GEM TN-92-77

Radiation Damage in Large Barium Fluoride Crystals

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March 1992

Abstract:

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RADIATION DAMAGE IN LARGE BARIUM FLUORIDE CRYSTALS

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ABSTRACT

The radiation damage of barium fluoride (BaF_2) crystals was investigated through the changes in their optical transmission before and after γ-ray irradiation. The correlation of radiation damage with crystal growth conditions revealed that the radiation damage is impurity and defect related. As impurity is concerned, when the contents of cationic impurities decrease to a certain tolerated level, oxygen and hydroxyl become most harmful. High density of defect such as scattering centers in crystal also resulted in radiation damage. Thanks to recent progress in BaF_2 crystal growth, an encouraging result of radiation test on large crystals has been achieved. On the mechanism of radiation damage, it is likely that the oxygen ion came from dissolved oxygen during irradiation is the cause of 190–250 nm absorption band and the formation of F color center is the origin of 500–600 nm absorption band. Another hypothesis by L.Y. Chen *et al.* suggests that the formation of U center after irradiation is responsible for the VUV absorption at 204 nm and IR absorption at 793.75cm^{-1} respectively.

INTRODUCTION

Considerable attention has been devoted to BaF_2 crystal since the discovery of the fast component in its scintillation light [1]. BaF_2 is the fastest scintillator known with its fast decay time of 600 ps at 220 nm wavelength, and has long been believed to be one of the most radiation resistant inorganic scintillators. In addition, BaF_2 has excellent time resolution, good detection efficiency and is not hygroscopic. All these advantages make BaF_2 favourable for the applications involving very high counting rates and severe radiation such as at the SSC.

After irradiation with high energy particles or other radiation sources, the coloration occurred in BaF_2 crystal resulting in the reduction of both its optical transmission and scintillation light output which is so called radiation damage. Therefore the radiation damage in BaF_2 crystal becomes an extremely important problem for its applications where the radiation dosage is rather high.

Although some research work [2] have been done in understanding the mechanism of radiation damage in BaF_2 crystal, many points still remain unclear. The purpose of present

article is to investigate the mechanism of radiation damage in BaF_2 crystals, especially for large size crystals from summarizing the results of various radiation tests with the hope to help improve the radiation hardness of BaF_2 crystal.

EXPERIMENT

The radiation hardness of BaF_2 crystals were investigated through the changes in their optical transmission before and after γ-ray irradiation. Two categories of samples were used. One category samples are in truncated pyramidal shape measuring 3×3, 4×4, 25 cm^3, which were prepared for the first prototype of GEM detector for SSC project. The other is 2.54cm dia.× 2.54cm long cylinder. All these samples were cut from ingots grown in a graphite crucible in a vacuum furnace at 10^{-5} torr level, then lapped and polished.

The irradiation of samples were carried out with a ^{60}Co source at Shanghai Nuclear Research Institute, Chinese Academy of Sciences. A Shimadzu UV-265 spectrophotometer was used to measure the optical transmission of small samples. For crystals more than 10 cm in length, a home made large compartment which has been cross-checked was used.

RESULTS AND DISCUSSION

The influence of impurities on radiation damage

A radiation test was performed on five samples a,b,c,d and e, each 2.54 cm long, taken from various places of a 2.54 cm dia.× 30 cm long cylindrical ingot along the longitudinal axis. (see left bottom of Fig. 1) The radiation dose is 1×10^5 rad. The transmission spectra for all these samples shown in Fig. 1 indicate that before irradiation all of them except sample e have good transmission with similar shapes in the region from visible to UV. However, after irradiation all samples were coloured in different purple tint and consequently various decrease occurred in their optical transmission that means the radiation damage for each sample is not identical. A distinguishable tendency is that along the longitudinal axis of ingot, the radiation damage is gradually increased. At the top corresponding to the end of crystal growth, it was even in dark purple and sharp absorption band was observed. Similar

