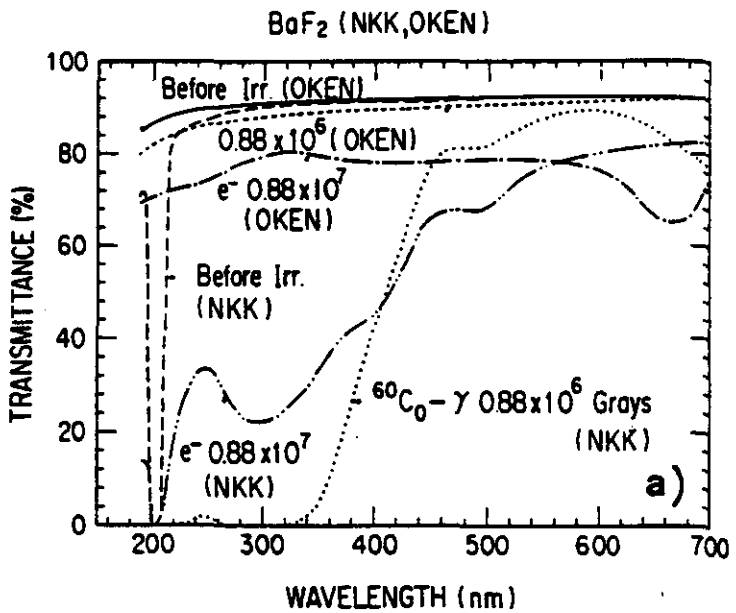
a) Percent transmittance of BaF_2 (NKK) as a function of the wavelength with the radiation near the 12 GeV proton beam line. The lines are solid (before irradiation), dashed (7.2×10^2 Gy), dotted (7.5×10^3 Gy) and dash-dotted (1.2×10^5 Gy).



c) Recoveries of the transmittance in BaF_2 (NKK) with illumination of the mercury lamp after irradiation by 1.2×10^5 Gy. The lines are solid (before irradiation), dash-dotted (after illumination of 12 h), dotted (after illumination of 1 h) and dashed (before illumination.)



b) Recoveries of the transmittance of BaF_2 (NKK) with ıpses of time after irradiation by 7.5×10^3 Gy. The lines are olid (before irradiation), fine dots (139 d after irradiation), lash-dotted (30 d after), dotted (6 d after) and dashed (54 h fter).



d) Percent transmittance of BaF_2 for the electron bean and the gamma rays. The crystals of NKK are shown b dashed (before irradiation), fine-dotted (gamma rays of 0.88×10^6 Gy) and dash-double-dotted (electrons of 0.88×10^7 Gy lines. The crystals of OKEN are shown by solid (before irradia tion), dotted (electrons of 0.88×10^6 Gy) and dash-dotte (electrons of 0.88×10^7 Gy) lines.

Fig.4 Transmission and recovery data from ref.[21].

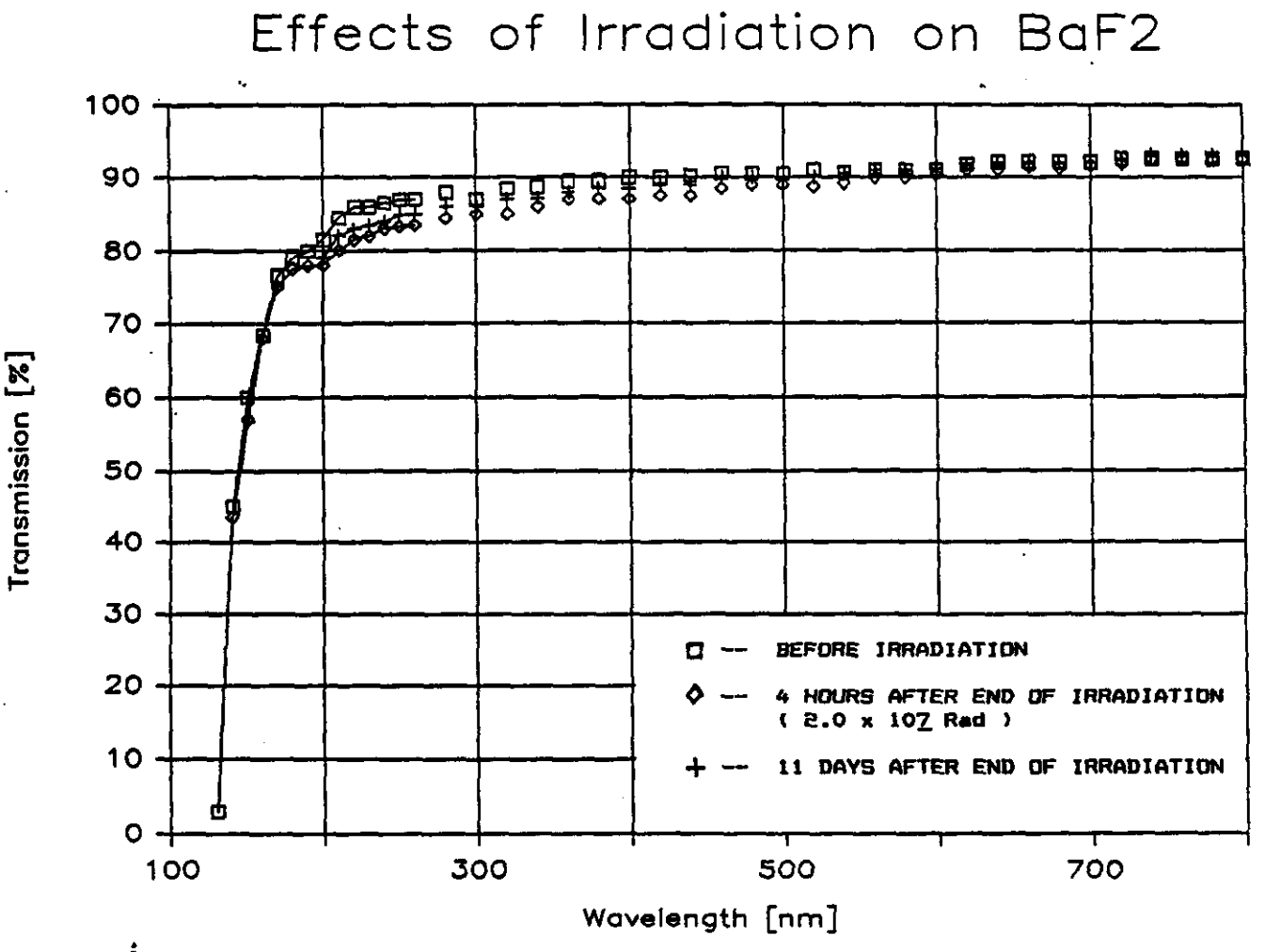


Fig.5 Transmission and recovery data for irradiated 1" dia. x 0.5" long BaF_2 crystal from ref.[25].

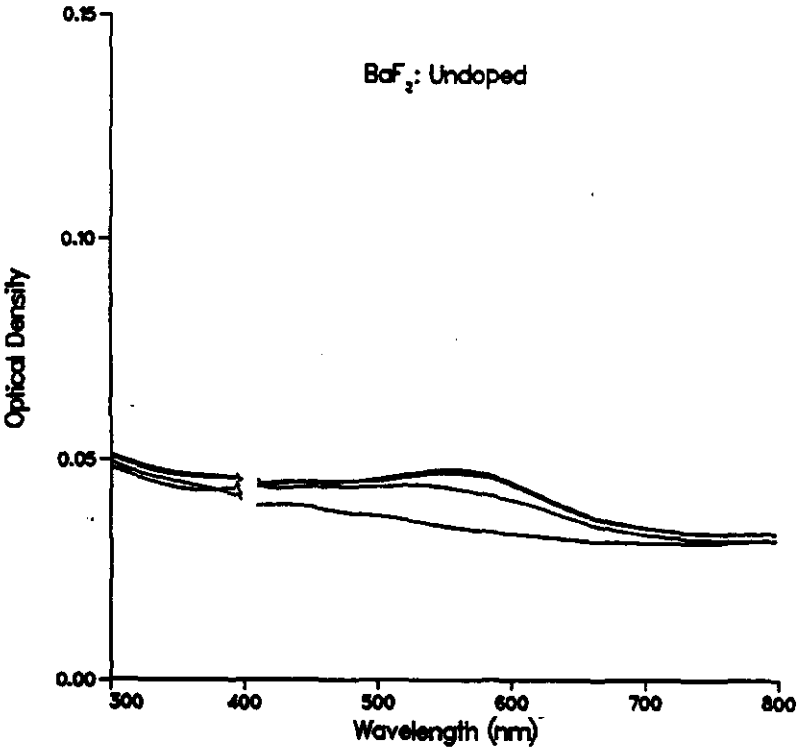


Fig.6a Transmission spectra for pure BaF_2 measured during irradiation for accumulated doses of 0, 5x10^4, 10^5 and 10^6 rad.

