GEM TN-92-129

Radiation Effect in Hydrolyzed Barium Fluoride Crystal

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June 18, 1992

Abstract:

With SCC-DV-X_α theoretical calculations, we have found that U, OH^-, O^- and O^{2-} centers would be the potential causes of γ-irradiation damage in BaF_2 crystals. For better understanding of their behavior in actual processes, radiation effects in hydrolyzed BaF_2 was investigated. Thermal annealing of BaF_2 samples in air above 900° C was performed. The characteristics of optical absorption curves of samples before and after γ-irradiation with doses of 1 x 10^6 rad were determined in the VUV, UV and IR regions. The results demonstrate that OH^- ion can be incorporated into BaF_2 by means of hydrolysis, with an absorption maximum at 192 nm and a complex absorption band in the IR region between 3100 ~ 3700 cm^{-1}. In the VUV region, the absorption edge shifts towards lower energy from 134 nm to 150 nm. The latter is close to that of the samples grown at low vacuum. After irradiation, several new absorption peaks at 204 nm and ~ 240 nm corresponding to U and O^- centers, respectively, were observed. An explanation is given in terms of OH^- and $O^{2-}\bullet V_\alpha$ decomposition through radialysis to form U, O^- and F-related centers, which correspond to the 793.75 cm^{-1} absorption in IR, ~ 240 nm and ~670 nm absorption bands respectively.

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Abstract

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1 Introduction

BaF_2 is the fastest scintillator known with its fast decay time of 0.6 ns at 220 nm wavelength, and could be used as electromagnetic colorimeter for high counting rates mesurement.

As we know most BaF_2 crystals generally available exist a serious radiation damage where the radiation dosage is high. The damage results in the reduction of both its optical transmission and scintillation light output, and become an extremely important issue for its application such as at the SSC. There are indications that the radiation damage in BaF_2 crystal relates to oxygen[1-3]. We believe that the hydrolysis process is a possible way for oxygen incorporated into the BaF_2. The purpose of the present work is to investigate the radiation effect in hydrolysed BaF_2. We hope it would be helpful to understand the mechanism of the radiation damage in BaF_2.

2 Theoretical Research

The electronic structures of impurities in BaF_2 were calculated with self-consistent-charge discrete variational method (SCC-DV-X_α)[4]. The calculations were performed on the embedded molecular cluster (EMC) models. In the case of anion impurity, the cluster was chosen with the form of $[ABa_4F_6]^{n+}$, where A was a substitutional impurity occupying a centric F^- site and n corresponded to the valence of the cluster. The basis functions employed were single site orbitals (SSO)[5]. The long-range coulomb interactions of BaF_2 crystal were included, by surrounding the EMC with point charge of $5 \sim 6$ shells.

Since it is known that hydroxyl and oxygen impurities could be incorporated into the bulk by means of hydrolysis process, particular attention has been paid to them. The absorption bands of color centres, hydroxyl and oxygen impurity centres are summarized in Tab. 1.

Tab.1 The absorption peaks of the color centres, hydroxyl and oxygen impurty centres

Color centres	λ (nm)	Color centres	λ (nm)	
F	611	O^{2-}	130	
			200	
M	720		290	
V_K	336	$O^{2-}\cdot V_a$	123	148
	750		127	188
U	206	$F_H(O^{2-})$	394	
OH^-	191		443	
O^-	175	$F_{2H}(O^{2-})$	365	
	230		539	
	413			

From the above results we know that U,OH^-, O^- and O^{2-} centres would be all the possible sources for the damage in BaF_2, since they have the absorption bands near 220 nm. But we need to make it clear what would be the main one that results in the radiation damage in actual process.

3 Experimental Results and Discussion

3.1 Experimental Procedure

The BaF_2 crystals used in our experiment were provided by Shanghai Institute of Ceramics. One is $1^{\#}$ BaF_2 grown in recent experiment, and the other is $2^{\#}$ BaF_2 grown at low vacuum. All the samples were processed to the thickness of 2 mm. Some were treated in air above 900 $^{\circ}C$. The characteristics of optical absorption curves of samples

before and after γ -irradiation were obtained in the regions of VUV, UV and IR with Acton VM 505, Graphicord UV-204 and Nicolet DX-V 5.07 Spectrophotometres. The radiation test was performed with the dose of 1×10^6 rad.