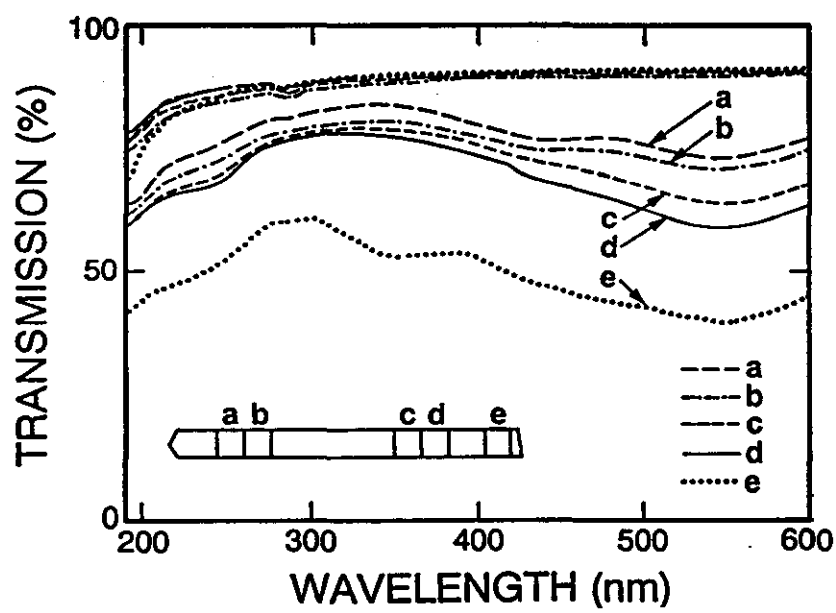

Figure 1: Transmission spectra measured before and after γ-irradiation (1×10^5 rad) for five samples, ϕ1"×1" long each, taken from a long crystal.

Table 1: Analytical results of BaF_2 crystal by AAS technique (ppm)

Impurity	Sample 1	Sample 2	Sample 3
Fe	0.50	0.44	0.41
Co	0.50	0.85	0.65
Cr	1.5	2.0	1.8
Mn	0.10	0.20	0.20
Ni	2.2	3.2	3.8
Ca	8.5	12	14
Mg	2.1	6.5	19
Sr	900	980	1300

Sample 1: taken from the bottom of crystal
Sample 2: taken from the middle of crystal
Sample 3: taken from the top of crystal

results have been obtained in radiation tests for other large crystals. These experimental results strongly support that the impurity is the main course of radiation damage . It could be explained by the crystal growth method we used i.e. the Bridgman-Stockbarger method which is based on a zone- refining principle. The raw material is placed in a graphite crucible which is then placed inside a vacuum furnace. The furnace has a temperature gradient which varies from above the melting point (1280°C) at the upper part to blow the melting point at the bottom. The crystal growth proceeds from the bottom to the top as crucible descents down. At the same time the impurities are forced to the top of ingot and concentrated over there. When the crystal was irradiated, its top part will naturally be coloured in dark tint due to the high impurity concentration thus resulted in large amount of radiation damage.

By using the AAS (Atomic Absorption Spectrometry) technique, we analysed cationic impurities such as transition metals and alkaline earth metals in three crystal samples which were taken at various sites from a 30 cm long ingot. The results listed in Table 1 show that the contents of transition metals such as Fe, Co, Cr, Mn, and Ni are within same magnitude of several tenth ppm to several ppm in whole ingot. It could be explained that while these elements are in a tendency to migrate towards the top of ingot during crystal growth, they

