JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 2, February 2007, p. 293 - 295

XRD and Raman spectroscopic study of Ru and Os doped $Bi_{12}SiO_{20}$ crystals

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Single crystals of $Bi_{12}SiO_{20}$ doped with Ru and Os (BSO:Ru and BSO:Os) with diameters of about 40 mm and lengths of 80-100 mm were grown by the Czochralski method. Slices of these crystals were studied by polarized Raman spectroscopy. Two-dimensional defects (probably stacking faults) were observed in the central core area of the BSO:Ru crystal by X- ray double crystal traverse topography, while the BSO:Os crystal was probably free of this defect. The specimens from the central part of the ingots were also investigated by single crystal X- ray diffractometry. Conclusions about the crystal perfection based on the research findings, were made.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: Crystal growth, Lattice defects, X- ray diffraction methods, Raman spectroscopy

1. Introduction

Crystals of $Bi_{12}SiO_{20}$ (BSO) have a sillenite type structure (space group I23) and are treated as a promising material for applications in linear and non-linear optics [1-3]. Large single crystals (diameter ≥ 50 mm and length ≥ 100 mm) and high quality, from undoped and doped BSO crystals, are usually grown by the Czochralski method [4]. The structural quality of the grown crystals is very often degraded by so-called "growth stripes" or "growth bands"- a structural defect that appears in the central core region of the ingot and is detected in optical microscopy images as darker lines [4]. Our previous investigations of BSO crystals by X-ray diffraction traverse topography (XRDTT) showed that these defects are probably some kind of stacking fault [5,6]. Researchers related the formation of such defects to the facet growth [3-6]. We present here the results of an investigation of BSO crystals doped with Ru and Os by two different X- ray diffraction methods and by Raman spectroscopy.

2. Experimental

BSO crystals doped with Ru and Os with diameters of about 40 mm and lengths of about 100 mm were grown by the Czochralski method along the [001] axis. More details of the crystal growth process can be found in [7]. Thick wafers of about 10 mm depth were cut nearly perpendicularly to the growth axis, precisely lapped and polished for the purposes of the present study.

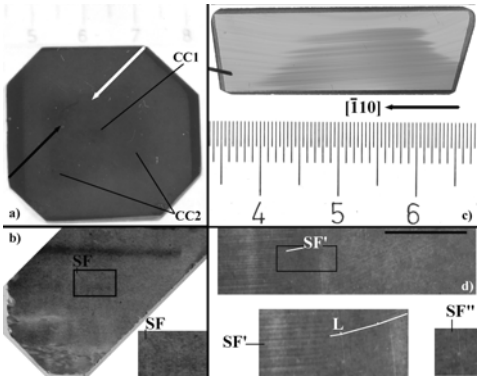

Fig. 1. a) Photography of the (001) surface of 8 mm thick BSO:Ru wafer. CC1 marks the central core area (the upper surface refferred to the plane of the sheet) and CC2 a similar area from the lower surface. The black arrow marks the [110] direction. b) A XRDTT image of the (001) surface viewed from the CC2 side ((006) reflection). Lower: a two times magnified rectangular part from the upper image. SF- denotes stacking faults lying in the (001) plane. c) A photograph of the (110) slice. d) A XRDTT image of the (110) surface- (660) reflection. SF and SF' denote stacking faults lying in (001) and (010) or (100), respectively. The marker represents 3 mm. Lower: a two times magnified part from the upper image near the SF'- and SF"-marked stacking faults and the L- marked line.

The wafers were examined by Raman spectroscopy at their surfaces that were declined from the growth axis at about 3° in BSO:Ru and less than 1° in BSO:Os crystals. Then, about 1 mm thick slices were cut parallel to (011) at a distance of about 5- 10 mm from the central axis of the ingot. The cutting plane is marked by arrows in Figs. 1 a) and 2 a), i.e. the central part of the ingot was not involved in the slices for further investigation. The (011) slices, as well the remaining pieces of the (001) thick wafers were examined by XRDTT. The results were the same as those presented in [6] for (001) surfaces- Figs. 1c) and 2c), as well as in [5] for (011) surfaces- Fig. 2d). Small pieces from slices were cleaved and examined by X-ray diffractometry.

