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RESOLUTION OF FACTORS RESPONSIBLE FOR DIFFICULTY IN GROWING SIN--ETC(U)
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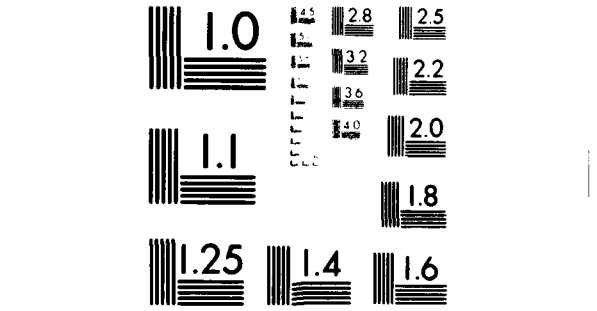
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Resolution of Factors Responsible for Difficulty in Growing Single Crystals of YAG

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INTRODUCTION:

In a ternary system like Al_2O_3-Y_2O_3-Nd_2O_3 it is naturally realistic to expect that numerous factors will contribute, each in its own way, to the complexity of growth problems of Nd:YAG single crystals which is a compound in the ternary system. However, extensive experimental study indicates that not many factors but rather a single factor has caused a derogative influence on the growth of Nd:YAG single crystals.

DEFINITION OF THE PROBLEM:

In 1980, Caslavsky and Viechnicki (1) reported that after melting of YAG, the structure of the melt undergoes a change, i.e., in spite of congruent melting of YAG there is no equilibrium between the solid and molten YAG. The non-equilibrium condition occurs on account of coordination change of 3/5 of the aluminum ions, which in the solid YAG structure are present in four-fold coordination, while in the melt they increase their coordination to six. On cooling such a melt, in which all YAG nuclei were destroyed, the coordination change is irreversible and the melt of YAG composition begins to solidify at 1855°C where yttrium aluminate (perovskite) commences to solidify as a metastable proeutectic phase. The solidification ends at 1700°C as a metastable eutectic mixture of 23.0 mol% Y_2O_3 and 77.0 mol% Al_2O_3. On the other hand, if a YAG nucleus, say a seed crystal, is present in the melt and latent heat of solidification is slowly withdrawn from the solid-liquid interface through the seed crystal, the YAG structure will perpetuate from the seed crystal on account of the melt converting into a YAG single crystal. It also was reported if the rate of solidification increases over a certain rate; precipitation of metastable proeutectic phase occurs and the amount formed is directly proportional to the rate of solidification. Further, it was suggested that presence of neodymia in the melt, as a dopant, somehow de-stabilizes four-fold coordination of the aluminum ions, therefore, the amount of second phase in the presence of neodymia increases with the rate of crystallization more rapidly than in the undoped melt.

To understand this phenomena, futher experimental evidence to explain the enhanced formation of scattering centers in doped YAG crystals was sought and is described in this paper.

EXPERIMENTAL METHODS:

a) Growth of the Single Crystals by the Vertical Solidification of the Melt (VSOM):

In this technique a cylindrical crucible of approximately 75 mm diameter and 125 mm height is used as a container. The seed crystal is placed in the middle of the bottom of the crucible which then is filled with the material to be melted. The crucible is positioned with its center on a water cooled heat sink, which in addition to serving as a support for the crucible, prevents the seed crystal from being melted and provides the means for controlled latent heat removal of solidification during the period of the crystal growth. Since the heat sink is now in the exact center of the cylindrical heating element, the crucible is heated evenly in the circumference, but there is an upward thermal gradient built into the element which is consequently reflected in the melt. Unlike most other crystal growth techniques there are no moving parts in the VSOM crystal growth technique. The driving force for crystallization in this technique is derived from the motion of the thermal field throughout the hot zone of the furnace. Elimination of moving parts combined with the upward thermal gradient in the melt gives to the VSOM technique a unique stabilization condition, i.e., there is practically no thermally induced flow inside the melt, and mechanically produced vibrations are absent.

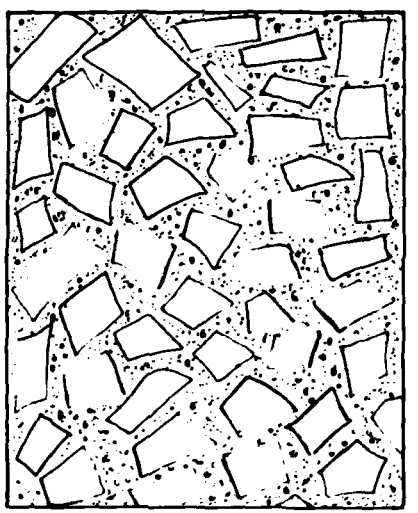
b) The Optical Differential Thermal Analyses (ODTA):

This technique was well described in (1) and since during the course of this investigation it was used only as a supporting method the reader is referred to the pertinent publication.

