RADIATION DAMAGE MECHANISMS IN SCINTILLATOR MATERIALS:
APPLICATIONS TO BaF2 AND CeF3

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ABSTRACT

Results from recent radiation damage studies in high quality BaF2 and CeF3 crystals are presented. Optical absorption and electron paramagnetic resonance (EPR) techniques are used to identify specific radiation damage mechanisms. Specific attention is given to the role of oxygen and hydrogen in the room temperature damage of BaF2. Also, Mn2+ ions are shown to change valence state in BaF2 during room temperature irradiation. Numerous optical absorption bands are created in CeF3 during irradiations at low temperature. These bands are associated with electron traps (either F centers or Ce2+ ions) and they thermal anneal below room temperature. An EPR spectrum, assigned to F centers, is observed in low-temperature irradiated CeF3.

I. INTRODUCTION

Nearly all scintillator materials exhibit radiation damage when exposed to sufficiently high radiation fields. There are, in general, two categories of damage mechanisms. In typical halide materials, the radiolysis process produces widely separated vacancies and interstitials (e.g., F centers and H centers) by an exciton relaxation mechanism. This process is present even in "perfect" crystals. A more pervasive, damage process involves the trapping of radiation-induced holes and electrons at native defects and impurities introduced into the crystal during growth. Transition-metal ions and rare earth ions are found in most scintillator materials at the part-per-million level. This is also true for hydrogen and vacancies. Ionizing radiation redistributes the electrons among these impurities and native defects, and the resulting valence changes result in unwanted optical absorption bands.

Spectroscopic techniques, such as optical absorption, luminescence, and magnetic resonance (EPR and ENDOR) provide sensitive, high resolution approaches to identify and characterize the various defects formed by radiation in scintillator materials. It is important to determine the model of each major defect and how it is produced and annihilated. Thermal stability is a key parameter since many defects are stable only at low temperature, but they still can cause significant transient absorption or luminescence at room temperature.

In the present paper, we describe a series of experimental results obtained from high-quality BaF2 and CeF3 crystal irradiated either at room temperature or below. A mechanism is proposed whereby OH- ions in BaF2 are dissociated by radiation to form an absorption band in the 200-nm region. The effects of low-temperature irradiation of CeF3 also is reported.
II. RESULTS FROM BaF₂ CRYSTALS

A. Low-Temperature Irradiation

Optical absorption and EPR results were obtained from a typical high-quality BaF₂ crystal irradiated near liquid-nitrogen temperature. In these low-temperature experiments, the sample size was 2 x 3 x 5 mm³ and the source of radiation was an x-ray tube operating at 60 kV and 30 mA. The optical absorption trace in Fig. 1, taken at 80 K after an irradiation at 80 K, shows a broad F center peak near 550 nm and a Vₖ center peak near 360 nm. Most, if not all, of the absorption around 200 nm was due to the silica windows on our low temperature optical Dewar. The most important features in Fig. 1 are the shifts of the F center and Vₖ center peaks from their quoted values in the literature. The literature values are 611 nm for the F center and 336 nm for the Vₖ center. These shifts suggest that the two defects may have a neighboring impurity that perturbs the defect.

Two intense EPR spectra are observed in a BaF₂ crystal after exposure to x rays at 77 K. Figure 2 shows these spectra taken at 77 K with the magnetic field along the [110] direction. The intense, widely-separated lines are from the Vₖ center and the weaker set of lines in the center region are from the F center. Even though the signals from the two centers appear to represent quite different concentrations, this is not the case because of differing linewidths. Actually, the two centers have comparable concentrations. When the magnetic field is along the [100] direction, the Vₖ center spectrum shows a splitting in the lines indicating there are two variations of Vₖ centers in the sample. Warming the sample to room temperature destroys all of the Vₖ and F centers that had been induced by the low-temperature irradiation.

