Investigation of structural defects in ytterbium doped calcium gadolinium aluminate crystals by means of the synchrotron and conventional diffraction topography

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A R T I C L E   I N F O

Article history:
Received 22 February 2017
Received in revised form 18 May 2017
Accepted 29 May 2017
Available online 29 May 2017

Keywords:
X-ray diffraction topography
Crystal lattice defects
Czochralski method
Femtosecond lasers

A B S T R A C T

Ytterbium doped calcium gadolinium aluminate (CaGdAlO₄) crystals, which is a perspective material for femto-second lasers, have been studied by means of synchrotron and conventional X-ray diffraction topography. The investigation was performed with a series of samples cut out perpendicularly and parallel to the〈100〉growth axis from the initial and end parts of CaGdAlO₄ crystals, both undoped and doped with different concentration of Yb. The synchrotron topographic investigation was performed at the European Synchrotron (ESRF) in transmission geometry using the radiation of rather short wavelength, while the conventional topographs were obtained in the back-reflection geometry by means of the double crystal method in Cu Kα₁ radiation. Some additional investigation was performed with polarization microscopy and high resolution X-ray diffraction omega scan. Apart from slightly pronounced segregation fringes and a core region the diffraction topographs revealed numerous volume defects, which most probably can be interpreted as solute trails. A characteristic feature of the presently observed volume defects were the details of the contrasts on their boundaries. These details suggested the presence of strong stress and the generation of the dislocations. The increase of the defect concentration with the increase in ytterbium concentration was observed.

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1. Introduction

Ytterbium doped calcium gadolinium aluminate (CaGdAlO₄–CALGO) crystal belongs to the oxide materials of the general composition ABCO₄ (where A = Ca, Sr, Ba, B = La, Nd, Pr, and C = Al, Ga) with perovskite-like structure. ABCO₄ are perspective substrate materials for high-temperature superconductor thin films, elements of thermal radiation receivers and other electronic devices, owing to their electrochemical and thermal properties and good lattice matching [1]. Unlike the other crystals of the family CALGO is a material considered for perspective applications in the technology of ultra-fast lasers with femto-second pulse duration [2–20]. There are only few papers describing the structural perfection of CALGO crystals [5,13,17,21]. The growth technology for these crystals, basing on the Czochralski method has recently been developed at the Institute of Electronic Materials Technology in Warsaw.

In the present work the defect structure of the CALGO samples was studied by means of various X-ray diffraction topographic methods and optical polarization microscopy. These methods are very sensitive to the lattice deformation and are very effective for studying of various oxide crystals grown by Czochralski method [22–35].

X-ray diffraction topographic studies provide valuable information about the real structure of crystals, deformation and crystal lattice defects. The defect structure depends on the type of crystal, the impurity content and its stoichiometry, growth conditions, as well as the additional thermal processing. The defects affect mechanical, electrical, optical, magnetic and chemical properties and for this reason the determination of structural quality of the crystals is very important.

The study was performed with crystals that exhibited various Yb dopant concentrations and with samples cut out from different regions of the crystal representing different stages of the growth process.

2. Experimental details

The single crystals of CaGdAlO₄ doped with ytterbium were grown by the Czochralski method at the Institute of Electronic Materials Technology in Warsaw. The investigation on growth conditions were carried out with a Cyberstar apparatus, equipped with an inductive heating. The thermal system was designed taking into account the melting point equal to 1830 °C and thermal conductivity coefficients (6.9 W m⁻¹ K⁻¹ and 6.3 W m⁻¹ K⁻¹, in a and c direction respectively).

The starting materials were prepared by mixing of 5 N pure Gd₂O₃, 5 N pure Al₂O₃ and 4 N pure CaCO₃ at stoichiometric ratios. The ytterbium dopant in the form of 5 N pure Yb₂O₃ oxide was added to the above...
mentioned compound, assuming that ytterbium ions substitute gadolinium ions and the ionic radii of these ions are similar. The mixture of the oxides and calcium carbonate was synthesized in a resistivity furnace by heating during 12 h at 1150 °C, then isostatically compressed and finally placed in the crucible. The diameter of the crucible was equal to 50 mm, its height was equal to 50 mm, and the thickness of the crucible wall was equal to 2 mm. The crucible was then placed in a thermal system which included an active afterheater with diameter equal to 50 mm, which was directly placed on the crucible. The crystals were grown under nitrogen atmosphere. The pulling rate was in the range of 1.0–2.0 mm/h, the rotation rate was 10–20 rpm, and the pulling direction was 〈100〉. Under these conditions single crystals with about 20 mm diameter and 55 mm length were grown (Fig. 1). The cooling time of the single crystal ranged from 12 h to 24 h.

