Growth and Investigation of α-LiIO₃ Single Crystals in the Presence of Additive Amounts of Permanganate-Ion

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Abstract: Single crystals of α - LiIO₃ are grown by the method of isothermal evaporation of the solvent in the presence of additive amounts of permanganate-ion. The chemical interaction between the permanganate-ion and the mother solution is found, as a result of it, the crystal contains manganese in the reduced form while the growth rate increases. The grown single crystals are of green emerald color, the crystal non-linear properties are preserved.

Keywards: Crystal growth, Lithium iodate, permanganate-ion dopands.

Dopants or the chemistry of the surrounding environment is a decisive factor both in creating the appearance of the crystal and in determining its homogeneity. The dopants effect is complex in nature, and currently there is no unanimously accepted viewpoint regarding the mechanism of this phenomenon. Dopants affect the growth and morphology of crystals in a very diverse way. Thermodynamically, the impurity shifts the equilibrium point between the crystal and the medium in accordance with the state diagram. Therefore, the preset saturation for crystal growth in the presence of a dopant should be determined taking into account the corresponding state diagram.

Kinetically, the dopant affects the transport of the matter in the medium, the processes occurring on the surface of the growing crystal and the structure of the solution. However, at uncontrolled dopant concentrations, its effect on the solution structure is very small. The dopant has the most powerful effect on surface processes [1], which is associated with the adsorption of its particles (ions, atoms, molecules) in various positions of the surface — in kinks, on atomically smooth parts of the face, etc.

The main scientific value of studying the kinetics of growth, morphology, and physical properties of crystals grown in the presence of controlled amounts of dopants is to establish the possible influence of the latter when they are uncontrolled in the mother liquor. Such dopants during the growth of a hexagonal-modified lithium iodate single crystal can be iron ions of the iron group (Fe, Mn, Cr, Ni) in different oxidation states. There are very few works [2,3] related to the growth of $\alpha - LiIO_3(Mn)$ single crystals in the presence of iron group metal dopants. In these studies, when examining $\alpha - LiIO_3(Mn)$ crystals from the optical absorption spectra, a single wide band was found with a maximum of 16800 cm⁻¹ in the entire frequency range studied. This is characteristic of both Mn^{3+} and Mn^{4+} in an octahedral environment, however, red luminescence is characteristic of Mn^{4+} , while Mn^{3+} ions in the visible spectral region do not luminesce. In the study of $\alpha - LiIO_3(Mn)$ crystals by the EPR method, Mn^{2+} ions were also found in the crystal, which could not be detected from the optical absorption spectra, apparently because of their low concentration in comparison with Mn^{3+} ions.

Nothing is known in literature regarding the behavior of other forms of oxidized manganese in the $LiIO_3 - HIO_3 - H_2O$ system. Meanwhile, this system is saturated with respect to IO_3 ions, as a result of which the redox potential of the IO_6^{-5}/IO_3^{-1} pair is greatly reduced and, upon introduction of the permanganate-ion into the system, oxidation of HIO_3 to H_5IO_6 and reduction of the permanganate-ion can be expected. Obviously, the latter process can have many intermediate stages, up to the formation of Mn^{2+} . The growing crystal will react and, possibly, will be able to capture that intermediate reduction product, which in its crystalline parameters is close to the structure of lithium iodate hexagonal modification and its distribution coefficient between the growing crystal and the medium is greater than unity.

In order to verify the assumptions made, as well as to influence the growth kinetics of the $\alpha - LiIO_3$ single crystal, we studied the effect of permanganate—ion on the growth rate and on the properties of the grown crystals.

We made an attempt to grow single crystals $\alpha - LiIO_3$ in the presence of potassium permanganate. Single crystals were grown on seeds under isothermal conditions at $40^{\circ}C$ in the "Iodate" crystallization apparatus using the new lid we developed [4,5]. Potassium permanganate was inputted into a saturated solution of lithium iodate in the form of a 0.1 normal aqueous solution. The *pH* of the solution was set with a saturated *HIO*₃ solution of 1.8 ± 0.01 . The dopant concentration varied in the solution within $4^{-10} \times 10^{-5} mol/liter$. After the addition of potassium permanganate, violet–pink solutions were obtained, from which we managed to grow three generations of well–faceted hexagonal single crystals of lithium iodate with an emerald green color, measuring 30mm along the X and Y axes and 70mm along the Z axis.

The color intensity of crystals of different generations was very different. The crystals of the third generation were almost colorless. A decrease in the color intensity of crystals along the Z – axis along the growth of crystals of the first and second generations was also observed. In another series of experiments, when third–generation crystals reached a size of 20mm along the Z – axis, potassium permanganate was added to the mother liquor, which led to a sharp increase in the green color of the crystals. As a result, the grown crystals of the third generation had a clear boundary separating the light green and dark green parts of the crystal, which indicates the dopant addition.

