On the Problems of Oxygen-related Impurity Induced Radiation Damage in the Barium Fluoride Crystal

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This report presents a mechanism of oxygen incorporation by the hydrolysis as OH^- ion rather than the oxidation. The theoretical model of radiation damage in BaF_2 is developed which UV absorption bands are chiefly caused by O^- related impurity centers formed from other oxygen-related impurities by the ionization. The explanations for several key observations are given. Finally, based on the mechanism of radiation damage we propose several methods to improve the radiation resistance of BaF_2 crystals.

1 Introduction

· The causes of radiation damage in BaF_2 crystals grown in China are focused on the oxygen-related impurities in recent research. The indirect observation of the correlation of oxygen with radiation damage had been carried out by SIC[1] and BGRI[2]. The studies of the radiation damage mechanism, especially the dominant roles of O^- and H_F^- have been carried out by Tongji Univ. and West Virginia Univ. An applicable radiation damage mechanism has been developed by theoretical studies[3] and basically verified by doping OH^- experiments[4] at Tongji Univ. and by electron paramagnetic resonance (EPR) experiments which clearly identified O^- and hydrogen atom in crystals at West Virginia Univ.[5]. In this report we will give a brief review of the radiation damage mechanism and explanations for several key observations, and bring forth some feasible measures to control the radiation damage in BaF_2. We are optimistic about the crystals of sufficient radiation hardness meeting the GEM specifications in future.

2   The States of Oxygen Impurities in BaF_2 Crystals

The questions that in which chemical states the oxygen impurities exist in the crystals and how they are incorporated into the bulk are first concerned in our studies of radiation damage. It is now verified that the hydrolysis is thermodynamically more favorable than the oxidation by our calculations and the experiments which showed much greater penetration of oxygen-related impurities into BaF_2 in the presence of H_2O compared with results of dry oxygen[3]. Furthermore reaction is only exothermic for impure crystals, in which the O^{2-} ion substitutional is stabilized by interaction with dopant ions especially rare earth ions.

- For the process of hydrolysis, a proposed mechanism of oxygen incorporation in crystal is that, as the initial step, a reducing reaction in which a hydroxyl ion replaces a lattice fluoride ion takes place at the surface,

$$H_2O_{(g)} + F_F^- \longrightarrow OH_F^- + HF_{(g)} \tag{1}$$
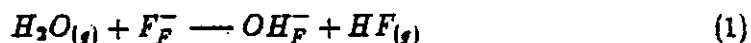
The energy of the reaction is estimated ~ 0.9 eV which is sufficiently small for the reaction to proceed at an appreciable rate at the higher temperatures.
Having replaced a lattice anion, OH^- may then migrate into the crystal by the normal anion migration mechanism. The activation energy for OH^- migration is close to that for F^- interstitial which was measured as ~ 1.0 eV. Thus the OH^- ion will uniformly diffuse through the bulk of crystal. The hydroxyl impurity is one of the oxygen-related impurities.

- Partial OH^- ions will take reaction with lattice fluoride ions at higher temperature,

$$OH_F^- + F_F^- \longrightarrow O_F^{2-} + \mathcal{V}_F + HF_{(g)} \tag{2}$$
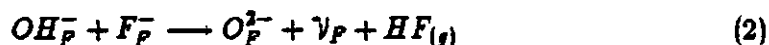
to produce HF and oxygen-vacancy dipole $(O^{2-} - \mathcal{V}_F)$ which is another form of oxygen-related impurities. The energy of reaction was calculated as ~ 0.6 eV for BaF_2 crystal.

- In general, BaF_2 crystals were contaminated by cation impurities, especially by rare earth impurities. The cation impurity exists in the more stable complex of next nearest neighbor cation substitutional-fluoride interstitial pair $(M_{Ba}^{3+} \cdot F_i^-)$ illustrated in