Since there are no absorption bands associated with the F center and the Vₖ center in the 200-nm region and since these defects are not stable at room temperature, we do not believe they are directly associated with the problems encountered in using BaF₂ as a scintillator.
B. Room-Temperature Irradiation

The important question in BaF$_2$ is the identity of the defect (or defects) responsible for the optical absorption in the 200 to 220 nm region following a room temperature irradiation. In addition to identifying the responsible defect(s), it would also be useful to determine the mechanism leading to the formation of the absorbing center(s).

From the extensive literature [1] on defects in alkaline-earth fluorides, i.e., CaF$_2$, SrF$_2$, and BaF$_2$, it is obvious that attention should be focused on two possible scenarios. The first of these involves substitutional impurity ions such as transition-metal ions (partially filled 3d shell) and rare-earth ions (partially filled 4f shell). These types of impurities can easily change valence state under irradiation and they have optical absorption bands throughout the visible and near ultraviolet. Every crystal is expected to have some of these impurities present, but the concentration may be very low if precautions are taken during preparation of the starting material for the crystal growth. The second possible scenario involves oxygen and hydrogen. These latter impurities can be introduced into the crystal from the atmosphere during preparation of starting materials and during growth.

A specific goal of our work at West Virginia University has been to obtain experimental evidence for one or the other of these two radiation damage scenarios. In this paper, we present results representing both possibilities. However, before reviewing these results, we describe in more detail how the oxygen/hydrogen mechanism might work.

First, we assume that oxygen and hydrogen are introduced into the crystal from the surrounding atmosphere during growth. The most likely mode of incorporation is OH$^-$ ions substituting for fluorine. Next, we assume that radiation at room temperature will do two things: 1) it will create via a radiolysis mechanism F centers and clusters of H centers and 2) it will dissociate the OH$^-$ ions into O$^-$ and H$_2$O centers. The rate of production of F centers is expected to be low, in agreement with the known difficulty of coloring barium fluoride. Thus, impurities that stabilize interstitials and allow F centers to be formed may play a critical role in the scintillator applications of barium fluoride. In support of this process we note that Bill and
Lacroix [2] observed O\textsuperscript{−} ions in CaF\textsubscript{2} after x-irradiation at room temperature. We then go on to suggest that a portion of the H\textsubscript{2}O centers that are produced by dissociating OH\textsuperscript{−} will, in turn, diffuse slowly through the lattice and recombine with F centers to form H\textsubscript{4}\textsuperscript{−} centers. These H\textsubscript{4}\textsuperscript{−} centers have a strong absorption band near 200 nm. In summary, we are suggesting a complex sequence of events beginning with OH\textsuperscript{−} ions and ending with H\textsubscript{4}\textsuperscript{−} centers as the mechanism for the production of ultraviolet absorption in barium fluoride. A crucial part of the sequence is the formation of F centers.

Based on the oxygen and hydrogen scenario, we suggest two ways to minimize the production of the 200-nm ultraviolet band. The obvious process is to prevent OH\textsuperscript{−} from entering the crystal during growth. Progress of this type has been made by the crystal growers. However, improvements in the crystal-growth procedures may fall short of achieving the desired levels of radiation hardness for future detectors. A second way to minimize the damage is to prevent the formation of F centers. This can perhaps be done by removing those impurities that stabilize the fluorine interstitials created coincidentally with the F centers. These impurities may be other alkaline-earth ions or they may be alkali ions.

1. Oxygen and Hydrogen Results

We have had only limited success in finding an EPR spectrum associated with either oxygen or hydrogen in the highest quality BaF\textsubscript{2} crystals following irradiation at room temperature. This is presumably because of the extremely low concentrations of any impurities in such crystals. Therefore, an alternate approach to studying oxygen and hydrogen was developed. Based on the work of Pena et al. [3], we introduced significant concentrations of oxygen and hydrogen into BaF\textsubscript{2} simply by heating the crystal in air. With samples treated in this manner, we explored the correlation between the presence of these impurities and the unwanted 200-220 nm absorption.