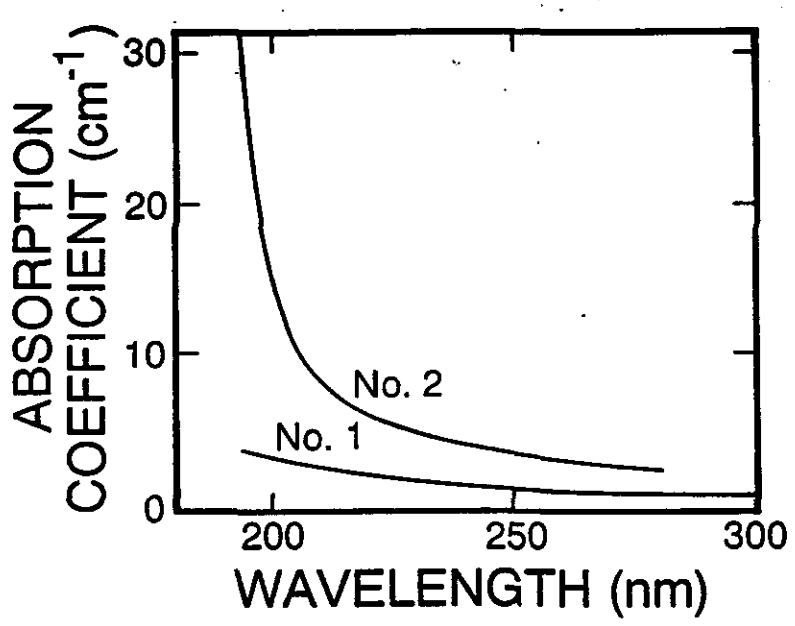

Figure 2: UV absorption of BaF_2 crystal with different oxygen content. No.1: low oxygen-containing sample; No.2: high oxygen-containing sample.

easily escape from the top because of the low boilling points of their fluorides. It is rather difficult at present to determine how much influence do these trace transition metals give on radiation damage of BaF_2 crystal. The contents of alkaline earth metals such as Ca, Mg and Sr in the crystals are relatively high and increase as crystal growth proceeds. It is, however, understood that due to their similarity to barium, other alkaline earth metals even in a rather higher contents may not have substantial influence on radiation damage of BaF_2 crystal.

For rare earth ions, we have tried to correlate the content of cerium in BaF_2 crystal measured by using ICP (Inductively Coupled Plasma) technique with the absorption peak at 290 nm because someone [4] has suggested that it is caused by cerium of several ppm or less. However, our analytical results on BaF_2 crystals with such an absorption peak show that no cerium has been found within the determining limit of 0.6 ppm. We have also not found intrinsic absorption band in UV region for other rare earth ions.

Among the anion impurities, oxygen and hydroxyl ions which are the most harmful impurities for radiation hardness of BaF_2 crystal could be easily introduced into the crystals. Fig. 2 shows the absorption of two crystal samples with different oxygen contents. It is evident that significant difference between these two samples is existed especially in the UV region. For high oxygen- containing sample, it is almost cut off at 220 nm.

The influence of defects on radiation damage

The transmission spectra of a tapered BaF_2 crystal in size of 3×3, 4×4, 25 cm^3 after γ-ray irradiation were measured through polished side surfaces at three points a,b and c. (see left part in Fig. 3) In general, curve b should locate in between curves a and c. However, the transmission of curve b is actually lower than that of curve c. And strong coloration could be found in the area around location b where high density of macrodefects such as a large number of scattering centers could be observed even by naked eye. (Fig. 4) It has been identified by microscopy that these scattering centers are 'negative crystals' with definite shapes and orientations. (Fig. 5) The perturbation of temperature in crystal growth furnace or impurity effect is directly leading to the increase of density of defects.

Mechanism of radiation damage

From above discussion, it is clear that the presence of impurities and defects in crystal

