Luminescence study of thermal treated and laser irradiated $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals

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Changes on the defect structure of $Bi_{12}GeO_{20}$ (BGO) and $Bi_{12}SiO_{20}$ (BSO) crystals induced by thermal treatments and laser irradiation have been studied by means of cathodoluminescence in the scanning electron microscope. The results have been compared to those previously reported for untreated and electron irradiated samples and recombination mechanisms responsible for some of the observed luminescence bands are discussed. Annealing of BGO samples causes the appearance of a new luminescence band at about 390 nm. The centers responsible for this band decorate the deformation slip bands in quenched BGO as observed in the cathodoluminescence images. The emission observed in BSO in the same spectral range is quenched during the annealing treatment. The annealing induced reduction of Bi ions to metallic Bi appears to be related to the quenching of a band at 640 nm observed in untreated samples. © *1998 American Institute of Physics.* [S0021-8979(98)07712-3]

I. INTRODUCTION

The sillenite structure compounds $Bi_{12}GeO_{20}$ (BGO) and $Bi_{12}SiO_{20}$ (BSO) belong to a class of materials with potential applications as photorefractive materials.[1] Since the photorefractive effect is related to the trapping dynamics of the photogenerated charge carriers,[2–4] the study of the nature and spatial distribution of electronic levels is of interest for the control of the optical properties of these materials and the development of their technological applications. Luminescence techniques, mainly photoluminescence (PL) and thermoluminescence, have been used in the past to characterize BGO, BSO, and other compounds appearing in the phase diagram of Bi_2O_3–MO_2 (M=Ge,Si,Ti).[4–12] Cathodoluminescence (CL) in the scanning electron microscope (SEM), which has been widely used to obtain spatially resolved information on the recombination properties of many semiconductors and insulating crystals, has been only occasionally applied to characterize crystals of the BGO and BSO systems. Nazarova *et al.*[13] reported CL-SEM observations of indented regions of $Bi_4Ge_3O_{12}$ single crystals, while in Ref. 12 this technique was used to study the core region of $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals. The difference in the luminescence behavior of the core region as compared with the crystal matrix could be studied[12] in as-grown crystals, but CL images did not show any contrast related to defects or growth features.

The interest in BGO and BSO crystals extends to their behavior during photon or electron irradiation as well as to their stability under thermal treatments. Santos *et al.*[14] reported surface damage of the crystals and the appearance of Bi microdrops as a consequence of annealing. In the same way, recent studies show that new phases are formed after thermal reduction with a Bi/M ratio lower than the initial one.[15] On the other side, x-ray[11,16] and electron[12] irradiation have been found to modify the defect related optical properties of BGO and BSO. In the present work, CL in the SEM is used to study the effect of vacuum annealing and of laser irradiation on the defect structure of $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals.

II. EXPERIMENTAL METHOD

BGO and BSO crystals were grown by the Czochralski technique. Details of the growth procedure have been previously described.[17,18] The starting materials were pure Bi_2O_3 and GeO_2 or SiO_2 (J. Matthey, Grade A1). The crystals were grown in a resistance furnace in Pt crucibles under atmospheric conditions. Samples were cut from the ingot, perpendicular to the growth direction, and polished with abrasive Al_2O_3 powder. Some samples were annealed in vacuum (10^{-2} Torr) at 750 °C during 4 h. Other samples were quenched in air from a temperature of 400 °C and a set of samples was irradiated in a vacuum of 10^{-4} Torr with a 514 nm line of an Ar^+ laser (175 mw/mm^2).

The CL measurements were carried out in a Hitachi S-2500 SEM at temperatures between 78 and 300 K with a 30 kV beam accelerating voltage. The experimental setup for the CL measurements consists of an optical lens that focuses the light on a guide at a window of the microscope. A

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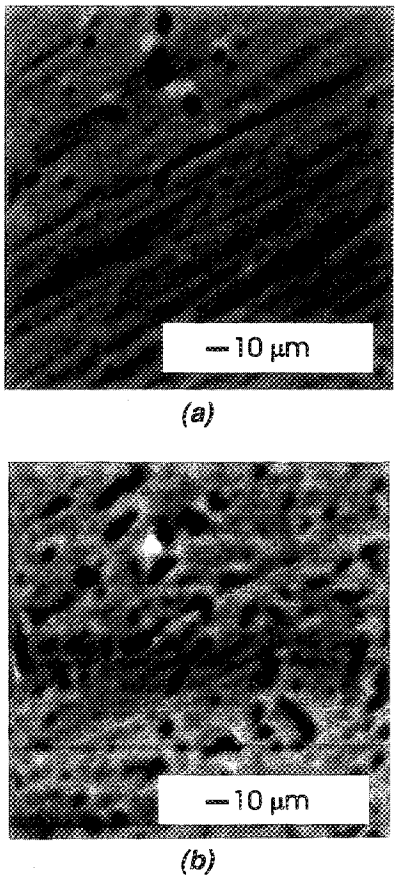

FIG. 1. (a) Secondary electron and (b) CL images recorded on the same area of a BGO annealed sample.

