Diffusion of Cobalt Ions into Crystals of Non-Stoichiometric Magnesium–Aluminate Spinel MgO·xAl$_2$O$_3$

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Magnesium–aluminate spinel crystals MgO·xAl$_2$O$_3$ have been grown by the horizontal directed crystallization method. The structure, phase and element composition of crystals were investigated using X-ray diffraction and scanning electron microscopy with a microanalysis system. The obtained MgO·xAl$_2$O$_3$ crystals have a spinel structure with $1 \leq x < 2$. The temperature stability of the spinel phase for different stoichiometry was established. Diffusion doping of magnesium–aluminate spinel crystals with cobalt ions through the gas phase using cobalt oxide as a diffusion source has been studied under the temperature treatment of 1300–1500°C. It was found that the penetration depth of the cobalt ions into the crystal body significantly increases with the increase of x. The diffusion coefficients of cobalt into MgO·xAl$_2$O$_3$ ($x = 1.00$) at 1300–1500°C and the efficient activation energy were estimated.

topics: MALO, non-stoichiometric magnesium–aluminate spinel, MgO·xAl$_2$O$_3$, cobalt diffusion

1. Introduction

Magnesium-aluminate spinel MgO·xAl$_2$O$_3$ (MALO, where x is the molar ratio of Al$_2$O$_3$ to MgO) in both crystals and ceramics form possess excellent chemical, thermal, dielectric, mechanical, and optical properties. These properties make MALO an attractive material for manufacturing substrates, optical windows, transparent armor, and infrared (IR) sensors [1, 2]. When doped with transitional metals, both stoichiometric (MgAl$_2$O$_4$, $x = 1.00$) and non-stoichiometric (MgO·xAl$_2$O$_3$, $1 < x < 3$) MALO compositions are promising matrixes for the manufacture of laser-active media (Cr, Ti etc.), as well as for passive Q-switching when doped with the Co^{2+} ions [3–5]. Usually, dopants penetrate MALO during crystal growth or synthesis of ceramic materials.

Introducing ions transition metal into the MALO crystals by gas-phase diffusion during high-temperature annealing is little studied. It is known that Cr ions can be introduced into stoichiometric MgO·Al$_2$O$_3$ crystals under significant pressure (up to 2 GPa) during annealing at 1100–1250°C [6]. To activate diffusion processes in the single crystals, higher temperature and pressure or other conditions are needed. Usually, a thin diffuse layer is formed on the surface of perfect single crystals. For example, when ZnSe, ZnS single crystals were doped with transitional metals during annealing, the thickness of the diffusion layer was 50–300 μm [7, 8].

However, when using ZnSe, ZnS polycrystals, the thickness reaches a few millimeters, because intense diffusion along the grain boundaries takes place [9]. At the same time, it is known that the incorporation of metal ions into complex oxides crystals can be achieved by annealing the crystals at high temperature with metal oxides as a source of diffusion [10, 11].

We assume that using non-stoichiometric spinel MgO·xAl$_2$O$_3$ activates the diffusion of Co^{2+} ions into the MALO crystal lattice due to the appearance of the cationic vacancies of V$_{Mg2+}$ [12, 13].

The present work deals with the investigation of the conditions of introducing the cobalt ions into the MALO crystal by the gas phase diffusion at high-temperature annealing.

2. Experimental

2.1. Crystal growth

MALO single crystals were grown by horizontal directed crystallization method (HDCM), which was developed at the Institute for Single Crystals to obtain the crystals of sapphite, Ti:sapphire, and rare-earth garnets [14, 15]. An initial charge consists of MgAl$_2$O$_4$ (99.7 wt%, 0.3 wt% Al$_2$O$_3$, Baikowski) powder compacted into tablets and annealed at 1500°C for 4 h. The growth process was carried out in a protective atmosphere based on an argon mixture and reducing additions of CO and H$_2$ under a total pressure of about 1 atm.

Samples $MgO \cdot xAl_2O_3$ with different x were obtained from two crystals grown at different crystallization rates v. At a lower crystallization rate, the deviation from the stoichiometry is greater because the evaporation from the melt is higher and the loss of magnesium is more sufficient. The molar ratio x increases along the crystal length from 1.00 to 1.30 at $v = 8$ mm/hr, and from 1.08 to 1.88 at $v = 3$ mm/hr.