A sample of BaF\textsubscript{2}, grown in China, was cycled through a series of heat treatments, radiations, and thermal anneals while monitoring the EPR and optical absorption spectra at each stage. Before the heat treatment, there were no identifiable EPR or optical absorption spectra. The sample was then heated in air, held at 730°C for 2 hours, and slowly cooled. This heat treatment induced a small amount of optical absorption in the 200-300 nm region, as shown in Figure 3, but no EPR spectra. A 30-minute exposure to x-rays at room temperature induced very intense absorption bands in the 200-300 nm region, as shown in Figure 3, and also induced very intense EPR spectra, as shown in Figure 4. The data in Figure 4 were taken at 60 K with the magnetic field parallel to the [100] direction. The two sets of sharp lines near 3100 Gauss and 3600 Gauss are due to atomic hydrogen while the two intense lines in the center of the spectrum, at 3250 and 3380 Gauss, are believed to be due to an oxygen center. Thus, the heat treatment in air obviously introduced large concentrations of oxygen and hydrogen into the crystal. Furthermore, the EPR spectra identifying oxygen and hydrogen centers appear to correlate with the absorption in the 200-nm region. This latter observation is further substantiated by a thermal anneal performed after the irradiation. Annealing the sample at
500°C for two hours removed nearly all of the radiation-induced ultraviolet absorption, as shown in Figure 3, and it also removed all of the radiation-induced EPR spectra.

After the initial experiment on a heat-treated sample, we repeated the work several times on additional samples, always with the same results. Briefly stated, irradiation at room temperature with x-rays produces extremely intense ultraviolet absorption bands in the 200-230 nm range if the sample has been exposed to air while at a high temperature (i.e., approximately 700°C). At the same time that the radiation-induced uv bands appear, we find an intense EPR spectrum due to hydrogen atoms in the BaF₂. This hydrogen atom is occupying an interstitial site, as opposed to a substitutional site. Additional EPR spectra produced by the irradiation of a heat-treated sample are attributed to oxygen centers although no definitive proof of such models have been obtained. It is important to note that these radiation-induced uv bands in a heat-treated sample are easily bleached when the sample is exposed to room light for several hours.
The above-described results are interesting and they suggest the need for additional experiments. Among the questions that need to be answered are: 1) What is an optimum heat treatment temperature to introduce oxygen and hydrogen into the crystal, 2) What is an optimum radiation dose to convert the oxygen and hydrogen into ultraviolet-active defects, 3) What anneal temperature is required to destroy the oxygen and hydrogen related ultraviolet absorption bands introduced by radiation, 4) What are the optical bleaching characteristics of these ultraviolet bands, 5) What is the exact nature of the oxygen center giving rise to the EPR spectrum, i.e., what is the model for this defect, and 6) Which is more important, oxygen or hydrogen, in producing ultraviolet absorptions.

2. Comparison of Heat-Treated and Untreated Crystals

Although much of our effort has focused on the post-growth incorporation of hydrogen and oxygen in BaF₂ during heat treatments in air, it is the radiation response of untreated, as-grown crystals that is the real question. It is important to determine whether the intense radiation-induced ultraviolet bands in the specially heat-treated BaF₂ samples are the same as the weak radiation-induced ultraviolet bands in the as-grown high quality BaF₂ crystals. In other words, do they originate from the same point defects, do they involve the same impurities, and do they have the same production mechanisms?