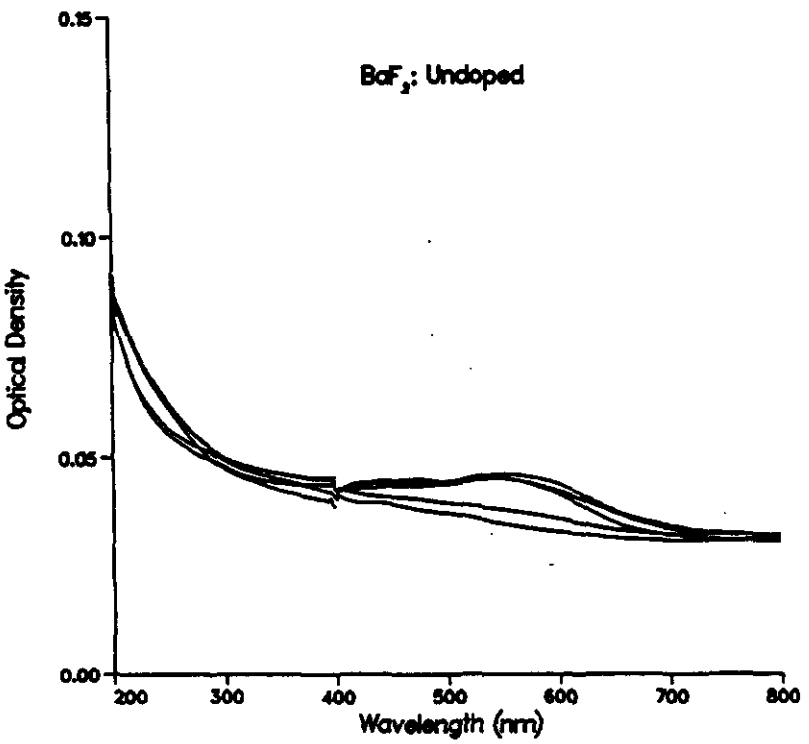


Fig.6b Transmission spectra for pure BaF_2 measured shortly after irradiation for accumulated doses of 0, 10^3, 10^4, 10^5 and 10^6 rad.

(from ref.[27])

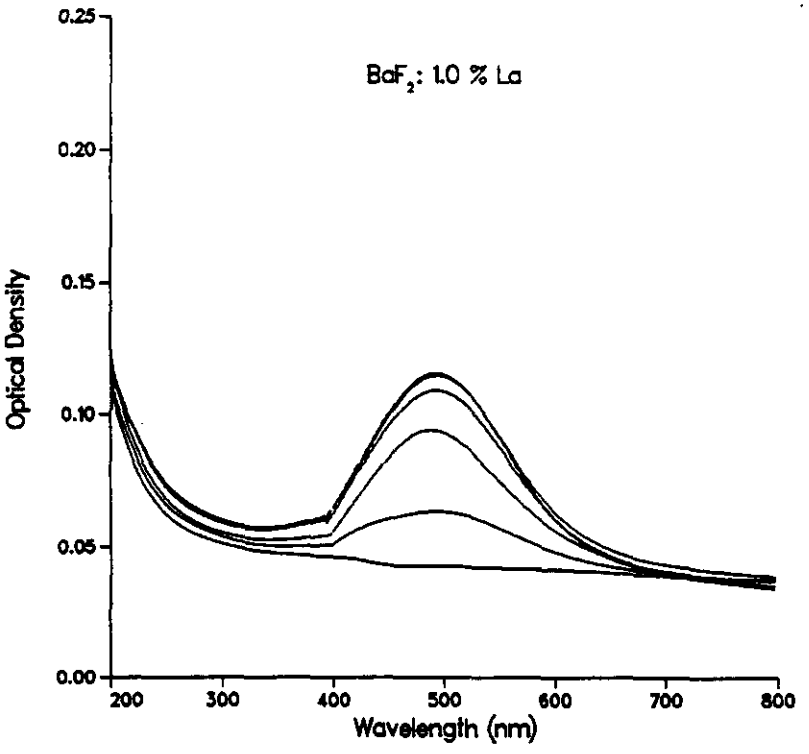


Fig.7a **Transmission spectra for 1% La sample measured shortly after irradiation for accumulated doses of 0, 10^3, $5x10^3$, $2x10^4$, 10^5 and 10^6 rad.**

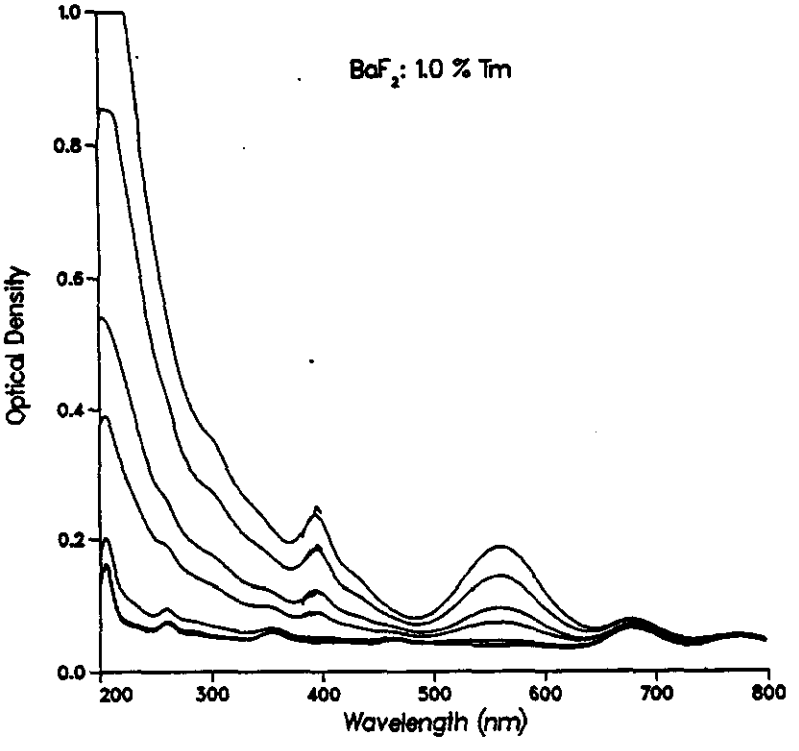


Fig.7b **Transmission spectra for 1% Tm sample measured shortly after irradiation for accumulated doses of 0, 10^3, 10^4, 10^5, $2x10^5$, $5x10^5$ and 10^6 rad.**

(from ref.[27])

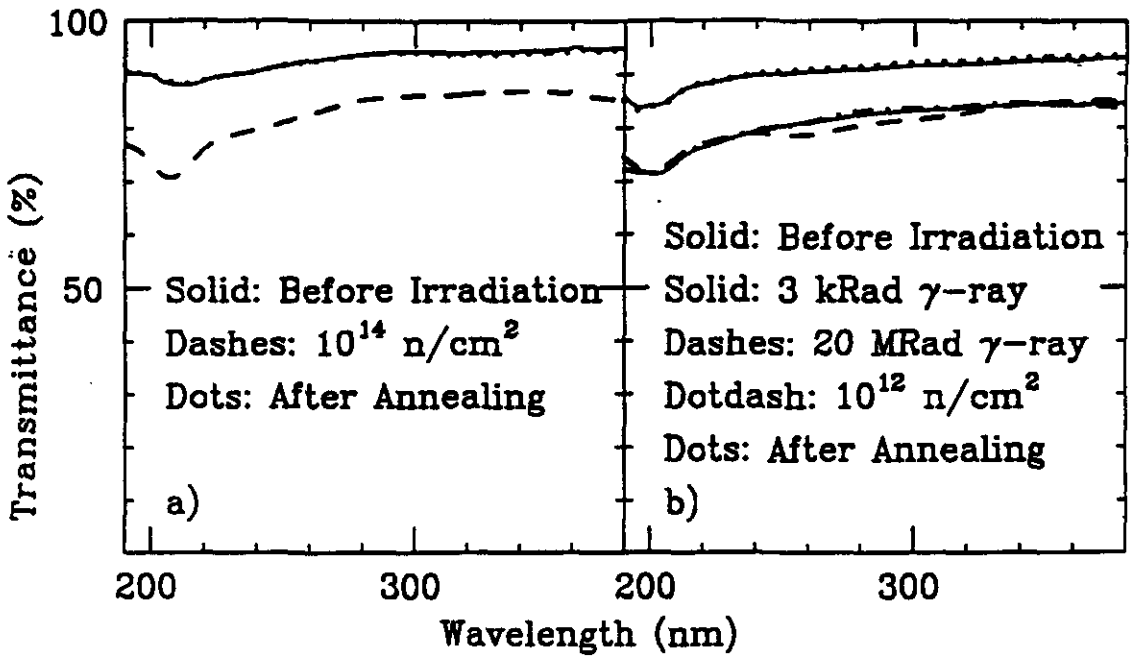


Fig.8 Transmittances before and after irradiation showing a) recovery from neutron damage; and b) typical saturation effect.

