Journal of Crystal Growth 483 (2018) 195–199

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

Control of optical properties of YAG crystals by thermal annealing

S. Tkachenko [a], P. Arhipov [a], I. Gerasymov [a], D. Kurtsev [a], S. Vasyukov [a], V. Nesterkina [a], N. Shiran [a], P. Mateichenko [b], O. Sidletskiy [a,*]

[a] Institute for Scintillation Materials NAS of Ukraine, 60, Nauky ave., 61001 Kharkiv, Ukraine
[b] Institute for Single Crystals NAS of Ukraine, 60 Nauky ave., Kharkiv, Ukraine

ARTICLE INFO

Article history:
Received 15 June 2017
Received in revised form 11 October 2017
Accepted 2 December 2017
Available online 5 December 2017
Communicated by R.S. Feigelson

Keywords:
A2. Czochralski method
A2. Single crystal growth
B1. Oxides
B2. Dielectric materials

ABSTRACT

Optical properties of YAG crystals grown and annealed under different atmosphere conditions have been compared. Simultaneously we have registered the surface composition of crystals and content of basic admixtures in the crystals grown under the reducing conditions. Unlike YAG grown under weakly oxidizing conditions in Ir crucibles and bleached under oxidizing annealing, YAG_{Mo} crystals grown in Mo crucibles under reducing Ar + CO atmosphere can be bleached by both oxidizing and reducing thermal annealing. The bleaching of YAG_{Mo} is not reversed by further annealing under any available conditions. Mechanisms of this phenomenon have been discussed, including a possible role of admixtures in elimination of color centers in YAG grown under the reducing conditions.

1. Introduction

Complex rare-earth oxides with the garnet structure, $Y_3Al_5O_{12}$, $Lu_3Al_5O_{12}$, are extensively used as hosts for solid state lasers, phosphors, scintillators. High melting temperatures over 1900 °C and need for expensive Ir crucibles and heat shields stimulates the development of garnet crystal growth technologies consuming cheaper materials, for instance, tungsten and molybdenum.

Quite often as-grown undoped $Y_3Al_5O_{12}$ (YAG) ingots crystallized from Mo crucibles in reducing atmosphere are colored. The causes of garnet crystals coloration, as well as conditions and methods of its elimination were analyzed in [1–7]. The appearance of coloration is attributed to an influence of reducing atmosphere, which is necessary to avoid crucible oxidation and melt contamination by its products. At the same time, reducing atmosphere calls the formation of vacancy-based color centers. As a rule, coloration is eliminated by post-growth thermal annealing in a certain atmosphere. Annealing calls formation/elimination of oxygen vacancies and change of valence state of admixtures with variable valence, which act as electron or hole traps. In the series of works on undoped and rare-earth doped YAG by Selim et al. [8–11] the existence of complex defects, or defect clusters consisting of aluminum and oxygen vacancies located near antisite defects has been suggested.

The mentioned results [1–7] were obtained on YAG crystals grown in Ir crucibles under the inert gas atmosphere, or in Mo crucibles under H_2 atmosphere. A method to grow garnets by the Horizontal Directional Crystallization under reducing Ar + CO atmosphere was developed in [12] and then elaborated by us for the Czochralski process [13,14]. This method has potential advantages over the growth under H_2, such as non-use of explosive hydrogen, and substitution of expensive ZrO_2 and corundum ceramics with graphite thermal insulation. Meanwhile, as we showed previously, Ar + CO atmosphere actively interacts with YAG crystal surface by the reaction (1) both during crystal growth and thermal annealing [14]:

$$Al_2O_{3(cr)} + CO_{(g)} \rightarrow Al_2O_{(g)} + Al_{(g)} + CO_{2(g)} \quad (1)$$

where the lower indices denote gaseous (g) and crystalline (cr) phases. Y_2O_3 is thermodynamically stable in the Al_2O_3 presence, and no its interaction with CO was noticed.

