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BRIDGMAN GROWTH AND PROPERTIES OF $\text{LuAlO}_3\text{-Nd}^{3+}$ LASER CRYSTALS

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Abstract - The solidification behavior of LuAlO_3 melts in Bridgman geometry is presented. The contribution of different growth parameters to crystallization of single phase LuAlO_3 are studied. Growth scheme for $\text{LuAlO}_3\text{-Nd}^{3+}$ crystals possessing improved laser properties is described.

1-Introduction.

LuAlO_3 (space group $D_{2h}^{16}\text{-Pbnm}$) is the end member of the rhombic rare-earth group (LnAlO_3 , where $\text{Ln} = \text{Y}$ or Ln ion between Gd and Lu). Five compounds from this group have been so far reported as laser host crystals, i.e. YAlO_3 , GdAlO_3 , ErAlO_3 , $(\text{Er,Lu})\text{AlO}_3$ and LuAlO_3 /1/, with lasing ions Pr^{3+} , Nd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Tm^{3+} /1,2/. Growth of $\text{LuAlO}_3\text{-Nd}^{3+}$ single crystals was first reported in /3/. A rod 18mm long and 5 mm in diameter cut from Czochralski grown material lased at $1.0832\mu\text{m}$ ($E_{\text{thr.}} = 8\text{J}$) and $1.3437\mu\text{m}$ ($E_{\text{thr.}} = 15\text{J}$) at 300K /4/ thus offering generation wavelength shift to long-wave part of the spectrum as compared with $\text{YAlO}_3\text{-Nd}^{3+}$ /1/. Owing to this potential usefulness of $\text{LuAlO}_3\text{-Nd}^{3+}$ can be extended if large size high-quality material is available. In view of results of M.Leduc, L.Shearer on optical polarization of helium atoms, $\text{LuAlO}_3\text{-Nd}^{3+}$ based lasers have prospects of application in this field. LuAlO_3 was prepared also by Bridgman technique /5/. More recently Nd^{3+} -doped optical quality material was obtained by this technique which reveal substantially better laser per-

formance /6/ than that reported by Czochralski grown material. This paper summarizes various aspects of Bridgman single crystal growth of $\text{LuAlO}_3\text{-Nd}^{3+}$ for laser applications.

2.-Experimental Details.

Vertical Bridgman technique has been used in the present work to study spontaneous solidification behaviour of LuAlO_3 melts and growth conditions of laser quality $\text{LuAlO}_3\text{-Nd}^{3+}$ crystals. The main experimental conditions were the same as described earlier in /5/. Additional variable parameters included cyclic melt overheating then solidification on cooling processes to study statistical characteristics of freezing end extra crystal annealing at the last stages of crystallization to study LuAlO_3 stability to high temperatures on cooling from the melting point.

3.-Results and Discussion.

The previous results of investigations of LuAlO_3 /3, 5, 7 - 9/ show that the main unclearness concerns nucleation and growth mechanism of this phase (it is formed assumingly when crystallization follows some metastable path on cooling of the melts in which the garnet and lutetium oxide phases are the most stable, while LuAlO_3 has even no stability field in subsolidus region of the phase diagram) and high temperature stability of LuAlO_3 upon cooling from the melting point (on heating from the room temperature crystalline LuAlO_3 readily decomposes at $\geq 1300^\circ\text{C}$, separating garnet and lutetium oxide phases).

Our experiments with melts 1cm^3 in volume have shown that by analogy with some metals the ability of melts to become supercooled before solidification occurs, depends on the overheating degree and its length. The supercooling degree increases with increase of the overheating temperature. The overheating length acts in the same direction as the overheating temperature. Note that LuAlO_3 phase originate only when solidification occurs at high ($\geq 100\text{ K}$) melt supercoolings with

respect to the melting point /9/. For comparison, $YAlO_3$ structure is readily formed on cooling of 1:1 melts irrespective to the freezing temperature /5/. The observed dependence together with results obtained for the melts with garnet composition /5/ show that probably no change in coordination number of cations occurs in the melts at high overheating temperatures. More evidently nucleus-size particles of stable phases which are present in initial melts disappear completely during overheating process giving way to simplicity principle /10/ to determine solid phase structure. In Bridgman growth the melt is cooled from the bottom so it is here where $LuAlO_3$ may originate first acting further as a seed crystal. Experiments have shown that after $LuAlO_3$ phase is formed the melt undercooling is being removed due to rapid solidification of the part of the initial melt and replacement of the interface up to the level corresponding to the equilibrium melting point of $LuAlO_3$. This means that solid $LuAlO_3$ which is nucleated at temperatures some ≥ 100 K below the melting point does not undergo any phase decomposition on heating from nucleation temperature to that close to the melting point. Growth runs which included additional crystal annealing at the cooling stage of the grown material have shown that $LuAlO_3$ conserves transparency with no signs of decomposition up to temperatures some 200-300 K below the melting point. At lower temperatures of annealing it undergoes complete phase decomposition as it is the case when $LuAlO_3$ is heated from the room temperature. However the observed behaviour of solid $LuAlO_3$ below the melting point cannot be considered as demonstration of thermodynamic stability of this phase in the mentioned temperature region. More evidently, the phase decomposition rate has a complex dependence on the temperature. It may be said that the rate of $Lu_3Al_5O_{12}$ nucleus formation in solid $LuAlO_3$ has a maximum at some temperature between 1700 and 1300C while at higher and lower temperatures it is going down. The amount of new phase is dependent on the rate of nucleus formation, their growth velocity and time interval, so at low temperatures the growth velocity, which is diffusion limited, is decreased due to decrease of atoms mobility. The observed stability of solid $LuAlO_3$ at higher temperatures needs additional investigations.

The properties of $LuAlO_3$, revealed in this investigation, show that crystal growth can be carried out by employing a scheme presented in Fig.1. It is based on the observed phenomena of conservation of the nucleated crystallization centers of $LuAlO_3$ at temperature increase, i.e. formation of these centers in supercooled melts and their conser-

vation during temperature increase close to the melting point.

Fig.1.- Growth scheme of LuAlO_3 single crystals. T_m -melting point, ΔT^+ -melt overheating, ΔT^- -melt supercooling. Arrows indicate the direction of temperature change at each stage of crystallization.

On this base conditions are found which offer crystallization to occur near the equilibrium, which in practice permit to obtain large size optical quality crystals of rhombic LuAlO_3 , as well as other metastable aluminates of the lanthanide family.

The next point shows that Bridgman technique is more preferable than Czochralski in view of application to LuAlO_3 growth. In Bridgman geometry the melt supercooling necessary to nucleate the metastable phase is self removed, while in Czochralski arrangement an empirical selection of thermal conditions is needed.

Spectral and generation experiments with Bridgman grown $\text{LuAlO}_3\text{-Nd}^{3+}$ /6/ have shown that these crystals have substantially better laser performance than those reported earlier for Czochralski grown material. In the pulse mode a rod 5mm in diameter and 40mm long lased at the wavelengths of the main and additional channels of Nd^{3+} ions at 1.0677 ($E_{thr.}=0.8$ J, 77 K), 1.0675(2 J, 300 K), 1.3429 (1.5 J, 100 K) and 1.3437 μ (3 J, 300 K).

4.-Conclusions.

The melt solidification properties of metastable LuAlO_3 are studied. Basing on obtained experimental results a growth scheme of $\text{LuAlO}_3\text{-Nd}^{3+}$ crystals using Bridgman technique is proposed, which permits crystallization to occur near to the equilibrium and to obtain large size material of improved optical and laser quality.

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