The difference between the color of the solution and the color of the crystal indicates that during the growth process, chemical reactions occur in the solution that change the charge or coordination of the dopant ion or both characteristics simultaneously. To identify the chemical interaction of the dopant with the mother liquor, the transmission spectra of the mother liquor were measured before and after the addition of potassium permanganate dopants in the wavelength range from 300 to 800*nm*. The transmission spectra are shown in Figure 1. As can be seen from the figure, the

characteristic absorption for permanganate disappears in time, which may indicate a chemical interaction of the dopant with the mother liquor. It could be assumed that permanganate – ion interacts with ions that contain iodine with a lower oxidation state and are present in solution as dopants. However, with the further addition of permanganate to the solution (third generation), the intensity of the green color of the crystals should not increase due to the dopants consumption of. This result indicates a direct interaction of lithium iodate with potassium permanganate. The nature of the ions entering the growing crystal, so far, can only be apprecieted by the green – emerald color characteristic of the manganate–ion.



Fig. 1. Transmission spectra: 1 – 0.002% potassium permanganate solution, 2 – saturated lithium iodate solution, 3 – saturated lithium iodate solution immediately after addition of permanganate, 4 – the same after 2 hours, 5 – the same, after 4 – hours.

During the growth of the $\alpha - LiIO_3$ single crystal with a dopant of potassium permanganate, the linear growth rate was measured. At the same time, the linear growth rate of pure lithium iodate was also measured under completely identical growth conditions. The results are shown in Figure 2. Curve 1 of Figure 2 corresponds to the linear growth rate of a lithium iodate single crystal from a pure solution, and curve 2 represents the same in the presence of a dopant. As can be seen from the figure, permanganate – ion and the chemical reactions associated with its presence accelerate the process. The grown doped single crystals were subjected to differential thermal analysis. The results of the differential thermal analysis of the first–generation $\alpha - LiIO_3$ doped single crystal are shown in Fig. 3. There is no displacement in $\alpha - \beta$ phase transition on the derivatogram, which indicates that the matrix of α – lithium iodate is preserved upon the dopant entering the crystal, and the

observed uneven coloring of the crystals along the Z axis is due to the fact that the distribution coefficient of the dopant is greater than unity.



Fig. 2. The linear growth rate of a lithium iodate single crystal of hexagonal modification: 1 - pure lithium iodate, 2 - doped lithium iodate.



Fig. 3. Derivatogram of doped lithium iodate.

For more convincing evidence of matrix retention and isomorphic entry of the dopant into the $\alpha - LiIO_3$ single crystal structure, nonlinear properties of first-generation crystals were studied. For these studies, a 30° section element with dimensions of $15 \times 11 \times 20mm$ (20mm is the optical length of the crystal) was cut from a crystalline boule of doped lithium iodate. The second harmonic generation from Nd^{3+} laser radiation ($\lambda = 1.064nm$) was studied. These studies showed that the angle of synchronism in the $\alpha - LiIO_3$ (*Mn*) single crystal was not changed (the accuracy of processing elements was $\pm 15'$) and the effect of second harmonic generation $\lambda (= 532nm)$ was preserved. The intensity of the second harmonic is partially reduced in comparison with the pure single crystal of lithium iodate. This can be explained by the absorption of the second harmonic

radiation by the crystal, which follows from the transmission spectrum of the doped single crystal of lithium iodate (Fig. 4).



Fig. 4. The transmission spectrum of doped single crystal of lithium iodate of the first generation.

The results of these studies show that the nonlinear properties of the $\alpha - LiIO_3$ (*Mn*) single crystal (which are very sensitive to any changes in the crystal structure) are fully preserved and are direct evidence of the isomorphic entry of manganate–ion into the $\alpha - LiIO_3$ single crystal matrix.

During mechanical processing, doped single crystals withstood various kinds of stresses better than pure lithium iodate single crystals, which can serve as indirect evidence for a decrease of various kinds of stresses, the formation of which is almost inevitable during growth.

The results obtained above give reason to consider permissible the use of permanganate – ion as an accelerator of the growth rate of a single crystal $\alpha - LiIO_3$, which is of great practical importance.

Conflict of Interest

There is no conflict of interest.

References

- [1] Adsorption et croisance cristaline. Parise: Edition du Centre Nat. de la. Recherche Sci., 1965.
- [2] Belyaev L. M., Grechushnikov B. N., Dobrzhanekiy G. F., Dymenko N. N., Martyshev Yu. N., Perekalina Z. B., Smorodina N. S. Investigation of the nature of the occurrence of impurity ions of an iron group in crystals by optical absorption spectra - Crystallography, 22, (1977), 650 (in Russian).
- [3] Bräuer A., Karthe W. ESR study of LiIO₃: Mn²⁺ Phys. Stat. Sol., 59, (1973), K131.
- [4] Atanesyan A.K., Balayan L.S. Regulation of growth rate of the lithium iodate (α LiIO₃) single crystal during the growth process. Materials of the 8-th International Scientific Conference Modern Methods of Diffraction Data Analysis and Actual Problems of X-ray. (2016), 17 (in Russian).
- [5] Atanesyan A.K., Balayan L.S., Hovhannesyan A.A. A crystallizer for Growing Monocrystals from Water Solution with Constant Rate of Growth. Reports of NAS and SEU of Armenia (ser. Technical Sciences), 41, N 2, (1998), 207 (in Russian).