3. Results and discussion

It is clearly distinguishable in the optical photographs of the (001) surfaces of the thick wafers- Figs. 1 a) and 2 a), that the BSO:Ru crystal has a more darkened central core region [5,6] (marked by CC1 and CC2 in Fig. 1 a)). The optical photograph of the (011) surface of the BSO:Ru slice- Fig.1b), reveals that the defects that determine the central core in the beginning of the ingot grow and occupy about 70- 80 % of the lower parts of the crystal, and are revealed (in this section of the ingot) as dark lines parallel to (001). Therefore, all darkened areas should be considered as a central core. The dark lines in the central core are declined at about 3° and parallel to (001), while the more bright lines marked by L in Fig. 2 d) and declined at different angles ±(3-20)° occupy practically all other parts of the BSO:Ru crystal. The BSO:Os crystal is practically free of dark areas and lines- Figs. 2 a) and b).

The XRDTT images (Figs. 1 c and d) confirm that defects similar to the stacking faults found in [5] and [6] almost completely occupy the (110) and (001) surfaces of the BSO:Ru specimen. These defects are revealed as areas in dark contrast, covered by bright lines parallel to [010] in Fig.1 c), and as dark lines parallel to [110] in Fig. 1 d). The distance between the defects could not be determined, as the picture is very complex due to the super-positioned lines- the defect denoted as SF' in Fig. 1d) is split into three different lines in the two times magnified images- see Fig. 1d). The declined lines in dark contrast- Fig. 1 d) correspond to the dark contrasted lines in the optical photograph- Fig. 1 b), to a first approximation. The declination angle of these lines is changed in different areas- see the L-marked line in the two times magnified images in Fig. 1 d). Dark-contrasted spots, sometimes covered by lines parallel to [001], very similar to the images of stacking faults but lying in (010) or (100), are observed in positions where the declination angle is changed- Fig. 1 d). We made two suggestions about the nature of lines similar to the L-marked lines (Fig. 1d) in [5], but now we can confirm that the L-marked lines have a complex structure and, on the micrometer scale, arise from the contrast due to stacking faults lying probably in (010) or (100). In addition, the crystal lattice in the lower corner of the (001) surface (see Fig. 1 b)) is strained and this can be related to the observed diameter change in this area as well as in the orientation of the crystal. The XRDTT image of the (001) surface of the BSO:Os crystal confirms the absence of defects similar to those observed in the BSO:Ru crystal- see Figs. 1 b) and 2 b).

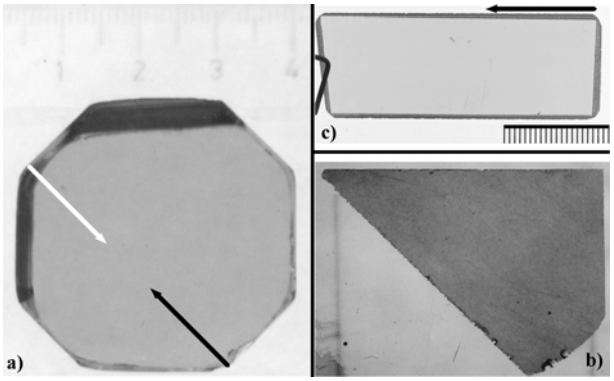

Fig. 2. a) A photograph of the (001) surface of the 8 mm thick BSO:Os wafer. The black arrow marks the [110] direction. b) A XRDTT image of the (001) surface- (006) reflection. c) A photograph of the (110) slice. The marker represents 10 mm.