Figure 5 shows the optical absorption from two high-quality BaF₂ samples grown in China. The treated sample had dimensions of 3 x 10 x 10 mm³ and was held at 800°C for 4 hours in air to introduce the oxygen and hydrogen into the crystal. This treated sample was x-rayed for 2 hours at room temperature and then its optical absorption spectrum was measured at room temperature. This resulted in the upper curve in Figure 5: it has significant absorption throughout the visible and near ultraviolet with an extremely intense peak going off scale below 230 nm. In contrast, the untreated sample had much larger dimensions (40 x 40 x 40 mm³) and was irradiated for 72 hours in a 60Co source on the campus of West Virginia University. The total gamma ray dose was approximately 1 to 2 Mrads. The lower trace in Figure 5 shows the radiation-induced optical absorption at room temperature from this sample.
untreated sample. There are small bands, with some structure, in the visible and near ultraviolet, and a weak, yet measurable, absorption in the 190 to 230 nm region. These results in Figure 5 suggest that radiation at room temperature produce similar effects, except in magnitude, in untreated samples and samples that have been heated in air. Thus, these results suggest that oxygen and hydrogen play a major role in the radiation response of BaF$_2$.

EPR was used to further study the radiation response of untreated and treated BaF$_2$ crystals. An untreated crystal with dimensions of 20 x 7.5 x 7.5 mm$^3$ was irradiated for 24 hours at room temperature in the $^{60}$Co source. The most noticeable radiation-induced signals in the untreated sample were a series of lines forming an F-center spectrum. Also, we observed a very weak hydrogen atom signal. This latter EPR signal was barely observable; however, repeated traces convinced us that it was indeed real. Several other possibly oxygen-related signals were also present. For comparison, the radiation-induced EPR signals of the hydrogen atom and oxygen centers from the heat-treated sample were intense. This latter heat-treated sample was the same one used to obtain the upper optical absorption curve in Figure 5.

3. Observation of Manganese in As-Grown Crystals

A large Chinese-grown BaF$_2$ crystal having dimensions of approximately 7 x 8 x 19 mm$^3$, was used in an EPR search for impurity ions. Spectra were taken before irradiation, after a $^{60}$Co irradiation at room temperature to a dose exceeding 1 MRad, and after a thermal anneal for one hour at 500°C. In the as-grown sample, we saw a weak six-line EPR spectrum extending from 3050 gauss to 3550 gauss. These equally split lines represent a hyperfine interaction with an $I = 5/2$, 100% abundant nucleus. From the literature, we are able to unambiguously identify this six-line spectrum as Mn$^{2+}$ substituting for a Ba$^{2+}$ ion. An additional line, most likely from Cr$^{3+}$, is located at the same magnetic field value as the fourth Mn line. The room-temperature irradiation destroys the Mn$^{2+}$ signal and produces an F center spectrum. Finally, heating the sample to 500°C in air for one hour restores the original Mn$^{2+}$ spectrum. For comparison purposes, we performed a similar set of measurements on a BaF$_2$ sample obtained from Solon Technologies (i.e., Harshaw) in Cleveland, OH. This sample had dimensions 2.5 x 8 x 29 mm$^3$. It contained the same Mn$^{2+}$ EPR spectrum as the previously discussed Chinese sample and the behavior as a function of radiation and thermal anneal were the same. Despite extensive searches, we were unable to find any EPR spectra from rare-earth ions in any of the BaF$_2$ samples.

Additional optical absorption measurements have shown that changes in the valence state of manganese correlate with the appearance of the 200-nm absorption in when BaF$_2$ crystals are irradiated at room temperature. Thus, we are left with two possible scenarios: one involves oxygen and hydrogen while the other involves manganese changing valence state. It is quite possible that the two aspects are interrelated.
III. RESULTS FROM CeF₃ CRYSTALS

We have made an initial study of point defects in CeF₃ using magnetic resonance and optical absorption techniques. Prior to this study, it was not known whether EPR techniques would provide useful information about defects in CeF₃. Fortunately, we are able to show that the EPR technique can be used to monitor and identify point defects containing unpaired spins in this material.