(from ref.[30])

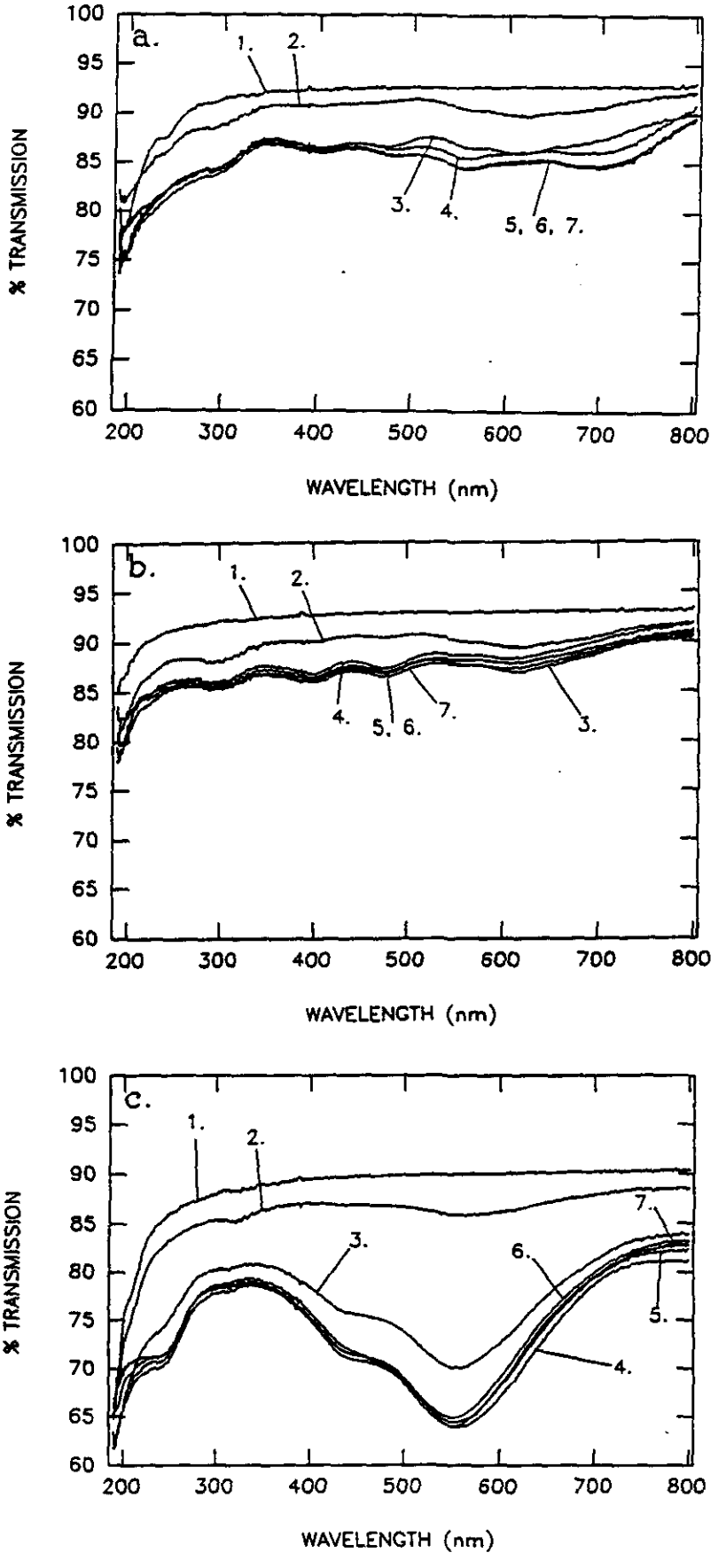


Fig.9 Transmission vs. wavelength for samples 1-3 (a-c) for doses of (1) unirradiated, (2) 10^3, (3) 10^4, (4) 6×10^4, (5) 2.7×10^5, (6) 9.0×10^5 and (7) 4.7×10^6 rad. Note expanded vertical scale (from ref.[32]).

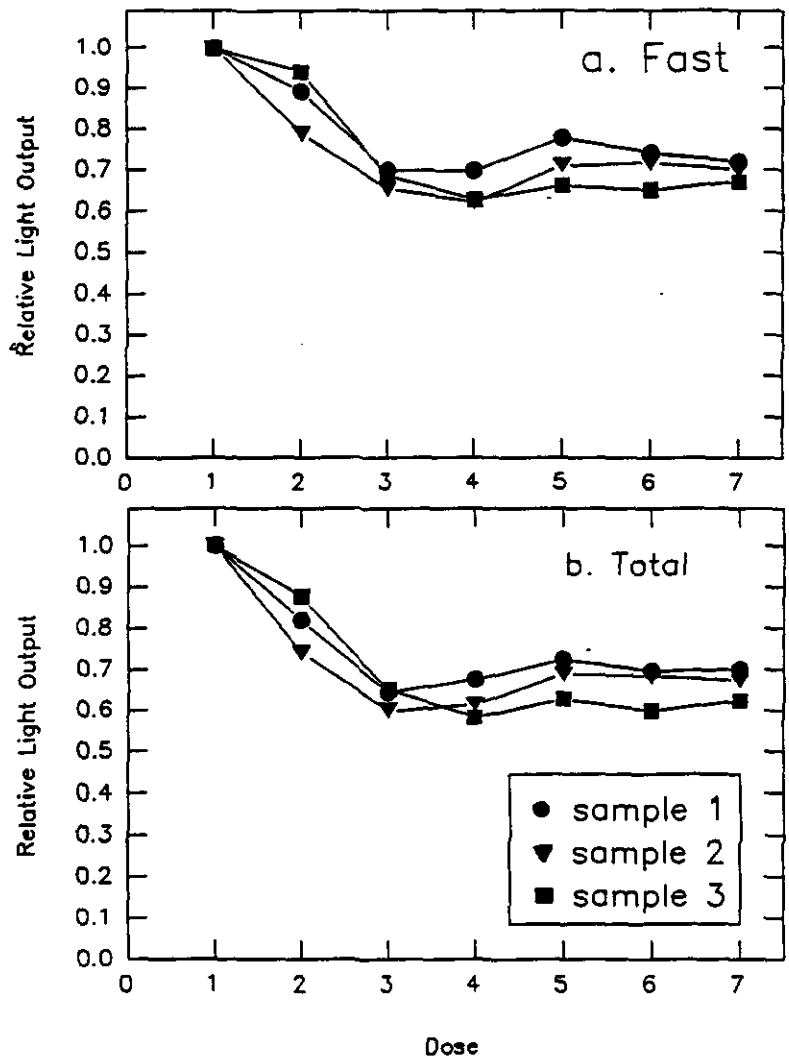


Fig.10 Relative change in light output of samples 1-3, (a) fast, (b) total, for doses of (1) unirradiated, (2) 10^3, (3) 10^4, (4) 6×10^4, (5) 2.7×10^5, (6) 9.0×10^5 (7) and 4.7×10^6 rad (from ref.[32]).