3.2 Optical Absorption Spectra of Hydrolysed BaF_2

The UV absorption curves of $1^{\#}$ sample which had been treated in air with different time were shown in Fig. 1. From these spectra we can see that the absorptions at low wavelength are much strong. These phenomena are quite similar to the absorption in large BaF_2 generally available. When we prolonged the heating time, an absorption peak at 192 nm appeared. The position was just situated at OH^- absorption band obtained by our theoretical study. We proposed that OH^- can incorporated into BaF_2 by means of hydrolysis process.

The absorption band in IR region between $3100 \sim 3700$ cm^{-1} obtained in our experiment also shown the present of OH^- in hydrolysed BaF_2 (see Fig. 2). It is known that OH^- occupying a fluoride site in BaF_2 has an absorption band at 3630 cm^{-1} corresponding its stretching mode.[2] While the OH^- act as an interstitial trap to form OH^--interstitial centre, the O-H valence bond is elongated and shifts the corresponding absorption band towards low energy.

For the hydrolysed BaF_2 crystals, their VUV absorption edges shift towards lower energies from 134 nm to 150 nm (see Fig. 3). the edge of $2^{\#}$ sample grown at low vacuum is situated at 148 nm near to the hydrolysed BaF_2. It seems to be reasonable to consider that the $2^{\#}$ sample is contaminated by hydroxyl or oxygen impurities.

From the above results we get an impression that OH^- are very easy to enter into BaF_2 crystals by means of hydrolysed process,and oxygen probably can also get into the bulk through this process to form O^{2-}-V_a centre.

3.3 Radiation Effect In Hydrolysed BaF_2

The absorption spectra from VUV to UV between hydrolysed and as grown BaF_2 before and after γ -irradiation were shown in Fig. 4 and Fig. 5. From the spectra we can see that the hydrolysed one exists a serious radiation damage. although no obvious absorption at 192 nm was found before irradiation. The results indicate that only a small

amount of hydroxyl or oxygen impurities can lead to a serious radiation damage in BaF_2. Concerning our theoretical analysis, we proposed that after irradiation the absorption bands of hydrolysed BaF_2 situated at 204 nm and ~ 240 nm corresponded to U and O^- centres respectively, which might be produced by the following radiolysis processes.

(1) The OH^- was decomposed through radiolysis to form U and O^- centres

$$OH^- \longrightarrow \begin{cases} H_i^0 + O_s^- & \text{or} \\ H_s^- + O_i^0 \end{cases}$$

This hypothesis was further confirmed by the the absorption at 793.75 cm^{-1} in IR spectra (see Fig. 6) originated from the U centre.

(2) The O^{2-}-V_a was decomposed through radiolysis to form O^- and F-related centres:

$$O^{2-} + V_a \longrightarrow O^- + F$$

The absorption spectra of hydrolysed BaF_2 before and after irradiation are shown in Fig. 7. The spectra demonstrate that after irradiation three absorption bands appeared. The absorption at ~ 240 nm and ~ 670 nm can explained by O^- and F-related centres.

4 Conclusion

From above discussion, it is emerged a clear picture that hydroxyl and oxygen impurities are very easy to enter into BaF_2 by means of hydrolysis process, and only a small amount of hydroxyl and oxygen impurities can result in a serious radiation damage in BaF_2. The mechanism of radiation damage in hydrolysed BaF_2 can be explained in Tab. 2.

Tab.2 The mechanism of radiation damage in hydrolysed BaF_2

Before Irradiation		After Irradiation
OH^- : 192 nm	$\longrightarrow$	U : 204 nm O^- : ~240 nm
$O^{2-}V_a$: 148 nm	$\longrightarrow$	O^- : ~240 nm F-related centre : ~670 nm

If we can find a way that can destroy the above radiolysis processes. The radiation damage resulted from hydroxyl and oxygen impurities can be controlled.

It is obvious that hydroxyl and oxygen impurities are harmful to the radiation damage in BaF_2. On the other hand, it should be considered that the radiation damage in BaF_2 could also be affected by other trace elements. Their effects will be further investigated in our next work.

Acknowledgements

The authors would like to acknowledge Prof. Z. W. Yin, Prof. P. J. Li for providing BaF_2 and their stimulating discussions. This work was supported by the National Science Foundation of China and the contract **191-750-31**.