(a): $(M_{Ba}^{3+} \cdot O_F^{2-})$

M_{Ba}^{3+}

F^-

O_F^{2-}

$\mathcal{V}_F$

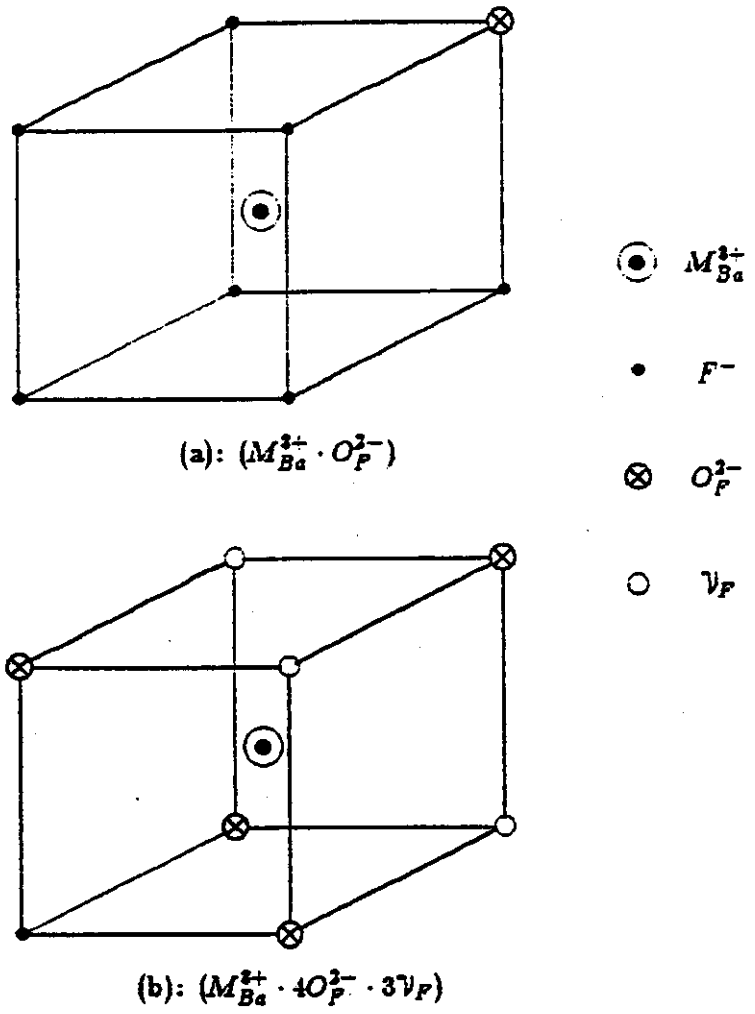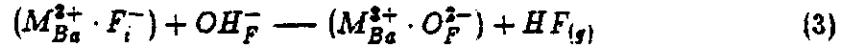(b): $(M_{Ba}^{3+} \cdot 4O_F^{2-} \cdot 3\mathcal{V}_F)$

Figure 1: The structure of the oxygen compensators

Fig.1(a). Thus the OH^- ion will diffuse through the crystal to the dopant interstitial complexes and reaction occurs at the trivalent ion site,

$$(M_{Ba}^{3+} \cdot F_i^-) + OH_F^- \longrightarrow (M_{Ba}^{3+} \cdot O_F^{2-}) + HF_{(g)} \tag{3}$$
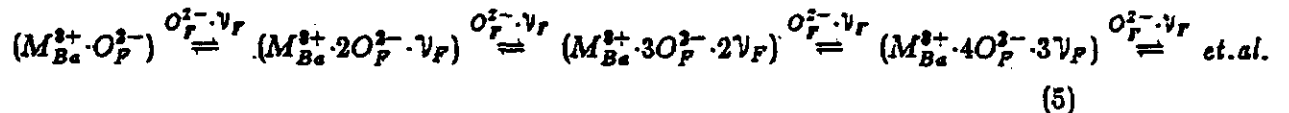
to generate the $(M_{Ba}^{3+} \cdot O_F^{2-})$ cluster plus internally produced HF and obtained energies of ~ 2.7 eV for BaF_2 crystal. We conclude therefore that for the hydrolysis reaction, kinetic barriers are present only for the hydrolysis reaction at the surface and for diffusion of the OH^- anion through the lattice. We estimate the energies for both these processes as ~ 0.9 eV. Reaction of F_i^- with OH_F^- in eq.(2) is highly exothermic as well as $F_i^- - \mathcal{V}_F$ recombination in eq.(3), which should provide enough of a driving force to overcome these kinetic barriers.

While the substitutional O_F^{2-} ion is expected to be immobile. At higher temperature, the diffusion of O_P^{2-} ion may more rapid. Another pathway could involve the migration of O_F^{2-} to form the oxygen compensation $(M_{Ba}^{3+} \cdot O_F^{2-})$ cluster. It is to say that O_F^{2-} ion can migrate to the trivalent dopant such as rare earth impurity (requiring the presence of $\mathcal{V}_F$ defects) to recombine with $(M_{Ba}^{3+} \cdot F_i^-)$ defect pair at the trivalent ion site,

$$(M_{Ba}^{3+} \cdot F_i^-) + O_P^{2-} + \mathcal{V}_F \longrightarrow (M_{Ba}^{3+} \cdot O_F^{2-}) + F_F^- \tag{4}$$