The X-ray investigations were carried by a powder XRD with a Siemens D500 diffractometer (Co K_α emission, graphite monochromator, Bragg-Brentano geometry, point scintillation detector $5 \leq 2\theta \leq 110°$, $\Delta 2\theta = 0.02°$). The Rietveld method was used to adjust the XRD patterns.

The determination of the elemental composition of the obtained crystals was carried out with the scanning electron microscope JSM-6390LV (JEOL, Japan) (SEM) equipped with X-max microanalysis system (Oxford Inst., United Kingdom). Studies were carried out at an accelerating voltage of 15 kV in the low vacuum mode to minimize charge-surface effects. As standards, the single crystals of stoichiometric MALO were used, on which the error of determining concentration was evaluated. For the quantitative analysis, correction of matrix effects using the XPP method (extended Puchou/Pichoir method) was used, which allows the chemical composition to be determined with an accuracy of 0.1 wt%.

Samples in the form of tablets of Ø 5 mm and a thickness of 1 mm with x from 1.00 to 1.88 were cut out of the crystals. The tablet surfaces were ground, mechanically, and chemically mechanical polished using silica. These samples have been used to study temperature stability.

2.2. Diffusion cobalt ions

Experiments on Co diffusion were performed in a closed sapphire container placed in a ceramic crucible with aluminum oxide powder between the walls (Fig. 1a). MALO tablets of Ø 5 mm and a thickness of 1 mm have been cut from the grown crystals with x from 1.00 to 1.61. The tablet surface was ground and polished using a diamond abrasive ACM 2/1. The surface roughness Ra was ≤ 5 nm,
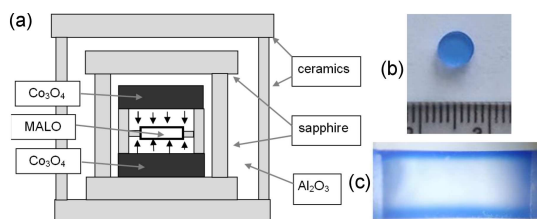

Fig. 1. The scheme of closed container (a) for annealing together MALO tablets and Co_3O_4 tablets, (b) MALO tablet after annealing, (c) a cross-section of the MALO tablet ($x = 1.61$).
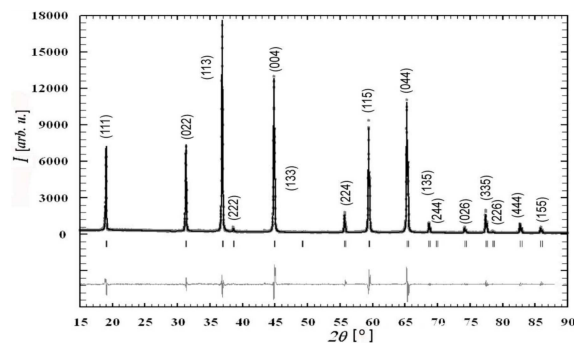

Fig. 2. Rietveld refinements of the XRD patterns of MALO crystals ($x = 1.08$).

flatness $\leq \lambda/8$, parallelism ≤ 30". The source of cobalt ions was cobalt oxide vapor. The tablets were prepared by pressing the Co_3O_4 powder and the following sintering at 800°C/1 h. The MALO and Co_3O_4 tablets were placed into a container and annealed at 1300–1500°C for 24 h in air. At temperatures higher than 900°C Co_3O_4 transformed to CoO.

The cobalt penetration depth in MALO was obtained using scanning electron microscope JSM-6390LV (JEOL, Japan) with a microanalysis system (Oxford Inst., United Kingdom). This was done by making a cross-section of the MALO tablet and analyzing the cobalt concentration perpendicular to the tablet surface. The accuracy of determining cobalt is up to 0.1 wt%.

