Single crystal growth of $\text{LuAlO}_3\text{-Ti}^{3+}$ and $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ by the vertical Bridgman technique and their optical properties

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Abstract - A selective self-seeding process has been used to grow optical quality $\text{LuAlO}_3\text{-Ti}^{3+}$ single crystals in the vertical Bridgman configuration. Thermal conditions of melt preparation and crystal cooling are discussed in respect to their affecting the solid phase structure. Conventional Bridgman scheme has been used to grow $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$.

Employment of different techniques in oxide crystal growth provides comparison important to understanding of various mechanisms governing solid phase formation and material properties. The vertical Bridgman technique is among those widely used in research of oxide-based laser crystals for many years now [1, 2]. In the present work it has been applied to titanium doped compounds which after the demonstration of $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ as a useful tunable and high gain material [3] have become a subject of extensive investigations. The interest around rhombic aluminates (LnAlO_3 , $\text{Ln}=\text{Y}$, Gd-Lu ; space group $\text{D}_{2h}^{16}\text{-Pbnm}$) with Ti^{3+} ions is concentrated upon material science and spectroscopy research because of very low estimated pumping efficiency ($\text{YAlO}_3\text{-Ti}^{3+}$ [4]). For that reason it may add information investigation of other aluminates belonging to this group. The Bridgman-grown $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ crystals may present applicational interest in se-

lectively pumped lasers utilizing small size rods with a given Ti^{3+} doping.

A selective self-seeding process, developed earlier for $\text{LuAlO}_3\text{-Nd}^{3+}$ /5/, has been used to grow optical quality $\text{LuAlO}_3\text{-Ti}^{3+}$ crystals in the vertical Bridgman configuration. In brief, this method assumes that the melt overheating degree (ΔT^+) and the time of heating in the molten state, if selected correctly, impart the change in the melt property resulting in perovskite phase nucleation, while garnet phase is nucleated under usual conditions of melt preparation. Perovskite phase growth under conditions near to the equilibrium is provided due to observed /5/ stability of this phase in the temperature region between spontaneous solidification temperature (T_{sp}) and that of the melting point (T_{m}).

Pre-reacted material was used which was prepared by melting the component oxides and Ti_2O_3 (0,5 at.%) under hydrogen atmosphere to insure the threevalent state of titanium. Under correctly selected growth conditions transparent single crystalline material is readily obtained with colour varying from light yellow to brown along the crystal length. As it may be suggested that the possible Ti^{4+} amount does not change within each separate crystal, the latter evidences of relatively low distribution coefficient of Ti^{3+} in LuAlO_3 . The absorption coefficient measured at the blue-green absorption band of Ti^{3+} increases approximately by a factor of 2.5 over the crystal length of 50 mm. Inclusion free crystals with low intensity of growth striations enriched with Ti^{3+} have been obtained at crucible lowering rates less than 2 mm/h.

The knowledge of the two following factors is important to provide correct growth conditions. They concern the extent of scattering in T_{sp} values and the exact figure of T_{m} . The former describes the solidification behaviour of overheated melts upon their cooling and must be recognized as contributing to scattering in originating crystal height. The latter is important to determine the position of the solid-liquid interface necessary for accurate selection of temperature gradients below the interface.

Fig.1 shows the statistical solidification behaviour of LuAlO_3

Fig.1 Statistical solidification pattern of overheated LuAlO_3 melt.

melts (overheating temperature $\Delta T^+ = 100\text{K}$, the time of heating in the molten state $\tau = 30$ min; 110 consecutive runs) where N is the number of tests in which the melts have solidified at certain values of ΔT^- ; ΔT^- - is the melt undercooling. As equivalence exists between the ΔT^+ and τ values in their affecting the melt property /6/, the lowest possible values of ΔT^+ are desirable to diminish losses of titanium oxide from the melts and melt interaction with the crucible material. The pattern given in the Fig.1 does not change significantly for different combinations between ΔT^+ and τ values if conditions /6/ required for melt property change are fulfilled.

The melting temperature, by definition, is a temperature of equilibrium phase transition of the solid to the liquid state. Since the rhombic aluminates of

end member rare-earth ~~elements~~ undergo phase decomposition on heating from the room temperature that occurs far below the melting point, the measured values of T_m will correspond to multiphase mixtures ($\text{R}_3\text{Al}_5\text{O}_{12}/\text{R}_2\text{O}_3$ or $\text{R}_3\text{Al}_5\text{O}_{12}/\text{R}_4\text{Al}_2\text{O}_9$) /7/ but not to the perovskite phase. The scheme which is normally used in the selective self-seeding process, described above, suggests that in order to escape phase decomposition the T_m values are measured directly after solidification at T_{sp} . The measured value of T_m (LuAlO_3) using this approach is $1900 \pm 15^\circ\text{C}$ /8/.

The spectroscopic and optical properties of $\text{LuAlO}_3\text{-Ti}^{3+}$ (which are described in some details in /6/) are almost the same as for $\text{YAlO}_3\text{-Ti}^{3+}$ /4/ and $\text{GdAlO}_3\text{-Ti}^{3+}$ /9/. Two broad bands in the blue-green region are present in the absorption spectra which are associated with Ti^{3+} ions. Due to stronger crystal field the position of fluorescence band in $\text{LuAlO}_3\text{-Ti}^{3+}$ is shifted to shorter wavelengths as compared with $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ /9/. In comparison with $\text{YAlO}_3\text{-Ti}^{3+}$ it is shifted by $5\text{-}10\text{ cm}^{-1}$ to longer wavelengths. A

broad infrared absorption band is located around 900 nm which by analogy to those present in $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ and $\text{YAlO}_3\text{-Ti}^{3+}$ may be referred to $\text{Ti}^{3+}/\text{Ti}^{4+}$ pair centers /10/. No appreciable change in absorption band intensity has been so far found in crystals treated by UV, X-ray and γ -ray (^{60}Co) radiations demonstrating a high stability of the material with respect to impurity ions valent states present and thus complicating the colour center identification. Annealing experiments have been performed at temperatures below 1000C under enclosed hydrogen atmosphere and in the air. These results, if informative, will be presented later. Single crystals of $\text{Al}_2\text{O}_3\text{-Ti}^{3+}$ (0,5 at.% in the melts) have been grown employing conventional Bridgman scheme at crucible lowering rate of 1,5 mm/h, seed orientation $\perp \vec{c}$. Pink coloured crystals have been obtained under argon-hydrogen atmosphere with 14 mm in diameter and up to 80 mm long free of solid and gas-bubble inclusions in the most of their volume. The value of 0,1 wt.% for Ti^{3+} concentration in the crystal middle sections was estimated using the plot of absorption coefficient at 490 nm in the π polarization as a function of Ti^{3+} given in /11/. The use of molybdenum and tungsten as construction metals for heaters and crucibles plus presence of hydrogen results in very low O_2 partial pressure so the fraction of Ti^{4+} ions may be only very small. Preliminary results show that the crystal properties are close to those reported for the vertical-gradient-freeze technique /11/.

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