The investigated CALGO single crystals contained various concentrations of the Yb dopant, namely without doping and respectively with the 4 at.% 5 at.% 8 at.% of Yb. The samples were cut out from two series of crystals. With the described topographic investigations strong stresses and the generation of dislocations were detected. This made us change some growth parameters in a second growth series. We decreased the growth rate and increased the cooling time.

The investigated samples corresponded to the section of the whole crystals cut-out from their various regions - representing different stages of the crystal growth process. The samples were cut-out perpendicularly and parallel to the 〈100〉 growth axis. All samples were mechanically and chemically polished and thinned down to the thickness of about 1 mm.

The characterization of the defect structure was performed by means of conventional X-ray double-crystal back-reflection diffraction topography, white beam transmission high-energy synchrotron radiation (SR) topography (BM05 station at the ESRF), high resolution X-ray diffraction omega scan and polariscopic microphotography realized using crossed polarizers. A common feature of all of X-ray diffraction topographic methods is that the sample is set to Bragg diffraction and the diffracted beam is recorded in the photographic emulsion or the high resolution electronic imaging device (camera). The resulting images are called topographs and show the interior (transmission geometry) or the near-surface layer (reflective geometry) of the sample. In the case of a defect free single crystal the topograph reveals a homogenous blackening, constant local intensity in the image. Lattice defects usually cause disorder of wave field propagation in the crystal, which locally alters the intensity of the diffracted radiation, resulting in a “diffraction contrast” in the topograph. Topographs presented in this work are negatives: a darker image part means higher intensity in the diffracted beam.

The main research techniques were:

1. Back-reflection double crystal topography using a conventional radiation source and Cu Kα1 (λ = 0.154 nm). The set-up contained a strongly asymmetric cut germanium monochromator which used the 511 reflection (Bragg angle of approx. 45° and the angle of entry of about 9°). On the samples reflections with as small as possible asymmetry were chosen. The elimination of the Cu Kα2 component was realized with a slit between source and monochromator.

2. Synchrotron white beam topography in transmission geometry at the ESRF. The method provides a set of topographs forming a specific

![Initial part of the crystal](image1)

![Final part of the crystal](image2)

Fig. 1. Representative CaGdAlO4 single crystals doped with 4 at.% of ytterbium grown by the Czochralski method at the Institute of Electronic Materials Technology.

Fig. 2. (a–b) White beam synchrotron transmission topographs of the undoped calcium gadolinium aluminate (CaGdAlO4) samples cut out perpendicularly to the growth axis 〈100〉: (a) initial part of the crystal, (b) final part of the crystal; (c) polariscopic image of the sample cut out from the initial part of the crystal. A indicates blocks separated by small angle boundaries which provided significant displacement of the fragments of images in the synchrotron topograph. B some evident cracks distinctly visible in the polariscopic image which provided only very weak contrast and very small displacement of images in the topograph. C — long linear contrasts which may be connected with dislocations or glide bands. X denotes the projection of the incident beam direction.
Laue-graph in one single exposure — recording the reflections from many families of lattice planes. This is because of the continuous spectral distribution of radiation of a bending magnet. Different topographs correspond to different reflections and different wavelengths. The advantage of the method used at a synchrotron is obtaining a large number of topographs at a very short exposure time (a few seconds) as well as the easy way to select and change reflections and wavelength. All synchrotron topographs were recorded on AGFA STRUCTURIX D2 SC films. All presented topographs are negative prints, i.e. a higher blackening corresponds to higher X-ray intensity.