The current work is focused at comparative study of YAG crystals grown by the Czochralski method in Ir and Mo crucibles and annealed under different conditions. The ways to control the optical and UV-transmission by heat treatment conditions are discussed. Simultaneously we controlled the surface element composition in YAG crystals and concentrations of some admixtures in them.

2. Experimental

Effect of thermal annealing on YAG optical properties was studied on samples fabricated from the crystals grown from Ir crucible (YAG_{Ir}) under weakly oxidizing atmosphere, as well as from

* Corresponding author.
E-mail address: sidletskiy@isma.kharkov.ua (O. Sidletskiy).

https://doi.org/10.1016/j.jcrysgro.2017.12.002
0022-0248/

crystals grown from Mo crucible (YAG_{Mo}) under reducing conditions. In the both cases the same batches of Al_2O_3 and Y_2O_3 powders with the purity of 99.99% were taken as the raw materials. The starting oxides were mixed, pressed and dried under air at 120 °C. The pressed pellets were sintered under air at 1200 °C to grow YAG_{Ir}, and sintered under Ar + CO atmosphere at 1600 °C to grow YAG_{Mo}. The growth chamber was filled with Ar gas with the purity of 99,999%. ZrO_2 thermal insulation ceramics was used for the YAG_{Ir} growth, and graphite thermal insulation was used for the YAG_{Mo} growth. The size of YAG_{Ir} crystal was of 110 mm in length and 30 mm in diameter (Fig. 1). The typical size of YAG_{Mo} crystals was of 60 mm in length and 30 mm in diameter. The growth process with automated crystal diameter control was provided by a weight sensor. While the diameter was well controlled at growth of YAG_{Ir}, the process for YAG_{Mo} was less stable, evidently, due to low thermal gradient above the melt called by induction heating of graphite thermal insulation. The diameter instabilities call the wavy roughness of the side surface. Some additional details of the crystal growth process we described in [14].

Then, the samples fabricated from the YAG_{Ir} and YAG_{Mo} crystals were heat treated under the following conditions:

- Oxidizing annealing: air, 1200 °C, Pt equipment, Al_2O_3 heat insulation, induction heating.
- Reducing annealing: T = 1500–1850 °C. The chamber was pumped out up to 10 Pa, and filled with argon. The reducing conditions (Ar + CO) were formed by the interaction of residual oxygen with graphite thermal insulation and graphite heater.

Two or more samples fabricated from the same crystal were annealed simultaneously under the same conditions. One of the samples was taken for optical measurements. Another one was shot for the illustration of sample color.

The admixture content in crystals was controlled by an ICAP 6300 Duo AES ICP spectrometer method (the latter procedure is described in detail in [15]) and a LEA-S500 laser analyzer of element composition. The carbon concentration in YAG crystals was determined using a LECO CS844 analyzer.

The condition and element composition of the ~50 μm thick surface layer after the annealing were controlled using a scanning electron microscope JSM 6390 LVX equipped with a MAX^N X-ray microanalysis system. The absorption spectra of polished samples were measured using a Specord 40 spectrophotometer.

