

Revealing the morphological peculiarities of $Y_3Al_5O_{12}$:Nd laser ceramics by ion beam sputtering

O.M.Vovk, M.A.Chayka, P.V.Mateychenko, R.P.Yavetskiy, D.Yu.Kosyanov, S.V.Parkhomenko

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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The morphological peculiarities of $Y_3Al_5O_{12}$:Nd laser ceramics prepared by vacuum sintering of co-precipitated nanopowders have been revealed by ion beam sputtering of the ceramics surface. Inclusions with a cross section up to 5 μm located between the grain boundaries as well as pores and grain boundaries were detected on the surface of $Y_3Al_5O_{12}$:Nd ceramics treated by ion sputtering since sputtering rate of these inclusions is much lower compared to bulk of ceramics. Qualitative elemental composition of inclusions is same as that of $Y_3Al_5O_{12}$:Nd ceramics. It was suggested that the inclusions were formed as a result of local deviation from stoichiometry $Y_3Al_5O_{12}$ during processing of ceramics and have different phase composition compared to the parent garnet phase. The concentration of revealed inclusions which is higher the one of pores.

Особенности морфологии лазерной керамики $Y_3Al_5O_{12}$:Nd, синтезированной методом вакуумного спекания соосажденных нанопорошков, выявлены при помощи ионного травления поверхности керамики. Включения с поперечным сечением до 5 мкм, локализованные между границами зерен, наряду с порами и границами зерен проявились на поверхности керамики $Y_3Al_5O_{12}$:Nd в результате ионной обработки благодаря более низкой скорости распыления включений по сравнению с основной массой керамики. Качественный элементный анализ свидетельствует, что включения состоят из таких же атомов (Al, Y, O и Nd), как и керамика $Y_3Al_5O_{12}$:Nd. Высказано предположение, что включения образуются в результате локального отклонения от стехиометрии $Y_3Al_5O_{12}$ в процессе получения керамики и имеют фазовый состав, отличающийся от фазы граната. Концентрация включений значительно выше концентрации пор.

Виявлення особливостей морфології лазерної кераміки $Y_3Al_5O_{12}$:Nd при розпиленні іонним променем. *О.М.Вовк, М.А.Чайка, П.В.Матейченко, Р.П.Явецький, Д.Ю.Косянов, С.В.Пархоменко.*

Особливості морфології лазерної кераміки $Y_3Al_5O_{12}$:Nd, яку синтезовано методом вакуумного спікання співосаджених нанопорошків, виявлено за допомогою іонного травлення поверхні кераміки. Включення з поперечним перерізом до 5 мкм, що локалізовані між границями зерен, нарівні з порами та границями зерен проявилися на поверхні кераміки $Y_3Al_5O_{12}$:Nd в результаті іонної обробки завдяки більш низькій швидкості розпилення включень у порівнянні з основною масою кераміки. Якісний елементний аналіз свідчить, що включення складаються з тих саме атомів (Al, Y, O та Nd), як і кераміка $Y_3Al_5O_{12}$:Nd. Зроблено припущення, що включення утворюються в результаті локального відхилення від стехіометрії $Y_3Al_5O_{12}$ в процесі одержання кераміки і мають фазовий склад, що відрізняється від фази гранату. Концентрація включень значно перевищує концентрацію пор, що дозволило зробити висновок про їх суттєвий вплив на властивості лазерної кераміки.

1. Introduction

Since 1995, when Ikesue et al.[1] demonstrated lasing with average output power of 70 mW with Nd-doped $Y_3Al_5O_{12}$ (YAG) ceramic gain media, the continuous progress of many scientific groups has leaded to achieving of more than 100 kW lasing power on laser ceramics [2]. The main features of ceramics affecting laser quality of material have been established. Transparency is one of the most important characteristics of the laser ceramics determined by the scattering of light on the ceramic inner structure. It is widely recognized that optical inhomogeneities of ceramics, such as pores, act as the main light scattering centers affecting its performance [3], while grain boundaries with width below 1–2 nanometers do not contribute to the light scattering. The crystal structure is another factor affecting its transparency. Laser ceramics are typically synthesized from optically isotropic crystals, i.e. crystals with cubic symmetry (for example MgO, Y_2O_3, YAG, and $MgAl_2O_4$ (spinel)). Ceramics of optically anisotropic crystals possess additional light scattering due to birefringence, which typically occur at the grain boundaries when light passes from one grain to another having different orientation [4].

YAG crystallizes in cubic crystal structure which belongs to the garnet group. YAG is among other three crystalline phases of yttria-alumina system, with the other two being yttrium aluminum monoclinic $Y_4Al_2O_9$ (YAM) and yttrium aluminum perovskite $YAlO_3$ (YAP). The presence of the latter two phases in YAG gain media can cause significant light scattering and thus degradation of the properties and functional response of the material [5].

