Time-resolved study and molecular dynamics simulation of defect centers in BaFX (X = Cl, Br) crystals

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Abstract

Some new evidence to determine the origin of the F-aggregate centers located in the near-IR region in BaFX (X = Cl, Br) crystals is demonstrated through a series of measurements and molecular dynamics simulations. Moreover, a new method to determine the concentration of the F centers in the photostimulable materials is also demonstrated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Barium fluorohalides; F-aggregate centers; Time-resolved study; Molecular dynamics

1. Introduction

BaFX (X = Cl, Br) has a matlockite structure consisting of layers in the sequence $F^- – Ba^{2+} – X^- – X^- – Ba^{2+} – F^-$ perpendicular to the crystal *c*-axis. The presence of such a layered structure, and the production of two types of F centers, $F(F^-)$ and $F(X^-)$, by X-ray irradiation, give rise to various interesting phenomena in a europium-activated BaFX system [1].

The present paper reports some more new experimental evidence regarding the origin of the F-aggregate centers as well as their optical properties by using BaFX, $BaFCl_{1-x}Br_x$ mixed crystals, and various impurities (Eu^{2+}, O^{2-})-doped BaFX crystals. A picosecond time-resolved absorption study is demonstrated to obtain more detailed information on the dynamics of the F and F-aggregate centers. Moreover, a new method to determine the concentration and oscillator strength of the F centers in the photostimulable materials is also demonstrated. Finally, some characteristics of vacancy-jump motions, and the anisotropy in ionic conductivity in host BaFX crystals are examined by means of molecular dynamics (MD) simulations on the atomic level.

2. Experimental

Various single crystals, i.e., doped (Eu^{2+}, O^{2-}) and undoped BaFX, produced at Vinogradov Institute of Geochemistry, Academy of Sciences of Russia were used. The color centers were produced at room temperature by X-ray irradiation from a tungsten target, being operated at 30 kV and 20 mA. The time-resolved absorption apparatus [2] consisting of a pump and probe light source, a polychromator, and a streak camera enabled us to observe time-resolved absorption spectra with 50 ps time resolution. As the pump light, the fourth harmonic (266 nm) generated from an actively–passively mode-locked Nd : YAG laser with a three-stage YAG amplifier, delivering pulses with a full-width at half-maximum intensity (FWHM) of 25 ps, was used to excite a sample. The continuum probe light from UV to near-IR was generated with a Xe tube focused by the fundamental pulses. Using this apparatus, we can observe both temporal and spectral profiles of transient absorbance with only a single laser shot.

3. Results and discussion

3.1. Optical properties and the origin of near IR centers

Fig. 1 represents the optical absorption spectrum of $BaFBr : Eu^{2+}$ irradiated by X-rays at 290 K. It may

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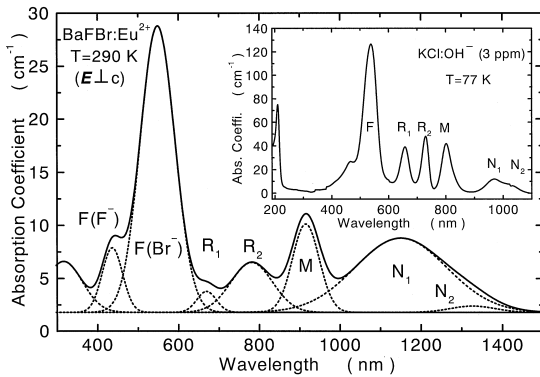 *E-mail address:* laser@kenroku.kanazawa-u.ac.jp (T. Kurobori)

Fig. 1. Absorption spectra of BaFBr : Eu^{2+} at 290 K recorded immediately after X-ray irradiation. The decomposition of the spectra into the bands is shown by the dotted lines.
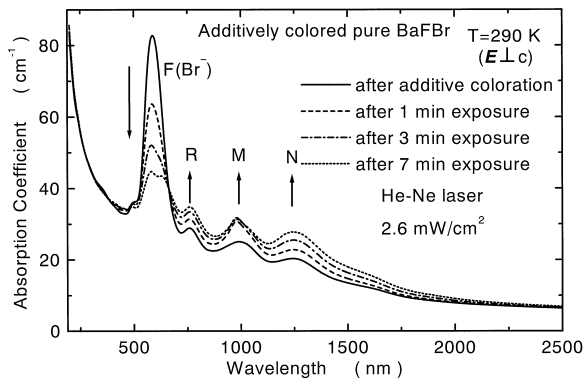

Fig. 2. Absorption spectra of additively colored pure BaFBr at 290 K recorded immediately after additive coloration (solid line) and after the F band exposure to a He–Ne laser (broken lines).
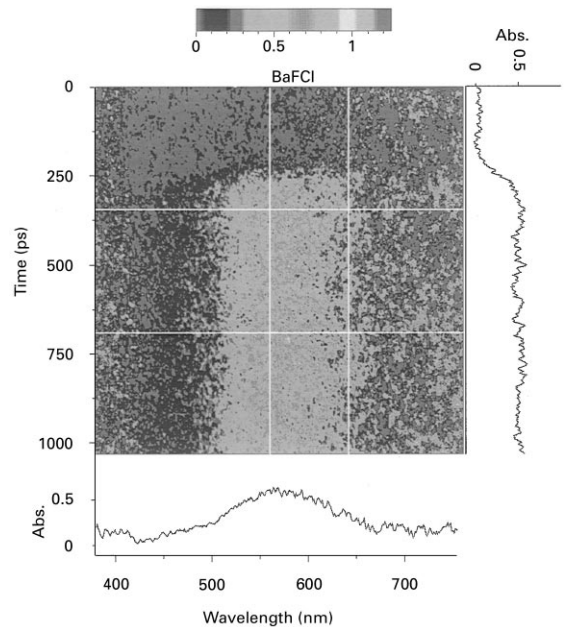

