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The growth of Mg_2TiO_4 single crystals using a four-mirror furnace

ALEKSANDAR GOLUBOVIĆ*# and MARKO RADOVIĆ

University of Belgrade, Institute of Physics, Pregrevica 118, P. O. Box 68, 11080 Belgrade-Zemun, Serbia

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Abstract: A single crystal of Mg_2TiO_4 was grown by the travelling solvent float zone (TSFZ) method. The lattice parameter a = 0.8444(8) nm was determined by X-ray powder diffraction analysis. The optical properties of the Mg_2TiO_4 single crystals were studied using spectroscopic ellipsometry. The obtained results are discussed and compared with published data.

Keywords: Mg_2TiO_4; crystal growth; single crystal; four-mirror furnace; spectroscopic ellipsometry.

INTRODUCTION

Magnesium orthotitanate, Mg_2TiO_4, has been used as a heat resistor, a dielectric for microwave technology, a capacitor for temperature compensation and as a refractory material.[1] Mg_2TiO_4 is a cubic crystal with a crystal structure of the inverse spinel type.

Mg_2TiO_4 is a metastable system. It can be obtained below 800 °C, but it decomposes to $MgTiO_3$ and MgO on further heating.[2] Mg_2TiO_4 crystallizes in the cubic system, with a $Mg(MgTi)O_4$ inverse spinel structure, in which magnesium occupies both tetrahedral and octahedral sites but titanium occupies only octahedral sites. The sites formula can be written as $(A_{1-x}B_x)^{tet.}(A_xB_{2-x})^{oct.}O_4$, where x is called to inversion parameter. In the present case, the spinel is named to (inverse) since x is equal to 1.[3] Mg_2TiO_4 single crystals could be grown by the Verneuil Method, but there are considerable difficulties due to fact that the chemical composition of Mg_2TiO_4 is covered by the primary crystallization field of MgO before Mg_2TiO_4 during cooling.[4] This problem can be solved using the travelling solvent float zone (TSFZ) method.[4] The TSFZ method is essentially identical to the floating zone method, with the exception that the chemical com-

* Corresponding author. E-mail: golubovic@ipb.ac.rs
# Serbian Chemical Society member.
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position of the grown crystal is appreciably different from that of the melt zone. The aim of the present research was to obtain Mg_2TiO_4 single crystals using a four-mirror furnace and determine their optical properties using ellipsometry.

EXPERIMENTAL

The apparatus used for crystal growth was a four-mirror furnace FZ-T-10000-H-HR-I-VPO-PC (Crystal System Corp., Japan). The apparatus has a mirror the shape of an ellipsoid and the focus positions are occupied by halogen lamps. The upper charge feeding and the lower seed holding shafts are located so that the other focus position is always occupied by the melt zone, into which the charge is dissolved and from which crystallization takes place on the seed. The crystal growth was performed in the chamber isolated by a silica glass tube for atmosphere control. An external camera was fixed at a position enabling the solid–liquid boundary to be observed during the crystal growth run and this is presented in Fig. 1.

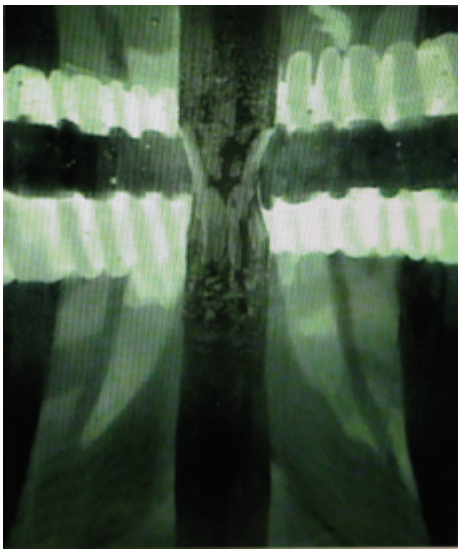

Fig. 1. A view of the floating zone in the display of the four-mirror furnace during a crystal growth run.

Powders of MgO (p.a., Centrohem) and TiO_2 (99.9 % pure, Degussa) were mechanically mixed in the molar ratios of 2:1 and 3:2 for preparation of the materials of the Mg_2TiO_4 charge and the solvent zone, respectively. Each of the mixed batches was placed into a sealed rubber tube and hydrostatically pressed (Crystal System HPTS-M-2000-W hydrostatic press) under a pressure of 80 MPa to give a rod of the desired diameter and length (approximately 10 and 100 mm, respectively). The rods were then sintered at a temperature of 1300 °C (the seed, exactly the solvent zone) and 1500 °C (the charge). In this way, the obtained rods had a density of approximately 85 % of the theoretical value.