Etching of solid surface with ion beam with energies up to 10 keV is sensitive to a number of characteristics of crystal structure due to different sputtering of crystal surfaces by ion beam in various crystallographic directions. Typically, defective area of the crystals is sputtered more intensively [6]. This phenomenon provides basis to revealing the boundaries in ceramics, because they have higher defects concentration than the bulk volume. Dependence of ion etching on crystalline orientation is more pronounced with increasing a glance angle between the surface and the beam direction for the anisotropic crystals. At the angles of 6–10° this dependence just appears, thus such geometry is used of ion polishing of surfaces to study by various methods including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Increasing the sputtering angle to 15–20° reveals large-sized crystal defects and inhomogeneities in the ceramics, while minor ones are not appeared [7, 8].

Appearing the morphological peculiarities in YAG:Nd laser ceramics such as pores, structural inclusions, grain boundaries is a function of the ceramic processing. A detection of these peculiarities should be carried out by diverse techniques complemented one other to determining later function which allows producing high quality ceramics.

This paper is devoted to detection different kind of morphological peculiarities in YAG:Nd laser ceramics resulted on ion sputtering of the surface. Special attention was paid to the revealing inclusions in this ceramics. That was carried out in first time to our knowledge and couldn't detect so easy by the thermal etching and Electron Probe Micro Analysis (EPMA) used traditionally.

2. Experimental

Samples of YAG:Nd (2 at. %) laser ceramics prepared by vacuum sintering at 1700°C for 12 h of co-precipitated nanopowders [9] were used in the study. Rods with diameter of 3 mm and height of 2 mm were cut from the original pallet. This rod was glued to the holder and was consecutive grinded on abrasive papers with 22, 13, 8.4 μm grains, the polishing on amorphous alumina was the latest step before ion treatment. Ion sputtering was carried out with argon ion (E = 4 keV) at glace angle of 15° during 12 h. The ion gun with saddle configuration of electrical potential was utilized. This gun was assembled into vacuum camber of VUP-5 (SELMI, Ukraine) vacuum station. The samples surface was investigated by SEM (JSM 6390LV, JEOL, Japan). Element composition of the surface was determined with Electron Probe Micro Analysis (EDS X-Max^N-50, Oxford Analytical, Great Britain).

3. Results

The polished surface of YAG:Nd laser ceramics was treated by ion sputtering during 12 h under fixed glance angle of the ion beam. After ion sputtering this surface was investigated by SEM and EPMA.

SEM image of the surface of YAG:Nd laser ceramics after ion sputtering is shown in Fig. 1a. Some details of this image obtained at higher magnification are pre-

