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DEFECT FORMATION AND VUV LUMINESCENCE IN BaF₂

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Nominally pure BaF₂ single crystals were investigated at 77 K with optical absorption and electron paramagnetic resonance to understand the mechanism of radiation damage. We find that X-irradiation at 77 K of undoped BaF₂ produces $V_k$- and $F$-centres having absorption bands at 3.4 and 2.3 eV respectively.

Keywords: Barium fluoride; Absorption; EPR

1. INTRODUCTION

BaF₂ single crystals are applied as scintillation materials for gamma ray detection in many high-energy physics experiments. Fast timing is possible with these crystals because the very short decay time of about 0.8 ns of luminescence at 195 and 220 nm which is due to cross-luminescence transitions. BaF₂ also has an intense, slow emission component at 300 nm with a decay time of about 620 ns at room temperature.

In recent years most of the attention has been focused on the scintillation mechanism in this crystal. Nevertheless, there are many outstanding questions on the processes of the radiation defect creation in undoped and doped barium fluorides. The basic part of the studies has been made thirty years ago (see for example [1]) and interpretation of the results was complicated by the problem of sample purity. Frankly, this problem always remains unsolved.

Alkaline earth fluoride crystals which have not been deliberately doped with impurities are much less susceptible to coloration at room temperature by X-rays than most alkali halides. Undoped CaF₂ and SrF₂ crystals may be colored by X-rays much more readily at 77 K than at room temperature but the coloration efficiency, especially in the case of CaF₂ is still much slower than in most alkali halides. Only a weak spectrum of self-trapped holes was visible after the X irradiation for 11 h at 20 K of pure CaF₂ crystals; no trace of $F$-centers could be found [2]. This small concentration of $V_k$-centers may arise from residual concentrations of electron trapping impurities in the crystals.

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The sole exception is the crystals of pure BaF$_2$. After X-irradiation of undoped BaF$_2$ crystals at 77 K intensive absorption bands at 3.4 and 2.3 eV are found. In the early works it was suggested that the absorption responsible for the peak at 3.4 eV is associated with the presence of a broad EPR line with $g = 1.98$ in the irradiated crystals which arises from trapped electrons. Authors concluded that the centers responsible for this band may be associated with an unknown chemical impurity in the crystals [3].

This paper contains results of an investigation of radiative point defects in undoped BaF$_2$ crystals. We find that X-irradiation at 77 K of undoped BaF$_2$ produces $V_k$- and $F$-centres having absorption bands at 3.4 and 2.3 eV respectively. Therefore, this absorption is associated with intrinsic defects rather than with an unknown chemical impurity.

2. EXPERIMENTAL TECHNIQUE

The crystals of undoped BaF$_2$ were grown using the combined Shteber-Stocbarger method. The samples were of high optical quality and no indication of oxygen contamination. The absorption spectra were taken with a "Specord" spectrophotometer. The crystals were irradiated at 77 K by X-rays from a Pd tube operating at 40 kV and 50 mA for 30 min.

3. EXPERIMENTAL RESULTS

X-irradiated BaF$_2$ crystals at 77 K show optical absorption having two maxima at 3.4 (365 nm) and 2.3 eV (540 nm) (Fig. 1). Mutual annihilation of the centers related with these absorption bands occurs below 130 K that correlates with thermal destruction of the $V_k$-centers.

When the undoped barium fluorides are X-irradiated at 77 K the $V_k$ center is predominant hole center formed and the TL spectrum exhibits the intense glow peak at about 110 K, which
is associated with the destruction of $V_k$ centers. Aside from this there are additional weaker features above 200 K [4].

The EPR spectrum of pure BaF$_2$ crystals after X-irradiation at 77 K is shown in Figure 2. It can be seen that X-irradiation of undoped BaF$_2$ at 77 K produces $V_k$- and $F$-centers. The EPR spectrum of $V_k$-centers in our X-irradiated undoped BaF$_2$ has the same $g$ and $A$ values and general appearance as that of $V_k$-centers in BaF$_2$-Tm$^{3+}$ crystals [5]. However, no absorption bands at 3.7 eV, which, in authors view [5] was associated with $V_k$-centers are produced by X-irradiation at 77 K of the undoped BaF$_2$ crystals.

