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Color Centers in the Near Infrared Region in Crystals *M*FX (*M* = Ba, Sr; *X* = Cl, Br)

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Color centers with absorption bands in the near infrared region (peaking near 900 nm) in X-rayed *MFX* crystals have been found. They might be attributed to the aggregates of $F(X^-)$ centers which are similar to *M* centers in *MX* crystals. The interconversion among $F(F^-)$, $F(Br^-)$, and *M* centers in BaFBr crystals has been found. These aggregated color centers are stable and exhibit stimulable absorption bands in the region from 700 to 1000 nm. Therefore some solid state lasers can be used as stimulating light sources instead of He–Ne lasers for reading the information stored in PSL image plates made of these X-ray storage phosphors. © 1993 Academic Press, Inc.

Introduction

Eu^{2+} doped $BaFX:Eu^{2+}$ (X = Cl, Br) phosphors are excellent photostimulated luminescence (PSL) materials (*1*, *2*), and Sm^{2+} doped $MFX:Sm^{2+}$ (M = Sr, Ba; X = Cl, Br) are good spectral hole burning materials (*3*). In their physical mechanism, electron color centers play an important role. To dates, studies of color centers in these matrices have been limited to simple *F*-centers whose absorption band is located in the visible region 350–600 nm. Less attention has been given to other kinds of color centers in these matrices than in alkali halide *MX* crystals. This makes many important luminescent properties of *MFX* crystals ambiguous. Reviewing studies on color centers in *MX*, we noted that *F* centers are not alone, but can interact each other and aggregate to form other types of color centers. For example, when the *MX* crystal is stimulated into its F-centers' absorption band at room temperature, there appear some new absorption bands located in the near infrared region. These new bands have been attributed to *R* and *M* bands and they could transform into *F* band again when appropriate thermal and optical stimulation of those aggregated centers' bands was applied (*4*). These phenomenon have not been studied in *MFX* crystals yet. On the other hand, for the application of the PSL materials, a wide separation between the wavelengths of stimulating light and the emission light is required so that the stored information can be read out. It has been found that the bands of photostimulation spectra of $BaFX:Eu^{2+}$ (X = Cl, Br) are located between 400 and 600 nm (*1*, *2*), agreeing with the position of absorption bands of $F(F^-)$ and $F(X^-)$ centers in these matrices. It is thought worthwhile to study whether in these matrices

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there exist absorption bands in the near IR region just as in the case of *MX*. If there exist such absorption bands, it is possible to use certain solid state lasers instead of He–Ne gaseous lasers as stimulating light source so as to simplify the construction of reading devices in computed radiography and to avoid the interference of the stimulating light on PSL.

In this paper, the absorption properties of X-irradiated *MFX* crystals have been studied in the region 400–1000 nm. Several new absorption bands beyond 600 nm were found and their origin has been determined. The interconversion between different kinds of color centers under optical and thermal stimulation was also observed in BaFBr crystals.

Experimental

1. Growth of Crystal

Single crystals of BaF*X* and SrFCl were grown by programmable slow-cooling methods.

2. Optical Measurements

The measurements of absorption spectra were performed on these crystals subsequent to X-irradiation. A 150 W halogen tungsten lamp light modulated by a chopper of model 194A was used as a light source. The modulated light was dispersed and monochromized by a HRD-1 double grating monochrometer (with a 3M 210R grating) and then passed through the crystal. The transmitted light was received by a combination of a silicon diode sensor and an RK-5200 power ratiometer and recorded by an *X–Y* function plotter. Samples were previously exposed for 30 min to the X-rays generated from a Cu target operated at 40 kV, 20 mA. Unirradiated crystals were used as references.

The glow curve was measured by a dosemeter manufactured by Litemour Company of British.