The crystal structure was determined by single crystal X- ray diffractometry on an Enraf-Nonius CAD-4 diffractometer- according to the procedure given in [8]. The X-ray single crystal measurements were carried out on two specimens cleaved from the dark areas of the BSO:Ru as well as from one slice cleaved from the BSO:Os at room temperature. The crystal structure was refined at an R-factor of 2.00- 2.10 % for different specimens. The values of the lattice parameter were a_o= 1.0084 nm and a_o= 1.0091 nm for BSO:Ru specimens and a_o= 1.0073(8) nm for BSO:Os specimen. The determined lattice parameter of a new BSO:Os specimen cleaved from a BSO:Os slice bilaterally lapped to a thickness of 250- 300 μm, is a_o= 1.0090 nm. We can notdraw definite conclusions about the observed deviations in the lattice parameter, but it seems that it could be related to the observed two dimensional defects in the BSO:Ru crystal.

The Raman spectra were measured on a Dilor Labram spectrometer at 514.5 nm, the absolute accuracy being 1.5 cm^{-1}. The laser beam was focused with microscope optics to a spot of about 2 μm diameter on the surface of the crystal, in order to prevent the relaxation of the selection rules caused by the high optical activity of BSO. The samples were measured in an Z(XY)Z polarization geometry, where only *F* modes are allowed by symmetry. We performed spatially-resolved Raman measurements in the central core, the core and the circumference region of both crystals. The Raman spectra from all regions in both crystals turned out to be practically identical to those of undoped BSO (a sample spectrum is plotted in Fig. 3a)), except for the high-energy stretching *F* mode of the Si-tetrahedra. This is the only *F* mode in BSO exhibiting TO-LO splitting, and only the LO component is allowed in the present polarization geometry. However, the forbidden TO component also appears, due to its much higher Raman activity and a certain degree of lattice disorder. In this

case, the intensity ratio ρ=*I*(TO)/*I*(LO) may serve as a measure of the defect density. Our spatially-resolved measurements revealed, for all regions of the BSO:Os crystal, a ρ value centered at 0.4 with a symmetric distribution between 0.3 and 0.5. The same was found for the central core and circumference region of the BSO:Ru crystal. However, in the core region of the BSO:Ru (approximately 0.15D – 0.4D), the distribution of ρ values, while still centered around 0.4, was found to be strongly non-symmetric and varying between 0.3 and 0.7. This is depicted in Fig. 3 b). On the other hand, the close similarity of all spatially-resolved Raman spectra of both crystals, and especially the lack of intensity transfer from the *F* to the forbidden *E* modes, indicates that small-angle lattice mis-orientations [9,10] are below the detectable limits, in agreement with the XRD results.

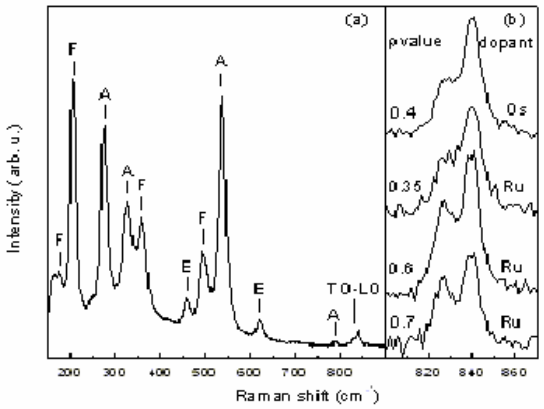

Fig. 3. a) Sample Raman spectrum representative of the spatially-resolved measurements in a Z(XY)Z polarization geometry on the BSO:Ru and BSO:Os crystals. b) Raman spectra of the high-energy antisymmetric stretching BSO mode as measured from the core region of the BSO:Os crystal (upper trace) and the BSO:Ru crystal (all three remaining traces). Note the substantial variation of the TO/LO intensity ratio in the core of the BSO:Ru crystal. The spectra were vertically shifted for clarity.

4. Conclusions

We confirmed the homogeneity and the high quality of the BSO:Os crystal and the higher defect concentration in the core region of the BSO:Ru crystal by several methods: Raman spectroscopy, XRDTT and X- ray diffractometry. The observed defects in the BSO:Ru crystal are two dimensional. It seems that they are some kind of stacking faults and occupy practically the entire crystal in some cases.

Acknowledgements

This work is financially supported by the Bulgarian National Scientific Research Found under contract No. F-1308.

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