Czochralski growth and characterization of MgAl₂O₄ single crystals

Andrzej L. Bajor, Marcin Chmielewski, Ryszard Diduszko, Jaroslaw Kisielewski, Tadeusz Lukasiewicz, Krzysztof Orlinski, Magdalena Romaniec, Wlodzimierz Szyrski

Institute of Electronic Materials Technology, ulica Wolczynska 133, 01-919 Warszawa, Poland

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ABSTRACT
MgAl₂O₄ (MALO) single crystals were pulled by the Czochralski method in [111] direction. The crystals were doped with Co (0.06–0.6 at% [charge compositions]), because Co²⁺ ions in tetrahedral positions exhibit non-linear optical properties, and, currently, Co-MALO seems to be the best saturable absorber in the eye-safe region (ca. 1.5 μm). By XRD powder technique a stoichiometric MALO was evidenced without admixtures of higher order spinels (MgAl₂O₄ and MgAl₇O₁₉). Also no excessive residual stresses have been discovered by different optical methods, and irrespective of the doping level we did not face any problem of cracking when cutting the crystals into wafers and other structures. In this work we have concentrated our efforts on investigation of thermal properties of MALO. Due to the 2nd order phase transition ca. 650 °C they seem to be of crucial importance in future thermal bonding of this material to the lasing host (Yb:Er-glass) expected just about this temperature.

1. Introduction

MALO has been a promising material in several applications, especially as substrate for GaN epi-layers and saturable absorbers in laser heads. It has a large thermal conductivity, and in spite of its large hardness it is easy to cut without cracking (unlike other researchers we have never experienced any problem of cracking). However, some of its disadvantages include large growth temperature (over 2100 °C) and a 2nd order phase transition ca. 650 °C. This last feature may play an important role in thermal bonding (TB) of MALO to a laser host material (e.g. Er,Yb glass) expected just about this temperature. Large temperature on the liquid interface is not far away departing from melting point (ab. 2420 °C) of Ir crucible used in the Czochralski growth of this spinel. Some attempts of different investigators were performed on lowering this temperature, either by adding scandum (ScMgAlO₄ – e.g. [1]), or by growing “higher order” magnesium spinels: MgAl₂O₇ [2] (1:2 spinel) and MgAl₆O₁₉ e.g. [3] (1:3 spinel). Although some researchers declare that the both work equally well or even better than MALO as saturable absorbers, from some other data it follows that this may not necessarily be so [see e.g. data on optical damage threshold in cit. [3]]. MALO (1:1 spinel because MgO and Al₂O₃ are mixed 1:1 in crucible) is still best resistant to laser damage ab. 1.5 μm. In this work we have concentrated on learning thermal properties of this spinel, because in the future we will continue with TB of MALO to Er,Yb glass, the purpose of which is to eliminate the air gap between the host and the absorber, as well as to eliminate two AR-coatings.

Structural homogeneity of MALO was checked by XRD and other X-ray techniques on samples cut from top and bottom of undoped and Co-doped crystals. This has not revealed admixtures of MgO, Al₂O₃ or “higher order” spinels, but a monocristalline spinel structure itself. Homogeneity of the crystals was also investigated by electron microscope, conoscope and plane and circular polariscopes. In several crystals we have additionally revealed a pair of plane-parallel surfaces that were also parallel to the growth axes. We measured transmission and refractive index distributions from bottom to top in these crystals. These investigations have shown that the crystals were grown without macroscopic defects, as well as residual stresses were of limited values.

Although all agree that MALO belongs to the cubic system, by no means this is still certain whether it belongs to Fd3m space group in temperatures below the 2nd order phase transition. We also have not answered this question yet. However, we begun our studies by measuring the following quantities as functions of temperature: elongation of the sample (and linear expansion coefficient), thermal diffusivity and conductivity, as well as specific heat. The mentioned phase transition has been confirmed to occur in undoped and in Co-doped MALO. However, from our experiments this is still unclear whether it occurs just at 650 °C. Needless to say, some other experiments will be needed to conclude on the nature of this transition.

Basically, it is said that Mg should occupy tetrahedral, while Al octahedral sites in the cubic lattice, respectively. However, it was...
quickly discovered that reverse population of Mg and Al (which is lower in natural than in industrial-grown spinels) is a real case in this crystal (See e.g. [4] – (Normal) \( \text{Mg}^4\text{Al}^3\text{O}_4 \Rightarrow (\text{Inversed}) \text{Al}^4\text{MgAl}_2\text{O}_4 \), where 4 and 6 denote tetra- and octahedral sites in the cubic lattice, respectively). Some authors (e.g. [5]) consider a “mixed” spinel \( \text{Al}_{1-x}\text{Mg}_x\text{Al}_2\text{O}_4 \) where \( x \) can be treated as a measure of this inversion. Origin of inversion (exchange of lattice sites) is the same like the origin of stoichiometry changes.