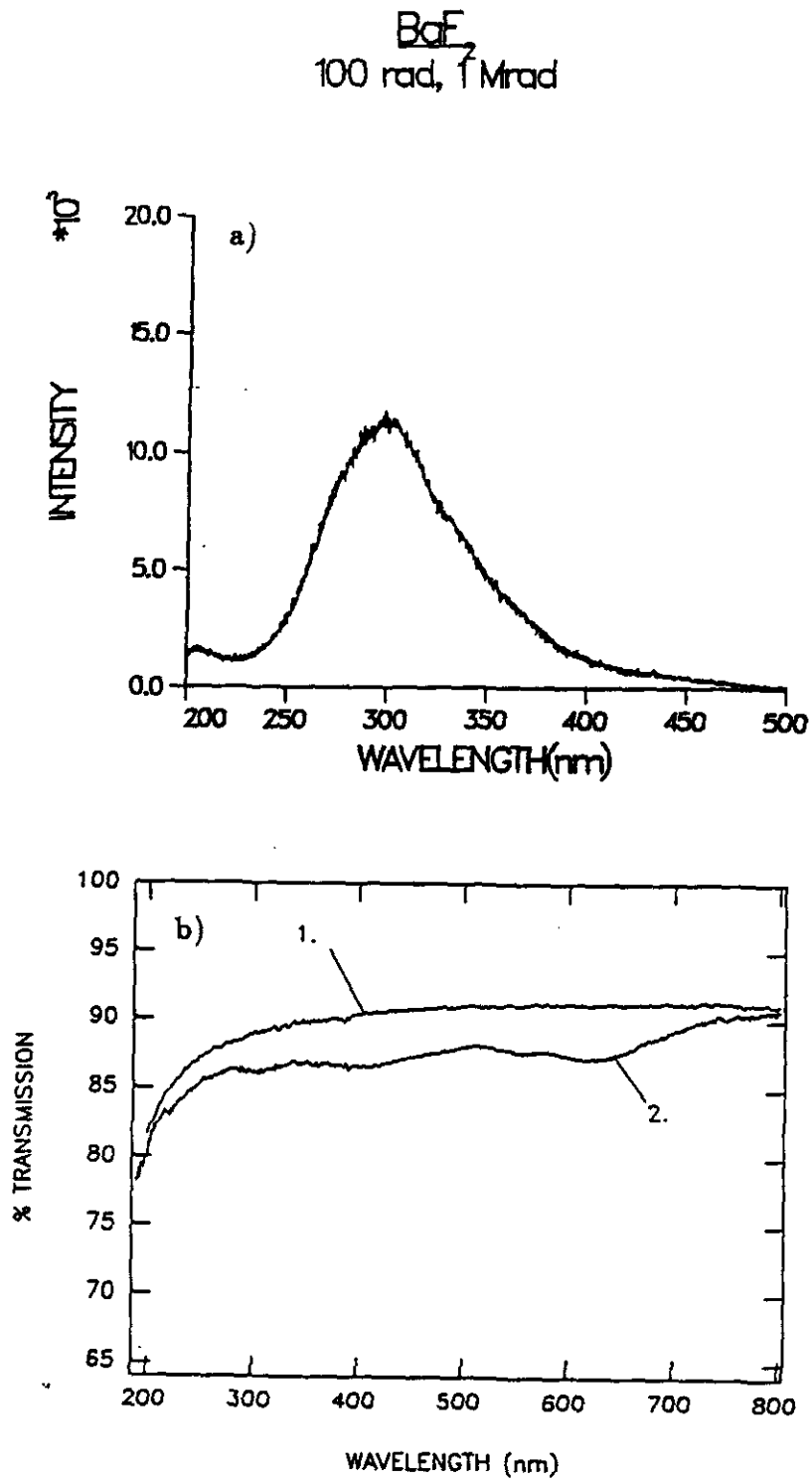


Fig.11 a) Scintillation emission spectrum for BaF_2 sample measured during irradiation. Curves for 100 rad and 10^6 rad are overlapping. b) Transmission spectra for same sample measured before and after irradiation of 10^6 rad (from ref.[32]).

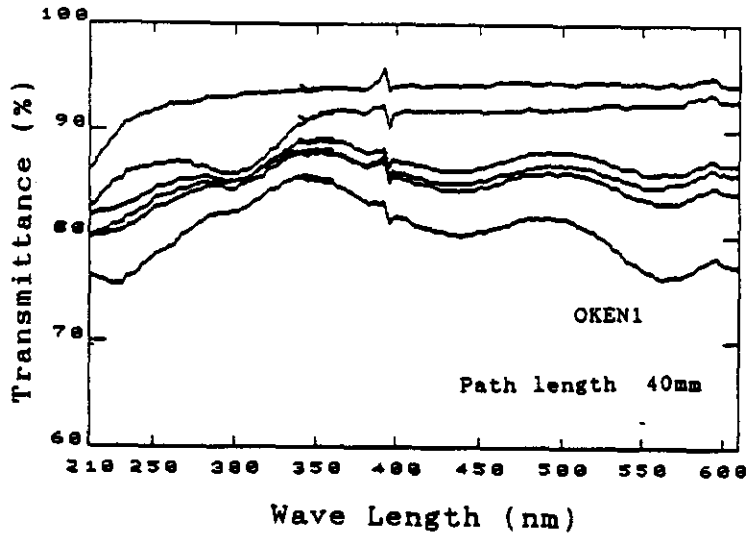


Fig.12a Transmittance vs wavelength for the path length of 40 mm for OKEN1. From the top to the bottom the curves correspond to the irradiations of 0, 0.6, 1.2, 2.5, 3.8 and 10.6×10^4 Gy.

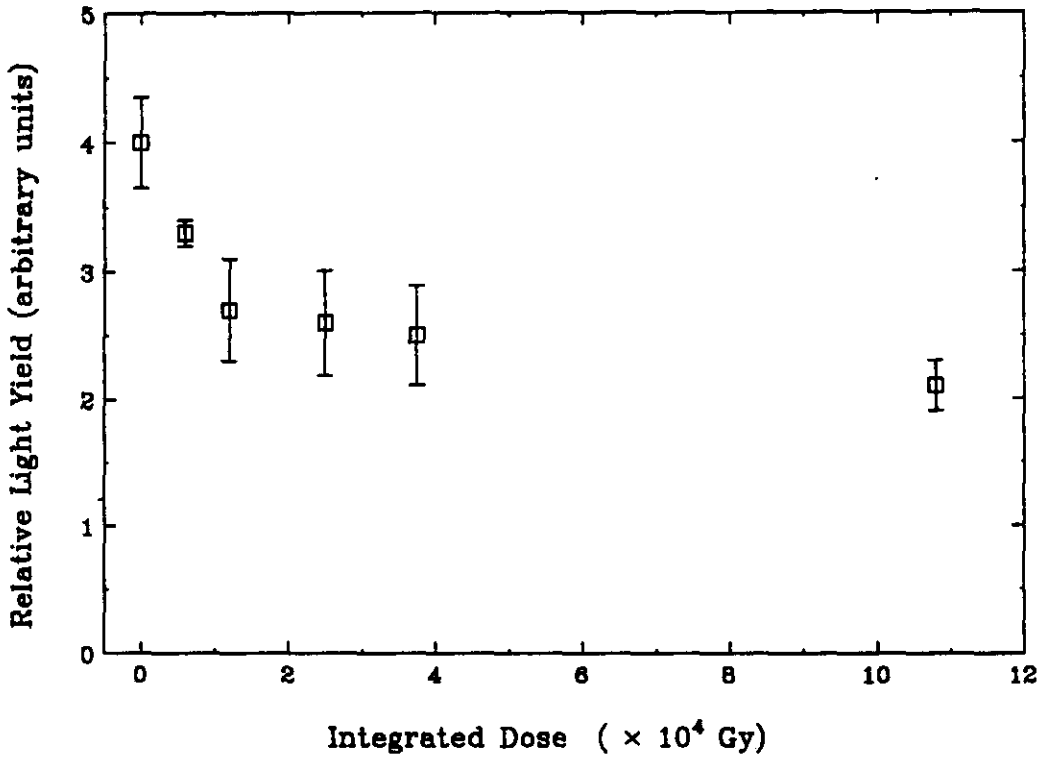


Fig.12b Light yield vs the integrated dose of γ-rays for OKEN1.