References

1. L.M.Wang, L.Y.Chen, M.Gu, K.H.Xiang,J.Du and X.Wu, The Optical and Radiation Damage Properties of BaF_2, BaF_2 Precision Electromagnetic Calorimeter Workshop, Shanghai and Beijing, China, May 27-June 1, 1991

2. P.J.Li, Y.Y.Xie, Y.L.Zhao and Z.W.Yin, Radiation Damage in Large Barium Fluoride Crystal, GEM TN-92-77

3. G.Chen, H.Xiao, S.Q.Man, J.Q.Zhang and S.X.Ren, Radiation Damage of Rare Earth Ions Doped Barium Fluoride Crystal, GEM TN-92-78

4. A.Rosen, D.E.Ellis, J. Chem. Phys. 65(1976) 3629

5. F.W.Averill, D.E.Ellis, J. Chem. Phys. 59(1973)6412

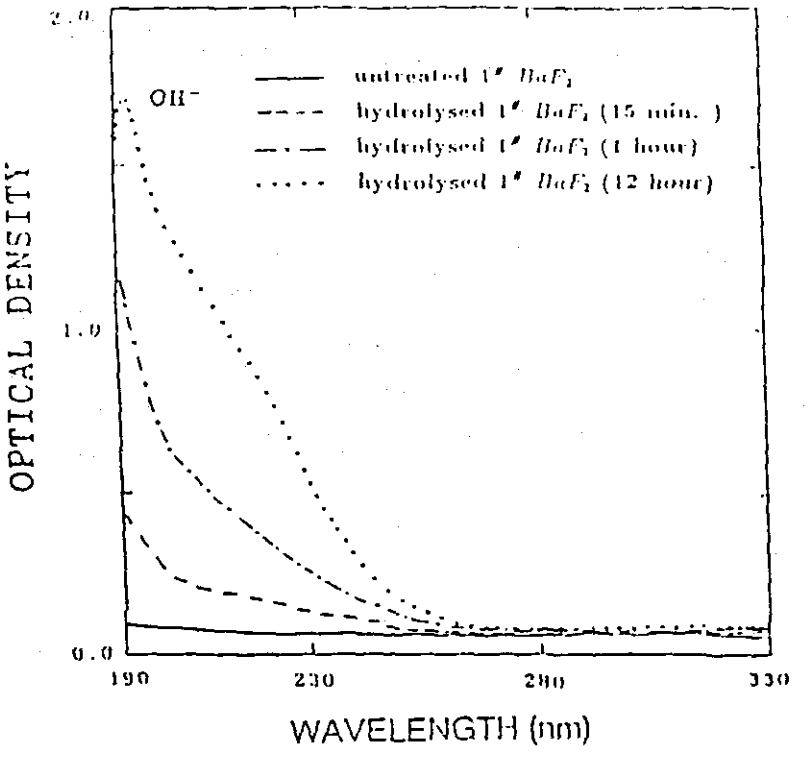

Fig. 1. Absorption spectra for different hydrolysed 1# BaF_2