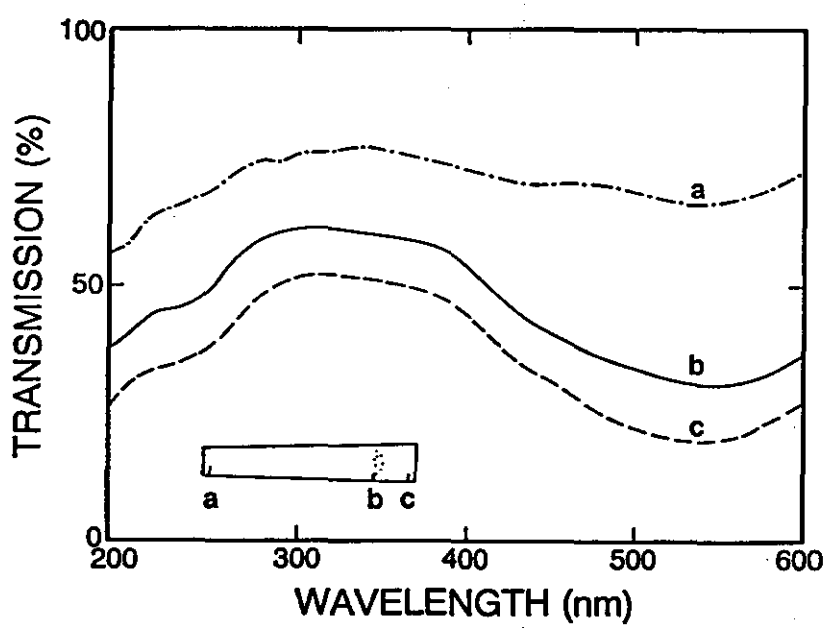

Figure 3: Transmission spectra measured at three different locations of crystal (3×3, 4×4, 25cm^3) after 10^5 rad γ-ray irradiation.

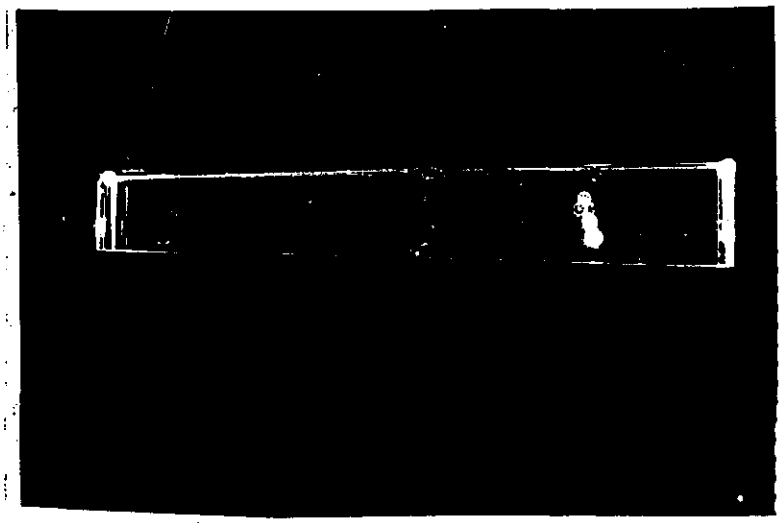

Figure 4: BaF_2 sample with macrodefects.

are the major reasons for radiation damage. As impurity is concerned, we also found that when the contents of cationic impurities decrease to a certain tolerated level, oxygen and hydroxyl become most harmful.

We have carried out a diffraction study with an electron beam in a diameter of 1000 angstroms focused on a crystal. Fig. 6a shows a perfect BaF_2 diffraction pattern taken just after starting a bombardment. This perfect pattern can be found nearly everywhere in the crystal indicating a low density of dislocation. After a few minutes, however, diffraction rings appear as shown in Fig. 6b. These rings have been identified as BaO. It is presumed that the oxygen atoms or molecules previously dissolved in BaF_2 crystals being transformed into oxygen ions during bombardment which then displace a fluorine atom at a lattice site and combine with barium ion into BaO.

When BaF_2 crystal was irradiated with ^{60}Co source, two broad absorption bands usually appear in 190–250 nm and 500–600 nm regions respectively. It is likely that the oxygen ion came from dissolved oxygen during irradiation is the cause of the 190–250 nm absorption band. During irradiation, the fluorine vacancy in the crystal is easily to trap one or two electrons forming a F color center. The formation of F color centers is probably the reason