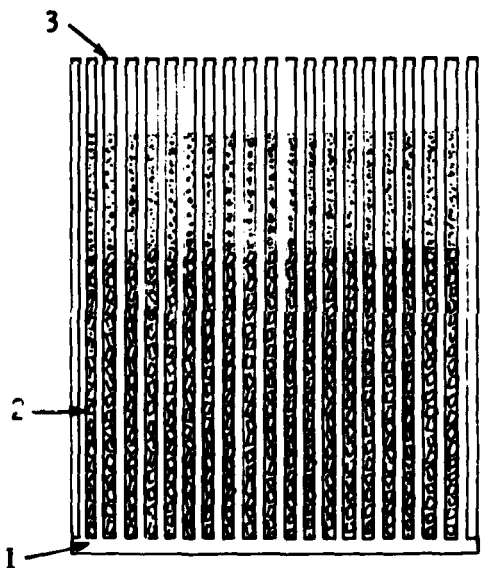
c) Experimental technique to reveal the influence of $NdAlO_3$ on the Solidification of Nd:YAG Melt:

From the figure 1a and 1b it is apparent that when the growth parameters are well controlled, the difference in the amount of scattering centers in single crystals of YAG and Nd:YAG grown by VSOM method are in both cases minimized or absent. Therefore, to study the factors responsible for the formation of second phase particles from single crystals is difficult. Owing to this fact it was decided to study the differences of solidification of unseeded doped and undoped melts of YAG composition.

Except for the absence of the seed crystal, the solidification process was exactly the same like it is used by growing single crystals by VSOM technique. The 75 x 125 mm molybdenium crucible was filled with material prepared by a process developed for the preparation of charges for growing YAG crystals as described in (2). The crucible was placed in VSOM crystal growth furnace and heated at a rate of 50°C/h



a. YAG



b. Nd : YAG

1. Single Crystal of $YAlO_3$
2. $YAlO_3$ + Al_2O_3 Crystals
3. $YAlO_3$ Dendrite

Figure 1. MELTS SOLIDIFIED WITHOUT THE SEED CRYSTAL.

until 1940°, the melting point of YAG, was reached as indicated by a thermo-arrest on the ODTA. At this point, the temperature increase was lowered to 5°C/h and after the thermo-arrest ended, about 90 minutes later, the temperature of the melt was increased to 2050°C. The melt was kept at this temperature for 18 hours to insure that no solid particles were present within the melt. Then the melt was cooled down at a rate 0.3°C/h until the entire content of the crucible was solidified as measured by the ODTA.

RESULTS:

a) Solidification of the undoped melt. During the temperature decrease the ODTA zero line remained stable until 1970°C, at which point a very sharp large exothermic maximum revealed spontaneous nucleation in the entire mass of the melt contained in the crucible. The solidification material removed from the crucible was in the form of large $YAlO_3$ crystals interspersed with much finer Al_2O_3 crystals. The overall appearance of the material was similar to a rapidly solidified mixture of high melting oxides (see fig. 1a).

b) Solidification of the doped melt. Material of composition $Y_{2.97}Nd_{0.03}Al_5O_{12}$ (corresponding to 1at% Nd:YAG single crystals) was melted and solidified as described for the undoped melt. However, significant differences were observed by ODTA solidification of the doped melt as compared to the undoped melt. At 1825°C an exothermic maximum was observed similar in character and magnitude to one which indicates freezing of the last liquid, during the regular crystal growth. The last liquid during crystal growth freezes at 1925°C since it is richer in yttria, due to the incongruent evaporation of alumina. The solidification of the unseeded melt follows the metastable crystallization path, hence, the exothermic maximum at 1825°C indicates freezing of a liquid richer in the Al_2O_3 than the YAG melt. With the further temperature decrease at 1700°C a second small exothermic maximum is observed due to the freezing of the metastable eutectic; this maximum is never obseved during the crystal growth process.

The appearance of a solid ingot obtained by solidification of an unseeded doped YAG composition melt is quite different to the undoped one. The entire bottom of 75 mm diameter solid ingot was transparent to the height of about 5 mm. The x-ray analysis revealed that it was a single crystal of $YAlO_3$ with the (110) crystal plane parallel with the bottom of the crucible. Since the $YAlO_3$ single crystal grew from the melt of different composition, the constitutional supercooling consequently instituted dendritic growth. The perovskite dendrites continued to grow until the composition of the metastable eutectic (23.0 mol% Y_2O_3 and 77.0 mol% Al_2O_3) was reached at 1700°C. At this point the metastable eutectic mixture solidified. In consequence of 22% of negative volume change, due to the liquid-solid transformation of the eutectic liquid, the level rapidly descended which revealed a "forest" of perovskite dendrites all parallel to each other with the dendritic axis

in the [001] direction. This indicated that all of the densities were seededby the single crystal found on the bottom of the ingot. The metastable eutectic mixture was found in the spaces among the dendrites (see fig. 1b).