In [6] a review of earlier papers on disorder problem in MALO has been provided. It was said that as early as 1932 Barth and Posnjak noticed that chemical formula for the normal spinel cannot reproduce the obtained X-ray diffraction patterns. However, since then no-one tried to abolish theory on MALO belonging to Fd3m. In consequence, it has been treated so by many, until it became apparent that a phase transition occurs ca. 650°C. This problem was later reconsidered in [7] when it became clear enough that cationic disorder in MALO has a significant impact on several parameters, like bulk modulus and the coefficients of thermal expansion. In cit. [8] apart from calculating the minimum lattice energy to occur for Fd3m point group, Raman spectroscopy data which are suggesting that MALO’s symmetry is lower than Fd3m at room temperature, as well as diffraction (Laue), which, on the other hand, confirms this to be just Fd3m, was recalled. So, the problem is still open for further discussion and experiments.

In [9] expansion coefficient of MALO between 30 and 800°C was measured and compared to a couple of earlier results obtained also in a polycrystalline specimen. An abrupt decrease in the expansion coefficient ca. 650°C of \( 1 \times 10^{-6} \text{K}^{-1} \), which is a large value when one is thinking of adjusting it to that of Er3+:Yb3+ glass, was observed. In [10] analysis of various spinels, including MALO, in terms of crystallographic parameters, cationic radii, lattice energies and cations distributions in the lattice, was made. Important for us is their Fig. 5 in which degree of disorder \( x \) was plotted as a function of temperature of heat treatment. A significant jump in \( x \) occurred ab. 800 and 850°C in two MALO samples, respectively. In lower temperatures no increase in this disorder has been observed. In [11] samples of natural and artificial MALO were heated to 727°C. By two independent techniques significant changes in the ultrasonic resonance frequencies, from which also elastic moduli \( C_{ij} \) and other parameters were next determined, were observed. Temperature derivatives of the resonant frequencies, and, hence, a couple of material parameters changed abruptly just about 727°C. Transition temperature can be also traced from temperature derivative of the Raman bands near 720 and 770 cm\(^{-1}\). In conclusion the authors say that this transition is a matter of the ions migration (order-disorder process) enhanced by temperature.

Independently, in [5] MALO was studied by Brillouin spectroscopy. It was noticed that ca. 650°C MALO undergoes the mentioned phase transition. Noticeable influence at this temperature was observed on \( C_{11} \) and \( C_4 \) \((C_4 = (C_{11} - C_{12})/2)\), while there have not been such changes in \( C_{44} \) and in \( C_{33} \) itself. This transition could be also seen on isotropic compressional and shear velocities, on temperature dependences of the [100] longitudinal and [110] transverse velocities, as well as on some other parameters. Redfern and others [12] continued their earlier work [10] to get more precise data on this transition temperature and the mechanism itself. They considered earlier and their own results and faced a common problem of large temperature increments that were used in the past. Their work is a good basis for further studies, since they analyzed practically all papers and results that existed at that time and were either devoted to ordering–disordering, or just to practical experiments made on various samples. Their own analysis is comprising a thermodynamic model which seems to be good fitting to experimental data. From theoretical and experimental curves it follows that the transition occurs between 647 and 677°C. More precise data on this temperature were acquired a year later in [13]. Most probably for the first time the authors applied Raman technique to powders heated in temperatures between 27 and 1427°C, and noticed that the order-disorder process became detectable at 671°C.

A couple of years later Meducin et al. [14] continued their earlier experiments, including pressure-induced ordering–disordering. Lattice measurements at different temperatures and pressures are suggesting a certain hysteresis. They have shown that the inversion parameter strongly depends on pressure and that it has also a noticeable impact on the “threshold” when increase in \( x \) occurs. However, like many others, their work suffers from too large temperature increments to conclude more precisely on the transition temperature.

Finally, we may conclude that ceramic MALO, irrespective of its major drawback (usually low transmission), by no means is free from the same cationic disorder problem [15].

### 2. Preparation of crystals and samples

Rather unexpectedly, one can face the problem of a very limited literature on preparation of these crystals. Even in [16], in which the authors gave some details on Verneuil-grown MALO, and compared this to Czochralski-grown crystals, no such details were provided for the latter. Cockayne and Chesswas [17] were the first to declare that they grew MALO by Czochralski method. The authors of [2,3] tried to show boundary as well as optimal growth parameters themselves. Other researchers while discussing some (e.g. laser) problems rarely give a couple of data on Czochralski-grown MALO e.g. [18].

Problems associated with distribution (segregation) coefficient \( k_{\text{eff}} \) of Co in MALO will not be discussed in this paper due to shortage of space, although \( k_{\text{eff}} > 1 \) (sorry to say, but no-one has yet determined this in MALO) may result in a couple of problems, including inhomogeneous Co distribution in the crystal.

