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MICROSTRUCTURE AND MICROSEGREGATION IN SUBSTRATE GARNET MATERIALS

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ABSTRACT

Electron microscopy is used to study the microstructure of Gadolinium Gallium Garnet (GGG) and Calcium Gallium Germanium Garnet (CGGG), materials used as substrates for bubble garnet films. Isolated undissociated dislocations with Burgers vectors $\frac{1}{2}\langle 111 \rangle$ are characterised using dynamical contrast analysis. Microcracks ($\lesssim 1 \mu\text{m}$ in size) bounded by groups of dislocations are observed in both GGG and CGGG. The occurrence of small inclusions (and voids) in CGGG are also investigated. A model is developed to explain the formation of these precipitates due to microsegregation of vacancy-atom clusters.

INTRODUCTION

Ferrimagnetic garnets are prime candidates for thin film bubble memory devices. For such applications, single crystal magnetic garnet films are usually grown on nonmagnetic ceramic substrates (1) such as $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG). Recently, $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (CGGG) has also been demonstrated (2) to be an alternate substrate garnet material. Defects and inhomogeneities in the substrate materials are easily replicated in the epi-films that subsequently lead to device degradation (3). Very little is known about the microstructures of the substrate and the epilayer garnets and their role in such occurrences on a sub-micron scale. Microstructural features affecting other properties of garnets also have rarely been systematically characterised on a microscopic scale. In the present paper, we shall present results of an electron microscope study of microstructural features found in CGGG and GGG substrate materials and discuss the significance of these findings.

Much effort (4-6) has gone into the study of dislocations in various garnet structure compounds using techniques such as (i) optical birefringence (ii) etchpit and decoration techniques, (iii) x-ray topography etc. Unfortunately, none of these

techniques have the resolution to provide information on a microscopic scale. As mentioned in the preceding paragraph, no systematic work on the electron metallographic characterisation of dislocations in garnets has been done. The few attempts (7,8) at such studies have been hampered by the difficulties in obtaining interpretable contrast conditions (two beam cases) in the diffraction patterns due to the large unit cell of the garnet materials ($a_0 \sim 12\text{\AA}$). Below, we present the analyses of the Burgers vector of some dislocations in GGG using special contrast conditions available in HVEM (9) and the corresponding computer calculation of the image profile. As will be seen later, the study of dislocations occupies a central position for subsequent characterisation of other microstructural features in this investigation.

EXPERIMENT

Czochralski grown single crystal chips of GGG were obtained from Rockwell International, Ca. and CGGG samples were obtained from Philips, the Netherlands. The method of preparation of CGGG crystals was similar to the preparation technique described in ref. 3. Specimens for examination in the microscope were prepared by (i) ultrasonically drilling a 3mm disc from the single crystal chips, (ii) mechanically polishing these discs to a thickness of about $25\mu\text{m}$ and (iii) ion-thinning them until electron-transparent ($< 0.7\mu\text{m}$). The thin foils were examined in a Hitachi HU-650 high voltage electron microscope operating at 650kV.

RESULTS AND INTERPRETATION

(a) Study of dislocations: Figs. 1(a) and (b) show the contrast from a pair of dislocations in two different diffraction conditions. The computer image profile at x in Fig. 1a is shown in Fig. 1(c). From detailed tilting experiments and comparisons with the calculated image profiles, it is concluded that dislocations A and B are mixed in character and have Burgers vectors $\frac{1}{2}[111]$ and $\frac{1}{2}[\bar{1}11]$ respectively. No evidence of dissociation is seen. Fig. 2 shows an isolated dislocation loop in CGGG imaged in bright field (a) and weakbeam darkfield (b). Fig. 2a is an example of commonly encountered contrast conditions which make it difficult to draw conclusions regarding the geometry of the dislocations. Using other specialised techniques (9) however, these analyses become easier.

In the crystals examined here, only a few dislocation networks and isolated dislocations are observed, and the materials are, to a large extent, dislocation free (if one excludes dislocations associated with other defects).

(b) Study of microcracks: Both GGG and CGGG examined here show microcracking in them. Fig. 3 is taken from CGGG and the fringe contrast A arises due to the presence of two internal boundaries at the cracks. The cracks are in general curved and do not lie on any specific crystallographic planes. They are bounded by a group of sessile dislocations as shown in Fig. 3. Contrast analysis experiments show that different cracks have dislocations of different Burgers vectors ($\vec{b}$) bounding them. We have observed both $\frac{1}{2}\langle 110 \rangle$ and $\langle 100 \rangle$ dislocations bounding the cracks. No evidence of dissociation of the bounding dislocations around the crack tips has been observed. Details of the contrast from microcracks will be published elsewhere.

The cracks are very small in size and have never been detected with alternate techniques (7,8) by other investigators.

The specimen preparation technique used here is not known to introduce any microcracks in other ceramic materials (10) thinned by the same method. Also the observation of more numerous cracks (~10 times) in CGGG compared to GGG samples suggests that the specimen preparation technique might not be responsible for the introduction of these microcracks.

(c) Microsegregation: Inhomogeneous regions as in Fig. 4 are very frequently seen in CGGG. These range from $1000\text{\AA}$ to $5000\text{\AA}$ in size. Detailed stereo microscopic analyses show that the light patch P at the center of the inhomogeneity has a spherical shape. The region Q surrounding P is generally cylindrical with a noncircular cross section. These inclusions do not give rise to any detectable scattering in the selected area diffraction patterns in any orientation of the matrix and are thus interpreted to have the garnet structure (same as that of the matrix). There is a sharp boundary separating region Q from the matrix, and no strain contrast arising from the inclusion is detected. As in Fig. 5, some inclusions have a dislocation around them. But in most cases, dislocations are seen to be present with a configuration as at C in Fig. 4 or in Fig. 5. Not all the dislocations (the ones denoted by C in Figs. 4 and 5) have identical Burgers vectors. We have been able to determine that the $\vec{b}$ s for some of the dislocations are parallel to $\langle 112 \rangle$. Experiments to determine the $\vec{b}$ s for all the dislocations are in progress. Dynamical

scattering events as discussed earlier and in Ref. 9 have hampered these analyses.