Hamamatsu R928 photomultiplier and a North Coast EO-817L were used for detection in visible and near-infrared ranges, respectively. Spectra were recorded at 100 K with a computer-controlled Oriel 77200 monochromator. A thin carbon film was deposited on the samples to avoid charge effects.

III. RESULTS

In a previous work[12] the CL and PL behavior of untreated BGO and BSO crystals, grown under the same conditions as the crystals used here, was reported. In this section

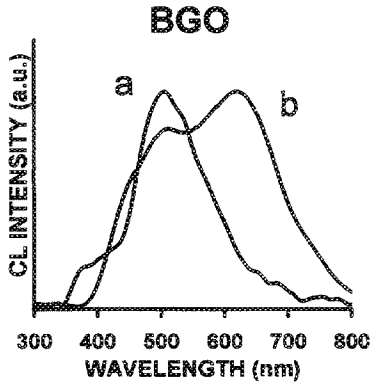

FIG. 2. (a) CL spectrum of a BGO annealed sample. (b) Spectrum of the BGO untreated sample is shown for comparison.

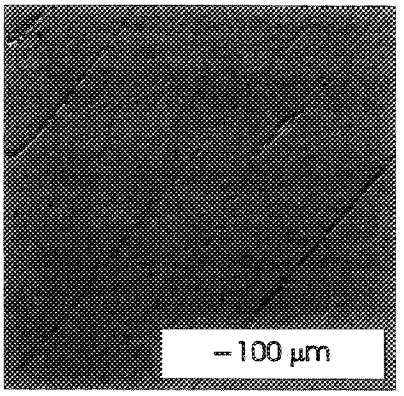

FIG. 3. Secondary electron image of a BGO annealed and quenched sample.

we describe the results relative to the thermal and irradiation treatments and compare them with those of Ref. 12 in the discussion section.

A. BGO

Annealing causes the appearance of rounded surface features observed in the secondary electron images [Fig. 1(a)]. These features present a dark CL contrast, as Fig. 1(b) shows, while the background of the sample surface shows a rather homogeneous CL emission. In Fig. 2 a representative spectrum of the annealed samples is represented together

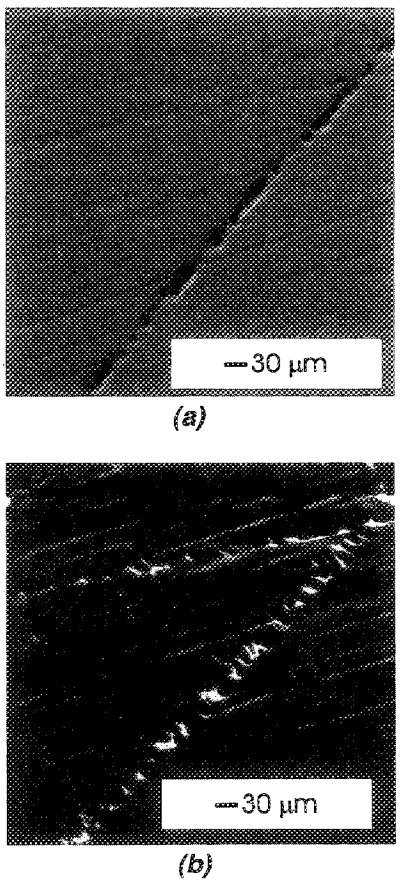

FIG. 4. (a) Secondary electron and (b) CL image of the same area of a BGO annealed and quenched sample, showing a luminescence slip band.

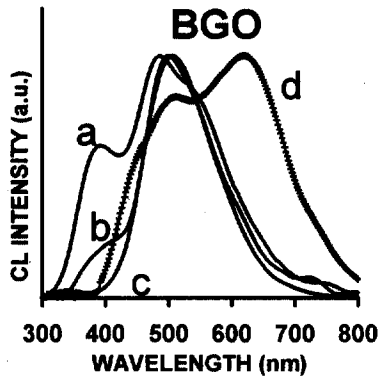

FIG. 5. CL spectra recorded on different zones of a BGO annealed and quenched sample: (a) on a line, (b) near a line, and (c) on a region without lines. (d) Spectra of the untreated sample is shown for comparison.