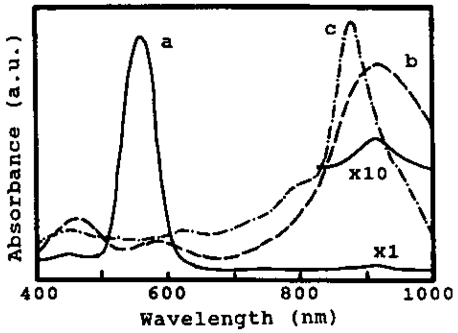

FIG. 1. Absorption spectra of BaFCl (a), BaFBr (b), and SrFCl (c) crystals X-rayed for 30 min.

Results and Discussion

1. Absorption Spectra of X-Rayed Crystals

Figure 1 shows the absorption spectra of BaFCl, BaFBr, and SrFCl crystals. In BaFCl, there are two stronger bands peaking at 450 and 560 nm which should be ascribed to *F* centers (*5*); meanwhile there appears a weaker and wider absorption band peaking at 910 nm. In BaFBr, in addition to two weaker bands of *F* centers peaking at 460 and 560 nm (*5*, *6*), there is a stronger and wider absorption band peaking at 920 nm in the region of 700–1000 nm. In SrFCl there exist four bands peaking at 450, 615, 800, and 870 nm. For SrFCl, under exposure to sunlight, the intensity of all bands decreases but the intensity of the strongest band peaking at 870 nm decreases more slowly than those of other peaks. In all these crystals, there are no absorption peaks in the range of 1000–2500 nm. And their absorption spectra do not change as rare earth ions are doped into the matrices.

2. Absorption Properties of BaFBr Crystal

(*1*) *Generation of color centers.* The absorption spectra of BaFBr crystals with different X-irradiation times are shown in Fig. 2. In the sample X-irradiated for 30 sec, there is only the band of the $F(Br^-)$ center

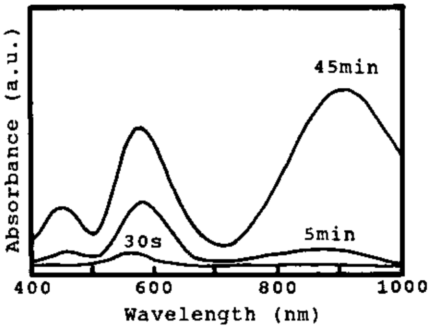

FIG. 2. Absorption spectra of BaFBr crystal X-rayed for 30 s, 5 min, and 45 min, respectively.

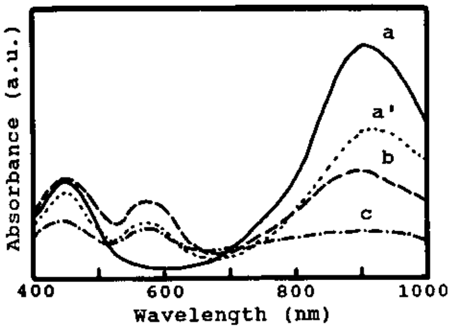

FIG. 3. Absorption spectra of BaFBr crystal X-rayed for 15 min (a') and then stored in dark for 10 days at RT (a), subsequent to sunlight bleaching for 1 min (b) and 10 min (c).

peaking at 580 nm. When the irradiation time is prolonged to 5 min, two new absorption peaks occur at 460 nm, attributed to the $F(F^-)$ center, and at 920 nm, which attribution is to be determined. The intensity of these peaks increases at different rate with increased irradiation time. As the crystal is X-irradiated for 45 min, the absorbance of the 920 nm band is greater than those of F centers whose absorbances increase more slowly.

(2) *Interconversion of color centers during optical and thermal stimulation.* The body color of freshly X-rayed BaFBr crystal is blue-violet. As the X-rayed crystal is stored in dark for several days, its color changes to brown–yellow. Under the bleaching by sunlight or by halogen tungsten lamp light, its color returns to blue-violet. This color interchange could take place alternatively for several times. Figure 3a presents the absorption spectra of BaFBr crystal X-irradiated for 15 min and then stored in the dark at room temperature for 10 days. It can be seen that the 580 nm band of the $F(Br^-)$ center almost disappears; instead the 920 nm band becomes predominant. As the above crystal is exposed to sunlight for 1 min, the absorbance of the 920 nm band decreases; meanwhile the band of the $F(Br^-)$ center at 580 nm appears again and the band of $F(F^-)$ center at 460 nm does not change obviously (Fig. 3b). As the exposure time to sunlight is prolonged further for 10 min, the absorbance of all bands decreases (Fig. 3c). Similar results were obtained by exposure of the above crystal to halogen tungsten lamp light. The bleaching effect of sunlight or halogen tungsten lamp light on the band peaking at 920 nm is more evident, because the strongest bands of both light sources are located near 920 nm. By the use of monochromatic light of 920 nm for bleaching, similar results to that by using sunlight for short-time bleaching have been observed.

