

<i>Cryst. Res. Technol.</i>	<b>34</b>	1999	5–6	615–619
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## On the Crystallization of Terbium Aluminium Garnet

Attempts to grow terbium aluminium garnet ( $Tb_3Al_5O_{12}$ , TAG) by the CZOCHRALSKI method lead to crystals of millimeter scale. Larger crystals could not be obtained. DTA measurements within the binary system showed that TAG melts incongruently at 1840°C. The perovskite ( $TbAlO_3$ , TAP) with a congruent melting point of 1930°C is the most stable phase in this system. The region for primary crystallization of TAP covers the chemical composition of TAG and suppresses the primary crystallization of the terbium aluminium garnet.

Versuche zur Züchtung von Terbium-Aluminium-Granat ( $Tb_3Al_5O_{12}$ , TAG) nach der CZOCHRALSKI - Methode erbrachten Kristalle mit Größen im Millimeter-Bereich. Die Züchtung größerer Kristalle mißlang. DTA - Messungen im binären System ergaben, daß TAG inkongruent bei 1840°C schmilzt. Der Perovskit ( $TbAlO_3$ , TAP) ist mit einem kongruenten Schmelzpunkt von 1930°C die stabilste Phase in diesem System. Das Primärausscheidungsgebiet von TAP schließt die chemische Zusammensetzung des TAG mit ein und unterdrückt die Erstkristallisation des Terbium-Aluminium-Granats.

Keywords: growth from melts, differential thermal analysis, laser materials, magneto-optical devices

### 1. Introduction

FARADAY isolators are a key component of many contemporary laser systems. They are used to prevent optical feedback leading to parasitic oscillations in multi-amplifier systems and frequency instabilities in laser diodes. The most important optical element of a FARADAY isolator is the FARADAY rotator providing a 45° rotation of the polarization plane of traversing light. The characteristics that one looks for in a FARADAY rotator material are a high VERDET constant, a low absorption coefficient, a low nonlinear refractive index and a high damage threshold. The most commonly used materials for the visible and near infrared regions are terbium doped glasses and terbium gallium garnet (TGG) single crystals. DENTZ et al. (1974) reported the VERDET constant of TGG to be 134 rad T<sup>-1</sup> m<sup>-1</sup> at room temperature and for a wavelength of 633 nm.

Already in the sixties RUBINSTEIN et al. (1964) measured and published the VERDET constants of several rare earth aluminium garnets that were grown from a lead oxyfluoride flux. Among these most promising for the application in FARADAY devices is terbium aluminium garnet (TAG) with a VERDET constant of 180 rad T<sup>-1</sup> m<sup>-1</sup> (room temperature, 633nm). This is caused by the electronic structure of the terbium ion i.e. the deep 5d bands and a wide range of transparency (WEBER 1986). More than a decade later KUZANYAN et al. (1982) used a directional solidification technique to grow TAG. In their experiments they met with serious problems connected with the concurrent crystallization of  $TbAlO_3$  (TAP, perovskite structure). These problems were explained by the action of impurities of the used

terbium oxide, e.g. by an appreciable concentration of the higher oxide  $TbO_2$  and a suspected lower melting point of the garnet phase.

Up to now, there are no reports in the literature about the successful growth of applicable TAG single crystals. Moreover, some of the information given until now seems to be questionable e.g. concerning the melting temperature and the melting behaviour.

## 2. Experimental

### 2.1. Crystal growth experiments

The stoichiometric mixture of the starting materials  $Al_2O_3$  and  $Tb_4O_7$  (5N and 4N5 purity, respectively) was sintered in a platinum crucible at  $1450^\circ C$  for several hours in air. According to the relevant literature (e.g. LEVIN, MCMURDIE 1975) it can be assumed that  $TbO_2$  contained in the reagents was entirely reduced to  $Tb_2O_3$  before the material was molten. The reduction process  $Tb^{4+} + e^- \rightarrow Tb^{3+}$  becomes obvious by a change of color from brown to white.