With additional oxygen incorporation, the formation of the higher order oxygen compensated sites will occurred,

$$(M_{Ba}^{3+} \cdot O_P^{2-}) \overset{O_F^{2-} \cdot \mathcal{V}_F}{=\!=} (M_{Ba}^{3+} \cdot 2O_F^{2-} \cdot \mathcal{V}_F) \overset{O_F^{2-} \cdot \mathcal{V}_F}{=\!=} (M_{Ba}^{3+} \cdot 3O_F^{2-} \cdot 2\mathcal{V}_F) \overset{O_F^{2-} \cdot \mathcal{V}_F}{=\!=} (M_{Ba}^{3+} \cdot 4O_F^{2-} \cdot 3\mathcal{V}_F) \overset{O_F^{2-} \cdot \mathcal{V}_F}{=\!=} et.al. \tag{5}$$

ENDOR studies[6] have identified the two major oxygen compensated sites as $(M_{Ba}^{3+} \cdot O_F^{2-})$ and $(M_{Ba}^{3+} \cdot 4O_F^{2-} \cdot 3\mathcal{V}_F)$ clusters (as shown in Fig.1 (a) and (b), respectively). These clusters correspond to the colloids (microscopic inclusions) was observed in the trace element and microstructural analysis at Charles Evans and Associates[6].

4

In summary, the oxygen-related impurities presenting in *as-grown* BaF_2 crystals may mainly be divided into following three type states:

- Hydroxyl groups: OH^-

- Oxygen-vacancy dipoles: $O_F^{2-} \cdot \mathcal{V}_F$

- Oxygen compensators: $(M_{Ba}^{3+} \cdot O_F^{2-})$ and $(M_{Ba}^{3+} \cdot 4O_F^{2-} \cdot 3\mathcal{V}_F)$ et. al.

3 The Electron Structure of O^--related Impurities

The mechanism for the absorption of the O^- impurity in BaF_2 is believed to be due to a charge-transfer transition between the impurity energy levels (O^- 2p) and the conduction band (Ba^{2+} 6s, 5d) or valence band (F^- 2p). The calculated electron structure of O^- impurity is illustrated in Fig. 2. Below the conduction band 1.2 ~ 2.6 eV the localized exciton bands are formed by hybridization between O^- 3s and Ba^{2+} 6s. It is clear that the absorption bands caused by the transitions between O^- impurity energy levels and conduction bands locate at the UV region of 200 nm ~ 270 nm which would degrade the transmission of the scintillate light of BaF_2.

4 The Process and Characterization of Radiation-induced Point Defects in BaF_2

Under irradiation by charged particles (e^-, p^+) and photons, the ionization is the predominant interaction with BaF_2 material. The processes of radiation-induced point defects in crystal are summarized in the following radiolysis:

1. The intrinsic color centers are created and annihilated under irradiation at room temperature. It is well known the F centers and V_k centers are unstable at room temperature due to their annealing temperature being about 40K and 120K, respectively. Although more than 1000 $F - V_k$ center pairs per photon are created. If not stabilized by other impurity traps, they will immediately annihilate at room temperature. The aggregated M centers from F centers will probably present in BaF_2. Their absorption peak positions were collected in Tab.1. It is to note that
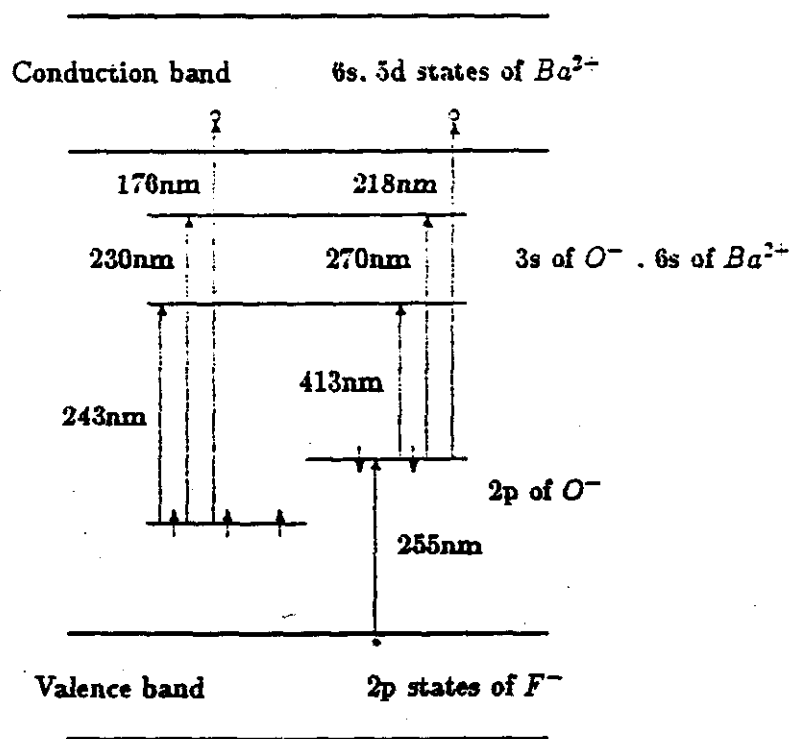
5

Figure 2: The band structure of $BaF_2 : O^-$ and the UV absorption mechanisms

the intrinsic lattice vacancies do not give rise to the absorption in the region between visible and UV light.