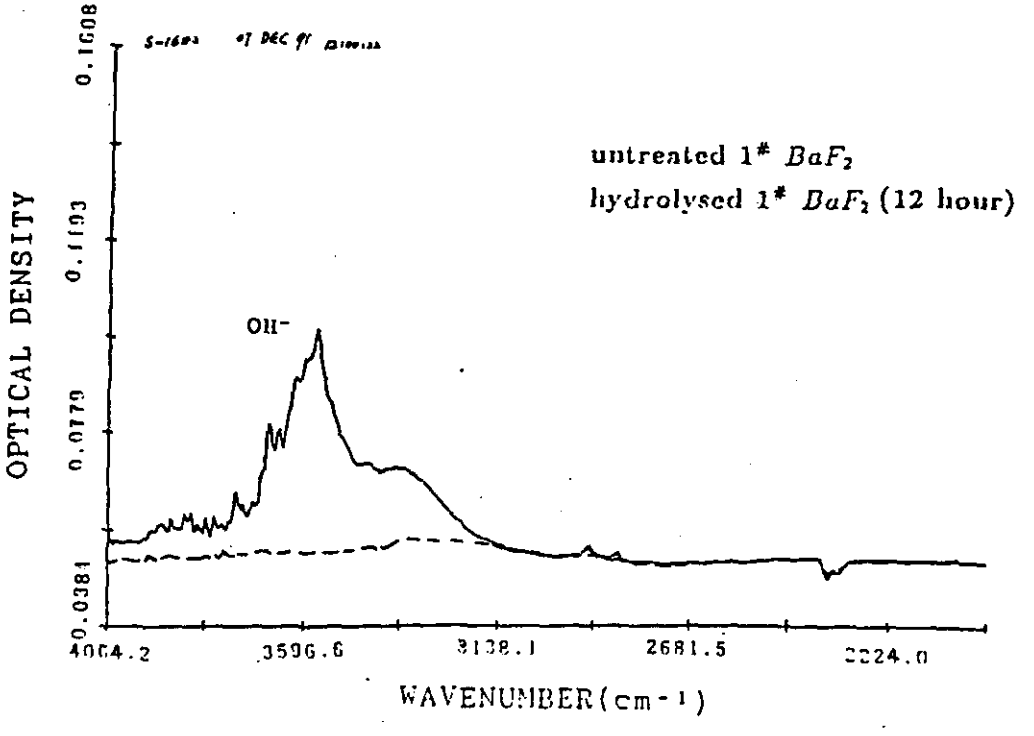

Fig. 2. Infrared spectra for hydrolysed and untreated 1# BaF_2

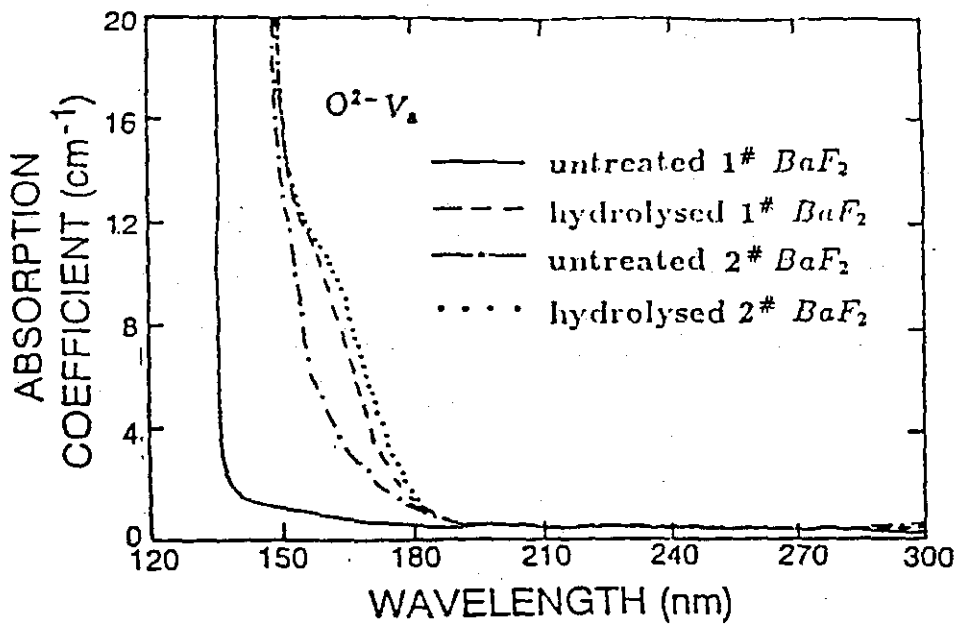

Fig. 3. VUV absorption for hydrolysed and untreated BaF_2

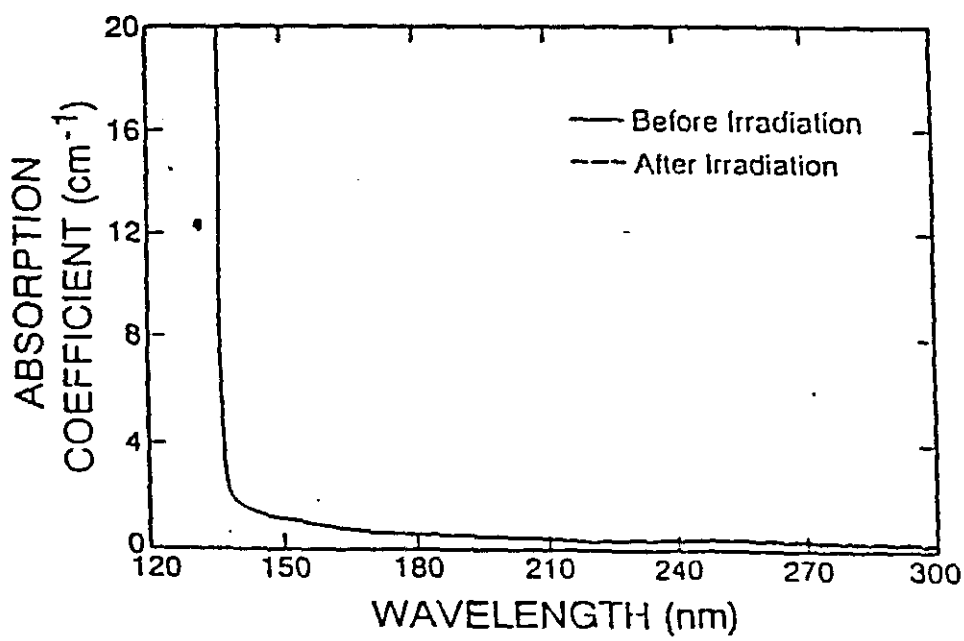

Fig. 4. Absorption spectra of 1# BaF_2 before and after irradiation

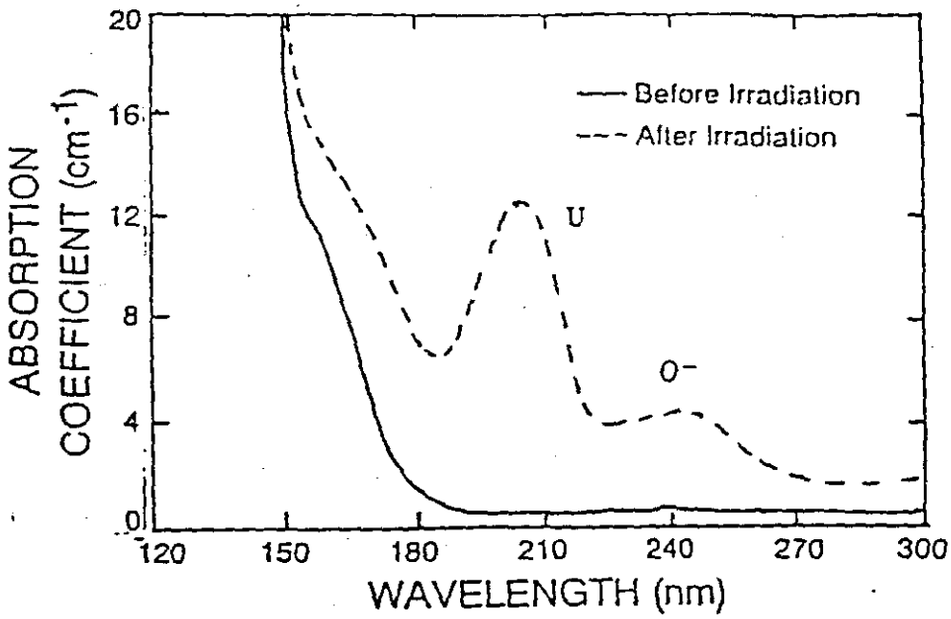

