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Optical Properties of $MgAl_2O_4$ Crystals Grown by Iridium-Free Technology

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It was carried out the investigation of optical absorption of magnesium–aluminum spinel ($MgAl_2O_4$) crystals. The crystals were grown by horizontal directional crystallization method in molybdenum crucible under the protective atmosphere Ar+(CO, H_2). The optical absorption spectra of $MgAl_2O_4$ crystals exhibit absorption bands (267 and 325 nm) caused by complexes of defects formed by oxygen vacancies and cations located in anti-sites. It is shown that annealing of crystals in an oxidizing environment at $T = 1500°C$ leads to the elimination of these absorption bands and the improvement of the optical properties of the grown crystals.

topics: magnesium–aluminum spinel, horizontal directional crystallization method, molybdenum, optical absorption

1. Introduction

Magnesium–aluminum spinel ($MgAl_2O_4$) is characterized by the combination of important physical properties — thermal, optical, and mechanical — that distinguish it from other crystalline compounds. Due to these characteristics, in particular, resistance to high temperatures (melting point 2135°C), high hardness (hardness is 7.5–8 on the Mohs scale), significant mechanical strength in a wide temperature range (135–216 MPa at room temperature, 120–205 MPa at 1300°C), relatively low coefficient of thermal expansion (9×10^{-7} K^{-1}), rather high thermal conductivity (25 W/(m K) at room temperature), resistance to chemical and radiation influences etc., spinel has been widely used in various industries and research [1–3]. An important advantage of spinel is the possibility of doping with transition metal ions, which opens up prospects for their use in optical devices, in particular in laser technology [4]. To date, spinel crystals are usually obtained by the Verneuil method [5, 6] and the Czochralski method [7, 8]. The disadvantage of the Verneil method is the significant thermomechanical stresses that lead to cracking of the crystals and the formation of blocks with misorientation angles of 0.1–4°. In addition, the technology of growing high-temperature crystals requires the use of hydrogen, which creates technical and other difficulties in ensuring safety in the production of crystals. A more promising method of obtaining $MgAl_2O_4$ crystals is the Czochralski method, but its technology uses expensive iridium crucibles. The disadvantage is the high growing temperature (over 2100°C), which is not much lower than the melting point of iridium (2420°C). Thus, the service life of a crucible is just a few processes. To solve these problems, it is necessary to develop iridium-free technology for growing crystals using other refractory materials for the crucibles.

Therefore, the aim of this work was growing $MgAl_2O_4$ crystals by iridium-free technology and study of the optical properties of the grown crystals.

2. Experimental

A new approach to the introduction of iridium-free technology was applied that consisted in obtaining spinel crystals using molybdenum or tungsten crucibles. These materials have much higher melting point than iridium (T_{Mo}=2620°C, T_W = 3420°C). In addition, these metals are much cheaper. Tungsten shows high stability, but from the technological point of view of crucible production, molybdenum is more suitable. Thus, further development of conditions for growing $MgAl_2O_4$ crystals was carried out for the molybdenum crucible. Molybdenum crucibles for growing crystals should be made by cold stamping from molybdenum sheet up to 0.5 mm thick.

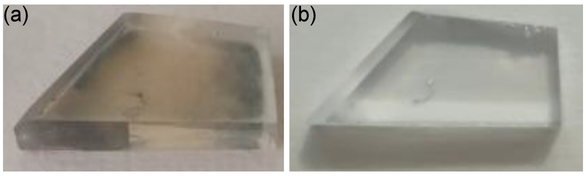

Fig. 1. Grown spinel crystal before (a) and after (b) annealing in air at temperature 1500°C.

The crystallization processes in molybdenum crucibles were carried out in the protective atmosphere Ar+(CO, H_2) at a pressure of 0.1 MPa by horizontal directional crystallization (HDC) method. The crystallization rate was 2–5 mm/h. Crystals dimensions were $40 \times 65 \times 25$ mm^3.