Tab.1 The absorption bands of intrinsic color centers in BaF_2

Color center	Absorption band λ (nm)
F	611
M	720
V_k	336
	750

2. The substitutional OH^- ion is decomposed through radiolysis to form substitutional O^- ion,

$$OH_F^- \overset{\gamma-ray}{\rightleftharpoons} O_F^- + H_i^0 \qquad (6)$$

subsequently, H_i^0 converts to the U center

$$H_i^0 + F \, center \overset{\gamma-ray}{\rightleftharpoons} H_F^- \qquad (7)$$

The radiation-induced decomposition of OH^- ion giving interstitial atomic hydrogen or U center as well as O^- centers has been observed in IR[3] and EPR[5] spectra in BaF_2 crystal. It can be assumed that during irradiation the interstitial hydrogen atoms are able to move a few fluorine cubes away from the O^- cites resulting in a distribution of the oxygen-hydrogen distances. That these reversible reactions of eq.5 and eq.6 are favorable at high temperature was observed in ESR experiment by J. I. Pena et. al.[7].

3. The $O^{2-} \cdot \mathcal{V}_F$ dipolar center will be converted into $O_F^- \cdot F$ center dipole which is instable at room temperature through radiolysis to generate O^- center and F center,

$$(O_F^{2-} \cdot \mathcal{V}_F) \overset{\gamma-ray}{\longrightarrow} (O_F^- \cdot F) \longrightarrow O_F^- + F \, center \qquad (8)$$
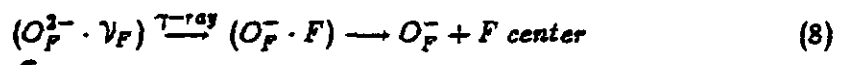
The F centers will be annihilated at room temperature. Then the isolated O^- substitutional will be formed rather than the oxygen-F center dipole. The $O^{2-} \cdot \mathcal{V}_F$

7

dipolar center may trap an electron to form $O_P^{2-} \cdot F$ center $(F_H(O^{2-}))$ which is instable

$$(O_P^{2-} \cdot \mathcal{V}_F) + e \xrightarrow{\gamma-ray} (O_P^{2-} \cdot F) \tag{9}$$
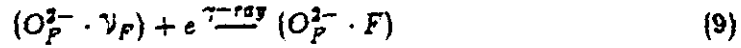
Trapping an F center the $F_H(O^{2-})$ center transforms the stable $F_{2H}(O^{2-})$ center: $(O_P^{2-} \cdot F_2)$ at room temperature.

$$(O_P^{2-} \cdot F) \xrightarrow{+F\ center\ 350K} (O_P^{2-} \cdot F_2) \tag{10}$$
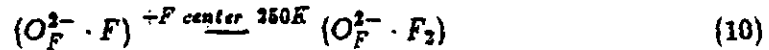
4. Because of the stabilization of oxide anions by trivalent cation dopants, oxygen incorporation occurs readily in impure crystals by a hydrolysis reaction. The species initially generated will be the $(M_{Ba}^{3+} \cdot O_P^{2-})$ center. On irradiation by γ-rays, the electron-hole pairs aggregate at the $(M_{Ba}^{3+} \cdot O_P^{2-})$ center to form $(M_{Ba}^{2+} \cdot O_P^{-})$ center which can be considered as O_P^- ion perturbed by M_{Ba}^{2+} cation. The difference between the optical absorption energy of $(M_{Ba}^{2+} \cdot O_P^{-})$ and that of isolated O_P^- ion, will be small. A model for the oxygen compensator is proposed to explain the experimental result which represented in Fig.3.

For the radiation-induced defects form the higher order oxygen compensators (such as $(M_{Ba}^{2+} \cdot 4O_P^{2-} \cdot 3\mathcal{V}_F)$), we are still difficult to understand them due to their complexity and for a moment we designate the radiation-induced defects form higher order oxygen-compensators as rose centers which are expected to have an absorption band about 500 nm. These centers will be predominant in heavy doped crystals.