Powder X-ray diffraction (XRD) was used for identification of crystalline phases, quantitative phase analysis and estimation of crystallite size and strain. The XRD patterns were collected using a Philips PW 1729 X-ray generator on a Philips diffractometer (PW1710) employing CuKα radiation. Step scanning was performed within the 2θ range from 5 to 70° with a step size of 0.06° and a fixed counting time of 0.41 per step. For product identification, the Fullprof computer program and JCPDS (ASTM) card files were used.

Ellipsometric measurements were performed using a high-resolution variable angle spectroscopic ellipsometer (SOPRA GES5E - IRSE) of the rotating polarizer type. The light source was a short arc Xe lamp while the detector was a photomultiplier tube.

RESULTS AND DISCUSSION

The formation of a steady TSFZ system for successful single crystal growth depends on the following three essential conditions: the degree of sintering of the charge rod, the growth rate, and the chemical composition of the charge rod. In a successful TSFZ crystal growth run, a steady solid–liquid interface is essential for avoiding the precipitation of foreign phases on the growing crystal. The phase diagram of the system MgO–TiO_2 was well described by Woerman *et al*.[5] This system is of interest because of the occurrence of four different eutectics. Such eutectics in this and other systems have been used to prepare some interesting two-phase materials. For example, when a liquid with a composition in the MgO--rich region is cooled from the eutectic temperature at 1707 °C, a material that consists of alternating lamellae of nearly pure MgO and Mg_2TiO_4 will be produced.[6] Other systems show different structures, which are determined in part by the interfacial energies. Of course, interfacial energies are usually not considered in the analysis of phase diagrams.

When the charge rod is in contact with the molten solvent zone under dynamic equilibrium, the liquid phase penetrates into the charge rod to the point where the temperature corresponds to the invariant situation. Consequently, that part of the charge rod is adjacent to the melt zone, thus causing an uneven solid–liquid interface. During floating-zone run, a too wide molten zone may result in the zone becoming unstable and precipitating, while a too narrow zone can lead to the formation of a bridge of solid (or partially solid) material between the growing crystal and the feed rod.[7] While this may not necessarily prevent crystal growth in all materials,[8] it can lead to strain being imparted into the growing crystal, especially if rotation is employed.

The growth rate is the second variable in the system and it was concluded after many experiments that the maximum growth rate of Mg_2TiO_4 single crystals was 2 mm h^{-1}. A higher growth rate resulted in opaque crystals due to foreign phase precipitation and incorporation, while a lower rate lead to many problems during the crystal growth run due to inappropriate surface tensions. The value of crystal growth rate of 2 mm h^{-1} is in accordance with literature data,[4] but the employed rotation rate of 5 rpm was not (the literature value is 30 rpm, [4] but using this value of the rotation, unstable experimental conditions were obtained in this study).

The third important condition for a successful Mg_2TiO_4 crystal growth run is the composition of the rods. The charge rod had the composition MgO:TiO_2 = 2:1, while the seed rod had the composition MgO:TiO_2 = 3:2. The composition of seed was chosen according to the composition obtained from the liquidus curve.[4]

Some authors[4] use solvent zone material in the shape of disk, which is put on the end of a pressed charge rod and then again hydrostatically pressed to give a charge rod with solvent material affixed. As the composition of solvent zone was unknown, it was decided that a seed should be made from the same material (the composition $MgO:TiO_2 = 3:2$).

Blue–grey crystals were obtained after the crystal growth run but after annealing for 12 h at 1000 °C in an oxygen atmosphere, the grown crystals became colourless and transparent. The structural properties were obtained using X-ray diffraction analysis of powdered samples. The unit cell of Mg_2TiO_4 was calculated by the least square method. The parameter of the cubic unit cell is given to be a = 0.8444 (8) nm, while the literature value is a = 0.84443 (4) nm, according to corresponding JCPDS card 87-1174. The XRD pattern of a powdered Mg_2TiO_4 single crystal is presented in Fig. 2.

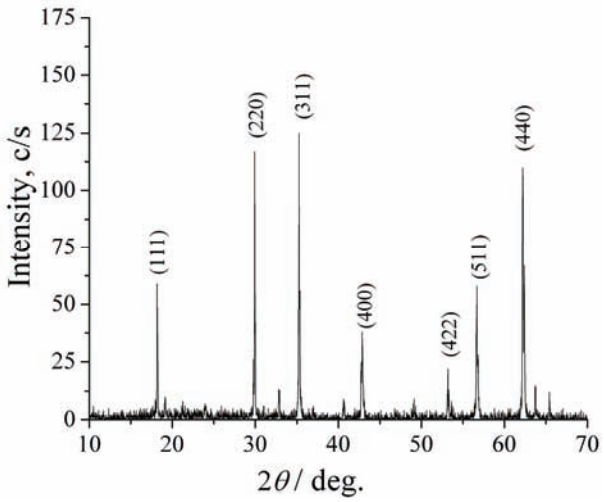

Fig. 2. XRD Pattern of the obtained Mg_2TiO_4 single crystal.