Fig. 3. Single shot streak image. The absorbance changes of pure BaFCl are measured by using a streak-camera and a monochromator after the 266 nm excitation.

be noted that the seven absorption bands as seen in Fig. 1 are observed at 456, 568, 656, 780, 912, 1127, and 1325 nm. The first two absorption bands have already been assigned to the F(F$^-$) and F(Br$^-$) centers, respectively. The other five absorption bands located at longer-wavelength side of the F band are tentatively assigned [3] to the F-aggregate centers like the R(= F$_3$), M(= F$_2$), and N(= F$_4$) centers, respectively, through comparison with the well-known aggregate centers in alkali halides, as shown in the inset in Fig. 1. The attribution of the F-aggregate bands to a cluster of the F(X$^-$) centers has been confirmed [4] through a series of measurements on their emission in IR, the process of aggregates formation in BaFCl$_{1-x}$Br$_x$ mixed crystals, and the non-recombination process in additively colored pure BaFBr. Fig. 2 shows the absorption spectra of pure BaFBr, which has been recorded immediately after additive coloration as well as after the F(Br$^-$) band exposure to a He–Ne laser for several minutes. It may be noted that the absorption coefficient of the F(Br$^-$) centers is

decreased, while that of the F-aggregate centers at 761, 981, and 1250 nm is increased. Further experiment is performed to determine the number of clusters of the F-aggregate centers. As a result, the F-aggregate bands at 860 and 1100 nm in BaFCl : K$^+$ are assigned to the F(Cl$^-$)$_2$ and F(Cl$^-$)$_4$ centers, respectively, in view of the equilibrium between the F(Cl$^-$) centers and the F-aggregate centers.

3.2. Determination of the optical constant of F centers

By using the well-known Smakula's formula, it is possible to determine the values of the oscillator strength f, of the F optical transition experimentally by measuring the F center concentrations, the refractive index, the absorption coefficient, and the full-width of the absorption band. Therefore, we measured these parameters and made an attempt to calculate the optical constants of BaFCl : Eu^{2+}. In particular, a new method to determine the concentration of the defect centers in photostimulable luminescent materials is demonstrated [5]. The method is based on a recombination model and the other factors which depend on the temperature and the distance between electrons and holes which are primarily useful in the analysis of afterglow decay curves. The method is representatively applied to BaFCl : Eu^{2+} and KCl : Eu^{2+} single crystals. The values of the oscillator strength are estimated to be $f = 0.80$ for the F(Cl$^-$)
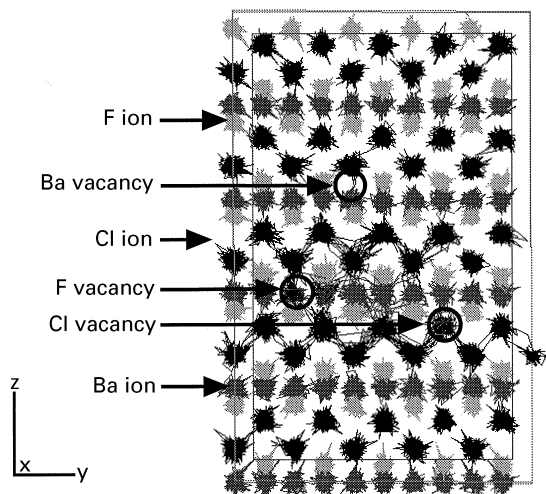
Fig. 4. The projection of the vacancy trajectories on the *yz* plane of Cl, F, and Ba ions in BaFCl simulated for 50 ps at $0.79T_m$.

centers in $BaFCl : Eu^{2+}$ and $f = 0.60$ for the F centers in $KCl : Eu^{2+}$.

3.3. Time-resolved absorption spectra

A two-dimensional streak image with temporal and spectral profiles of pure BaFCl, using only a single laser shot, is shown in Fig. 3. The time-dependent absorption changes and time-resolved spectrum are displayed graphically by setting up the vertical and the horizontal windows, respectively. It is found that the formation time of $F(Cl^-)$ centers in BaFCl was estimated to be less than 50 ps at room temperature by measuring the rise time of the transient absorption kinetics, which does not show any rise time broader than the instrument temporal resolution.

3.4. MD simulations

The MD simulation was performed for BaFX and $BaFX : O^{2-}$ containing 750 atoms in a cube with periodic boundary conditions [6,7]. The Schottky-type defects consisting of one metal ion vacancy and two halogen vacancies were arbitrarily introduced by removing an ion from each ionic site. Fig. 4 shows the typical vacancy trajectories of Cl, F, and Ba ions in BaFCl for a *yz*-plane simulated for 50 ps at $0.79T_m$, where T_m is the simulation melting temperature. The jump motions of Cl ions are observed to be more frequent, and a zig-zag motion between the two adjacent Cl planes was dominant.

The diffusion coefficients and the activation energy for the vacancy migration have been calculated. Furthermore, the probable mechanisms for the vacancy migration process and the anisotropy in ionic conductivity in BaFX have been discussed on the basis of structural considerations of the unit cell.

4. Summary

It is presented that the F-aggregate centers which appeared in the near-IR region of absorption spectra in BaFX are due to $F(X^-)$-aggregate centers. This attribution has been evidenced through a series of measurements and MD simulations.

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