In conclusion, the radiation-induced defects from oxygen-related impurities mainly are the following defects:

- the isolated substitutional O^- ions and the perturbed O^- ions corresponding to the 190-250 nm absorption bands

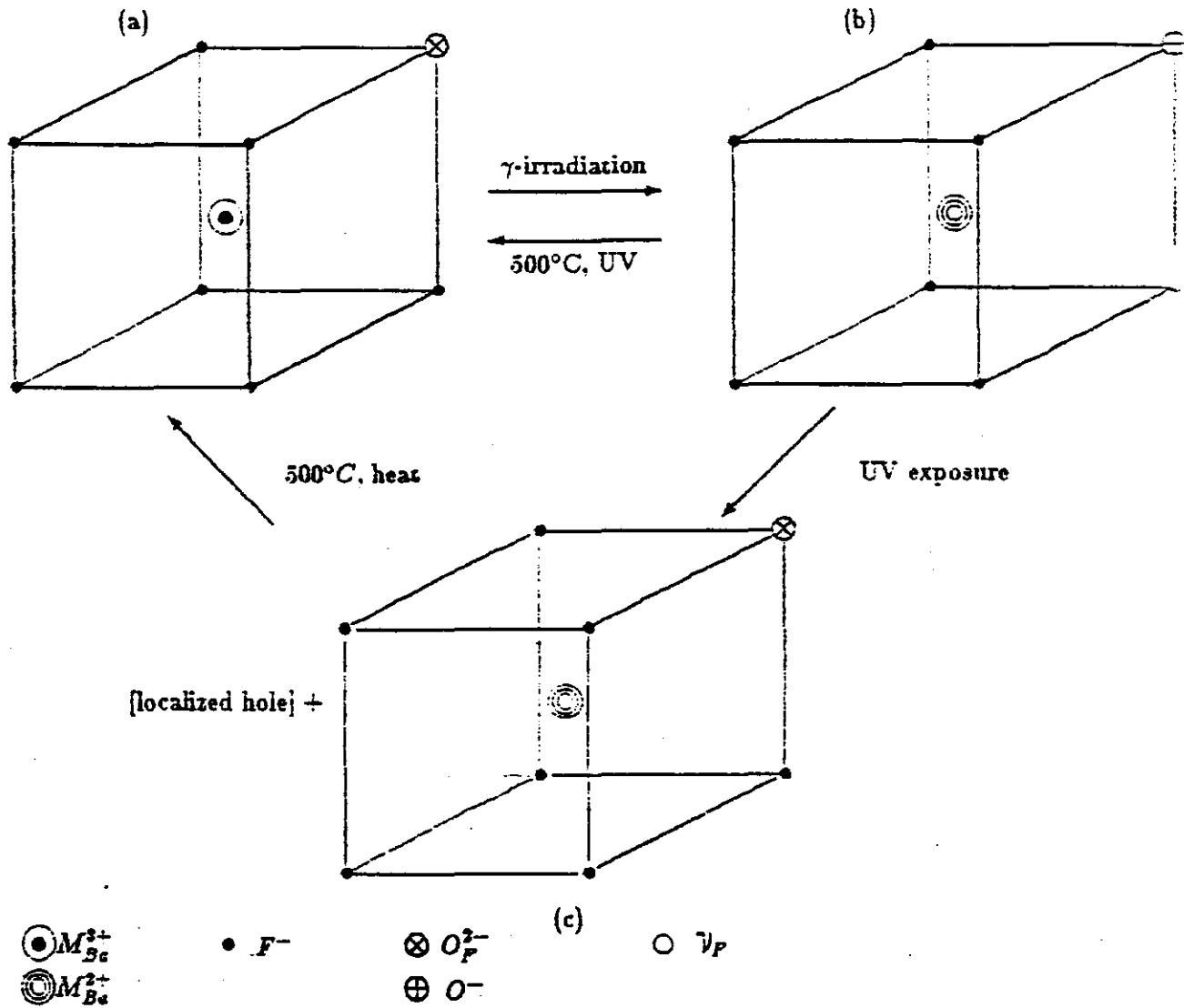- the $F_{2H}(O^{2-})$ and M center et. al. color centers corresponding to the visible absorption.

(a)

(b)

γ-irradiation

500°C, UV

500°C, heat

UV exposure

[localized hole] +

(c)

$\bigcirc\!\!\bullet\, M_{Ba}^{3+}$ $\bullet\ F^-$ $\otimes\ O_F^{2-}$ $\bigcirc\ \mathcal{V}_F$

$\bigcirc\!\!\bigcirc\, M_{Ba}^{2+}$ $\oplus\ O^-$

Figure 3: The Model of ionization and annealing of oxygen-compensater center in BaF_2

(a) $(M_{Ba}^{3+} \cdot O_F^{2-})$ center before γ-irradiation.

(b) $(M_{Ba}^{2+} \cdot O_F^{-})$ center (electron-hole aggregate) after γ-irradiation.

(c) UV exposure after post-γ-irradiation liberates the hole $(O^- \xrightarrow{UV} O^{2-} + hole)$ from the aggregate center. the hole diffuse and localizes at the lower-temperature traps.