The crystals had a brownish coloration, some cracks and inclusions of molybdenum and other phases of different sizes, which are unevenly distributed over the volume of the crystals. In the initial part of the grown crystals there were volumes up to $\approx$ 1–2 cm^3 of good optical quality, which allowed making samples for the study of optical properties. The experiments therefore showed the principled opportunity of obtaining the optical quality of spinel crystals by iridium-free technology. To determine the effect of growth conditions on the optical characteristics and the formation of crystal color centers, the grown crystals were annealed in different atmospheres. After the annealing in an oxidizing atmosphere at temperatures of 1500°C the crystals discolored (Fig. 1).

The optical absorption spectra of the crystals were measured at room temperature by means of a UV-Vis spectrometer (Optizen 3220, double beam) with a step of 1 nm.

3. Results and discussion

The optical absorption spectra of the grown crystal before and after annealing are presented in Fig. 2.

For crystal as-grown there are observed intense absorption bands peaked in UV spectral region at wavelength 220, 267, and 325 nm. Annealing in an oxidizing medium eliminates absorption bands 267 and 325 nm, which leads to discoloration of the crystals and improvement of their optical properties. This behavior may indicate the connection of the absorption centers in the grown crystals with anion vacancies. However, our data do not agree with the values of the optical transitions in spinel associated with the absorption of light by the anionic vacancies, i.e., 5.3 eV (λ = 234 nm) for F-centers and 4.75 eV (λ = 261 nm) for F^+-centers [8].

In [15] it was shown that all complex defects in $MgAl_2O_4$, formed by isolated intrinsic defects (the vacancies of oxygen (V_O), magnesium (V_{Mg}), aluminum (V_{Al}), oxygen interstitial (O_i), magnesium and aluminum antisites (Mg_{Al} and Al_{Mg})), have

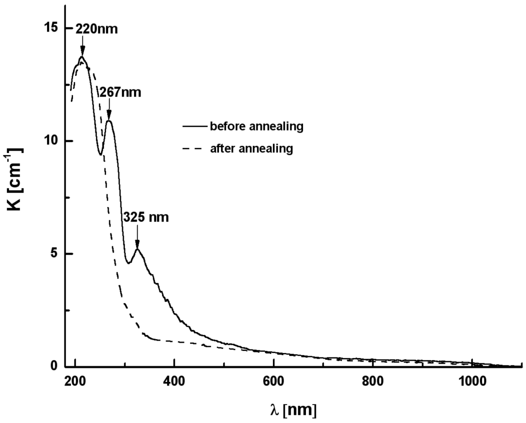

Fig. 2. Optical absorption spectra of the $MgAl_2O_4$ crystals grown by HDC before and after annealing.

low formation energy, and therefore are energetically competitive and more stable when compared with single defects. The absorption peaks at 267 nm and 325 nm observed in the experiment correspond to optical transitions, the values of which were calculated for the complexes formed by oxygen vacancies (V_O+ Al_{Mg}) and antisite defects (V_O+ Mg_{Al}). As for the peak at 220 nm, which is not affected by annealing in an oxidizing atmosphere (Fig. 2), its nature is not associated with the presence of anion vacancies or complexes formed by them.

The differences between the optical transitions corresponding to the complexes V_O+ Al_{Mg} and V_O+ Mg_{Al} and the experimental data on the peaks of the optical spectrum are 4 and 1.5%, respectively. These differences are due to the fact that the inaccuracy in the calculations of optical transitions in [15] for the band gap and Kohn–Sham Kohn–Shem energy levels that are introduced by intrinsic defects into the band gap, was approximately 5%.

4. Conclusions

Magnesium aluminum spinel crystals ($MgAl_2O_4$) were successfully grown by the method of horizontal directional crystallization in a protective atmosphere Ar+(CO, H_2). Optical absorption spectra investigations showed the presence of bands in UV spectral region. Post-growth annealing in an oxidizing atmosphere eliminated the absorption bands 267 and 325 nm. The data calculated for optical transitions in spinel crystals in [15] confirmed that these bands correspond to the optical transitions of the complexes formed by oxygen vacancies and antisite defects.

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