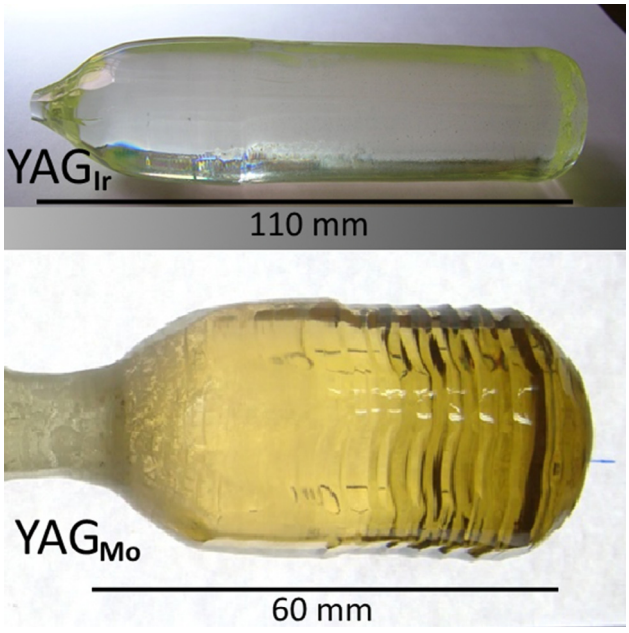

Fig. 1. Photos of typical as-grown YAG_{Ir} and YAG_{Mo} crystals.

3. Results

3.1. YAG_{Ir} crystals

The as grown crystal was visually transparent and did not contain visible inclusions and pores. The view of YAG_{Ir} sample (5 × 4 × 4 mm size) under sequential thermal annealing is shown in Fig. 2. The element composition of the crystal surface is $Y_{2,99}Al_{5,01}O_{12}$ and nearly corresponds to the garnet stoichiometry.

The absorption spectra of samples with the dimensions of 10 × 10 × 1 mm after the sequential annealing are shown in Fig. 3. The as-grown YAG_{Ir} are visually transparent but the intense absorption bands in UV range (205 and 255 nm) indicate the presence of Fe^{3+} ions (Fig. 3a).

The heat treatment under the reducing atmosphere leads to strong coloration with the gradient from black at the surfaces until grey in the center (Fig. 2 b). It corresponds to the notable absorption increase in the visible spectral range (Fig. 3, curve b). The revealed bands may be connected with the several kinds of centers (F-type and/or the impurities of Cr, Ti, Mo ions with variable valence [16,17]).

Nevertheless, the oxidizing annealing following the reducing annealing results in the complete visual discoloration (Fig. 2e). The 1 h annealing was sufficient to eliminate the coloration in the 5 × 4 × 4 mm sample pointing that color intensity gradient from the surface towards the bulk of the samples is caused by concentration and diffusion rate of oxygen vacancies under the given conditions. The absorption spectrum of the as-grown YAG_{Ir} after the oxidizing treatment is similar to the as-grown crystal spectrum, with slightly stronger peaks in UV bands attributed to the valence change of iron traces ($Fe^{2+} \rightarrow Fe^{3+}$) - Fig. 3, curve c). Therefore, the coloration and bleaching are reversible in YAG_{Ir}.

After the annealing the surface element composition modifies towards $Y_3Al_{3,6}O_{10}$ due to the chemical interaction of the surface with CO atmosphere as we showed in [14]. Crystal surface under the reducing annealing is depleted with aluminum and oxygen under the reducing annealing, but it not affects notably the bulk properties.

3.2. YAG_{Mo} crystals

The crystals grown in molybdenum crucible are colored. The weak yellow[1] color near the seed is gradually deepening to brown in the bottom (see Fig. 1). As-grown crystals are not uniformly colored as on may see in Fig. 4. We attribute the in uniform coloration to distribution of some unidentified admixtures. Meanwhile, under the prolonged oxidizing annealing the samples became completely bleached.

The absorption spectrum of the as-grown crystal is shown in Fig. 5. It demonstrates the intense broad band absorption in the UV range (190–300 nm), which consists of several peaks attributed to Fe^{3+} ions and F-type centers. According to the review [18], the additional peak at 370 nm (Fig. 5, curve a) is related to F^+-centers near oxygen vacancy, or Y^{3+} in Al^{3+} site. The latter band is not observed in YAG_{Ir} and should be caused by defects formed by the interaction with reducing atmosphere and, evidently, carbon occurrence in YAG_{Mo} crystal. In case of YAG grown in Mo crucible under reduced atmosphere the crystal contains carbon admixture

[1] For interpretation of color in Figs. 1 and 4, the reader is referred to the web version of this article.