As 580 nm monochromatic light is used for bleaching, the absorption intensity of the 580 nm peak decreases and that of the peaks at 460 and 920 nm increase (Fig. 4). This

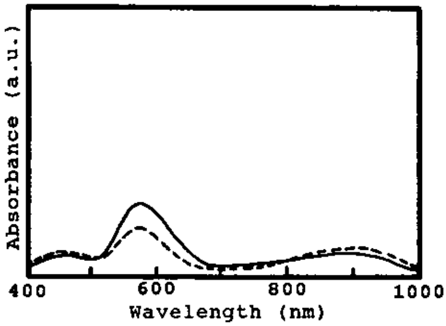

FIG. 4. Absorption spectra of BaFBr crystal X-rayed for 5 min (—) and then optically bleached by 580 nm light (----).

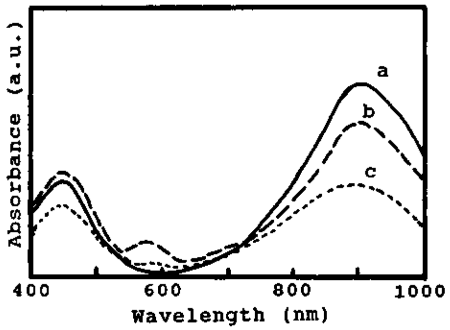

FIG. 5. Absorption spectra of BaFBr crystal X-rayed for 20 min and then stored in dark for 4 days at RT (a), subsequent to thermal bleaching at 340 K for 20 min (b) and then at 373 K for 20 min (c).

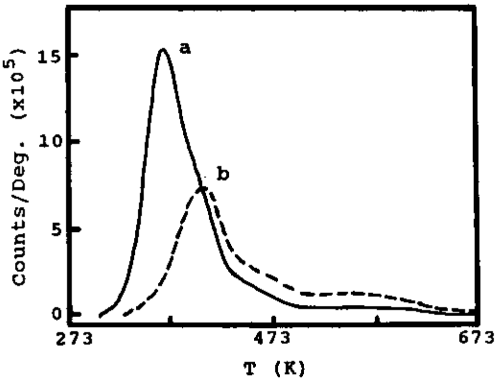

FIG. 6. Glow curves of BaFBr crystal X-rayed for 10 min (a) and X-rayed for 10 min and then stored in the dark for 3 days at RT (b).

indicates that part of $F(\text{Br}^-)$ centers transform to $F(\text{F}^-)$ centers and centers at 920 nm.

When the BaFBr crystal X-rayed for 20 min is stored in dark for 4 days and then is thermally bleached at 340 K for 20 min, its absorption band at 580 nm still remains, the absorbance of the 460 nm band increases slightly, and that of the 920 nm band decreases (Fig. 5b). As the crystal is further thermally bleached at 373 K for 20 min., the absorbance of all bands decreases, but there is still a weak absorption band of $F(\text{Br}^-)$ center and of 920 nm (Fig. 5c).

3. *Glow Curves*

The glow curves of BaFBr crystal X-rayed for 10 min is shown in Fig. 6. The strongest glow peak at 363 K which is ascribed to electron detrapping from $F(\text{Br}^-)$ (*6*), and two weaker shoulder locating at 404 and 450 K (Fig. 6a). When the crystal is stored in the dark for 3 days, its absorption band at 363 K disappears and the peak at 404 K attributed to $F(\text{F}^-)$ (*6*) appears obviously. The shoulders at 450 and 550 K rise a little at the same time (Fig. 6b). This result agrees with that of the absorption spectrum in which the absorption band of the $F(\text{Br}^-)$ center disappears as the crystal has been stored in dark for several days. Comparing the results of glow curves with those of the absorption spectrum, we think that the bands peaking at 450 and 550 K may be correlated with the centers of the 920 nm band. Further research is in process.