Fig. 5. Absorption spectra of hydrolysed 1# BaF_2 before and after irradiation

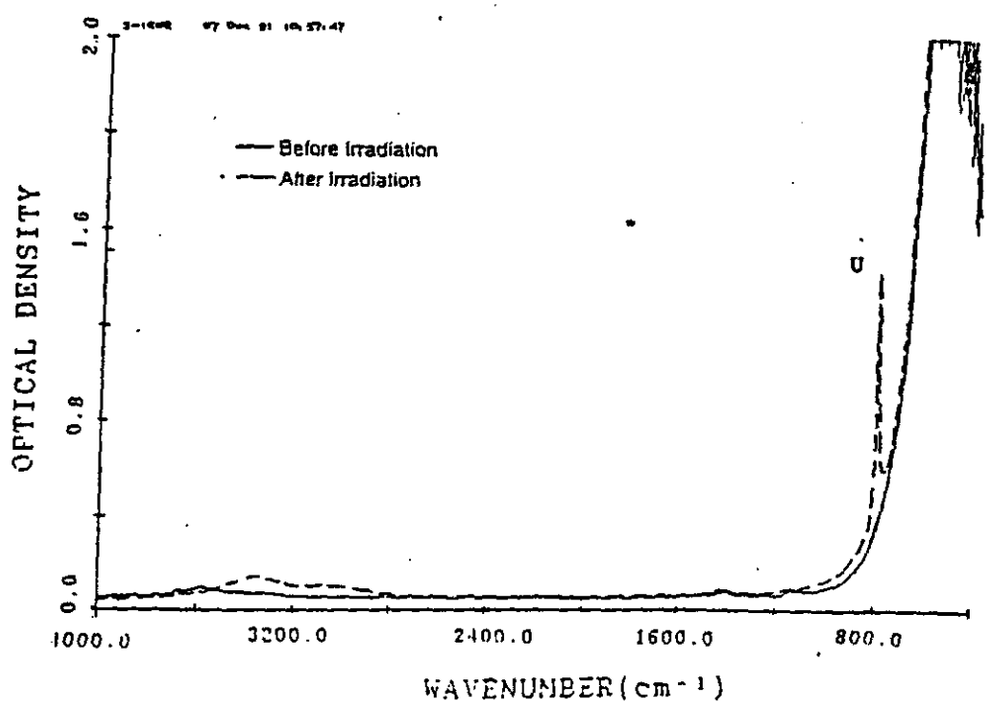

Fig. 6. IR Absorption spectra for hydrolysed 1# BaF_2 before and after irradiation

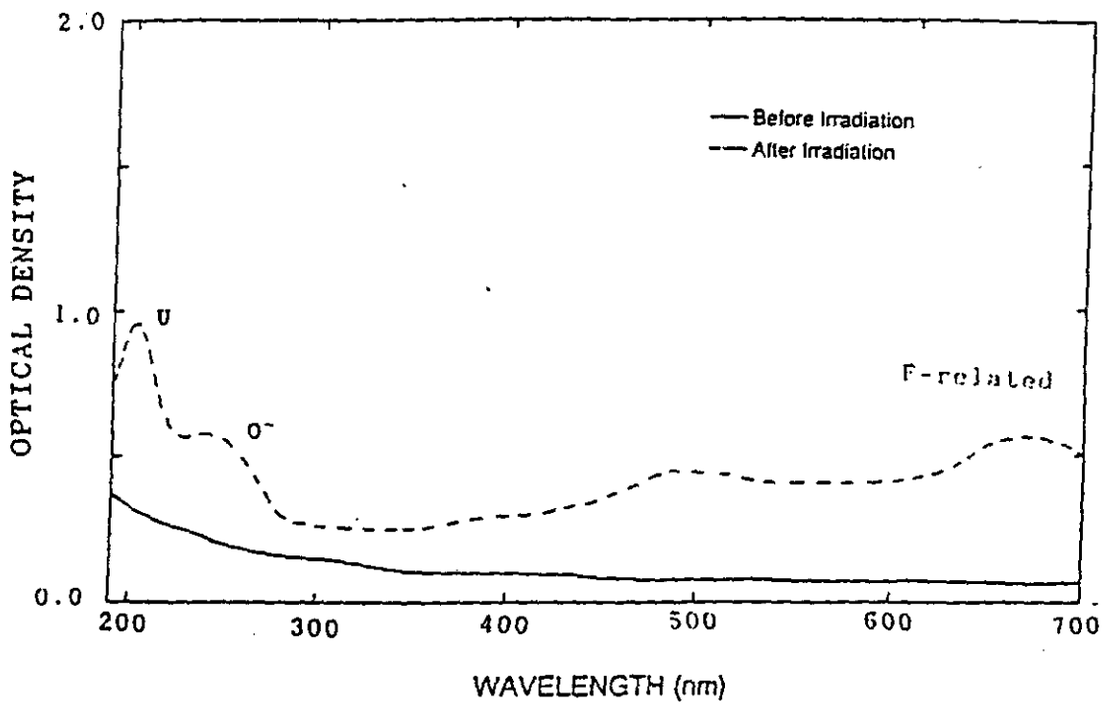

Fig. 7. Absorption spectra for hydrolysed 1# BaF_2 before and after irradiation