(d) Subsquently heating anneals the $(M_{Ba}^{2+} \cdot O_F^-)$ center by delocalizing of the retrapped holes and their recombination with M_{Ba}^{2+} of the center shown at "(c)", i.e. $(hole + M_{Ba}^{2+} \longrightarrow M_{Ba}^{2+*} \longrightarrow M_{Ba}^{3+} + TL)$. The remaining $(M_{Ba}^{2+} \cdot O_F^-)$ centers shown at "(b)", which have not been affected by UV photons, are completely annealled at 500°C by local recombination $O^- + M_{Ba}^{2+} \xrightarrow{500°C} O^{2-} + M_{Ba}^{3+*} \longrightarrow O^{2-} + M_{Ba}^{3+} + TL$.

The calculated absorption bands of impurities and radiation-induced point defects from oxygen-related centers are represented in Tab.2.

Tab.2 The absorption bands of oxygen-related impurities before and after irradiation

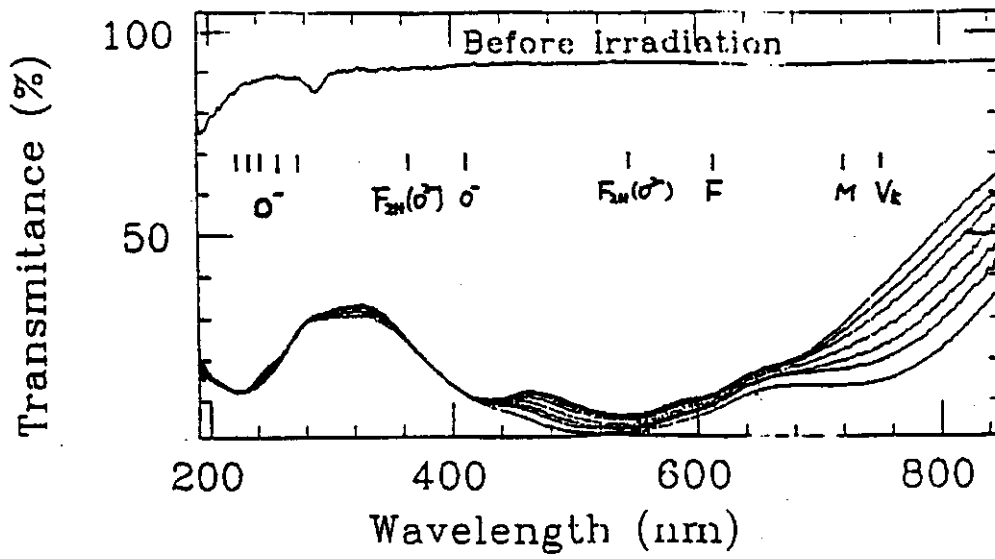| Oxygen-related impurities before irradiation	λ (nm)	Radiation-reduced oxygen centers	λ (nm)	
OH^-	191	O^-	176	
			218	230
O^{2-}	130		243	255
	200		270	413
	290	U	206	
$(M_{Ba}^{2+} \cdot O_F^{2-})$	?	$(M_{Ba}^{2+} \cdot O_F^-)$	200~270	
		Rose center	500 ?	
$O^{2-} \cdot \nu_F$	148	$F_{2H}(O^{2-})$	365	539
	188	$F_H(O^{2-})$	394	443

5 The Explanations for Several Key Observations

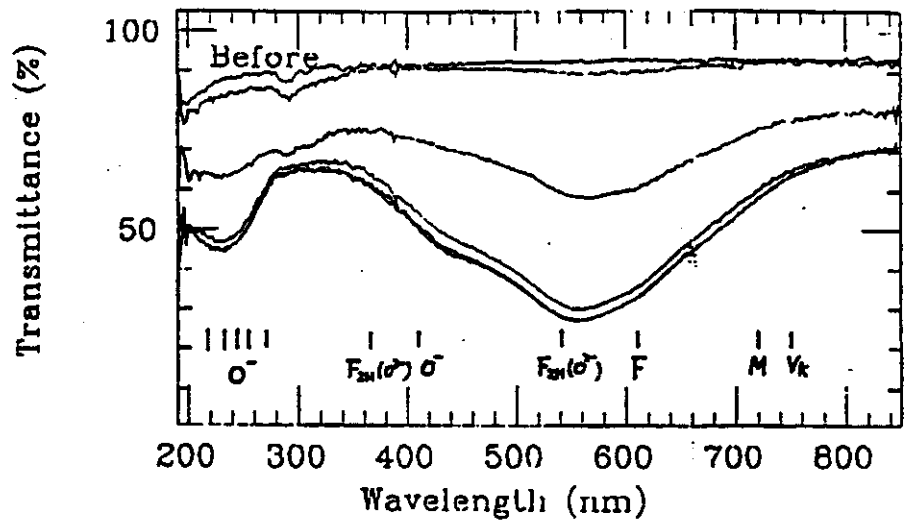1. Absorption spectra of γ-irradiated BaF_2.

   According to above analysis and Tab.2, we can give a satisfactory assignment of the absorption bands in Fig.1 and Fig.2 of [6] which is demonstrated in Fig.4.