Growth experiments were carried out applying an automated CZOCHRALSKI technique with rf induction heating. KUZANYAN et al. (1982) reported for TAG a high melting temperature of  $1860 \dots 1900^\circ C$ . Therefore an iridium crucible was used and consequently, growth was carried out under flowing nitrogen. In order to attain moderate temperature gradients and to avoid overheating of the melt an active afterheater was employed. Crystallization from the crucible bottom was avoided by an active bottom heater. The growth parameters were rather common for oxides, i.e. a pulling rate of  $1.5 \text{ mm/h}$  was applied. A  $\langle 111 \rangle$  oriented YAG crystal was used as seed.

In chapter 3 it will be shown that all attempts failed to grow bulk crystals from the melt. It must be assumed, that this circumstance is due to peculiarities of the binary phase diagram  $Al_2O_3 - Tb_2O_3$ .

### 2.2. Differential thermal analysis

The DTA measurements with 11 different  $Al_2O_3/Tb_2O_3$  mixtures were carried out using a NETZSCH STA 409C equipment with tungsten high temperature TG-DTA sample holder (W/W-Re thermocouples). As the growth of TAG single crystals was the main intention of this study, only the relevant part of the binary system  $Tb_2O_3 - Al_2O_3$  was investigated by DTA. The composition range under investigation ( $22 \dots 59 \text{ mol\% } Tb_2O_3$ ) included as well the garnet phase TAG ( $Tb_3Al_5O_{12} - x_{Tb_2O_3} = 0.375$ ) as the perovskite phase TAP ( $TbAlO_3 - x_{Tb_2O_3} = 0.500$ ).

To get well homogenized DTA samples it was necessary to melt the material in a first heating cycle. The measurements were performed with sample masses of typically  $50 \text{ mg}$  under flowing argon and with heating/cooling rates of  $10 \text{ K/min}$ . The onsets of the melting and crystallization peaks were observed to coincide within a tolerance of typically  $10 \text{ K}$ .

## 3. Results and discussion

The crystal growth experiments did not result in TAG single crystals of satisfying size and quality. Typically only a few cubic millimeters of transparent and colorless material was grown directly on the seed and could be identified as TAG by X-ray powder diffraction

analysis. Most of the crystallized material was opaque of brownish color with lots of small spires on the surface. X-ray analysis confirmed that this part was a two-phase solid composed of TAG and TAP.

According to these results one could assume that the congruent melting point of TAG simply does not coincide with the integer stoichiometric composition but should be shifted towards lower terbium concentrations. Indeed, this assumption could explain the two phase crystallization mentioned above. After the start with a stoichiometric TAG melt ( $x = 0.375$ ) lying between the two adjacent (congruently melting) phases the melt composition must follow the liquidus line until the binary eutectic is reached.

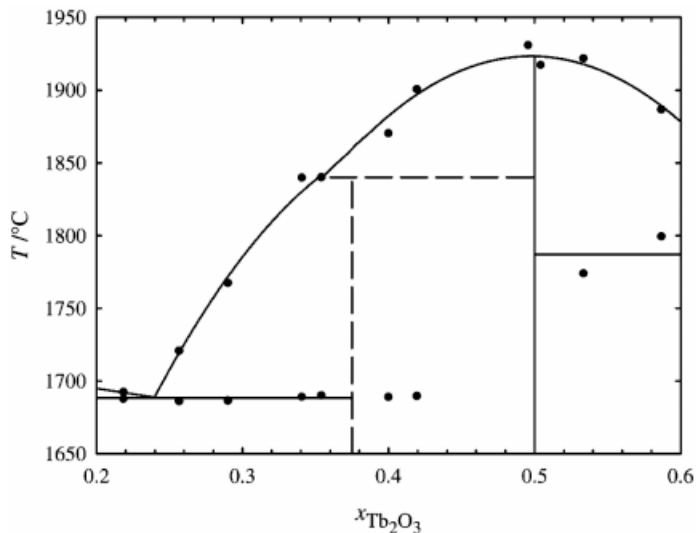


Fig. 1: DTA results within the  $\text{Al}_2\text{O}_3$  -  $\text{Tb}_2\text{O}_3$  system and constructed binary phase diagram. The dashed and full vertical lines indicate the compositions of TAG or TAP, respectively.