3. Simplified polarization microscopy consists in taking high-resolution macroscopic pictures. Samples were placed between crossed linear polarizers and the images were recorded using an Olympus camera with m 4/3 16 MP matrix and Sigma 2.8/50 macro lens. Differently from X-ray diffraction topography the polariscopic microscopy is sensitive to difference of main the stress tensor component and not much sensitive to the misorientation of the lattice [36–37].
Fig. 5. Polariscopic images of samples cut out from the calcium gadolinium aluminate doped with 4 at.% Yb, cut out perpendicularly to the growth axis [100]: (a) initial part of the crystal, (b) final part of the crystal. A — the volume defects in the central part of the crystal. B — the crack.

Fig. 6. Diffractometric curve in omega scan of the sample cut out perpendicularly to the growth axis [100] from the final part of the calcium gadolinium aluminate single crystal doped with 4 at.% Yb, CuKα radiation (λ = 0.154 nm), 031 reflection: a) central region of the sample, b) boundary region 2, c) boundary region 1.
4. High resolution omega scan (scan perpendicular to the diffraction vector) in 031 reflection of Cu Kα₁ (λ = 0.154 nm) radiation.

3. Results and discussion

Representative topographs of the samples cut out from the first series of CALGO crystals, both undoped and doped with different concentrations of Ytterbium ions are reproduced in Figs. 2–6.

The characteristic feature of the sample cut out from the initial part of the undoped crystal was the presence of cracks related probably with the high level of the residual stress. These cracks were visible both in the synchrotron diffraction topographs (Fig. 2a) and in the polariscopic images (Fig. 2b). One cannot exclude that apart from the cracks there were some blocks separated by small angle boundaries which provided significant displacement of the fragments of images in the synchrotron topographs (marked by A in Fig. 2a, b). The sample exhibited block structure composed of large grains with 0.5° disorientation. The boundaries between these blocks did not produce any significant contrast in the polariscopic micrographs. Contrary to that there were some evident cracks distinctly visible in the polariscopic image which provided only very weak contrast and very small displacement of images in the synchrotron topographs (marked by B in Fig. 2a, b). The topograph of the end part of undoped crystal reveals some long linear contrasts which may be related to dislocations or even glide bands (marked by C in Fig. 2c).

A very interesting defect structure was observed in the case of the crystal doped with 4 at.% Yb which was obtained with the first series of growth processes. As it may be noted in Fig. 3a, the initial part of the crystal contained a number of defects producing round contrasts (marked by A) surrounded by some “tails” most probably build of dislocations (marked by B). The most probable interpretation of the defects is the “solute trails”. These defects are in fact elongated rods of the material whose crystallization takes place later than the main part of the crystal as they contain the higher content of impurities decreasing their temperature of solidification. The solute trails are often formed behind not completely melt fragments incorporated to the growing crystals. The existence of the tails formed from dislocations is most probably caused by a significant stress connected with the rods of inclusions. Sample cut out from the end part of the crystal practically does not contain the solute trails but one can observe the tails of dislocations around the facets forming the core (marked by C in Fig. 3b).

The double crystal topograph of the sample cut out from the initial part of the crystal indicated distinct bending of the sample causing that only relatively narrow stripes of the crystal were reproduced (Fig. 4a). Contrary to that, the sample cut out from the end part of the crystal...
Fig. 9. (a–b) White beam synchrotron transmission topographs of the calcium gadolinium aluminate doped 4 at.% Yb, samples cut out parallel to the growth axis [100]; (c) polariscopic image. A — extended volume defects, B — segregation fringes, E — the glide band. X denotes the projection of the incident beam direction.

(Fig. 4b) was almost not bent providing a good reproduction of the whole sample and well reproducing the details of the defect structure, particularly the volume defects (marked by A), segregation fringes (marked by B), faceted regions (marked by C), some dislocations (marked by D) and glide bands (marked by E). The polariscopic images of both samples reveal relatively weak image of the defect structure, in particular some faceted regions and solute trails close to the core (Fig. 5a, b).

Diffraction profiles of the samples from the end part of the 4 at.% Yb crystals are shown in Fig. 6a–c. The measurements were made in three different regions of the sample. In the boundary regions 1 and 2 (Fig. 6b, c) the omega scans revealed only one relatively narrow maximum. The full widths at half maximum (FWHM) were respectively: 30.24 arcsec in the region 1 and 29.88 s in the region 2. In the central region of the sample (Fig. 6a) the main maximum was stronger and narrower (FWHM = 23 s), but an additional weak peak was clearly marked. The results indicate a relatively good crystallographic quality of boundary areas and presence of some misoriented regions in a central part of the sample. The evaluated misorientation was in the range of several arc minutes.