These experiments were repeated three times with the same results; the reproducibility of the experiments and their interpretation led to a mechanism of scattering centers formation in Nd:YAG single crystals.

EXPLANATION OF FORMATION OF SCATTERING CENTERS:

In the solid state the YAG structure, from the oxides components Al_2O_3 and Y_2O_3, forms quite easily at temperatures as low as 700°C. The kinetics of formation of the YAG structure is directly proportional to the temperature, and at the temperatures between 1700°C and 1800°C the stoichiometric mixture of the oxides reacts completely in two hours to the YAG structure. By contrast, when the oxide mixture is melted and then solidified no YAG is formed. This phenomenon is seen whether or not Nd_2O_3 is present. Nevertheless, if the melt is seeded and solidification performed under the controlled conditions, a single crystal of YAG is obtained. However, the experimentally determined growth rates needed to obtain scattering center free doped crystals, are at least three times lower than the growth rates for undoped crystals.

In reference (1) it was established that it was impossible to form YAG from an unseeded melt due to the fact that the aluminium ions are not willing to lower their coordination without external influence and will much rather form incongruently melting perovskite even from non-stoichiometric melt. The only mechanism which forces aluminum ions to the four-fold coordination is the dangling bonds protruding from the free surface of the seed crystal. Such dangling bonds in the most favored case can extend from the solid structure of the YAG only 12A. Therefore, the coordination change can take place only in close proximity to the free surface of the seed crystal. If the solidification rate exceeds the rate with which the coordination change can take place, the perovskite phase will crystallize simultaneouslywith the YAG. From all experimental work it is evident that the rate of change of the aluminum ions is the factor controlling the rate of the YAG structure formation. If this would be the only factor responsible for formation of the scattering centers in YAG, there should be no reason for Nd:YAG to grow scattering center free only at much lower rates than undoped YAG. From the experiments described in the previous paragraph, the following conclusion for enhanced formation of scattering centers in Nd:YAG is interpreted as follows:

$YAlO_3$-perovskite is the highest melting compound in the ternary system melting congruently without decomposition at 2110°C. It is highly probable in this ternary system that under sufficient supercooling $NdAlO_3$ will first form stable or supercritical nuclei, and this fact accounts for the difference in the crystallization behavior of unseeded

doped and undoped melts of YAG composition.

In the VSOM crystal growth arrangement the melt around the bottom part of the crucible nearest the heat sink is estimated to be cooler by 100° to 150°C than the melt farther away from the heat sink. During slow cooling of a melt of Nd:YAG composition there is enough time, in the locally supercooled area, for $NdAlO_3$ to nucleate and eventually form supercritical nuclei. With progressing cooling such nuclei will grow. However, in this melt there is not enough neodymium ions to sustain the growth of $NdAlO_3$ but since $NdAlO_3$ is istostructural with $YalO_3$ a heteroepitaxial boundary will be formed and $YAlO_3$ will continue to grow off as a single crystal until the constitutional supercooling will force dendritic growth.

In the VSOM technique it is impossible experimentally to measure the thermal gradient near the solid-liquid interface, but from experience gained working with this technique, it has been found that to control growth, the thermal gradient near the interface has to be very steep. In such steep gradient, however, nucleation of the $NdAlO_3$ still can occur according to a reaction

$$L_1 = L_2 + S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where L_1 is a liquid free of any solid particles while L_2 is liquid whose composition has changed due to the nucleation of $S = NdAlO_3$. Therefore, if the rate of the growth of Nd:YAG exceeds the transportrate of solid particles so that they cannot be carried away from the solid-liquid interface into the melt region where temperature is high enough to reverse reaction (1) to:

$$L_2 + S = L_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

then the $NdAlO_3$ particles will deposit by gravity on the solid part of the solid-liquid interface and will be embedded in it and will form scattering centers in the resulting single crystal.

CONCLUSIONS:

The enhanced formation of the scattering centers in Nd:YAG is attributed to the fact that the melting point of YAG is 170°C lower than the melting point of $NdAlO_3$. Further, since aluminium ions in the neodyium aluminate are present in six-fold coordination $NdAlO_3$ can easily nucleate near the solid-liquide interface where lower temperature favors reaction (1). Provided that the growth rate of Nd:YAG exceeds the kinetics of reaction (2), the second phase particles will precipitate in the growing Nd:YAG crystal and appear as scattering centers.