2. Long recovery time constant of BaF_2 crystal at 220 nm after γ-ray irradiation.

   From the discussion in Section 4, we understand that the absorption bands near 220 nm are caused by the isolated O^- ion and the perturbed O^- ion which are very stable at room temperature. But the isolated O^{2-} ion cannot exist in crystals because of not preserving its electroneutrality and in its higher 2nd electron affinity. The hydrogen atoms nearby the O^- ions are move to a few fluorine cubes away from O^- ions resulting in a difficulty for the reversible reaction of equation 6 to occur. We conclude therefore that, under visible light exposure at room temperature, the

Transmittance (%)

Before irradiation

O^- $F_{2H}(O^-)$ O^- $F_{3H}(O^-)$ F   M V_k

50

200   400   600   800

Wavelength (nm)

Transmittance before and 0, 39, 69, 108, 150, 180
and 210 days after 1M Rads irradiation

100

Transmittance (%)

Before

50

O^- $F_{2H}(O^-)$ O^- $F_{3H}(O^-)$ F   M V_k

200   300   400   500   600   700   800

Wavelength (nm)

Transmittance before and after 100, 1k, 10k, 0.1M
and 1M Rads irradiation

Figure 4: The asignment of absorption bands of BaF_2 crystals

absorption bands at ~ 220 nm cannot be spontaneously bleached except for that of visible region caused by intrinsic color centers (such as F, M, V_k et. al). After exposure of UV ($\lambda < 250$ nm), O^- ion will be excited to liberate a localized hole

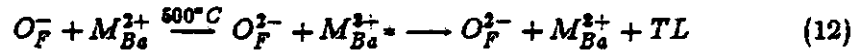$$O^- \xrightarrow{UV} (O^{2-} + localized\ hole) \longrightarrow O^- \tag{11}$$
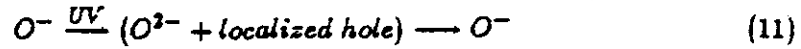
Under room temperature the localized hole cannot diffuse away from oxygen ion and will get retrapped into the oxygen ion.

For the dopant-oxygen compensator $(M_{Ba}^{2+} \cdot O_F^-)$, a similar model of annealing of the aggregate center is elucidated in Fig.2. The UV exposure at temperature higher than 370 °C will liberates the hole from the localized cite resulting in partial recovery of UV absorption.

3. No permanent damage by either photon or neutrons

- Fig.3 illustrates that the $(M_{Ba}^{2+} \cdot O_F^-)$ aggregate center will be recovered into $(M_{Ba}^{3+} \cdot O_F^{2-})$ center by recombination

$$O_F^- + M_{Ba}^{2+} \xrightarrow{500^\circ C} O_F^{2-} + M_{Ba}^{3+*} \longrightarrow O_F^{2-} + M_{Ba}^{2+} + TL \tag{12}$$

where TL designates the thermoluminescence.

- At high temperature, the substitutional O^{2-} ions are able to move rapidly in crystal resulting in destroying the $F_{2H}(O^{2-})$ centers.

- For isolated O^- ion, it will recombine with F center in annealing procedure at ~ 450 °C to form the $(O^{2-} - \mathcal{V}_F)$ center.

$$O_F^- + F \xrightarrow{heat} (O_F^{2-} \cdot \mathcal{V}_F) \tag{13}$$

We make therefore conclusion that all radiation-induced point defects and lattice point defects can be completely annealed at 500°C.

4. No or very small damage caused by fast neutrons

The interaction of neutron and solid state is mainly the elastic collision and inelastic which don't involve the ionization of matrix in contrast to the charged rays. These collisions should create the lattice vacancies to enhance the concentration of fluorine vacancies which could increase the light scattering rather than the absorption. The increase of scattering is limited after neutron-related at $10^{14} n/cm^2$. For the oxygen-induced defects, the concentration of the $(O^{2-} \cdot \mathcal{V}_F)$ dipole will be increase due to the conversion from OH^- ion rather than O^- ion could be generated. Indeed, the effect of fast neutron irradiation is very insignificant due to its small collision cross-section, resulting in very small damage.

6 Improving Radiation Resistance

From the discussion given above, it is clear that a number of radiation effects are seen in BaF_2 crystals grown in China, which could be caused by a few of impurities, especially the oxygen-related impurities. The intrinsic color centers (F, V_k and M etc.) and little number of point defects (F^- vacancy and interstitial F^- ion) are quite innocuous for the transmission of BaF_2 in the region of the scintillation emissions after irradiation, although a pronounced absorption band could be produced in the visible at low temperatures. Lots of trace cations (include Sr impurity) also do not apparently affect the transmission of BaF_2.