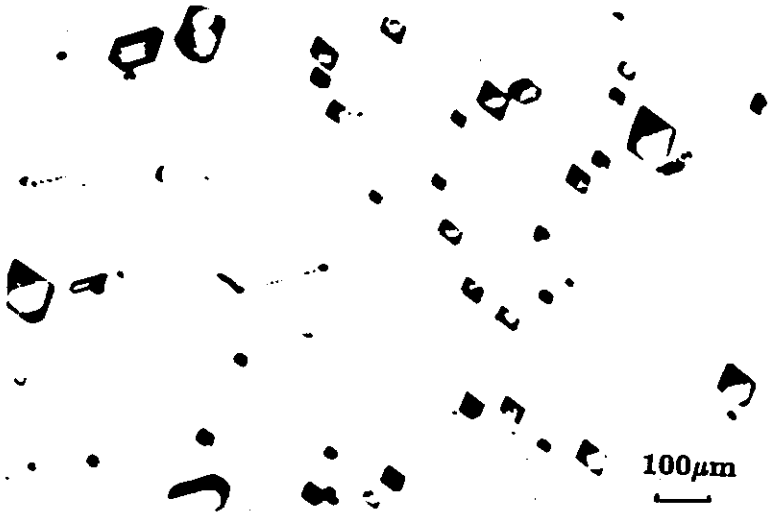

Figure 5: 'Negative crystals' in BaF_2 crystal (×100).

Figure 6: 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.

for 500–600 nm absorption band.

It is already known that the damaged crystals could be recovered with exposure to UV light from a mercury lamp, sunlight or roomlight. It could be explained that the electrons trapped by F color centers which formed during irradiation escape from the centers with the energy of UV light thus destroy the F centers and the crystal is bleached. There is another probability that during the exposure to UV light, the irradiation induced oxygen ions lose their electrons thus return to original oxygen atoms or molecules.

Recent study [5] revealed the effect of OH^- on radiation damage in BaF_2 crystal. A piece of good sample from Shanghai Institute of Ceramics, Chinese Academy of Sciences was heated in moisture at 700°C for 12 hours. The surface hydrolysis and subsequent migration of OH^- ion into crystal produced an OH^- doped sample.

$$BaF_2 + 2H_2O \rightarrow Ba(OH)_2 + 2HF$$

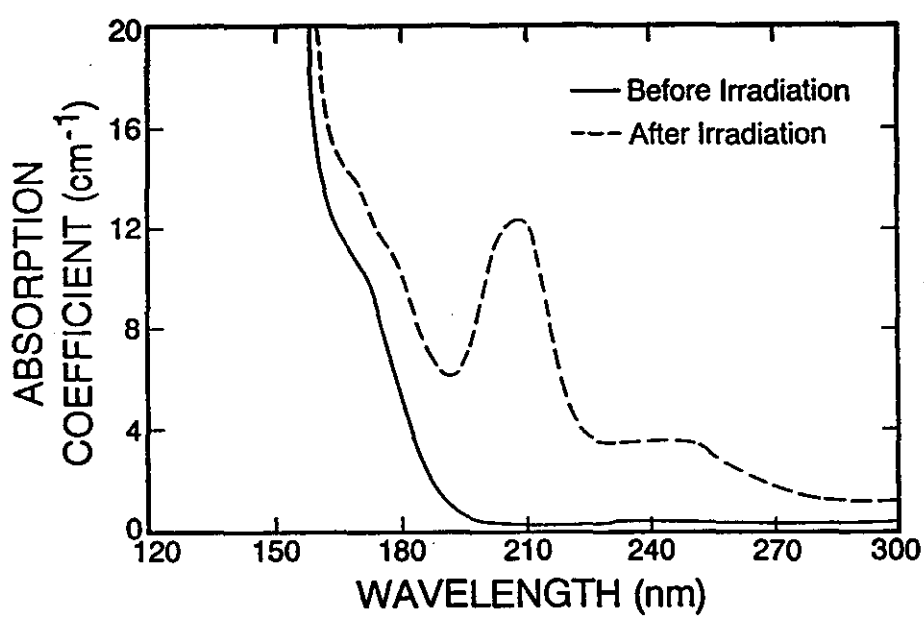

Figure 7: UV absorption of BaF_2 :OH^- crystal.