(from ref.[33])

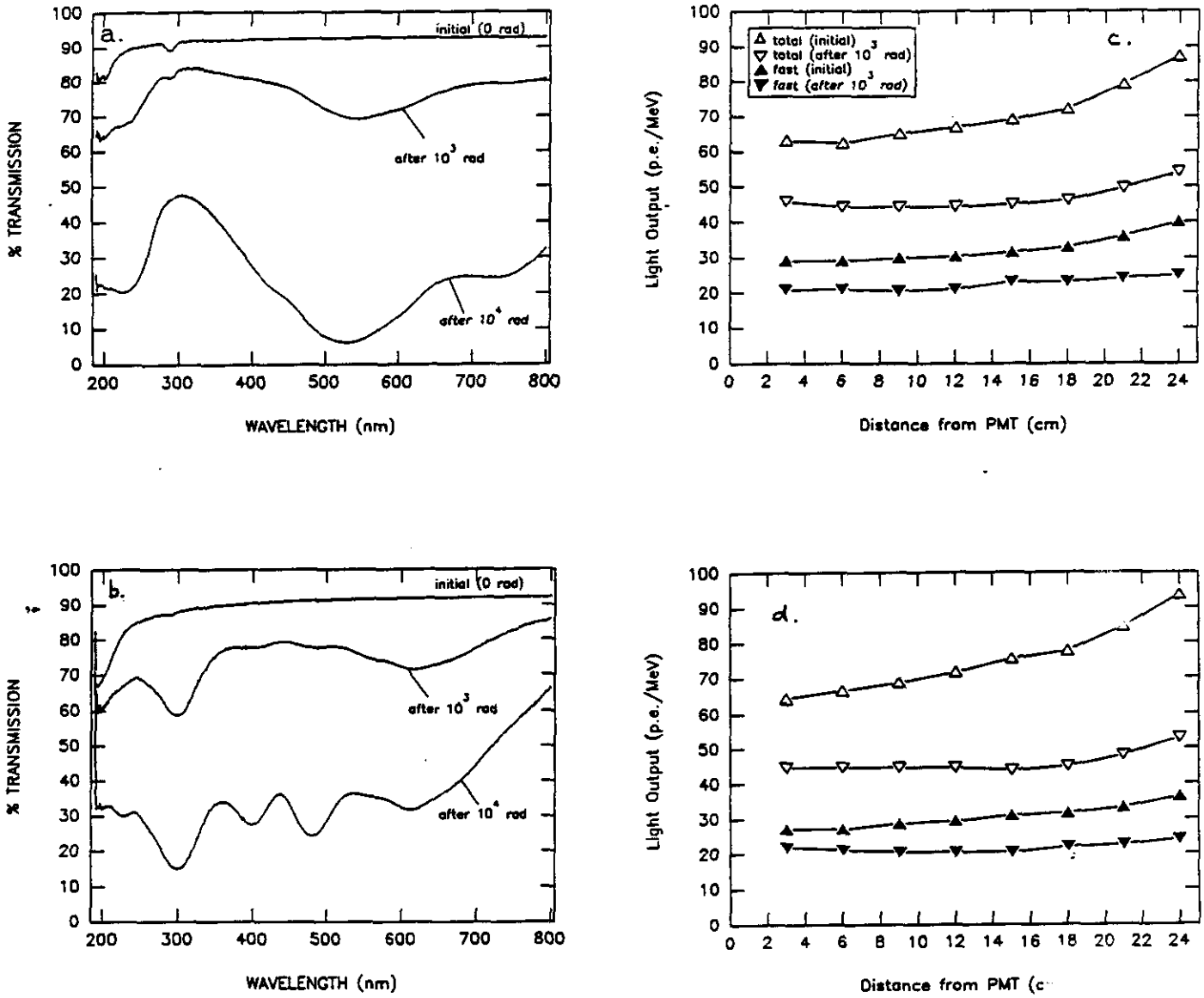


Fig.13 Transmission spectra of 25 cm BaF_2 trapezoids measured after 10^3 and 10^4 rad, (a) SIC sample (b) Korth sample. Change in light output as a function of position along the 25 cm BaF_2 trapezoids after 10^3 rad, (c) SIC sample (d) Korth sample.

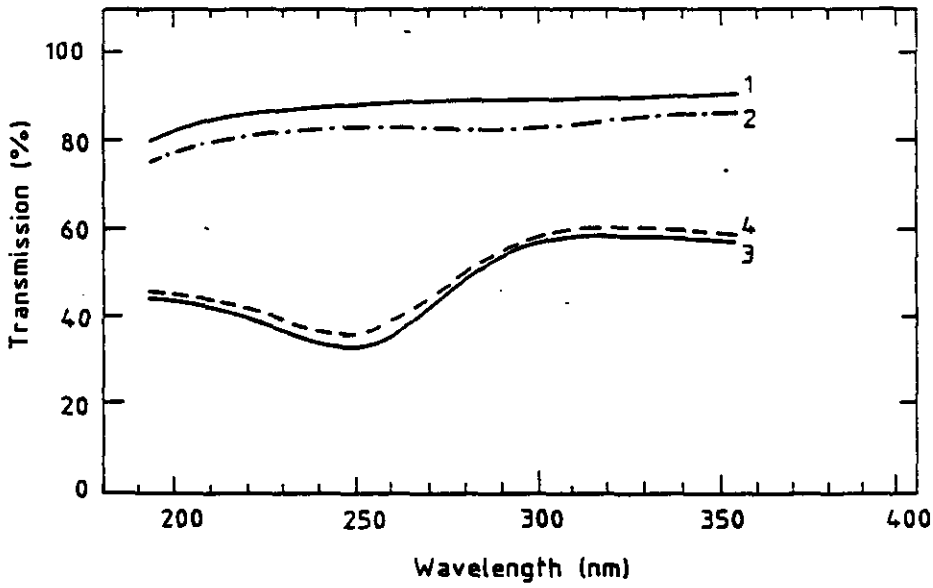


Fig.14 Transmission of a BaF_2 crystal as a function of wavelengths: 1) Before irradiation; 2) after 0.5 MGy; 3) after 1.7 MGy; 4) after three weeks recovery.

(from ref.[35])

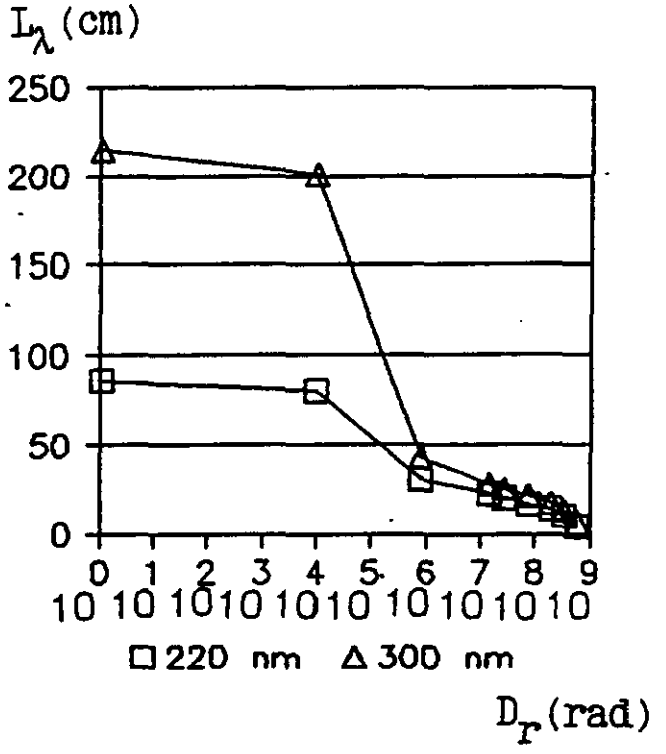


Fig.15 The dependence of $L_\lambda = f(D_r)$. Here D_r is absorbed dose ($E_\gamma \approx 1.25$ MeV).