First (undoped) MALO was grown on iridium wire. By X-ray technique it was evidenced that it was grown in [111] direction. XRD patterns (e.g. Fig. 1) have shown that there were no admixtures of other order spinels. This crystal became the source of seeds for next processes. The crystals were pulled from 50 mm diameter Ir crucible in Cyberstar Oxypuller arrangement. Important feature of the reactor was associated with applying an active after-heater, as well as due to large temperature we also used
zirconia grog and blankets from the “top-shelf”. In our works we benefitted from earlier information on a distinguished problem, namely of a relatively small yield while cutting the boules into wafers ([3] – only 20% of unbroken wafers was taken as the criterion of success in wafer preparation). Possibly, the excessive resolved shear stress (RSS) might have been a problem in their experiments. Therefore, we have decided to grow 1 in. diameter crystals only, and to thermally isolate the reaction chamber to the “greatest possible extent”, just to avoid thermal losses and to lower the temperature gradients on the liquid–solid interface and in the crystals themselves. Reduction of diameter aims at reduction of residual stresses (the RSS is directly proportional to the square of the diameter in Czochralski-grown crystals).

So, after limiting the diameter, we decided to use active after-heater, which is a very important part of the reactor, because it helps also to limit temperature gradients in these parts of crystals that have already emerged from the liquid (cone and middle part). The active after-heater is also very helpful in limiting temperature gradients in finally extracted from the melt crystals, which, by all means undergo then a certain thermal shock.

MgO, Al2O3 and Co3O4 high-purity powders (at least 4.5 N) were pressed on the isostatic press. In every (new) batch in which we pulled 6 or 7 crystals, small portions of the pressed powder were added to the crucible and after a couple of consecutive meltings, the final melting was ended by inserting MALO seed into the melt. We began with the lowest (0.06) and by adding suitable quantities of Co3O4 after each process, we continued until the largest Co concentration (0.6 at% in the melt) was reached. Before each processes, the air was pumped away from the reactor, and after that it was exchanged by a high purity N2.

Pulling rate was kept between 1.8 and 2.2 mm/h, while rotation rate was varied between 12 and 18 (usually 15) rpm. After automatic extraction of a crystal from the melt a 24 h cooling time was usually applied. Although even in such case there have not been problems of cracking, we pulled also two crystals with enhanced cooling time (78 and 82 h, a very small cooling rate in the first 48 h) for some future experiments.

Standard procedure in sample preparation was to cut off the conical and tail parts perpendicularly to the growth direction and polish the two end faces. However, we had also to discover a relation between morphology and crystal orientation. Although it may seem odd, only one paper on this problem exists [3]. Its authors gave only a couple of drawings of front view (conical part) of faulted and properly grown [111] oriented MALO, the latter showing 3-fold symmetry. No crystallographic directions were, however, marked on their drawings. We have also faced a 3-fold symmetry, although in many cases the cross-section of the cone was a hexagon, rather than triangular-like figures shown in cit. [3]. In the majority of cases we observed 3 thin scratches on the cones in our crystals, separated by 120°. They continued toward the tail, and closer the tail they were, also “thicker” they became. By X-ray studies it was quickly evidenced that the scratches lied in planes in which also [100], [010] and [001] directions lie, respectively. This also means that one may use these scratches for orienting crystals, since the three mentioned directions are equivalent in the cubic lattice.

A typical as-grown MALO (in the center) and two other boules prepared for testing of their optical (in)homogeneity are shown in Fig. 2. After such examination the boules were later cut into pieces: thin (ab. 1.5 mm) wafers that were usually cut perpendicularly to [111], 8 × 8 and 4 × 4 mm2 structures, as well as 5 × 5 × ca. 20 mm3 rods for thermal investigations.

3. Investigation of structural and optical homogeneity of MALO

In Fig. 3 one can see a “thick” isogyres cross, the arms of which, although slightly deformed, are parallel to polarizer’s and analyzer’s optical axes, respectively. From our experience we know that the thicker the arms of the cross are, the smaller are also residual stresses (difference of radial and tangential principal stresses). On the other hand, however, a decrease of refractive index from tail to top could be seen in all crystals (Fig. 4). The indices were determined by measuring a shift of the light beam induced by tilting the crystals with two plane-parallel surfaces on their perimeters, like these shown in Fig. 3, by a certain angle vs. the beam, which, primarily, was perpendicular to the surface area [20]. Accuracy of the method (ca. 0.001) cannot explain differences in the refraction index between tail and cone. Although further studies are needed, the effect may be due to a certain Co-distribution along the pulling axes, and/or to larger concentrations of dislocations (as well as residual stresses themselves) in the tail parts compared to that of the cones in Czochralski-grown crystals.

