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**PECULIARITIES OF COLORATION PROCESSES IN LiNbO₃:Fe
CRYSTALS UNDER HIGH TEMPERATURE
REDUCING/OXIDIZING ANNEALING**

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The work presents experimental results of an *in-situ* investigation of optical absorption of LiNbO₃:Fe during reducing (95%Ar+5%H₂) and oxidizing (O₂) high-temperature treatments in the temperature range from 20 to 800°C. The absorption spectra measured *in-situ* at high temperatures in reducing/oxidizing atmospheres as well as the kinetics recorded at fixed wavelength during rapid replacement of gas atmospheres have been analyzed. The origin of the changes in optical absorption caused by the reducing/oxidizing treatments is discussed in terms of hydrogen and oxygen ion diffusion and the point defect structure of the material.

Key words: lithium niobate; thermochemical treatment; reduction and oxidation kinetics; optical spectroscopy; point defects.

As it is known, the changes of optical properties of lithium niobate single crystals under influences of external electro-magnetic fields and temperatures are caused by processes in the subsystem of point defects in the crystal structure [1, 2]. Particularly, the photorefractive properties of LiNbO₃ depend on the presence of polyvalent ions, most of all by Fe ions [2]. These ions are always present in the crystal as an uncontrolled impurity. Besides, LiNbO₃:Fe crystals are grown specially as a material for holographic recording [2, 3].

Iron ions in LiNbO₃ are observed in two charge states: 2⁺ and 3⁺ [3] and the effectiveness of optical information recording depend on Fe²⁺/Fe³⁺ ratio. This fact caused a great interest to recharge processes of Fe ions under the influence of external factors, particularly, reducing/oxidizing annealing. In most cases, the changes in optical absorption that take place in LiNbO₃:Fe crystals upon high temperature treatments [3-9] have been studied at room temperature after a certain cooling procedure. We know only two works [10, 11] where *in-situ* investigations of optical absorption were carried out for Fe-doped LiNbO₃ crystals in the spectral region of absorption of the Fe ions, however in a narrow temperature range. Authors of [10] studied the absorption changes at the

spectral range of 0,4–2,5 μm during heating the crystal up to 150°C, whereas in [11] the changes in the absorption band of Fe^{2+} with maximum at 0,5 μm was studied at the temperatures up to 350°C. At the same time in [12] we have investigated the changes of optical properties of nominally pure LiNbO_3 crystals directly during high-temperature ($T \sim 20\text{--}800^\circ\text{C}$) treatment in different atmospheres.

Here we present the results of the *in-situ* investigations of optical properties of congruent $\text{LiNbO}_3\text{:Fe}$ crystals during reducing/oxidizing annealing. The analysis of the obtained experimental data is based on the comparison with the ones obtained previously [12] for nominally pure congruent LiNbO_3 , that allows to determine the role of Fe-ions in the reducing/oxidizing annealing of $\text{LiNbO}_3\text{:Fe}$ crystals.

$\text{LiNbO}_3\text{:Fe}$ crystals were grown by the Czochralski technique in air from platinum crucibles. Concentration of Fe ions in charge was 0,2 at.%. Samples for experiments were prepared as Y-cut polished plates with 0,8 mm thickness. The optical *in-situ* experiments have been performed using a specially designed high-temperature furnace placed in a Perkin-Elmer Lambda 900 spectrophotometer with spectral range 0,2–3 μm (50 000–3 333 cm^{-1}). The furnace allows to heat samples from room temperature up to about 1000°C in a certain gas atmosphere. The temperature controller ensures a linear heating program with the maximal rate of 5 K/min as well as the temperature stabilization at a desired temperature. The construction of the furnace allows rapid (~ 1 min) switching of gas atmospheres in the furnace and the registration of the subsequent reduction/oxidation (redox) kinetics at a certain wavelength. The absorption spectra were registered in the reducing (5% H_2 +95%Ar) and oxidizing (pure O_2) atmospheres. Detailed scheme of the experiment is described in Ref. [12]. The absorption spectra of the crystals at $T > 400^\circ\text{C}$ were corrected on the value of the heat radiation of the furnace.