(from ref.[36])

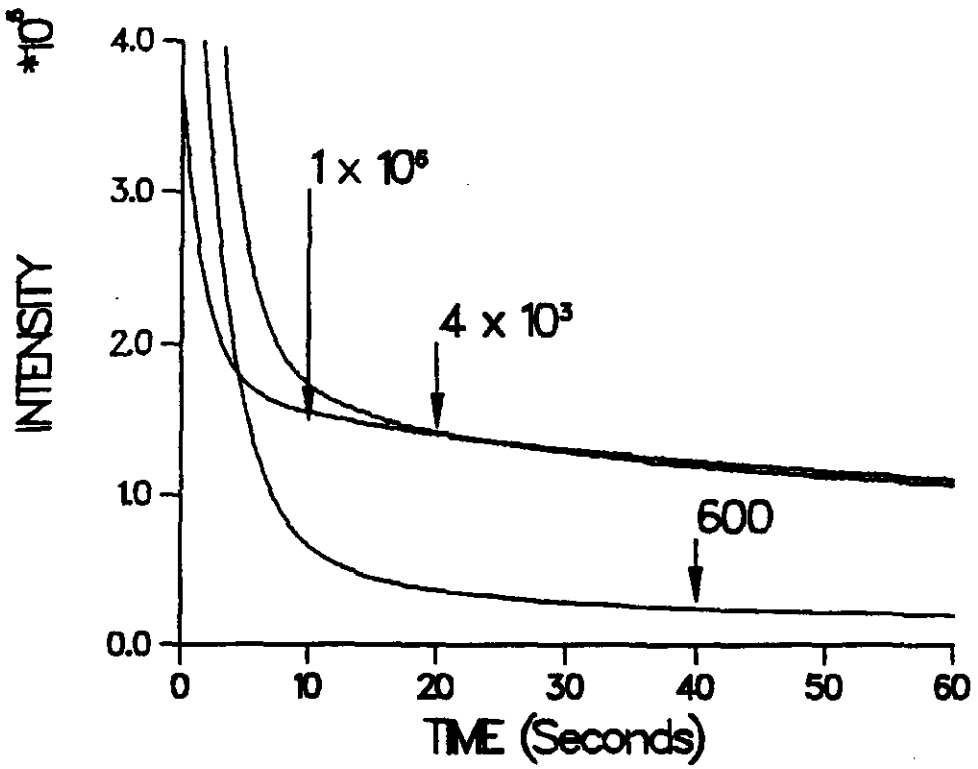


Fig.16 Phosphorescence decay spectrum after doses of 600, 4 x 10^3, and 1.0 x 10^6 rad (from ref.[32]).

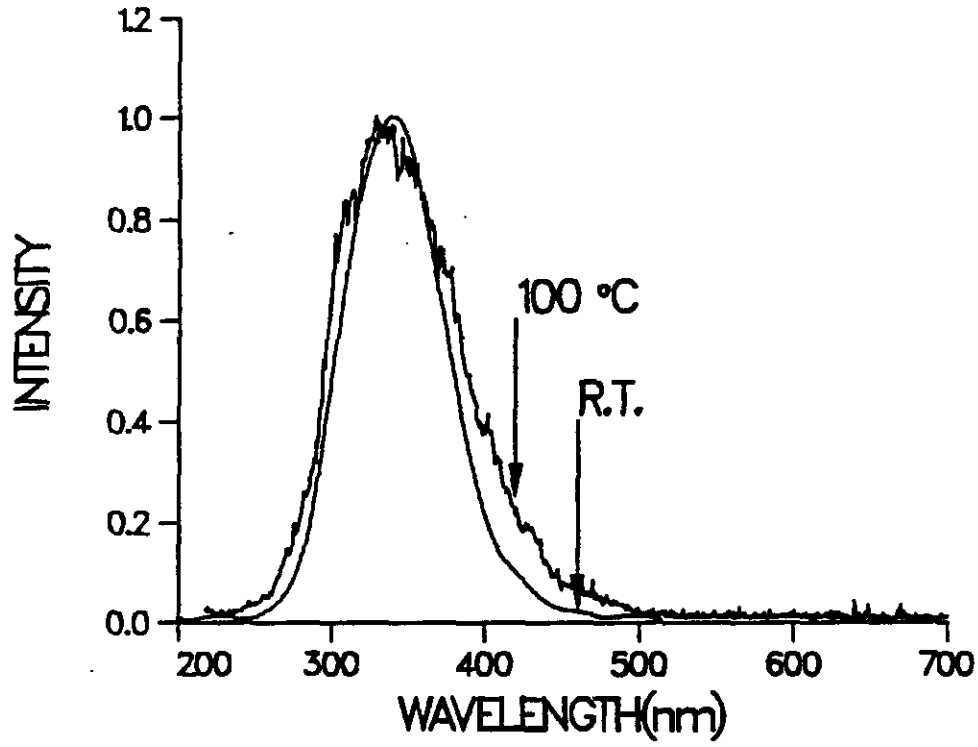


Fig.17 Phosphorescence emission spectrum measured with a sample kept at room temperature and a sample heated to $100°C$. Both curves are normalized to 1.0 at the peak (from ref.[32]).

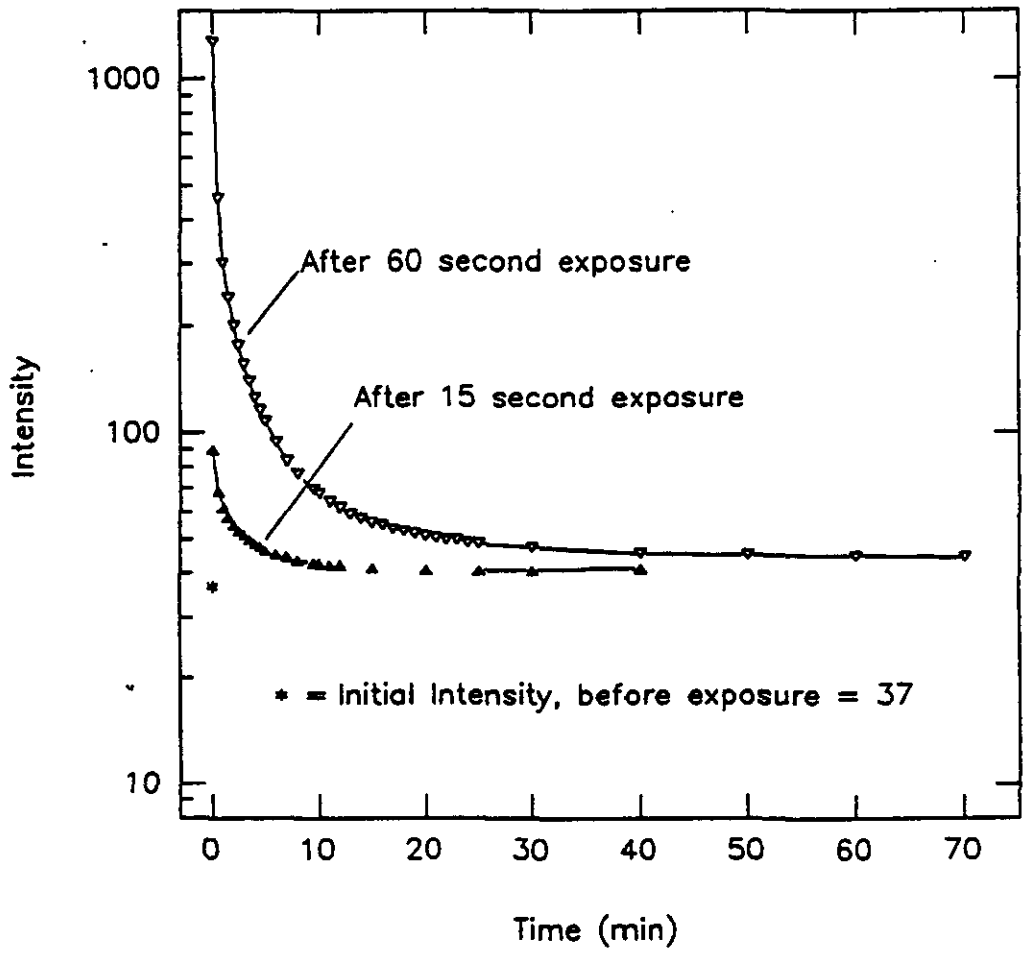


Fig.18 Phosphorescence intensity and decay in an irradiated crystal after several exposures to roomlight. The intensity prior to exposure to roomlight is also indicated (from ref.[32])