The Crystal Clear collaboration at CERN has focused on the role of fluorine vacancies in the radiation response of CeF₃, and the results of our investigation support that approach. Also, all of our data are in agreement with the contention that the usual radiolysis damage mechanisms (i.e., those that allow ionizing radiation to create anion vacancies in the alkali halides) do not work in CeF₃. The fluorine vacancies that participate in the radiation response of CeF₃ are formed, most likely, during growth because of the need to charge compensate other defects. Thus, it should be possible to produce CeF₃ crystals that are intrinsically radiation hard. Achieving this goal will require a concerted effort involving the correlation of improvements in growth procedures with the spectroscopic identification and monitoring of radiation-induced defects.

The data we report were taken from two samples of CeF₃ provided by Optovac. One was referred to by Optovac as undoped and the other was labeled 0.5% Ba-doped. In their as-received condition, both were 1-cm diameter disks with 2-mm thickness. The crystal orientations of the two disks were not specified. We used a small diamond saw to cut an EPR sample 2 mm wide from the side of each disk. This left approximately 85% of each original disk for the optical absorption measurements.

A. Optical Absorption

Optical absorption data taken from the undoped CeF₃ sample is shown in Figures 6(a) and 6(b). Trace a in Fig. 6(a) was taken before irradiation. Then the sample was irradiated for 30 minutes at approximately 20 K. This causes the crystal to turn completely black to the eye. Trace b in Fig. 6(a) was taken immediately after the irradiation and shows two very intense and broad absorption peaks, one near 490 nm and the other near 715 nm. Trace c was taken after the first anneal step to 80 K. Each anneal step consisted of heating the sample, while in the closed-cycle helium refrigerator, to the specified temperature and holding it at that temperature for five minutes before returning it to the 20-K base temperature. The broad absorption has decreased in trace c and a sharper band has appeared at 680 nm. Trace d was taken after an anneal to 100 K. Again, the broad absorption bands decrease by a small amount. Trace e was taken after another anneal to 120 K and it is significantly different from the earlier traces. Essentially all of the two broad absorption bands has disappeared, leaving a series of less intense sharper bands extending from 320 nm to 680 nm.

Figure 6(b) shows the results of continuing to room temperature the thermal anneal of the undoped sample. Note the change in vertical scale between Figures 6(a) and 6(b). Trace f was taken after an anneal to 160 K. A band near 785 nm has appeared and the absorption in
Figure 6(a). Thermal anneal of low temperature irradiated CeF$_3$.

Figure 6(b). Thermal anneal continued.

The 300-to-500-nm region continues to change. Traces g, h, i, and j show the anneal progressing through the 180, 220, 260, and 300 K steps, respectively. Absorption disappears at each step. After the 260-K step, the largest peaks remaining are at 340 and 385 nm, and these correspond to the bands observed by other investigators after a room-temperature irradiation.

Optical absorption data taken from the Ba-doped CeF$_3$ sample is shown in Figures 7(a) and 7(b). Trace a was taken after a 30-minute irradiation at 20 K. It shows the same two broad and intense bands, around 500 nm and above 700 nm, that were present in the undoped sample immediately after irradiation at 20 K. As shown in trace b, absorption is increasing in the 300-to-400-nm region as the two broad bands anneal. This "conversion" of absorption from the visible into the near ultraviolet continues through the 80 and 100-K anneal steps. Continuation of the anneal data in Fig. 7(b) shows that the two broad bands, around 500 nm and above 700 nm, have essentially disappeared after the anneal to 120 K. This is similar to the undoped sample. However, after the 120-K anneal, there is still significant absorption in the red and near-ir region (i.e., between 600 and 800 nm) for the Ba-doped sample. The combination of strong absorptions in the blue and the red cause the sample to appear green to the
The absorption in the 300-to-500-nm region continues to drop as the anneal proceeds through the 140, 160, 180, 215, and 260 K steps. In contrast, the absorption in the red and near-ir doesn't decrease significantly until the 260-K step. Finally, after the 300-K anneal, the remaining absorption has peaks at 340 and 385 nm, just as was observed by other investigators who irradiated their samples at room temperature.