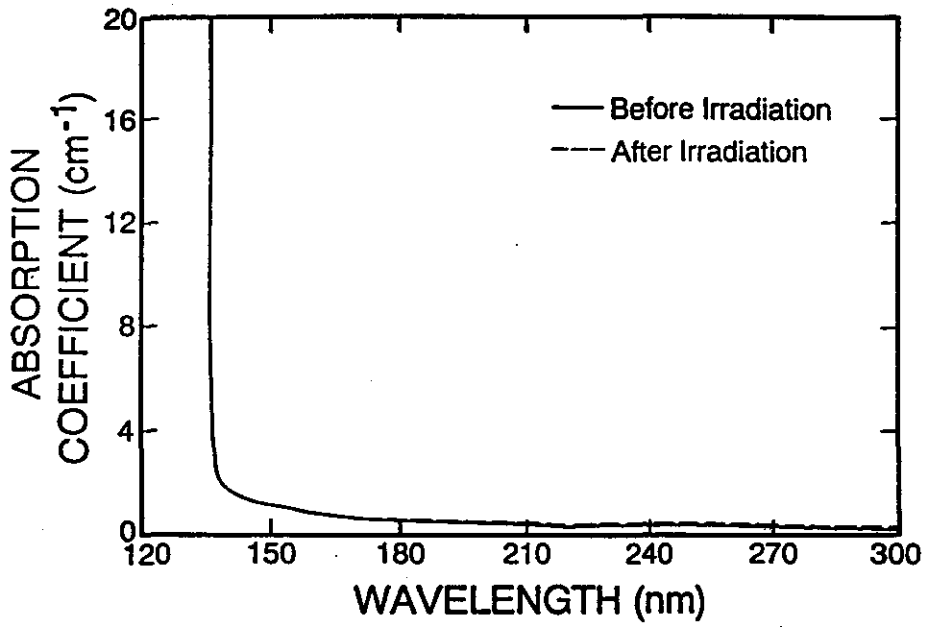

Figure 8: UV absorption of undoped BaF_2 crystal.

The comparison of absorption measured before and after γ-ray irradiation between this sample and two undoped samples showed that OH-doped sample exhibits obvious absorption band. (Fig. 7 and Fig. 8) It was at 192 nm before irradiation and shifted to 204 nm after. It was suggested that OH^- was decomposed through radiolysis and an U center was formed:

$$OH^- \rightarrow H_i^0 + O^- \quad or \quad H_s^- + O_i^0$$

H_i^0 is interstitial hydrogen atom; H_s^- is substitutional hydrogen ion; O_i^0 is interstitial oxygen atom. The U center is the product of H^- occupied in a fluorine vacancy. This was further confirmed by an IR absorption at 793.75 cm^{-1} originated from the U center.

CONCLUSION

From the information presented in this article, it is evident that the radiation damage

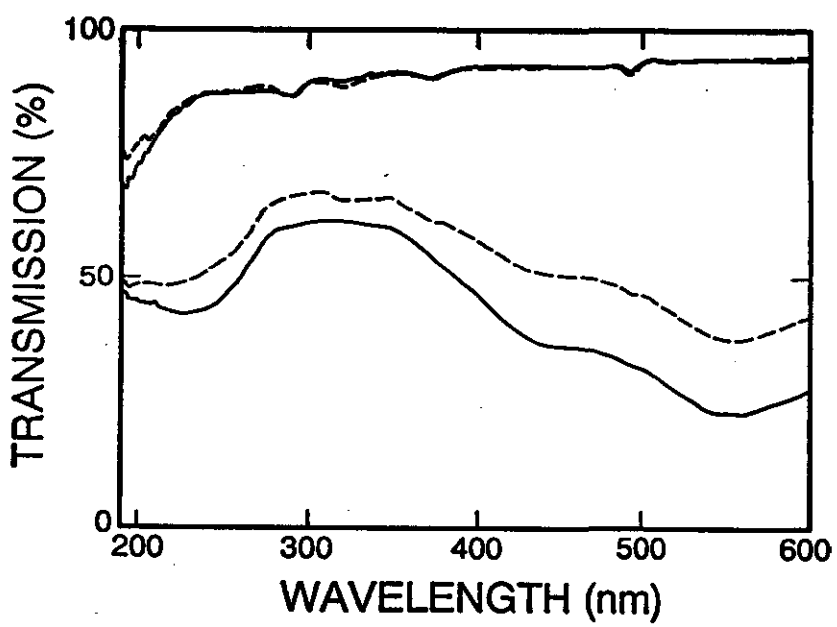

Figure 9: Transmission spectra for BaF_2 samples, 3×3, 4×4, 20cm^3 (dash) and 3×3, 4×4, 26cm^3 (solid), before and after 1 Mrad γ-ray irradiation.