The absorption spectra of $\text{LiNbO}_3\text{:Fe}$ crystal measured at different temperatures during heating in reducing atmosphere are shown in fig. 1. The absorption edge of the crystal at room temperature is located near 27500 cm^{-1} , while in nominally pure LiNbO_3 crystals it is observed in more high-energy region (near 35000 cm^{-1}). This shift of the absorption edge to the low-energy region in $\text{LiNbO}_3\text{:Fe}$ crystals is evidently connected with the presence of Fe-ions that is confirmed by the literature data [7]. In the spectral region of 25000–5000 cm^{-1} the $\text{LiNbO}_3\text{:Fe}$ crystal is transparent. Increasing of the temperature leads to linear shift of the fundamental absorption edge of $\text{LiNbO}_3\text{:Fe}$ crystal to the low-energy spectra region (fig. 1).

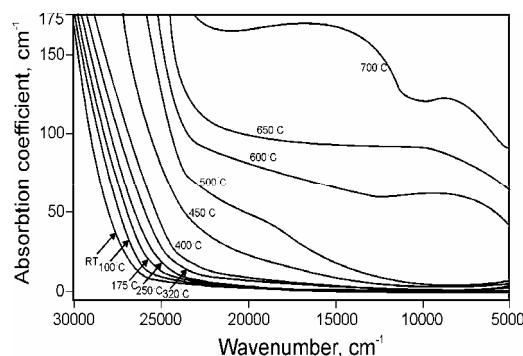


Fig. 1. Optical absorption spectra of an as-grown $\text{LiNbO}_3\text{:Fe}$ crystal registered during heating in reducing atmosphere at different temperatures

The main peculiarity of $\text{LiNbO}_3\text{:Fe}$ crystals in comparison with nominally pure LiNbO_3 during heating in reducing atmosphere consists in earlier beginning of optical absorption increase in the wide absorption band with a maximum near $20\,000\text{ cm}^{-1}$. As it is seen from fig. 2, the optical absorption of $\text{LiNbO}_3\text{:Fe}$ starts to increase at the temperature about 300°C , whereas in pure LiNbO_3 the changes of optical absorption begin at about 450°C [12]. At that the changes in pure LiNbO_3 is initially observed at more low-energy absorption band with a maximum near $10\,000\text{ cm}^{-1}$. The absorption band with a maximum near $20\,000\text{ cm}^{-1}$ is observed in [3–4, 6, 8] and is connected with intervalence transition $\text{Fe}^{2+} \rightarrow \text{Nb}^{5+}$.

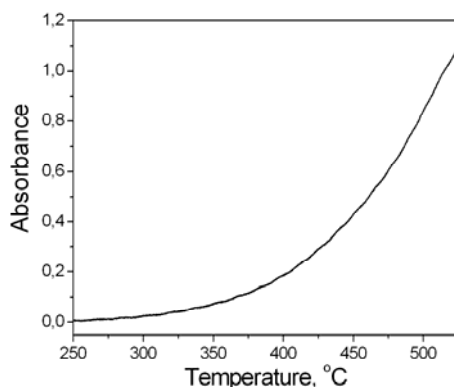


Fig. 2. The changes of optical absorption at 20000 cm^{-1} during heating of $\text{LiNbO}_3\text{:Fe}$ crystal in a reducing atmosphere

During further heating of $\text{LiNbO}_3\text{:Fe}$ samples in reducing atmosphere as well as in case of nominally pure LiNbO_3 crystal, the wide absorption band in the infrared spectral region arises at temperatures higher than 600°C (fig. 1). However, the maximum of this band is shifted to more low-energy region ($8\,000\text{ cm}^{-1}$) in comparison with pure LiNbO_3 . Further heating in reducing atmosphere leads to increasing of absorption in the visible spectral region – in the band located near $15\,000\text{ cm}^{-1}$. This band is also shifted to low-energy region in comparison with similar absorption band in nominally pure LiNbO_3 crystals, where it is located near $1\,6000\text{ cm}^{-1}$.

Similarly to pure LiNbO_3 crystals, the process of absorption centers formation both in IR and visible regions has got an activation character. However, it is impossible to determine parameters of the process of the absorption centers formation, because the absorption in the bands grows up continuously even at a constant temperature. Such a behavior of the absorption can be explained by the fact that formation of the absorption centers is originated from a diffusion process that takes place continuously.

Heating in oxidizing atmosphere does not lead to formation of absorption bands in visible and near IR- regions of the crystal spectra.