The weak EPR $F$-centre lines in BaF$_2$ are superimposed on intensive EPR lines of $V_k$ centers. No absorption band at 2.03 eV (611 nm), which in authors view [3] was associated with $F$-centers, is produced by X-irradiation at 77 K of the undoped BaF$_2$ crystals. The absorption band at 2.03 eV (611 nm) is only found in the BaF$_2$ crystals doped with lanthanum X-irradiated at 77 K. Thermal and optical destruction of the EPR spectrum correlates with thermal and optical destruction of the centers responsible for the absorption bands at 3.4 and 2.3 eV. From this it may be concluded that X-irradiation of undoped BaF$_2$ at 77 K produces $V_k$-centers with absorption band at 3.4 eV and $F$-centers with absorption band at 2.3 eV. The absorption band at 2.3 eV probably arises from an $F$-centre which is associated with negatively charged fluorine interstitials in distinction from the absorption band at 2.03 eV (611 nm).

In BaF$_2$ crystals a fast ultraviolet emission with two main maxima at 6.3 and 5.6 eV under x-ray excitation or particle irradiation is due to cross-luminescence transitions. In our previous work [6] we found that in the BaF$_2$ crystal doped with lanthanum a weak additional high-energy emission appears and its intensity grows with increasing La-doping. The emission arises from a radiation transition between the electron state of the interstitial $F_i^-$-ion, its electron state is located in the forbidden band at low concentration of lanthanum, and the outermost Ba$^{2+}$ 5p core band.

In the BaF$_2$ crystals doped with yttrium the high-energy emission band is also detected. As in the case of La-doping, a slow component of the luminescence at 4.0 eV, which is caused by self-trapped excitons, is suppressed by doping with $Y$. In both cases the high-energy emission, as the main cross-luminescence, is temperature independent at least from 77 to 300 K.

![EPR spectrum of pure BaF$_2$ crystal after x-irradiation at 80 K, B \( \parallel \langle 100 \rangle \).](image)
Unfortunately, in our previous work [6] the wave-length scale of our monochromator was in error. Now we present the revised spectra (Fig. 3) of the high-energy emission band which has maximum at about 7.5 eV.

In pure BaF$_2$ crystals under X-ray excitation at both 77 and 300 K the high-energy emission band is not observed. However, in some cases the high-energy emission band with maximum at about 7.5 eV was detected using 6 keV electron excitation [7] or synchrotron irradiation [8] of pure BaF$_2$ crystals. The emission is observed in the temperature range below 120 K. This temperature behavior is not similar to that of the cross-luminescence. This is due to the fact that the negatively charged fluorine interstitials can be created not only by doping with trivalent ions, but also by radiation damage.

4. CONCLUSION

X-irradiation of undoped BaF$_2$ at 77 K produces $V_k$-centers and F-centers. The $V_k$-centers and F-centres begin to disappear due to mutual annihilation at 100 K and have completely disappeared by 130 K. The strong resistance of undoped BaF$_2$ to coloration by X-rays at room temperature is apparently due to recombination of electrons and holes created by the irradiation.

The production efficiency of $V_k$- and F-centers by X-rays in our undoped BaF$_2$ at 77 K is at least an order of magnitude greater than in undoped CaF$_2$. This suggests, in contrast to CaF$_2$, that interstitial anion-vacancy pairs with sufficient separation to trap electrons may be created by X-rays in BaF$_2$.

$$e^0 \rightarrow e^0(F^-H) \rightarrow \alpha - I$$

The anion vacancy can then trap an electron to become an F-center.

$$\alpha - I + e^- + e^+ \rightarrow F^- + F_i^- + V_k$$
The distinctions between the absorption spectrum of the X-ray induced $F$-centers in BaF$_2$ and that of the $F$-centre in additively colored BaF$_2$ could be due to anion interstitials.

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