A majority of rare earth impurities give rise to the absorption at UV, but it was shown that lanthanum at the trace amount level < 1ppm did not seriously affect the radiation hardness. It should to note that trivalent rare earth impurities in BaF_2 crystal are known to enhance oxygen incorporation which degrades the radiation resistance of BaF_2. Therefore, to reduce or to eliminate the rare earth impurities is favorable. In principle, there is no reason that the transmission of the γ-ray radiated BaF_2 is less than 70% ~ 80%.

- Reactive Atmosphere

From the discussion in Section 3. We have known that oxygen incorporation in BaF_2

occurs by hydrolysis rather than oxidation. The hydrolysis reaction is presumed to follow a three-step process involving an intermediate OH^- species. Water gas plays a more significant role in these reactions than pure oxygen. An important feature of the hydrolysis reactions is the internal generation of HF. Of course, the hydrolysis reactions will in principle produced at sufficiently low partial pressure of HF. To depress the oxygen- incorporation into the bulk, the decrease of partial pressure of water and increase of one of HF in atmosphere which needn't the high vacuum, will be favored. The reducing reactive atmosphere can be obtained by replacing the oxygen scavenger agent by $NH_4F \cdot HF$ in the growth conditions.

- Cation Dopant Effects on Oxygen-related Color Center Formation in BaF_2

  Cation dopant effects on radiation damage have been extensively investigated, particularly for the rare earth and transition metal dopants[2]. The conclusion was that no dopant could apparently improve the radiation damage. Here we propose several potential dopants which could control the formation of O^{2-}-related color center according to our analysis.

    - Several cations (Li^+, Mg^{2+}, Sc^{3+} et. al.) may inhibit oxygen compensation formation. There may be a competition between these cations and rare earth ions for the available oxide ions resulting in their tight binding with O^{2-} ion without inducing O^- ion. Hence, the effects of these cation impurities depress the UV absorption when their concentration in the crystal becomes significantly larger (on the order of 100 ppm or more) than the corresponding concentrations of color centers and OH^- ions.

    - Particularly to note that, apart from above inhibition of oxygen compensation formation. Aluminum could be an efficient oxygen scavenger with the interconversion

    $$(O^{2-} \cdot \mathcal{V}_F) + (Al^{2-}_{Ba} \cdot F_i^-) = F_F^- + (Al^{3+}_{Ba} \cdot O_F^{2-}) \tag{14}$$
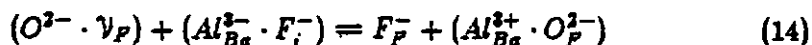
    displaced well to the right. Additionally, aluminum could form separate phase of its own which might impede oxygen incorporation onto BaF_2 surface.
    The doped crystals are being grown at SIC and BGRI.

- Removing of OH^- and O^- Ions in BaF_2 Crystals

  For the *as-grown* BaF_2 crystals contaminated by hydroxyl and oxygen impurities, it seems possible to remove the OH^- and O^- ions from crystals. From the discussion given above, the migration of OH^- and O^- in crystals very readily occurs at room temperature. The kinetic barriers for diffusion of OH^- and O^- which are assumed to be identical to their interaction with lattice ions are estimated as 0.9 eV slightly less than 1 eV for F^-. It is to say that the diffusion coefficients of OH^- and O^- are slightly greater than that of F^-. This situation indicates us to exert an external force on the crystals to expel the OH^- and O^- impurities. The exertion of strong electric field is under our recent investigation. The fundamental result is interesting.

  In conclusion, based on the full understanding of the mechanism of radiation damage in BaF_2, to solve the problem of radiation damage is very promising

References

1. P. J. Li, *et. al.*, **GEM internal note GEM TN-92-77**, March 1992;
   Z. W. Yin, Talk given in First East Asia/Pacific - US Symposium on SSC, May 1992.

2. G. Chen, *et. al.*, **GEM Internal note GEM TN-92-78**, March 1992.

3. L. M. Wang, *et. al.*, *The Optical and Radiation Damage Properties of Barium Fluoride Crystals*, Talk presented in Shanghai BaF_2 Workshop, Shanghai, May 1991.
   L. Y. Chen *et. al.*, *The Radiation Damage of BaF_2 Crystals*, talk prepared for GEM BaF_2 Panel meeting, Shanghai, December 1991.
   L. Y. Chen *et. al.*, **GEM internal note GEM TN-92-129**, June 1992.

4. L. Halliburtoon *et. al.*, *Identification and Characterization of Radiation-Induced Point Defects in BaF_2*, University of West Virginia Optoelectronics Group Technical Reports, April - June 1992.

5. Reddy T. R.; *et. al.* **Phys. Lett. A 36**, 231, 1971.

6. Ren-yuan Zhu, *"Answers to PAC'S Questions Concerning Barium Fluoride"*, July 6, 1992

7. J. I. Pena, *et. al.*, **J. Phys. Chem. Solids, vol. 49**, 3, 1988.