3. Results and discussion

3.1. Characterization of MALO crystals

The size of the grown MALO crystals was $110 \times 70 \times 20$ mm³. At least half of each crystal was transparent and did not contain visible inclusion. The results of the diffractogram processing by the Rietveld method are presented in Fig. 2. The row of vertical bars shows the reflection Bragg positions; the bottom line shows the difference between the observed and calculated intensity in every point. No foreign phases were revealed in the transparent part of the crystals which had a spinel structure with x from 1.00 to 1.88. MALO belongs to the cubic space group $Fd3m$; the lattice parameter for $x = 1.08$ is $a = 8.08258(8)$ Å. Analysis of the turbid part of the ingot revealed an extra phase of Al_2O_3 in the form of corundum with $R3c$ symmetry.

3.2. Determination of the thermal stability interval for MALO crystals

The spinel structure of $MgO \cdot xAl_2O_3O$ is wide, with alumina ranging from 50 to 88 mol.% [16]. The temperature intervals of the spinel phase stability depend on the degree of non-stoichiometry. The phase diagram MgO—Al_2O_3 shows that with the increase of composition non-stoichiometry, the
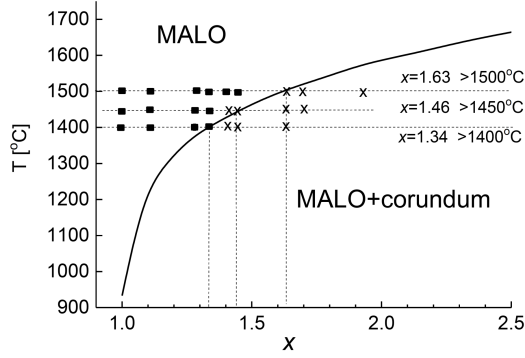
Fig. 3. Temperature of phase stability MgO·xAl$_2$O$_3$ for different x.

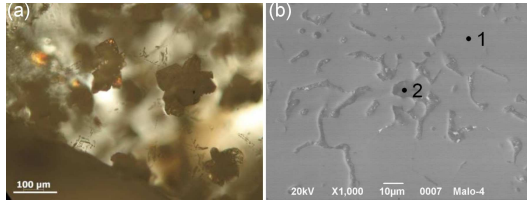Fig. 4. Decomposition of MALO (initial $x = 1.69$) after annealing at 1450°C/24 h/air (a) optical microscope, (b) SEM: $(1 - x) = 1.45$, $(2 - x) = 3.48$.

Fig. 5. Distribution of the cobalt across MALO crystals (thickness 1 mm) with different x after air annealing at 1500°C for 24 h.

spinel stability temperature becomes greater. At annealing below stability, the temperature spinel decomposes into a magnesium-rich phase and corundum. Figure 3 shows the MALO temperature stability curves as a function of x, calculated from the MgO—Al$_2$O$_3$ phase diagram presented in [16]. These temperatures were refined for our MALO crystals. For this a series of spinel samples with x from 1.00 to 1.88 were annealed at 1400–1500°C for 10 h. All initial samples were optically transparent. In Fig. 3, the samples that remained transparent after heat treatment are marked with black circles, and those with detected opacity and inclusions of foreign phases are marked with crosses.

The inclusions of acute-angled shape were observed in the volume of crystals. For samples with the same x, the size of inclusions increased as the annealing temperature decreased. When the annealing of samples with different stoichiometry, more inclusions appeared with the increase of x. Annealing at temperatures below the stability temperature for the corresponding x results in the decomposition of the spinel phase into magnesium-rich spinel in comparison with the initial composition and another aluminum-rich phase.

Figure 4 shows images of the spinel (initial $x = 1.69$) after annealing at 1450°C for 24 h. Element analysis showed that the matrix phase contains more magnesium than the original sample with $x = 1.45$ (Fig. 4b, point 1). The inclusions consist of an alumina-rich phase and $x = 3.48$ (Fig. 4b, point 2).
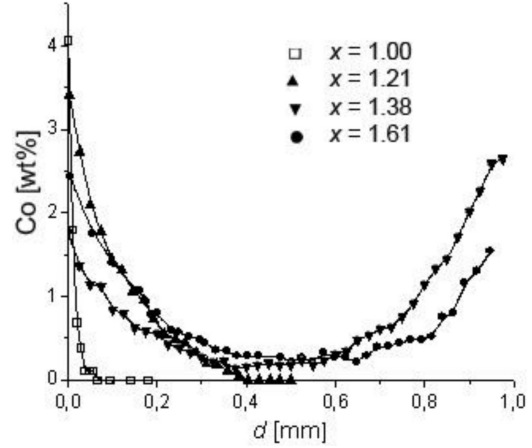
It was found that the temperature stability of MgO·xAl$_2$O$_3$ phase increases with the increase of x. The MALO phase with $x > 1.34$, $x > 1.46$, and $x > 1.63$ is stable at temperatures above 1400, 1450, and 1500°C, respectively.

