Growth of MgF₂ Optical Crystals and Their Ionic Conductivity in the As-Grown State and after Partial Pyrohydrolysis

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Abstract—MgF₂ single crystals have been grown from melt by the Bridgman technique in a fluorinating atmosphere. To control the presence of oxygen impurity, it was first suggested to measure the ionic conductivity in MgF₂ crystals by impedance spectroscopy. The characteristics of ionic conductivity of “as grown” (i.e., without thermal treatment) crystals and crystals obtained by commercial vacuum technology practically coincide: the volume conductivity \( \sigma_v = 1.4 \times 10^{-7} \text{S/cm} \) at \( T = 773 \text{K} \) and the ion-transport activation energy \( E_a = 1.40 \pm 0.05 \text{eV} \). Annealing MgF₂ crystals during electrophysical studies upon heating from 293 to 823 K in vacuum (residual pressure \( \sim 1 \text{ Pa} \)) for 4 h led to their partial pyrohydrolysis. The influence of this thermal treatment of MgF₂ crystals on their optical transmission is studied in the wavelength range of 115 – 300 nm.

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INTRODUCTION

MgF₂ single crystals are construction optical materials for the vacuum UV (VUV) spectral range [1]. Under industrial conditions they are grown by directed crystallization from melt using a vacuum \((\sim 10^{-2} \text{ Pa})\) technology [2, 3] which allows for the incorporation of oxygen impurity, which remains in the crystal bulk volume as an isomorphous impurity and/or second-phase (oxide) particles, and leads to the formation of Mg(OH)₂ and MgO films on the surface. In all cases the oxygen impurity adversely affects the VUV transparency of crystals.

The pyrohydrolysis (interaction with \( \text{H}_2\text{O} \) vapor at high temperatures) of a grown MgF₂ crystal also affects its optical properties [3–5]. The initial stage of \( \text{MF}_2 \) pyrohydrolysis is not visualized if oxygen isomorphously enters the crystal to partially substitute for fluorine. Carrying pyrohydrolysis to the second-phase segregation manifests itself as a loss of the optical quality of crystal and is accompanied by changes in some physical properties, in particular, optical transmission, thus limiting the practical application of these crystals. The Mg(OH)₂ – MgO surface film, which is formed under partial pyrohydrolysis and cannot be observed visually, sharply deteriorates the optical characteristics of MgF₂ single crystals in the short-wavelength range [5]. The study of the fluoride pyrohydrolysis kinetics [6] showed that MgF₂ belongs to easily hydrolysable crystals; only AlF₃ and BiF₃ are even less stable.

To use MgF₂ single crystals in practice as construction optical elements in the VUV spectral range, it is necessary to reduce the amount of oxygen-containing impurities to minimum both in the bulk and on the surface of crystals. Currently there are no fast and simple methods for determining the presence of oxygen impurities in fluoride crystals, except for directly investigating optical transmission in the short-wave spectral range. However, this method is not confirmed by other independent techniques, at least for MgF₂ single crystals. Since the fluoride ionic conductivity is “sensitive” to structure defects in the anionic motif, the presence of oxygen impurity in the fluoride should manifest itself in the features of ion transport in partially hydrolyzed crystals.

Magnesium fluoride crystallizes into the rutile \((\text{TiO}_2)\) structure type, tetragonal system, sp. gr. \( P4\text{I}2/\text{mmm} \). MgF₂ crystals belong to wide-band gap insulators (the band gap is \( E_G \sim 13 \text{ eV} \) [7]). The electric conductivity \( \sigma \) of difluorides \( \text{MF}_2 \) \((M = \text{Mg, Mn, Zn})\) with a rutile-type structure has an ionic character; the most likely charge carriers are interstitial anions and anionic vacancies [8, 9] formed according to the Frenkel mechanism. The anisotropy of ionic conductivity is found in \( \text{MF}_2 \) crystals \((M = \text{Mg, Mn})\) [8, 10] (the measurements were performed in the directions parallel \((\sigma_{||})\) and perpendicular \((\sigma_{\perp})\) to the crystallographic axis \( c \)); the highest conductivity is observed for \( \sigma_{||} \). The mechanism of ion transport in \( \text{MF}_2 \) with a rutile-type structure has not been studied.

The reproducibility of \( \sigma \) data for \( \text{MF}_2 \) crystals \((M = \text{Mg, Mn})\) [8] was observed only when heating to a temperature of \( \sim 400^\circ\text{C} \), above which the material begins to interact with water vapor. The \( \sigma \) value depends to a
greater extent on the oxygen content in vapor. This reaction occurs despite the fact that experiments are carried out in a “water-free” inert gas atmosphere.