The optical properties of an Mg_2TiO_4 single crystal were studied using spectroscopic ellipsometry in the 1.5–6 eV photon energy range at a 70° angle of incidence. The extraction of refractive index (n) and extinction coefficient (k) from the ellipsometric data was performed using a two-phase model. The spectral dispersions obtained for n and k are shown in Fig. 3.

Since inverse spinels have a direct band gap (E_g),[9] the value of E_g for the Mg_2TiO_4 single crystal was evaluated from the general relation:

$$\alpha E = b\sqrt{E - E_g} \quad (1)$$

where E is the photon energy, b is a constant related to the density of states in conduction band and α is the absorption coefficient derived from extinction coefficient k through the relation:

$$\alpha = \frac{4\pi k}{\lambda} \quad (2)$$

where λ is the wavelength of light.

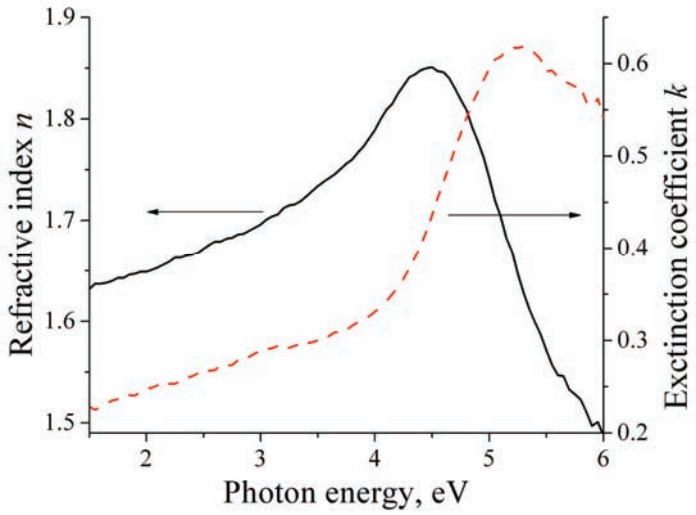

Fig. 3. The photon energy dependence of the refractive index and extinction coefficient for the Mg_2TiO_4 single crystal.

A plot of $(\alpha E)^2$ *vs.* photon energy is shown in Fig. 4. The linear extrapolation towards zero energy gives the value of E_g = 4.25 eV for the direct band gap transition, which is comparable with previously reported results,[10,11] (E_g = 4 eV) and (E_g = 4.4 eV), respectively. The position and slope of the optical absorption edge makes this material a suitable UV-B light absorber.

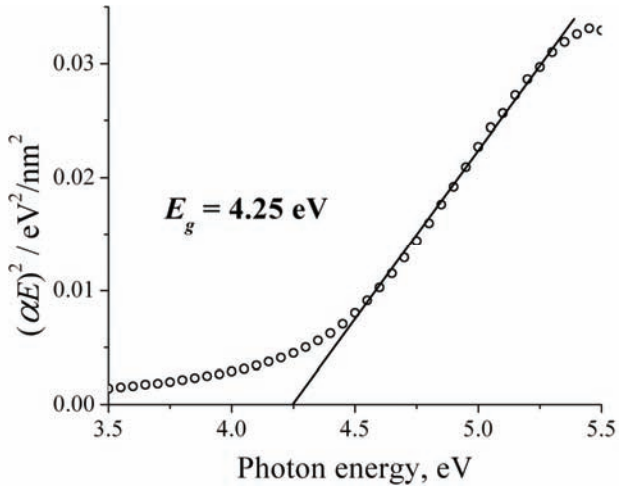

Fig. 4. A plot of $(\alpha E)^2$ *vs.* photon energy, showing the linear extrapolation towards zero energy.

CONCLUSIONS

Good quality Mg_2TiO_4 single crystals were obtained using a four-mirror furnace. The optimum experimental conditions, crystal growth rate of 2 mm h^{-1} and rotation rate of 5 rpm, were experimentally obtained. The unit cell of parameter a = 0.8444 (8) nm and the value of the band gap energy of 4.25 eV for the obtained Mg_2TiO_4 single crystal were in good accordance to data reported in the literature.

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И З В О Д

РАСТ МОНОКРИСТАЛА Mg_2TiO_4 ПОМОЋУ ПЕЋИ СА ЧЕТИРИ ОГЛЕДАЛА

АЛЕКСАНДАР ГОЛУБОВИЋ и МАРКО РАДОВИЋ

Универзитет у Београду, Институт за физику, Прегревица 118, п. пр. 68, 11080 Земун

Монокристал Mg_2TiO_4 је добијен методом лебдеће зоне са путујућим растварачем (TSFZ). Параметар јединичне ћелије, a = 0,8444 (8) nm, је одређен помоћу дифракције x-зрака на праху. Оптичка својства монокристала Mg_2TiO_4 су проучавана елипсометријом. Добијени резултати су дискутовани и упоређивани са подацима из литературе.

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