We also examined MALO by means of electron microscopic (Zeiss-Auriga) investigations. After examining an entire [111]-cut wafer for its homogeneity, a spread distribution of atoms on wafer’s areas has been performed in 11 small areas on each wafer separated by a constant increment (e.g. Fig. 5).
4. Thermal properties

Results presented in [19] suggest that at least thermal conductivity may, although rather insignificantly, be depended on orientation, i.e. that it may be anisotropic in basically isotropic crystal. Although these may also be influenced by measurement errors, to be absolutely certain of an (or non-) influence of orientation on thermal properties, we have decided to use different orientations of samples in case of investigation of thermal parameters of MALO.

The measurements, including also dependence of (linear) expansion coefficient on temperature, were performed in an automated dilatometer DIL402PC. We made 11 measurements of undoped MALO to get a standard curve of elongation which could be next compared to that in Co-doped crystals. Co-doped samples were measured ab. 5 times each and the average result was next compared to that of the undoped crystal. Specific heat was measured in a Simultaneous Thermal Analyzer STA 449 F1 Jupiter, while thermal conductivity and diffusivity were measured by LFA (Laser Flash Analysis; e.g. [21]) in an automated diffusimeter (all of the mentioned arrangements were made by Netzsch-Gerätebau GmbH).

Although the project is far away from the end, we demonstrate here our preliminary results, because even now they seem to be useful in investigation of the phase transition. In Fig. 6 one can see that this transition occurs ca. the same temperature, namely 650 °C, in undoped [111], as well as in 0.085 at% of Co doped [111] and [1-14] oriented rods. In our future experiments we will try to determine whether this transition temperature is dependent on Co doping. Having the mentioned problems in our minds, we have applied small (20 ± 1 °C, and 10 ± 1 °C around 650 °C increments). Although thermal diffusivity and conductivity of MALO is expected to decrease with increase of temperature, a certain increase in this conductivity (not shown in the paper), as well as in thermal diffusivity (Fig. 7) above ca. 650 °C can be seen in lightly (0.085 at% of Co) doped crystals. One of the [1T4] oriented samples may suggest that the phenomenon is “sharp” in its nature, and, in fact, a doubled concentration of Co (Fig. 8) may confirm this suspicion at the moment.
reach, and the same, however at a small rate, decrease in conduction and diffusion may be ideal for investigation of such a relation may occur. Besides, it seems that plots of thermal conductivity in 0.16 at% of Co doped (charge composition) [111] oriented MALO on temperature. Two samples were cut from top and one from the bottom part of the boule.

5. Summary and discussion

In this paper we have presented preliminary results on growth and investigation of MALO single crystals. Due to limited space we have shown only a fraction of these results, and especially we have concentrated on displaying thermal properties which seem to be very important due to future works on TB of MALO to Er Yb glass. Although we are still not sure that this is exactly 650 °C we confirmed the 2nd order - disorder process to occur ca. 650 °C, and possibly at slightly larger temperature, which falls in the anticipated range of the future TB process. Decrease in the linear coefficient of thermal expansion (1.2 \times 10^{-6} K^{-1}) in undoped and in lightly Co-doped MALO (Fig. 6) is comparable to that obtained in [9] undoped MALO (1 \times 10^{-6} K^{-1}) at the transition temperature. However, we are still not sure whether this will change with Co concentration. In Fig. 8 the phenomenon may be abrupt in nature, like suggested in [11]. However, e.g. Fig. 7 this may not necessarily be such. We have also observed rather not sharp changes of specific heat (\(C_p\) - not shown in this paper) with increase in temperature. The phenomenon began just at 650 °C with a small dip in \(C_p\) followed by a constant increase of ab. 7% of the absolute value at 700 °C when the maximum was reached, and the same, however at a small rate, decrease in \(C_p\) between 700 and 1200 °C. Therefore, it will be important to answer a question whether concentration of Co (0.06 - 0.6 at% in the melt) may influence this and other thermal phenomena. From the point of view of commercial practice, one may modify Co-doping to a certain extent, since initial transmission of the saturable absorber can be adjusted to a desired value by varying also its thickness. So, therefore, learning of the mentioned thermal parameters and their dependence on Co-doping is even more important from technological (TB of MALO to Yb Er glass) than from lasing site of the problem. Plots of 0.085 and 0.16 at% of Co (in the melt) doped MALO shown in this paper are suggesting that such a relation may occur. Besides, it seems that plots of thermal conductivities and diffusivities may be ideal for investigation of the mentioned phenomenon, since a more pronounced differences can be seen on these plots compared to those of e.g. \(C_p\) that have been mentioned above in others’ works.

Another very important task will be to find in the future a relation between absorption coefficient and concentration of Co in order to receive (a practically unknown value of the absorption cross-section of Co^{2+} ion in MALO single crystals – a very important parameter in laser technique.

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