The purpose of the DTA measurements within the system  $\text{Al}_2\text{O}_3$  -  $\text{Tb}_2\text{O}_3$  that were reported in the previous chapter 2.2 was to find the expected congruently melting composition of TAG. The result was surprising since contrary to what had been reported (and believed) before. The expected liquidus maximum of TAG could not be found and hence, one has to take note of the fact that in the considered system the garnet phase is not a congruently melting one! Both heating and cooling curves could be used to construct the relevant part of the binary phase diagram (Fig. 1). The DTA results can be summarized as follows:

- For all 7 compositions with  $0.22 < x < 0.42$  only one eutectic temperature  $T_{\text{eut}}^{\text{left}} = (1688 \pm 2)^\circ\text{C}$  was found. This is surprising, as on the left or right side of the composition TAG ( $\text{Tb}_3\text{Al}_5\text{O}_{12}$ ,  $x = 0.375$ ) different eutectic temperatures for the eutectics  $\text{Al}_2\text{O}_3/\text{TAG}$  or  $\text{TAG}/\text{TAP}$  should be expected, if TAG was indeed a congruently melting compound. Only 2 compositions on the  $\text{Tb}_2\text{O}_3$  rich side of TAP ( $x = 0.53$  and  $x = 0.59$ ) were investigated. Here an eutectic temperature  $T_{\text{eut}}^{\text{right}} = (1787 \pm 15)^\circ\text{C}$  could be found. The large experimental error is probably due to the small peak size, especially for  $x = 0.53$ .

- The liquidus shows only one maximum close to the composition TAP ( $x = 0.50$ ,  $T_{\text{liqu}} = 1931^\circ\text{C}$ ). All liquidus temperatures for  $0.4 < x < 0.59$  can be fitted by a parabola with apex at  $x = 0.498$  and  $T_{\text{liqu}}^{\text{max}} = 1923.3^\circ\text{C}$ . The parabolic fit becomes much worse, if the liquidus temperatures for  $0.257 < x < 0.354$  are included, as the slope  $\partial T_{\text{liqu}}/\partial x$  is flatter in this composition range left from TAG.

-According to the lever rule it should be expected, that the peak areas of both eutectic and liquidus peak,  $A_{\text{eut}}$  and  $A_{\text{liqu}}$ , change linearly with  $x$ . An at least satisfying linear dependency could be found on both sides of TAP for  $A_{\text{eut}}$  (dashed lines in Fig. 2). The observation, that from both sides  $A_{\text{eut}} = 0$  is not reached at  $x = 0.50$  seems to indicate, that the compound TAP has a finite homogeneity range; but this hypothesis should be confirmed by additional investigations.

The separate linear fits of  $A_{\text{liqu}}$  at both sides of TAP are intersecting at  $x = 0.498$ . This is exactly the same composition as obtained for  $T_{\text{liqu}}^{\text{max}}$ , thus indicating, that this peak is indeed due to the melting/crystallization of TAP. From Fig. 2 it becomes obvious, however, that the slope  $\partial A_{\text{liqu}}/\partial x$  changes from  $61 \mu\text{V s} / \text{mg}$  ( $x > x_{\text{TAP}}$ ) to  $15 \mu\text{V s} / \text{mg}$  ( $x < x_{\text{TAP}}$ ).

From the DTA measurements a peritectic decomposition temperature  $T_{\text{per}} = 1840^\circ\text{C}$  of TAG can be assumed.

One could propose, that the observation of the eutectic peak at  $T_{\text{eut}}^{\text{left}} = 1688^\circ\text{C}$  for 2 compositions with  $x > 0.375$  (cf. Fig. 1) indicates, that the chemical composition of the incongruently melting TAG is shifted to  $\text{Tb}_{3+z}\text{Al}_{5-z}\text{O}_{12}$  ( $z > 0$ ). However, the observation of this peak for the sample with  $x = 0.42$  would result in the unexpected high value  $z = 0.36$ . DIGIUSEPPE et al. (1980) reported for the gadolinium gallium garnet the congruently melting composition  $\text{Gd}_{3.05}\text{Ga}_{4.95}\text{O}_{12}$ . The corresponding value  $z = 0.05$  can be regarded typical for many garnets.