These inclusions are also often seen to be aligned in linear arrays along $\langle 100 \rangle$ and $\langle 110 \rangle$ crystallographic directions. However, no dislocations connecting them are observed. In addition, of the inclusions which occur in arrays, some show regions similar to those at P and Q in Fig. 4 (or 5), while some do not exhibit the light patch P. Nevertheless, none of these particles have structures different from that of the matrix. Dislocations are generally associated with precipitates which do not contain the light patch. From contrast behaviour of the light patches, they are believed to be voids.

DISCUSSION

The method of characterising dislocations as outlined in section III, although rather specialised, does not suffer from the problems that other investigators have encountered (7,8). It offers sufficiently high resolution so that the materials can be microscopically characterised and examined for any localised defects. In the present work, close examination of the images at high resolution (using weak beam and high order bright field techniques (9)) failed to show any dissociation of these dislocations to partials (11), or any other structural defects such as those observed in other ceramic ferrites (12).

The dislocations bounding the microcracks are seen to have Burgers vectors different from those of the isolated dislocations. Microcracks are believed to be formed due to the generation of thermal stresses during crystal growth and are probably very undesirable in device applications. Nevertheless, more work is needed to ascertain the exact origin of these cracks and their effect on the epi-films.

The "white" precipitates in CGGG encountered by Damen et al. (2) are believed to be identical to the ones reported here. The crystals used for both their study and the present study originated from the same source; however, due to resolution limitations, Damen et al. (2) were not able to identify the microstructural features in question. From the results presented in section III, it is suggested that the inclusions in Fig. 4 (or 5 or 6) are due to microsegregation of one of the components present in the material. Assuming the activation energies for the formation and migration of a vacancy-atom (V-A) pair to be low, such a pair would form and diffuse through the lattice easily, segregating to form a large cluster.

Eventually, when enough V-A pairs have combined, the vacancies (V) dissociate and accumulate to form voids, while the atoms (A) segregate around them. The structure factor contrast from regions Q (in Figs. 4 and 5) suggest these regions may be richer in heavier elements compared to the matrix. Work is in progress to determine the composition of these aggregates. The above description is consistent with the observation that smaller aggregates do not have voids associated with them, but frequently have dislocations instead. Also, the formation of rows of these precipitates (2) as in Fig. 6 can be explained by assuming that they form on pre-existing dislocations via a mechanism of easy pipe diffusion.

The shape of the precipitates, observed in this study and the geometry of the associated dislocation configurations as in Figs. 4 and 5 are different from the models of stress gradients and deformation zones reported by Lal and Mader (12) or studied in detail by Mathews (13). Also the dislocation segments in Figs. 4 and 5 have different bs and hence can not be segments of loops which surround precipitates. Finally, unlike the Nd, Ir, or other reported inclusions in GGG (4,8,15), the present inclusions are much smaller in size, have a garnet structure, and probably do not form from contaminants in the melt crucible.

In conclusion, a combination of image profile contrast calculations, high order bright field and weakbeam darkfield imaging, and tilting experiments in the electron microscope are necessary for unambiguous characterisation of dislocations in garnet structure compounds. Although this has been demonstrated for only GGG and CGGG in this paper, the methods should be equally applicable for other garnet materials. Segregation problems of the kind discussed here are probably a consequence of the complex defect chemistry in these materials. More work is needed to ascertain the chemical composition of the segregates and to verify the present model for their formation. Finally, efforts must be made to explain the occurrence of the various kinds of structural defects reported here and by other investigators (4-7) in different garnets.

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FIGURE CAPTIONS

Fig. 1(a) and (b) are high order bright field images (B.F.) of two isolated dislocations A and B. (c) is the calculated image profile corresponding to point X (center of the foil), and for an undissociated dislocation with $b = \frac{1}{2}[111]$ in GGG.

Fig. 2 An isolated dislocation loop with $\vec{b} = \frac{1}{2}[111]$ on $(1\bar{1}0)$ plane in CGGG imaged in B.F. (a) and weak beam dark field (b). Foil normal near $[112]$ pole and the loop is viewed edge on. Some latex balls used for stereo microscopy on the foil surface are seen at A.

Fig. 3 B.F. image of an isolated microcrack in CGGG. The fringes A arise due to the two internal crack surfaces. The crack is bounded at its tips by groups of dislocations B.

Fig. 4 B.F. image of an inclusion in CGGG consisting of a spherical void (P) surrounded by a cylindrical region (Q) that is richer in a heavy element. Note the sharp boundary separating Q from the matrix. The dislocations C exhibit dynamical contrast and hence the images are smeared out.

Fig. 5 B.F. image of an inclusion similar to the one in Fig. 4. The void (P) is not exactly spherical. A dislocation loop D is present around the inclusion in addition to the dislocations C.

Fig. 6 A row of inclusions aligned parallel to $[100]$ direction. Whereas inclusions 2,3,4 are similar to the ones in Fig. 4 (or 5), inclusion 1 does not contain the void (P), but has a few dislocations only.

XBB 779-9469

Fig. 1

XBB 779-9464

Fig. 2

XBB 779-9465

Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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