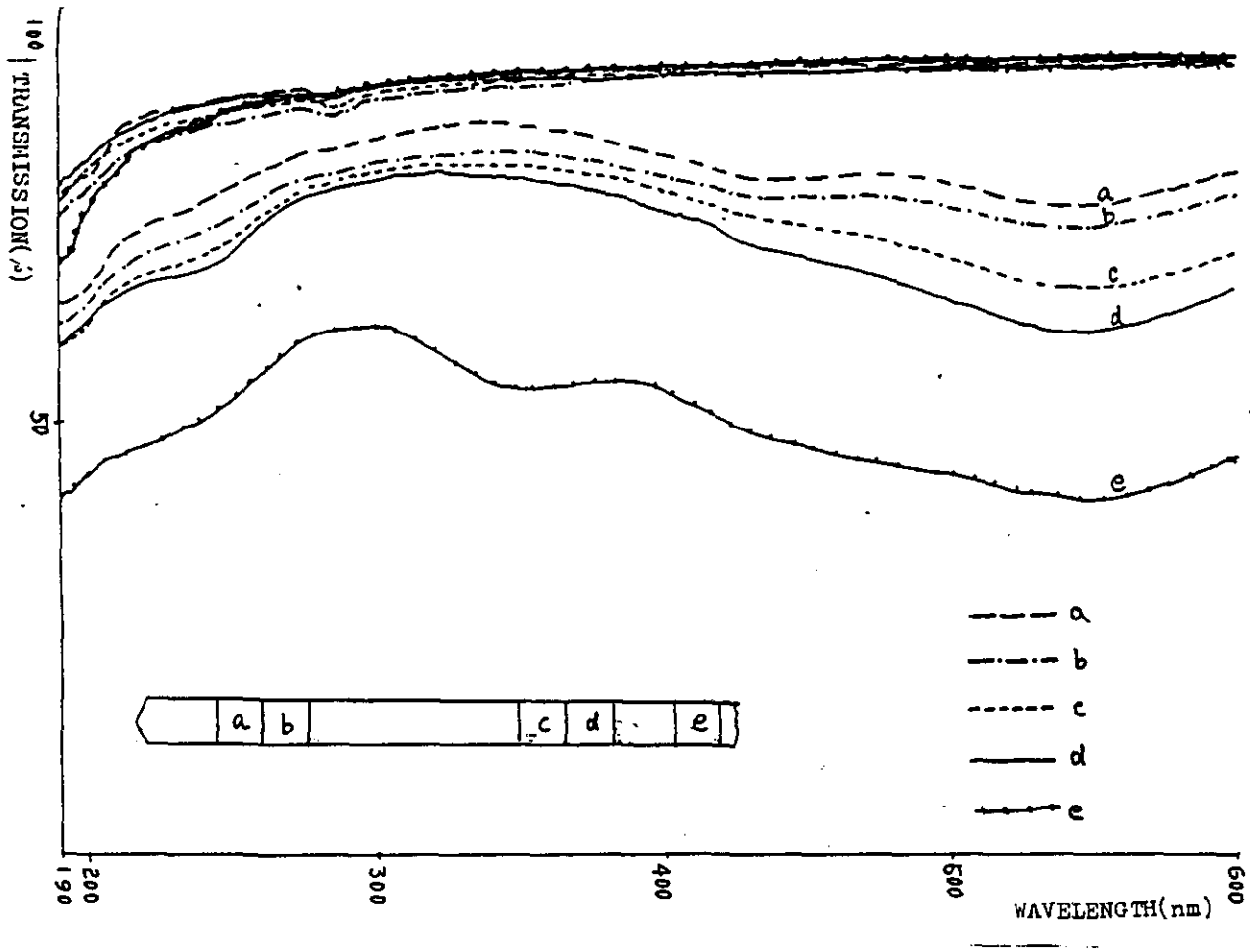


Fig.19 25 mm long crystal, r-ray irradiation: 1.6 MRad.
BaF_2 crystal cut from different sites of a 300 mm crystal

(from ref.[42])

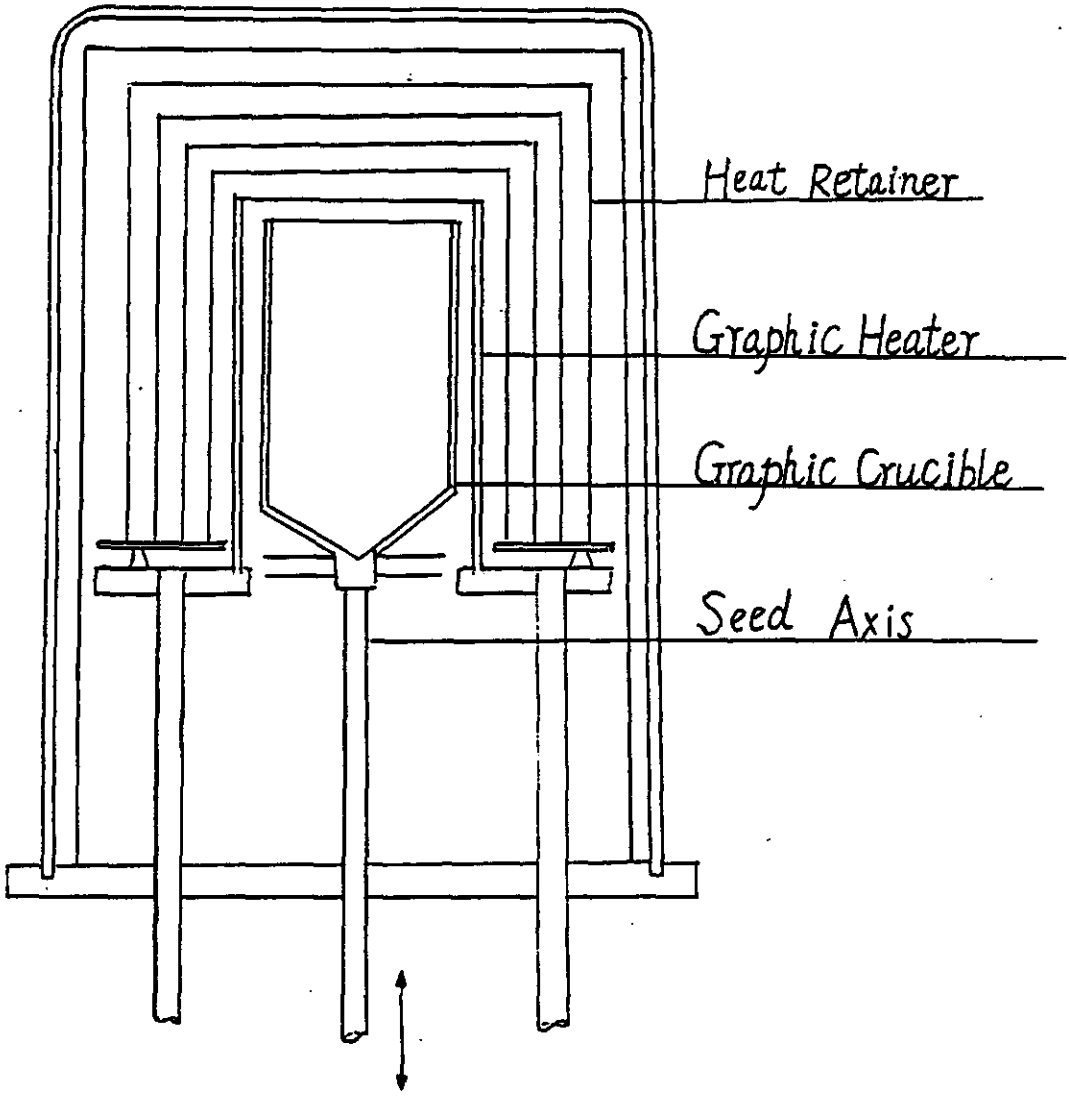


Fig.20 Schematic representation of a Stockbarger furnace (from ref.[44]).