The purposes of this study were as follows: to grow MgF₂ single crystals from melt by the Bridgman technique using a fluorinating atmosphere (in order to obtain VUV optical elements) and determine the stability of optical elements to bulk and surface pyrolysis in air upon heating by developing a method for comparing the optical characteristics in the VUV range with the ionic conductivity data.

EXPERIMENTAL

MgF₂ crystals were grown by the Bridgman technique in a fluorinating atmosphere in a graphite crucible on a seed oriented along the optical axis (the crystallographic axis c; [001] direction). Broken fragments of commercial MgF₂ crystals of MFU (magnesium fluoride ultraviolet) grade, obtained by vacuum technology according to OST (branch standard of the Russian Federation 3-3509-82), was used as a starting charge. The fluorinating atmosphere was formed by polytetrafluoroethylene pyrolysis products. The rate of lowering the graphite crucible with a melt was ~5 mm/h, and the crystal cooling rate was ~100 K/h.

A comparison was performed with a standard MgF₂ optical element (of MFU grade) obtained by the Bridgman method using commercial vacuum technology.

The samples studied were polished plates 2 mm thick cut normally to the [001] axis.

Phase composition of crystals was checked by X-ray diffraction (a Toshiba AFV-202 diffractometer, CuKα radiation). It was shown that the crystals grown belong to the rutile structure type with the following parameters of tetragonal unit cell: \(a = 0.4621 \pm 0.003\) nm and \(c = 0.3053 \pm 0.003\) nm.

Optical transmission in the range of 115–300 nm was recorded with the aid of a VMR-2 vacuum monochromator at room temperature.

Ionic conductivity of crystals in direct current (\(\sigma = \sigma_{dc}\)) was measured by impedance spectroscopy in a frequency range of \(5–5 \times 10^2\) Hz (a Tesla BM-507 instrument). The measurement system was described in [11]. Graphite Dag 580 and silver Leitsilber pastes were used as inert electrodes. The electrical measurements were carried out in a temperature range of 293–829 K. The presence of the blocking effect of inert electrodes in the impedance spectra indicates the ionic character of \(\sigma\).

We denote the MgF₂ crystal obtained by commercial vacuum technology and the crystal grown under laboratory conditions using a fluorinating atmosphere as A and B, respectively.

RESULTS

Transmission spectra \(T(\lambda)\) of as-grown MgF₂ crystals obtained by the commercial technique in vacuum (curve 1) and crystals grown using a fluorinating atmosphere (curve 2) are shown in Fig. 1. The application of a fluorinating atmosphere improves the transparency of MgF₂ crystals in the range \(\lambda < 250\) nm. The short-wave transmission edges (at a transmission level of \(\sim 30\%\)) are 125 and 120 nm for crystals A and B, respectively. The optical transmission spectrum of crystal A is in a good agreement with the results of [1]. The use of a fluorinating atmosphere to grow fluoride crystals (instead of the necessity of supporting high vacuum at a level of \(10^{-2}–10^{-3}\) Pa [9, 12]) is more technological and makes optical elements less expensive.

Dependences of the conductivity \(\sigma(T)\) of as-grown MgF₂ crystals upon thermal cycling are shown in Fig. 2, which presents the following data on conductivity: four heating–cooling cycles for crystal A (Fig. 2a) and one temperature cycle for crystal B (Fig. 2b). Due to the low conductivity of MgF₂ fluoride, the volume resistivity of as-grown samples was recorded by a Tesla BM-507 impedancemeter (with the upper limit of resistivity measurements of \(10^7\) \(\Omega\)) only after heating them to 720–730 K.

The \(\sigma\) values of crystals A and B coincide during the first heating (Fig. 3). However, the \(\sigma\) data for these crystals obtained upon cooling and the \(\sigma\) values measured for crystal A during the second and third cycles are not reproduced and exceed the \(\sigma\) value obtained during the first heating. The lateral surfaces of single crystal A were mechanically cleaned before the measurements in the fourth temperature cycle. As a result, the \(\sigma\) values obtained for this sample during the fourth

![Fig. 1. Optical transmission spectra T(\(\lambda\)) of MgF₂ crystals: (1) as-grown crystal A, (2) as-grown crystal B, (3) crystal B after heating to 823 K in vacuum (~1 Pa) for 4 h, and (4) crystal B after surface mechanical treatment. The crystal thickness is 2 mm.](image-url)