Microhardness and brittle fracture of garnet single crystals

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Hardness and fracture toughness were measured using the Vickers microhardness test in the low load range from 25 to 100 g near to the fracture threshold for near-perfect single crystals of garnets. The influence of crystal growth parameters, calcium impurity content and crystallographic orientation of Gd$_3$Ga$_5$O$_{12}$ (GGG) and Ca$_3$Ga$_2$Ge$_3$O$_{12}$ (CaGeGG) samples was investigated. Fracture starts with radial cracking from indent corners followed by lateral fracture of two distinct modes. The mean hardness of [1 1 1] oriented GGG is $H = 13$ GN m$^{-2}$, for [1 1 1] oriented CaGeGG it is $12$ GN m$^{-2}$, the average fracture toughness being $K_c = 1.2$ and 0.8 MN m$^{-3/2}$, respectively for the two crystals. Impurity doping slightly increases the strength of the material. Among the investigated crystals (1 1 1) faces are the least strong, the (1 0 0) face has maximum $H$ and $K_c$ values for CaGeGG. The constraint factor, $\phi$, and yield stress, $Y$, were deduced from the measured hardness data, giving $\phi = 2.2$ and $Y$ about 7 GN m$^{-2}$.

1. Introduction
Garnets are ionic crystals with cubic crystal structure of a general formula A$_3$B$_5$O$_{12}$. The elementary cell contains 8 formula units with 160 ions. The cations fill three different kinds of sites inside oxygen ion polyhedra. The crystal structure is loose enough to make possible the substitution of cations in a wide range of valencies and ionic radii. In consequence, materials with predetermined properties can be tailored from garnets.

Naturally occurring garnets are minerals, isomorphous mixed silicates and they are used as gemstones. Their Moh's hardness is in the range 7 to 7.5, compared with 8 for spinels and 9 for sapphire (corundum). It is known from jeweller's practice that they are brittle with no definite cleavage planes.

Synthetic garnets of composition R$_3$M$_5$O$_{12}$, where R denotes a rare earth ion and M is a metal cation, are widely used as materials for microwave devices (Y$_3$Fe$_5$O$_{12} =$ YIG), laser host crystals (Y$_3$Al$_5$O$_{12} =$ YAG) and magnetic storage materials in bubble memory devices (epitaxial layers of substituted YIG). For bubble memory and integrated device application a thin garnet film is needed that can be grown epitaxially on a single crystalline substrate with the same crystal structure and lattice parameter. Gd$_3$Ga$_5$O$_{12}$ (GGG) is the most widely used substrate material, along with other, less expensive candidates like Ca$_3$Ga$_2$Ge$_3$O$_{12}$ (CaGeGG).

GGG crystals are grown as boules of 2 or 3 inch diameter from the melt at about 2000 K by the Czochralski method, then sliced by a diamond saw, lapped and finally polished chemico-mechanically to obtain a perfect, featureless, flaw-free, near-atomically smooth surface. These crystals are practically defect-free, having dislocation and inclusion densities below 10 cm$^{-2}$ [1].

However, one of the most serious problems during GGG growth, substrate machining, and wafer dicing is the cracking and/or breaking of the crystals. In view of this, it is surprising that no systematic study seems to have been published regarding the mechanical properties of garnets.

Heinz et al. [2] published data on the physical properties of Dy$_3$Ga$_5$O$_{12}$ and GGG crystals together with the hardness values of 13.50 and 12.50 GN m$^{-2}$ for DyGG and GGG, respectively.
Measurements were made at 300 g load, with an error of 35%. Ehman [3] investigated the work damage during surface preparation of crystals, important as substrates for microelectronic devices. For (111) oriented GGG he measured a Knoop microhardness of 1098. Details of the measurement were not given.

The aim of our work was to study the hardness and fracture characteristics of nonmagnetic garnet single crystals in dependence of the conditions of growth, impurity content and crystallographic orientation. Knowledge of these parameters seems to be very important not only for machining such crystals, but for preventing fracture during growth and device fabrication. At the same time these garnets are good model materials for brittle fracture theory, as they are single crystals of cubic crystal structure, they are elastically isotropic, homogeneous, without internal defects (dislocations, inclusions, flaws) their surface is atomically smooth, and massive samples can be investigated. These crystals are colourless and transparent in visible light, making visual, microscopic observation very easy. As a consequence, simplifying assumptions and approximations of the theory can be proved and approved in this case.

2. Experiments

The investigated crystals were grown by the Czochralski method, with a fully automatized diameter control, along the [111] crystallographic direction.

Three groups of crystals were investigated.

Group A: Gd$_2$Ga$_5$O$_{12}$ crystals, each grown under slightly different conditions (A4 was cracked during cooling).

Group B: calcium doped GGG. Doping with calcium changes the front of crystallization and drastically reduces the number of dislocations via oxygen vacancy formation, already at the lowest level of doping [4]. The calcium content of the melt was 0, 10, 20, 30 ppm for crystals B1 to B4, respectively.

Group C: Ca$_3$Ga$_2$Ge$_3$O$_{12}$ crystals, surfaces parallel to various crystallographic faces.

After growth, boules were cut into wafers, polished and cleaned in accordance with bubble memory device requirements [1]. Growth defects of crystals, as cores, facets, inclusions and disruptions, were measured due to the stress-induced birefringence contrast in the optical microscope between crossed polarizers [1]. The thickness of wafers of groups A and C was 0.5 mm, for group B it was 1 mm. All samples except C1 and C2 had a (111) oriented surface.

Microhardness measurements with a Vickers indenter were performed in a Neophot-2 microscope (Zeiss, Jena) with an mhp-100 microhardness tester. The maximum applied load was 100 g, above which intensive cracking (conchoidal fracture) occurred. The minimum load (20 g) was above the threshold of radial cracking. Indentation sizes and crack dimensions were measured either at ×1000 using a dry objective of N50 in the same microscope, or at ×1700 from microphotographs. The statistical average and its dispersion were calculated from a minimum of three indentations at each load, taking into account each radial and/or lateral crack length. The curve fitting was done by regression analysis (least squares fit), and the correlation of each fit was calculated.

Measurements were made in air. This can be justified by the simplicity of the experiments; however it is known that ferrites are usually weakened by moisture. Processes connected with grain boundary effects are excluded in our case, but the lowering of surface tension is not. As the indentation depth is above the critical value for creep (see [5]), it is not likely that the results were influenced by this effect.

As garnets have no preferred cleavage planes, the orientation of the indents was accidental, with subsequent indents made along a row, having parallel diagonals on each crystal. Repeated measurements along other directions did not give significantly different results.

The indenter was applied quasi-statically, the loading time was typically 5 to 10 sec. The specimen remained under load for 5 sec, because acoustic emission associated with cracking in accordance with the experiments of Lankford and Davidson [6], occurs immediately upon application of the load. We were not able to decide if radial cracks extended upon unloading, but in some cases abrupt expansion of lateral cracks was observed even 20 to 40 sec after unloading.

3. Results

3.1. Morphology

Indentations from the Vickers pyramid were