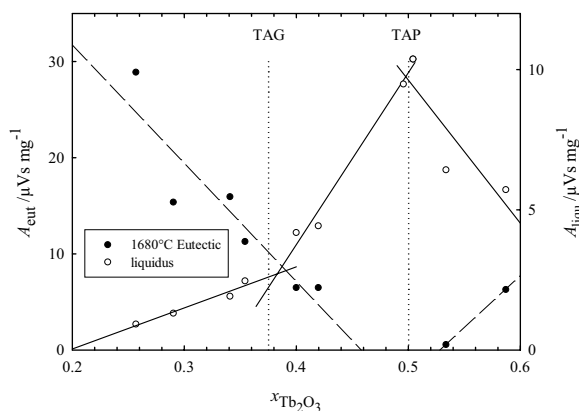


Fig. 2: Area of the liquidus peak size (1692...1931°C - full line) and of the eutectic peak size (1688°C left from TAP;  $\approx 1790^\circ\text{C}$  right from TAP - dashed line) vs.  $x_{\text{Tb}_2\text{O}_3}$ .

Accordingly, a better explanation for the  $1688^\circ\text{C}$  peak at  $x > 0.375$  seems the assumption, that the samples did not obtain the state of thermodynamic equilibrium during the DTA runs: If a melt with e.g.  $x = 0.4$  is cooled, crystallization of TAP takes place from  $T_{\text{liqu}} = 1880^\circ\text{C}$  down to  $T_{\text{per}} = 1840^\circ\text{C}$ . At this temperature TAP, TAG and a melt with  $x \approx 0.354$  are in equilibrium and the peritectic reaction  $\text{TAP} + \text{melt} \rightarrow \text{TAG}$  should consume melt. It must be expected, that a total equilibration can not be obtained during the DTA runs due to the high cooling rate of  $10 \text{ K/min}$ , as this reaction between a solid and a melt is diffusion controlled. Hence, parts of the melt remain and lead to the  $1688^\circ\text{C}$  peak due to eutectic crystallization.

#### 4. Conclusions

The DTA measurements within the binary system  $\text{Al}_2\text{O}_3 - \text{Tb}_2\text{O}_3$  showed, that the

incongruent melting behaviour of TAG is responsible for the unsuccessful attempts to grow single crystals of this substance with considerable size. The small amounts of only a few cubic millimeter crystallized from an undercooled melt. Such crystallization seems possible, as at the composition of TAG ( $x_{\text{Tb}_2\text{O}_3} = 0.375$ ) the liquidus temperature is only  $\approx 15$  K higher than  $T_{\text{per}}$ .

The different thermodynamic stability and the resulting different melting/decomposition points of the garnet and perovskite phases in related binary systems seem to be crucial problems for the growth of the garnets: YAG crystallizes easily from  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$  melts, as the melting point of the garnet ( $T_{\text{m}}^{\text{YAG}} = 1970^\circ\text{C}$ ) is considerably higher than the melting point of the perovskite ( $T_{\text{m}}^{\text{YAP}} = 1875^\circ\text{C}$ , ABELL et al. 1974). The growth of GGG from  $\text{Ga}_2\text{O}_3/\text{Gd}_2\text{O}_3$  melts is more difficult, as the garnet ( $T_{\text{m}}^{\text{GGG}} = 1740^\circ\text{C}$ ) melts below the perovskite ( $T_{\text{m}}^{\text{GGP}} = 1807^\circ\text{C}$ ). Here an overheating of the melts leads very often to the metastable crystallization of GGP even below TGGG (DIGIUSEPPE et al. 1980). The case of the  $\text{Al}_2\text{O}_3/\text{Tb}_2\text{O}_3$  system presented in this work is even worse: The high thermal stability of the perovskite ( $T_{\text{m}}^{\text{TAP}} = 1930^\circ\text{C}$ ) is combined with peritectic decomposition of the garnet at  $T_{\text{per}}^{\text{TAG}} = 1840^\circ\text{C}$  and prevents congruent crystallization of the garnet.

#### *Acknowledgements*

The authors express their gratitude to M. Bernhagen for technical assistance.

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(received July 6, 1998; accepted July 17, 1998)

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