B. Magnetic Resonance (EPR)

Because CeF$_3$ is an intrinsically paramagnetic material, there is a background EPR signal in all samples due to the 4f$^1$ electron on each cerium ion. As expected for a paramagnet, the intensity of the extremely broad signal goes as $1/T$. We also used a SQUID to measure the magnetic susceptibility of the CeF$_3$ as a function of temperature from 5 K to near room temperature. This data verified that no magnetic ordering occurred and that the material behaved as a classic paramagnet over this temperature range.
A one-hour irradiation at 77 K induces defect-related signal near $g = 2$. Figure 8, taken from the Ba-doped sample, shows this radiation-induced spectrum. There are at least seven resolved components in this spectrum which, most likely, are due to hyperfine effects with fluorine nuclei associated with the point defects. The $g$ value of this spectrum is 2.0018 and is very near the free-electron $g$ value of 2.0023. Also, there is no measurable angular dependence associated with this radiation-induced spectrum. Additional investigations must be performed before a final identification of the responsible defects can be made; however, several observations can be made immediately. The nearly-free-electron $g$ value and the lack of angular dependence strongly suggest that the EPR signal is due to F centers or related defects. Because of the complexity of the spectrum in Figure 8, we believe there is probably more than one type of F center contributing.

The radiation-induced EPR spectrum shown in Figure 8 thermally anneals when the sample is returned to room temperature. As the anneal proceeds, the F-center spectrum narrows, thus indicating that one or several of the various types of F centers are annealing at an earlier stage than other types of F centers.

C. Radiation-Damage Mechanism

Even though our data on CeF$_3$ comes from defects that are stable only at lower temperatures, we believe that these defects will play an important role in determining the radiation response of the CeF$_3$ crystals at room temperature. Monitoring the evolution of defects during a thermal anneal (after a low-temperature irradiation) provides one of the few ways to understand the defect structure of a material. An even more important point involves the transient behavior of point defects in CeF$_3$ following a burst of radiation. The broad absorption bands that are stable after a low-temperature irradiation also will be present, in a transient mode, after a room-temperature irradiation. The lifetime of these defects may only be of the order of tenths of milliseconds at room temperature, but that may be sufficient to interfere with the operation of a high-radiation-field scintillator. Thus, it is important to understand the origin of all defects, even though they may not be stable at room temperature.
In general, our data can be explained as follows. Ionizing radiation (whether it be x-rays, gamma rays, or particles) creates uncorrelated free electrons and holes in the lattice. We expect the holes to be trapped on Ce$^{3+}$ ions and form Ce$^{4+}$ ions. The resulting Ce$^{4+}$ ions are a closed shell configuration and give no EPR signals since they are not paramagnetic. The free electrons produced by the radiation are most likely trapped at various fluorine-vacancy complexes. These fluorine-vacancies are formed during the growth of the crystal to serve as charge compensators for different impurities, either divalent impurities or oxygen ions. We note that the presence of fluorine vacancies has been previously suggested by members of the Crystal Clear collaboration, and we totally agree with this suggestion. In addition to requiring fluorine vacancies for charge compensation of impurities, thermodynamic considerations may require that a small but significant concentration of fluorine vacancies and cerium vacancies occur during the high-temperature growth of the crystals. In a variation of this mechanism, it is possible that the electrons are trapped in the form of Ce$^{2+}$ ions in the otherwise perfect lattice at the low irradiation temperatures.

The various fluorine-vacancy complexes will resemble the traditional "F centers" found in alkali halides and other simple halides and oxides. These F centers may be perturbed by an adjacent barium or other divalent impurity, an adjacent oxygen ion, or an adjacent cerium vacancy. Even within the perfect lattice there are several variations of F centers possible. Each of these F-center variants could have a different thermal stability. A systematic investigation of the radiation-induced EPR and optical absorption spectra will help explain the trends governing F-center formation and decay.

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