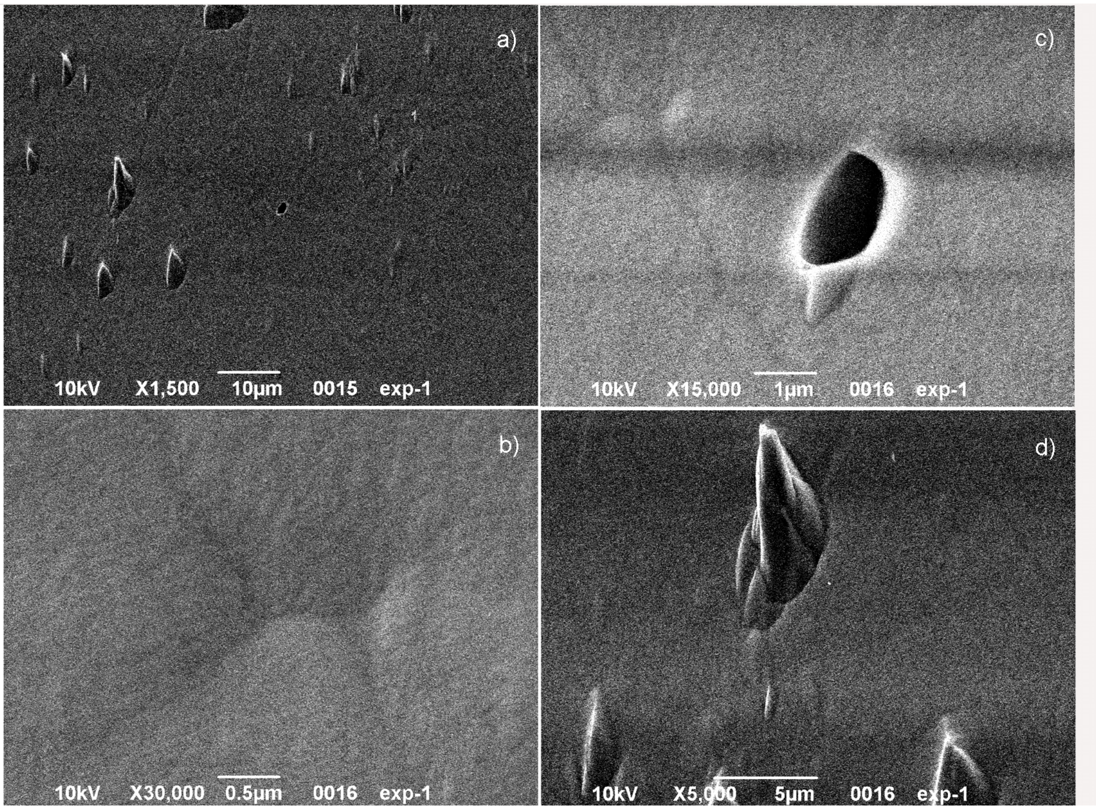

Fig. 1. SEM images of the surface of $Y_3Al_5O_{12}$:Nd (2 at. %) laser ceramics after ion sputtering for 12 h (Ar^+ ions, E = 4 keV, glance angle of 15°): a — general view; b — grain boundaries; c — pore; d — inclusions.

sented in Fig. 1b–d for the better viewing. The sample surface is generally smooth; the main structural peculiarities observed on the surface are grain boundaries, pores, and inclusions. The inclusions that stack out as pyramidal structures on the surface are presented in much higher concentration compared to the pores. The value presenting ratio of concentration of inclusions to concentration of pores is more than 10:1. EPMA of the smooth area of surface showed the following content of host constituents: 24.9 at. % Al, 14.3 at. % Y, 59.9 at. % O, 0.9 at. % Nd, corresponding to YAG:Nd (2 at.%) atomic composition of ceramics.

Fig. 1b shows the grain boundaries of ceramics after ion sputtering. Although they appeared much weaker than after thermal etching [10], this image demonstrates that ion sputtering can also be used for identification of grain structure of the optical ceramics. To identify the structure by thermal etching the long exposure times at high temperatures are usually required which can results in grain coarsening due to recrystallization. Ion sputtering procedure takes some time also, but the sample surface isn't heated to high temperatures thus avoiding recrystallization of the ceramics. The larger magnification of this image also shows that the grain surface is not perfectly smooth, but consists of irregularities with characteristic linear dimensions ranging from 100 to 500 nm. These inhomogenities do not have preferred orientation; consequently, they do not depend on the ion beam direction either.

Fig. 1c shows SEM image of the pore. It can be seen that the pore does not locate at the grain boundaries. The cross section of the pore is ellipse-like with axes sizes of 1 and 2.2 μm. Fig. 1d shows the inclusions revealed into the bulk of ceramics. These inclusions look like the structures of conical shape with a base in the form of an ellipse. The longer axis of the ellipse is directed along the incident sputtering ion beam. The inclusions height reaches 6 μm that allows one to estimate the thickness of the layer removed from the surface by the ion sputtering because the later should be higher or equal to the inclusions height. We suppose that conical shape of inclusions may be formed during the ion sputtering. The inclusions are located at grain boundaries, which are clearly seen from Fig. 1d. We failed in determining the quantitative element composition of the inclusions by EPMA since their surface is no right oriented. A qualitative analysis showed that the inclusions consist of Al, Y, O and Nd atoms only, as well as YAG:Nd ceramics.

SEM image of cleavage of the sample is shown in Fig. 2. It can be seen that the grain form irregular polyhedra without any elongation, the spatial distribution of grains are quite chaotic, i.e., it can be assumed that this ceramics has no texture. The grain size of YAG ceramics ranges from 10 to 25 μm.

4. Discussion

Selected sputtering geometry, namely, the glance angle of 15°, allowed us to reveal grain boundaries, pores and inclusions in YAG:Nd laser ceramics as the main defects at this scale. Among the three sorts of revealed peculiarities the cone-like inclusions are of the greatest interest. Their concentration on the treated surface is much higher compared to that of the pores and therefore they may impact significantly the ceramics properties. As it was shown before the grain boundaries do not affect the light scattering in ceramics essentially [3]. Thus the inclusions may be a major factor decreasing the optical quality of our ceramics. Such inclusions can be identified after the mechanical polishing and thermal etching of the ceramics surface [11], while EPMA mapping allows one to additionally analyze the composition of each grain that reaches the interface and determine the distribution of elements on the surface. After ion sputtering surface inhomogeneities can be detected at sufficiently large areas more easy.