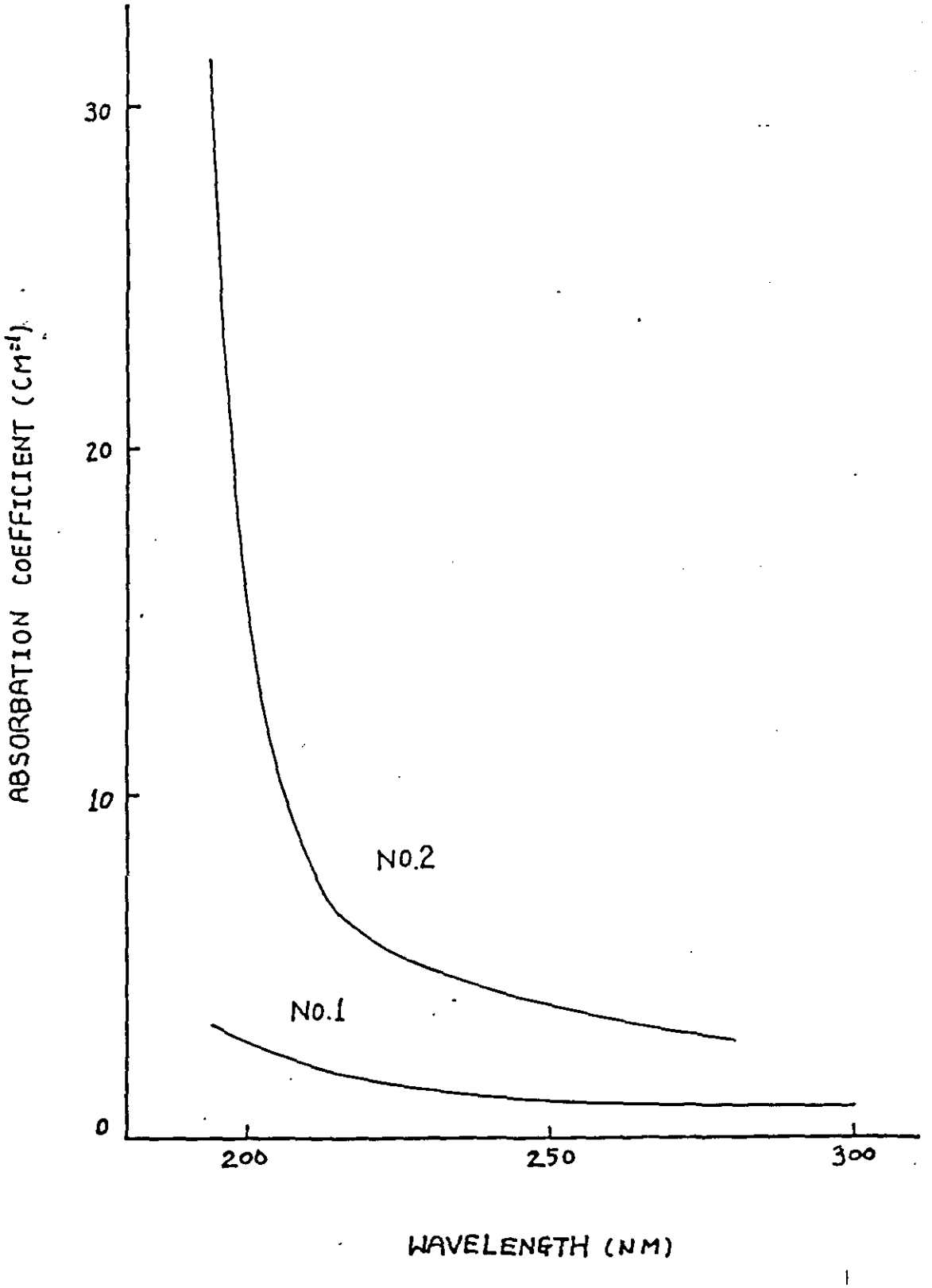


Fig.21 UV absorption edge of BaF_2 crystal with different oxygen content

(from ref.[42])

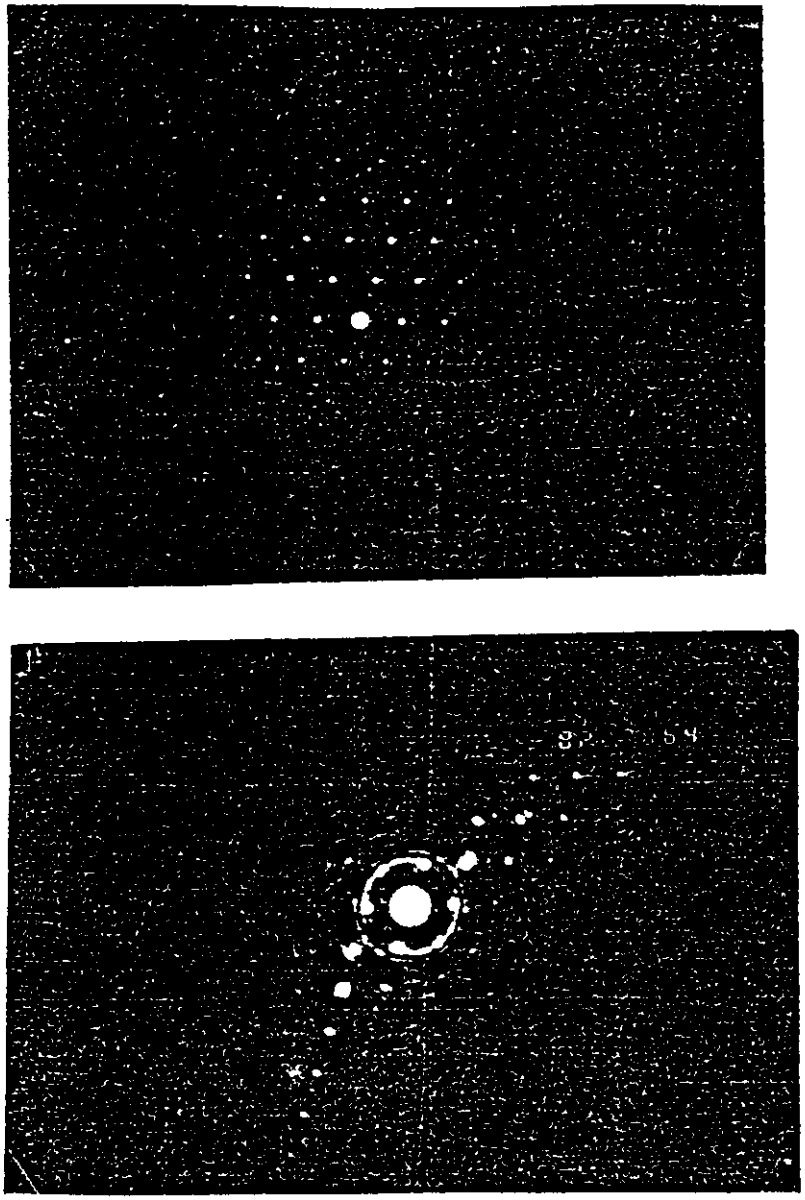


Fig.22 Electron diffraction patterns of BaF_2 crystal

(a) Just start bombardment of electron beam on crystals
(b) After certain time of bombardment of electron beam, pattern shows appearance of BaO rings

(from ref.[42])

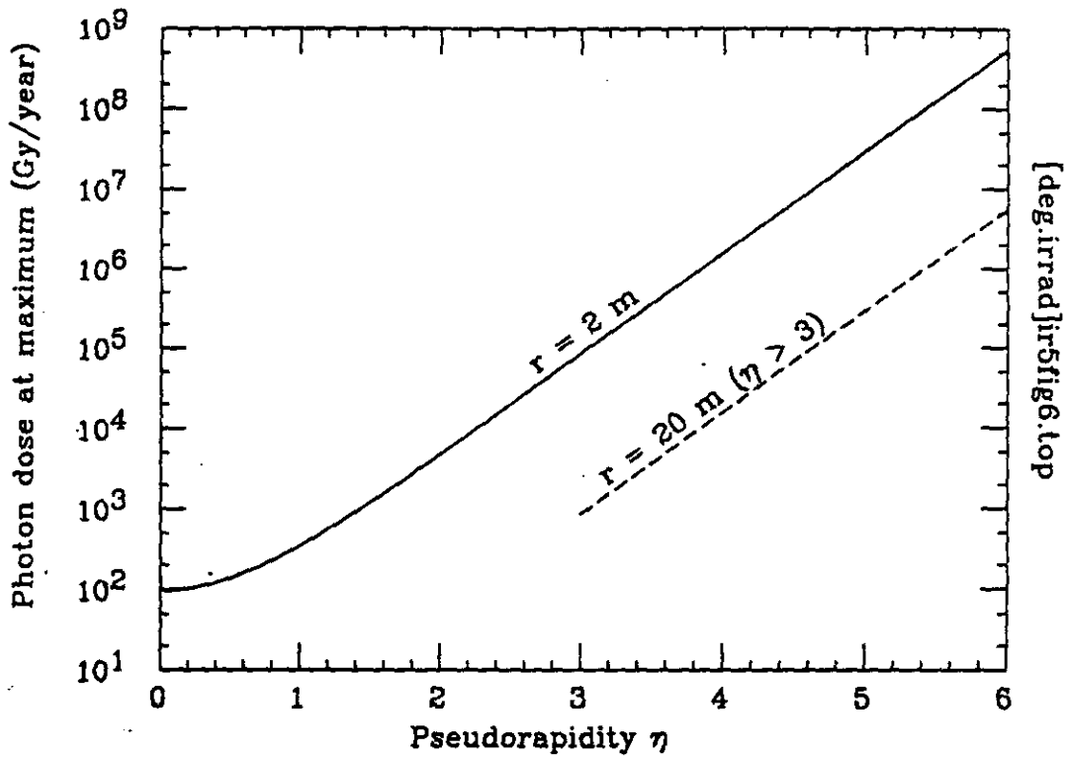


Fig.23 The maximum dose from incident photons. The full curve assumes the maximum occurs at 200 cm. The other curve is calculated for 20 m, typical of forward detectors.

From ref.[59]. Note: dose levels on the y-axis should be corrected ***downward*** by a factor of 1/3 as given in a later erratum.