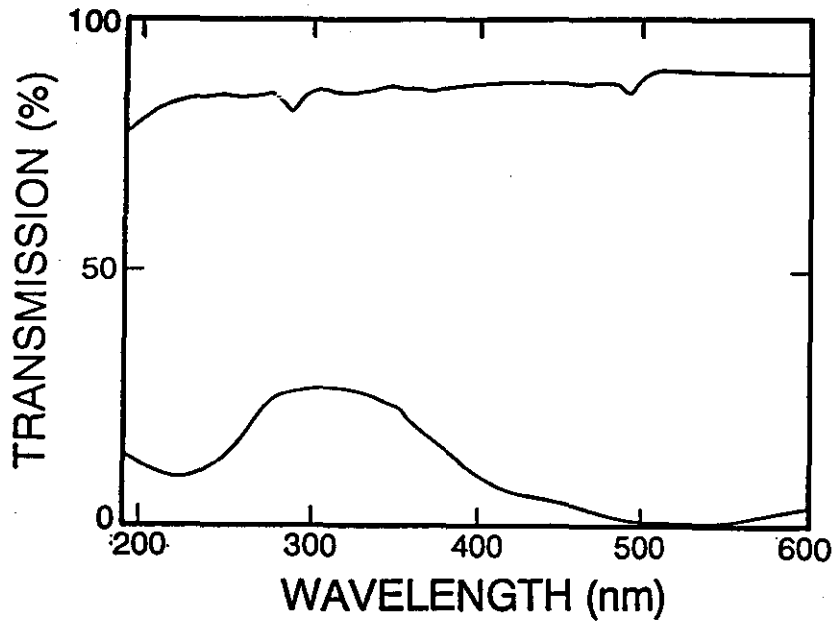

Figure 10: Transmission spectra for sample (2×2, 3×3, 25cm^3) of previous batch, before and after 1 Mrad γ-ray irradiation.

of BaF_2 crystal is impurity and defect related. The intrinsic radiation hardness of pure BaF_2 may be quite good. As impurities is concerned, the contents of cationic impurities such as transition metals, rare earth and alkaline earth metals should be lowered to a certain amount for which there is no criterion yet at present. For anionic impurities, much attention should be given to oxygen and hydroxyl, although the detection and elimination of trace of them are rather difficult. On the other hand, measures should be taken to eliminate the defects as possible as we can. There is no doubt that the less imperfection in crystal will make it more harder to radiation. Recently thanks to the progress in our BaF_2 crystal growth experiment, an encouraging result of radiation test on large crystals has been achieved. (see Fig. 9 and Fig. 10) We will make further effort along this direction to improve the radiation hardness of large BaF_2 crystals.

ACKNOWLEDGEMENT

The authors are indebted to the AAS Group and ICP Group of SIC for performing chemical analysis measurements and to Dr. Song Xiangyun from TEM Lab. of SIC for the help with diffraction study. Many useful discussions with Drs. R.Y. Zhu and Z.Y. Wei from CALTECH are greatly appreciated.

References

[1] M. Laval *et al.*, *Nucl. Instr. and Meth.* **A206** (1983) 169-176.

[2] A.J. Caffrey *et al.*, *IEEE Trans. on Nucl. Sci.* **33** (1986) 230-234.

[3] S. Majewski *et al.*, *Nucl. Instr. and Meth.* **A260** (1987) 373-376. P.K. Chakraborty and K.V.Rao., *J. of Mater. Sci.* **22** (1987) 587-591. A. Murakami *et al.*, *Nucl. Instr. and Meth.* **A301** (1991) 435-444. C.L. Woody *et al.*, *paper presented at the IEEE Nuclear Science Symposium, Santa Fe, New Mexico, Nov. 5-8, 1991.*

[4] H. Xiao *et al.*, *paper presented in GEM BaF_2 Panel Meeting, Beijing, Dec. 12, 1991.*

[5] L.Y. Chen *et al.*, *paper prepared in GEM BaF_2 Panel Meeting, Shanghai, Dec. 14, 1991.*