As was shown below (see Fig. 2), the ceramics is not textured, i.e. the output of different crystallographic planes on the surface of polished section is equally probable. The surface of ceramics (see Fig. 1) observed after ion etching is substantially flat indicating that the most of crystallographic planes of the YAG:Nd ceramic sputters with the same rate under the configuration of the ion processing used. We assume that it is due to cubic crystal structure of YAG.

The question is what is the origin of the inclusions sticking out from the surface? Several possible explanations could be considered. First, a new crystal phase is formed at the grain boundary during the ceramics processing, and this phase is more resistant to ion sputtering than YAG. Second explanation is that there are some crystallographic orientations of YAG grains which have different sputtering rates. Finally, these grows may be formed during ion sputtering of ceramics due to redeposition. The last explanation seems to be unlikely according to the following reasons. The redeposition phenomenon is often observed during sputtering of metals or alloys [6], and the redeposited structures usually grow towards the ion beam as whiskers. In our case, the grown structures have almost normal orientation to the surface with a slight slope only. During ion etching surface is sputtered through individual atoms, and considering multicomponent phase such as YAG we can hardly assume that a phase of the same qualitative composition is formed. Concerning the second explanation of the inclusion origin, we believe that even if there are specific orientations in the cubic crystals, which would be much worse sputtered by ion beam, it should not lead to significant differences in the dissipation rate and to formation of the large-sized inclusions. However, this question requires more detailed study.

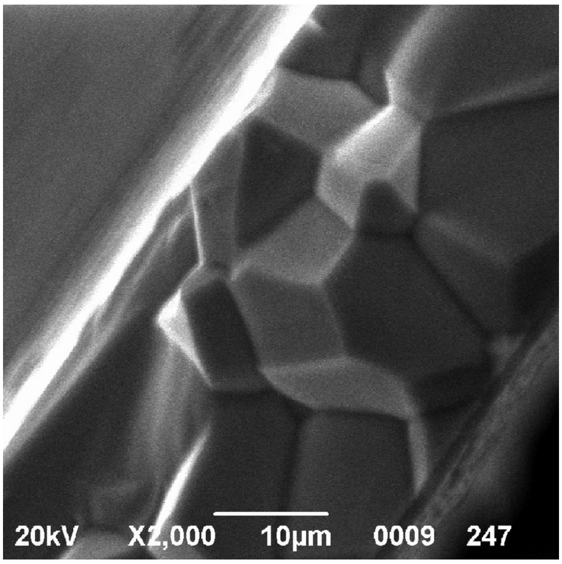

Fig. 2. SEM image of the cleavage of $Y_3Al_5O_{12}$:Nd (2 at. %) laser ceramics.

Most likely these defect areas represent the new phase consisting of Al, Y, O and Nd atoms which is characterized by different from the cubic crystals structure. The YAG ceramics processing is very sensitive to the composition of the powder mixture and even a slight deviation from YAG stoichiometry leads to formation of the impurity phases such as YAM or YAP [5, 12]. Some speculation concerning formation of these phases could be done. The ceramics consists of single crystalline grains which coarsening and recrystallization occur during a sintering process. The local deviations from YAG phase stoichiometry originated, for, example, from local inhomogenities of YAG coprecipitated powders, results in accumulation of intermediates at the grain boundaries until the break up of growth of YAG grains happens. After that the new phase (YAM or YAP) appears along the grain boundary depending on deviation from the stoichiometry degree. These phases are anisotropic and it seems that size of the inclusions is large enough to cause significant light scattering in YAG ceramics and affect its laser performance.

5. Conclusions

The morphological peculiarities of $Y_3Al_5O_{12}$:Nd laser ceramics prepared by vacuum sintering of co-precipitated nanopowders have been revealed by ion beam sputtering of the ceramics surface. Inclusions with a cross section up to 5 μm located between the grain boundaries as well as pores and grain boundaries were detected on the surface of $Y_3Al_5O_{12}$:Nd ceramics treated by ion sputtering since sputtering rate of these inclusions is much lower compared to bulk of the ceramics. Qualitative elemental composition of the inclusions is same as that of $Y_3Al_5O_{12}$:Nd ceramic. It was suggested that the inclusions were formed as a result of deviation from stoichiometry during processing of $Y_3Al_5O_{12}$ ceramics and have different phase composition compared to the parent garnet phase. Early it was established that pores most affected on the laser ceramic performances. But in our case the concentration of the revealed inclusions is much higher the one of pores. It allowed us to conclude that influence of the inclusions is significant.

Also it was shown that ion sputtering is quite sensitive to morphological peculiarities of the ceramics, especially to detect inclusions.

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