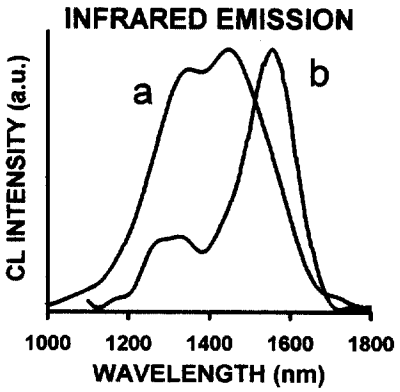

FIG. 7. Infrared CL spectra of (a) annealed BGO and (b) annealed BSO samples.

with a spectrum of the untreated samples as a reference. Comparison of both spectra shows that annealing causes the increase of a band centered at about 500 nm, which dominates the spectra of the annealed samples, and the reduction of the emission appearing at 620 nm in the untreated samples.

Figure 3 shows the secondary electron image of an annealed and quenched BGO crystal. A set of parallel lines are observed, which we suggest to be related to slip bands generated by stresses during the quenching. The rounded features present in the annealed samples are also observed here. A detail of a slip line is shown in the secondary electron and CL images of Fig. 4. In order to study the origin of the emission at the lines, CL spectra were recorded in the line, in its proximity, and in a region not containing lines. Figure 5 shows that the spectra depend on the region considered. The spectrum recorded at the line shows a higher contribution of the 390 nm band. This emission decreases in the region near the lines and is absent in the line-free regions. The 620 nm band, which dominates the visible spectrum of the untreated samples, is almost completely quenched by annealing followed by quenching, as already observed for the annealed samples. The main band of the treated samples, at about 500 nm, seems to split into two components at the slip lines.

Laser irradiation was not observed in the secondary electron mode of the SEM to modify the sample surface. CL spectra of the laser irradiated samples show enhanced emission in the blue-green range as shown in Fig. 6. In Fig. 6, spectra of untreated samples and of samples after electron irradiation in the SEM (from the results of Ref. 12) are included for comparison. In all the BGO treated samples, CL infrared emission bands at about 1340 and 1440 nm, not present in the untreated samples, were observed (Fig. 7).

B. BSO

As in BGO, the surface of the annealed samples shows the rounded features described above. After annealing, the CL spectrum appears dominated by a band centered at about 500 nm (Fig. 8), while the spectra of the untreated samples consist of a band at 620 nm and a weak blue emission. The behavior of BSO after irradiation is similar to that of BGO with an increase of the 500 nm band in the laser irradiated samples and emission at about 650 nm after electron irradiation (Fig. 9).

The different treatments induced, as in BGO, infrared CL emission bands at about 1340 and 1440 nm. In addition, annealed BSO presents a new band at 1560 nm.

IV. DISCUSSION

The rounded surface features produced by the thermal treatments of BGO and BSO in this work are similar to those described by Santos *et al.*[14] and have probably the same ori-

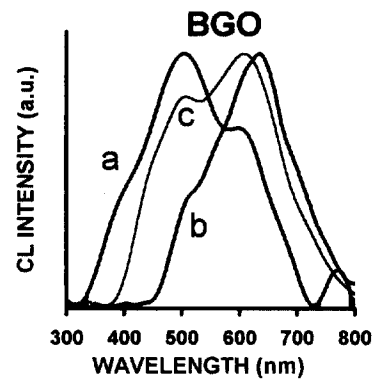

FIG. 6. CL spectra of (a) laser and (b) electron irradiated BGO samples. (c) CL spectrum of the untreated sample is plotted for comparison.

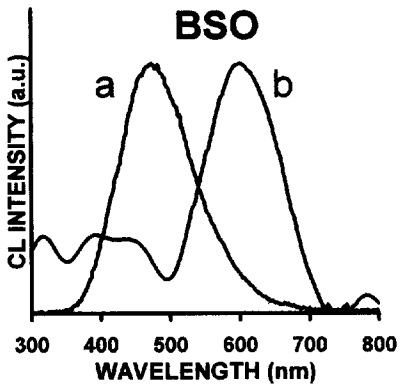

FIG. 8. (a) CL spectrum of a BSO annealed sample. (b) CL spectrum of a BSO untreated sample is shown for comparison.