3.3. Introducing the cobalt ions into the MALO crystals

Diffusion annealing of the MALO crystals with x from 1.00 to 1.61 was carried out from 1300 to 1500°C. The crystals are stable at these temperatures. The penetration depths of the cobalt ions into the crystal after temperature treatment are presented in Fig. 5. The thickness of the diffuse layer of cobalt d significantly increases with an increase of x. The value of x directly relates to the magnesium content and the number of cationic vacancies. The increase in x causes a decrease in the magnesium content and, therefore, an increase in the number of cationic vacancies. Thus, for $x = 1.00$, d is in the range of 0.05–0.07 mm, for $x = 1.21$, it increases to about 0.35 mm, and for $x = 1.38$, a thickness is equal to 0.50 mm (see Fig. 5). At $x = 1.61$, the thickness increases to 0.53 mm and the MALO sample became saturated by cobalt over the whole thickness.

An approximate estimation of the diffusion coefficients D of cobalt ions into MALO for stoichiometric spinel ($x = 1.00$) was carried out. The depth of the Co ions diffusion is very low and equals 0.03, 0.05, and 0.07 mm after annealing at 1300, 1400, and 1500°C, respectively, for 24 h. The diffusion coefficients D were calculated from formula

$$D = \frac{d^2}{4t}, \tag{1}$$

where t — annealing time. The values of D are $(2.6 \pm 0.9) \times 10^{-11}$ cm^2/s (1300°C), $(7 \pm 2) \times 10^{-11}$ cm^2/s (1400°C), $(1.4 \pm 0.4) \times 10^{-10}$ cm^2/s (1500°C).

Efficient activation energy E_a of diffusion was estimated based on the Arrhenius temperature dependence of the obtained diffusion coefficients by the formula

$$D = D_0 \exp\left(-E_a/(k_B T)\right), \tag{2}$$

where $k_B = 8.617 \times 10^{-5}$ eV/K is the Boltzmann constant, T — temperature [K], and D_0 is a pre-exponential factor. The value of E_a is 2.03 eV.

4. Conclusions

MALO crystals with $1 \le x < 2$ have been grown by HDC method. It was found the temperature stability of the spinel phase depended on the composition of the phase. Compositions with $x > 1.34$, $x > 1.46$, and $x > 1.63$ keep stability at temperatures higher than 1400, 1450, and 1500°C, respectively.

Diffusion doping of the MALO crystals with cobalt ions can be performed through the vapor phase, using the cobalt oxide as a source of diffusion under the temperature treatment at 1300–1500°C. The thickness of the Co diffusion layer increases with increasing the spinel non-stoichiometry. The penetration depth of the cobalt ions increases from 0.05 to 0.53 mm as x changes from 1.00 to 1.61 under annealing at 1500°C for 24 h. The lift of the diffusion rate occurs due to the increase in the number of cationic vacancies V_{Mg2+}. As result, the MALO crystals ($x = 1.61$, thickness $d = 1$ mm) with cobalt ions distributed into the whole internal volume of the sample were obtained.

The diffusion coefficients of cobalt into MALO ($x = 1.00$) at 1300–1500°C and efficient activation energy have been estimated. The values of D are $(2.6 \pm 0.9) \times 10^{-11}$ cm^2/s (1300°C), $(7 \pm 2) \times 10^{-11}$ cm^2/s (1400°C), $(1.4 \pm 0.4) \times 10^{-10}$ cm^2/s (1500°C), and E_a is 2.03 eV.

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