4. *Discussion*

On the basis of the above results, it is reasonable to think that the absorption band peaking at 920 nm in BaFBr crystal could be attributed to a complex of $F(\text{Br}^-)$ centers which is something like the *M* center in alkali halides (*4*). As we know, there are three models used to describe the *M* center in alkali halides. Seitz (*8*) proposed an L-shaped model which consisted of an *F* center and a pair of positive–negative ion vacancies. In the light of there being no permanent dipole moment in *M* center, Knox (*9*) revised the above model by suggesting that the *M* center was of reverse symmetry. Von Doorn (*10, 11*) presented another model in which the *M* center was an aggregate of two neighboring *F* centers. In that model there was an equilibrium between *F* centers and *M* centers; i.e., $2\,\text{F} \rightleftharpoons M$, and *M* centers had the second absorption band in the spectral region of the *F* band. Our experimental results suggest that in BaFBr crystal the *M* center might be the aggregate of two $F(\text{Br}^-)$

centers, agreeing with the model of Van Doorn.

We observed that the $F(\mathrm{F}^-)$ center at 460 nm changes along with the change of $F(\mathrm{Br}^-)$ and M centers. In Fig. 4, optical bleaching of an $F(\mathrm{Br}^-)$ center results in the increases of absorption intensities of both $F(\mathrm{F}^-)$ and M centers. During the thermal bleaching, the absorbance of $F(\mathrm{F}^-)$ center also changes (Fig. 5). There are two possible explanations for above results. One is that $F(\mathrm{F}^-)$ centers may be accompanied by M centers according to the model of Van Doorn (*12, 13*). The other is that $F(\mathrm{Br}^-)$ centers could be partially transformed to $F(\mathrm{F}^-)$ centers. The former proposal requires further investigation to confirm, while the latter case has been observed in BaFCl crystal (*7, 14, 15*).

In Fig. 1, there are absorption peaks at 910 and 870 nm for BaFCl and SrFCl, respectively. What is the origin of these bands? As we know, the peak wavelength of absorption band vs unit cell volume for the same kind of electron defects obeys the Ivey or Mollowo equation (*4*). For F-centers in MFX (M = Sr, Ba; X = Cl, Br) crystals, there exists a relationship between the peak wavelength of the F-centers' absorption band (λ(nm)) and unit cell volume (V(Å^3)) as follows:

$$F(X^-):\quad \lambda = 9.08\,V^{0.817} \tag{1}$$

$$F(\mathrm{F}^-):\quad \lambda = 1.55\,V^{1.18}. \tag{2}$$

Similarly, the absorption wavelengths near 900 nm in BaFCl, BaFBr, and SrFCl crystals obey the following equation:

$$\lambda = 288\,V^{0.232}. \tag{3}$$

Therefore the defects with absorption bands peaking near 900 nm in BaFCl and SrFCl crystals have the same property as that in BaFBr crystal; i.e., the absorption band peaking at 910 nm in BaFCl and that at 870 nm in SrFCl come from defects of the same kind as that in BaFBr and can be attributed to M centers.

5. *Conclusion*

The color centers with absorption bands in the near infrared region (peaking near 900 nm) in X-rayed MFX crystals have been found. They might be attributed to the complexes of $F(X^-)$ centers which are similar to M centers in MX crystals. Interconversion among $F(\mathrm{F}^-)$, $F(\mathrm{Br}^-)$, and M centers in BaFBr crystals has been observed. All these color centers are stable and exhibit stimulable absorption bands in the region from 700 to 1000 nm. Therefore some solid state laser beams can be used as stimulating light for scanning image plates made of these X-ray phosphors phosphors.

Acknowledgment

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