A similar defect structure as in the crystal doped with 4 at.% of Yb was observed in the crystal doped with 8 at.% of Yb. Fig. 7 presents the topographs and the polariscopic images of the initial (a, c) and end part (b, d) of this crystal. Both the samples were cracked. The cause of cracking is most probably residual stress connected with the dislocation bundles and volume defects.

The investigation of the samples cut out from the second improved series of the crystals included those cut out parallel to the growth axis. These samples allow following of the shape of the growth surface and the formation of defects during a certain period of the growth process.

Fig. 8 reproduces synchrotron transmission topographs of the samples cut out perpendicularly to the growth axis respectively from the initial (Fig. 8a) and the end (Fig. 8b) part of the crystal doped with 4 at.% of Yb. Fig. 9 presents the topographs and the polariscopic image of the sample cut out parallel to the growth axis of the same crystal. The characteristic feature visible in all these images are the segregation fringes (also called growth striations) (marked by B in Figs. 8b, 9) corresponding to the subsequent position of the growth surface as it may be easily follow in case of samples cut out parallel to the growth axis [100]. The another interesting objects are some volume inclusions (marked by A in Figs. 8–9) which, in case of the samples cut out parallel to the growth axis, are often parallel to the growth surface at some length. In the topographs of the samples cut out perpendicularly to the growth axis one can see mainly the inclusions of the oval shape. The elongated volume defects may correspond to the faceted growth caused by constitutional supercooling, but in some cases they can also be kind of the solute trails. Contrary to the volume defects detected in the first series of crystals, in the second series neither the strong contrasts due to deformed region nor the dislocation bundles were observed.

In the initial part of the crystal one can notice some strong stripe formed diffraction contrasts which most probably may be attributed to the glide bands (marked by E in Fig. 5a, b).

The topograph and the polariscopic micrograph of the sample cut out perpendicularly to the growth axis from the crystal doped with 5 at.% of Yb are shown in Figs. 10a, b. The investigation reveals some segregation fringes and also a certain concentration of the volume defects, some of them being most probably the solute trails.

The defect structure in the presently studied crystals seems to be different than in other oxide crystals including the SrLaGaO4 crystals belonging to the same family. In the last case the rod-shaped volume defects were sometimes observed but their concentration and morphology were usually different. Also the generation of dislocation connected with the volume defects was not present [22,32,33].

4. Conclusion

The aim of the study was the characterization of the structure defects in CaGdAlO4 single crystal. The studies included the examination of the crystals both undoped and doped with ytterbium. The investigation was performed by X-ray diffraction topographic methods, exploring both conventional and synchrotron X-ray sources. The X-ray diffraction topography is extremely sensitive to lattice deformation. However, the transmission synchrotron topography is practically not sensitive to the lattice parameter changes differently from the double crystal topography, which is sensitive both to the misorientation and lattice parameter changes.

The X-ray diffraction topographic and polariscopic investigation revealed segregation fringes, faceted regions, volume defects and dislocations. In particular they also reveal that the generation of dislocations and significant strains are often connected with volume defects most probably being the “solute trails”.
The strong stress and generation of dislocations indicated by the presently described topographic investigations were the motivation for decreasing the growth rate and increasing of the cooling time in growing the second series of crystals. The use of X-ray diffraction topography demonstrated better crystalline quality of investigated crystals of the second series.

The orientation of the samples cut out parallel to the growth axis made it possible to follow the shape of the growth surface and its evolution during the growth process.

We did not observe any systematical changes of the defect structure in the presently studied crystals with various concentration of ytterbium.

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**References**


**Fig. 10.** (a) White beam synchrotron transmission topograph of the calcium gadolinium aluminate doped with 5 at.% Yb sample cut out perpendicularly to the growth axis [100]; (b) polariscope image. A – volume defects (most probably the “solute trails”), B – segregation fringes. X denotes the projection of the incident beam direction.