From the experimental evidence it can be concluded that in the composition section on and near the tie line connecting $NdAlO_3$ and $Y_3Al_5O_{12}$ in the Nd_2O_3-Y_2O_3-Al_2O_3 ternary system, $NdAlO_3$ shows an inherent property to nucleate first. To eliminate the nucleation of $NdAlO_3$ during the crystal growth of Nd:YAG the thermal gradient near the solid-liquid interface has to be very steep while the melt temperature has to be kept above the temperature which prevents reaction (1). Simultaneously

the speed of the interface advancement has to be set below the thermally induced flow of the melt from the solid-liquid interface. Therefore, it is apparent that with the correct growth conditions scattering center free Nd:YAG single crystals can be grown by VSOM.

REFERENCES:

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2. Viechnicki, D.J., Caslavsky, J.L., American Ceramic Society Bulletin 58 (1979) 700.

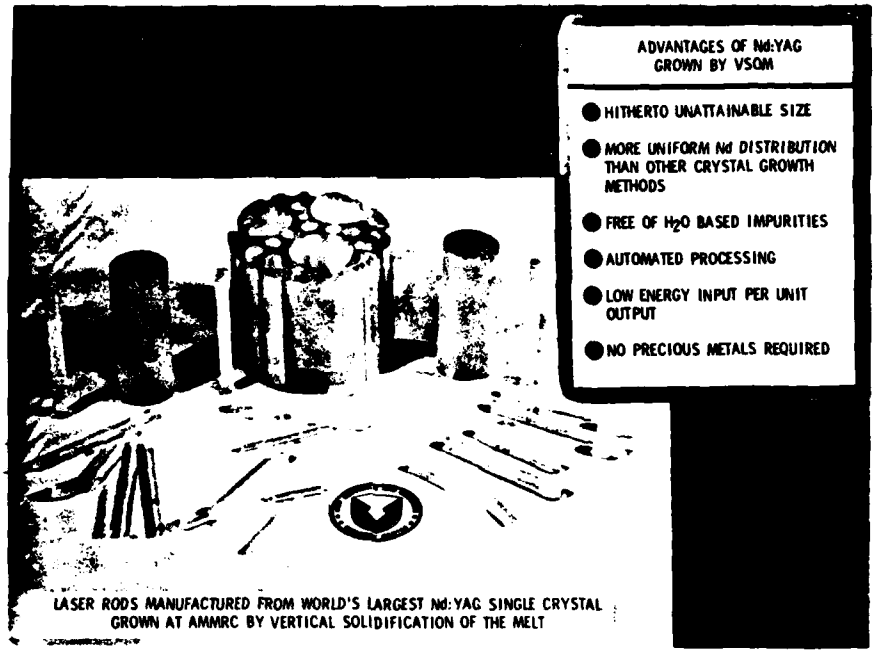

Figure 2

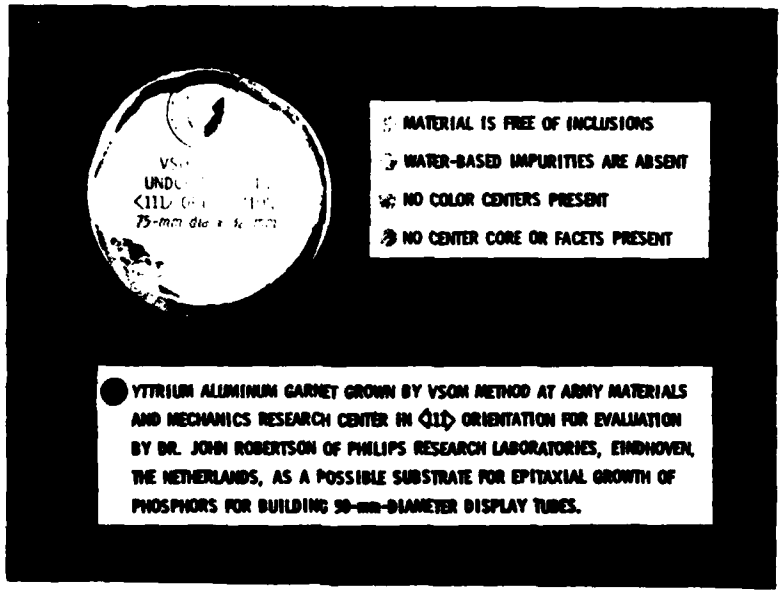

Figure 3


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