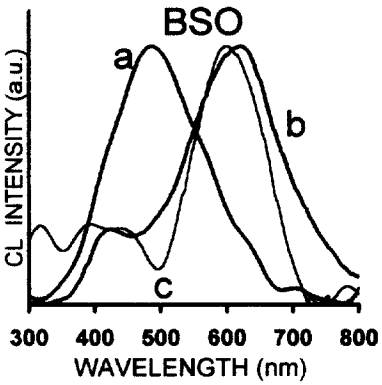

FIG. 9. CL spectra of (a) laser and (b) electron irradiated BSO samples. (c) CL spectrum of a BSO untreated sample is plotted for comparison.

gin. These authors reported the reduction of Bi^{3+} ions to metallic Bi after annealing above 400 °C in vacuum and the formation of metallic Bi microdrops on the surface. The presence of metallic microdrops agrees with their dark contrast observed in the CL images. In addition to the contrast changes in the CL images, thermal treatments cause variations of the CL spectra. In the following, the spectral changes induced by thermal treatments and by laser irradiation are discussed.

Spectra of untreated BGO and BSO do not show a resolved emission band in the blue spectral region, but annealing causes the appearance of a shoulder at about 390 nm in the CL spectra of the BGO samples. This emission is enhanced when annealing is followed by rapid quenching in air and appears mainly localized in the slip bands resulting from thermal stresses. This fact indicates that the 390 nm centers, which would involve impurities and/or native point defects, are generated during annealing and decorate the dislocations of the slip bands forming a Cotrell atmosphere. The effect of laser irradiation on the blue emission is similar to that of the annealing, with an increase of the 390 nm band, and can be explained by local heating caused by the laser beam. These results suggest that point defects, mobile at the annealing temperature, are involved in the luminescent centers responsible for the 390 nm.

The blue emission present in the BSO untreated samples has a different behavior. It is not stable under the same annealing conditions, as concluded from the CL spectra of annealed BSO in which no blue emission is observed. This behavior could be understood if one considers that the annealing temperature is much closer to the melting temperature for the BSO crystals (850 °C) compared with BGO crystals (950 °C).

The 500 nm emission, which is present in the untreated samples, increases during annealing and dominates the spectrum of all thermal treated samples. This behavior suggests that as in the case of the 390 nm band, the motion of the point defects at the annealing temperature contributes to the formation of the 500 nm centers. Irradiation in the SEM causes the reduction of this band, and the increase of the band peaked at about 640 nm, as described above and in a previous work.[12] The increase of the 640 nm emission was tentatively atributed[12] to changes in the charge state of Bi ions during irradiation. The decrease of the 550 nm emission can be either related to the same effect, if Bi ions are involved in the center, or to the appearance of the competing recombination channel related to the 640 nm center. Laser irradiation enhances the 550 nm band, showing that the effect of this treatment is, as in the case of the 390 nm band, similar to that of annealing.

The band at about 620–640 nm appears intense in untreated samples and is quenched by thermal treatments. This behavior is consistent with the suggestion[12] that the center responsible of this emission involves Bi ions. Annealing over 400 °C causes the reduction of Bi^{+} ions[14] and the appearance of Bi microdrops, which have been also observed in this work. Consequently, the concentration of centers involving Bi is reduced in accordance with the results of Zaldo *et al.*[15]

Annealing or irradiation induced luminescence changes in the visible range have been detected by CL but not by PL. This difference is due to the different excitation conditions of each technique, the latter being more selective. In the near-infrared range changes have been detected by both luminescence techniques. One of the bands present in the untreated samples, peaked at about 900 nm (reported previously in Ref. 12), and has been attributed[5] to a complex of oxygen and Ge or Si vacancies. The other infrared bands induced by thermal treatments, as those centered at about 1400 or 1560 nm, are to our knowledge reported for the first time. The present results do not enable us to obtain information on their nature.

V. CONCLUSIONS

Annealing of BGO causes the appearance of an emission band at 390 nm. The centers responsible for this band decorate the dislocations in quenched samples. Emission in the same spectral range, observed in untreated BSO, shows a different behavior and is quenched during annealing. Annealing causes quenching of the 640 nm band due to the reduction of Bi ions to metallic Bi that appears in the form of microdrops in the annealed samples. The same treatment enhances the emission band centered at about 500 nm. Centers responsible for luminescence in the near-infrared range are generated during annealing but their nature is unknown.

ACKNOWLEDGMENTS

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