At the sufficiently high temperatures, the change of the annealing atmosphere from reducing to oxidizing one leads to bleaching of the absorption bands, i.e. the crystal becomes transparent again. A cycling of the atmospheres from oxidizing to reducing one (and vice versa) results in the formation and bleaching of the absorption bands, so the redox processes have got the reversible character.

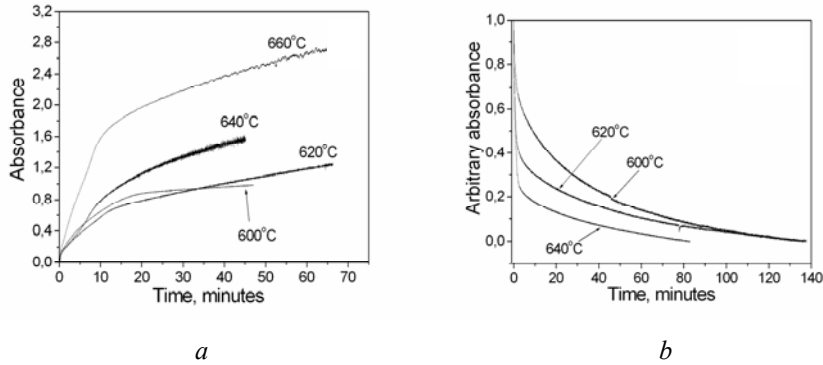


Fig. 3. Time dependent absorbance change of a $\text{LiNbO}_3\text{:Fe}$ crystal during reduction (*a*) and oxidation (*b*) registered at $14\,000\text{ cm}^{-1}$ at different temperatures. Initial points are shifted for all curves to same value

The kinetics of the redox processes for the absorption bands 8000 cm^{-1} and 14000 cm^{-1} at different temperatures are shown in fig. 3–4. As it is seen from figs. 3, *a*, 4, *a* on the reduction kinetics one can observe some delay in the reduction process that becomes visible in saturation of the crystal coloration (even some bleaching of the crystal). After that the process of the crystal coloration becomes monotonous again. Obviously, such peculiarities of reduction kinetics are caused by the presence of Fe-ions in the crystal. At the same time any analogous peculiarities are not observed on the oxidation kinetics for both absorption bands (figs. 3, *b*, 4, *b*). This behavior of the reduction kinetics can not be explained unambiguously at the time, though it is possible to make certain assumptions. It can be assumed that reduction of Fe-ions takes place at the initial stages ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$). At the same time the quantity of free electrons formed owing to the diffusion of oxygen from the crystal is too small. That's why re-trapping of the electrons by the Fe-ions from polarons takes place and it explains the delay (extremum) in the reduction process. After all the Fe-ions have been reduced, the reduction kinetics become monotonous again and are determined only by the polarons formation similar to nominally pure Ln [12].

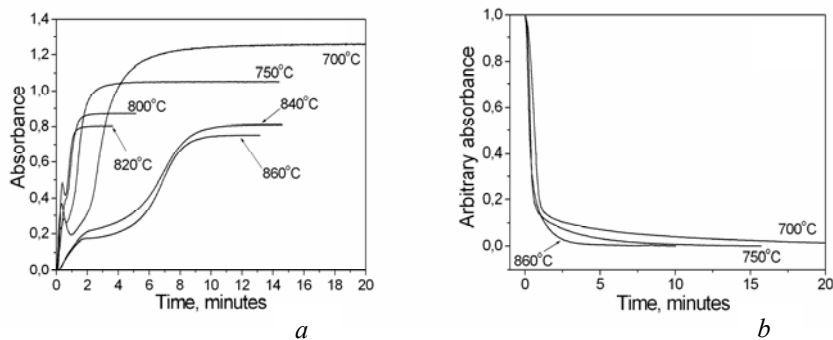


Fig. 4. Time dependent absorbance change of a $\text{LiNbO}_3\text{:Fe}$ crystal during reduction (*a*) and oxidation (*b*) registered at 8000 cm^{-1} at different temperatures. Initial points are shifted for all curves to same value

One more peculiarity of $\text{LiNbO}_3\text{:Fe}$ crystal in comparison with pure LiNbO_3 one is observed cooling in reducing atmosphere. As it was shown in [12], when undoped LiNbO_3 is cooled in reducing atmosphere to room temperature both from 600°C (when only the low-energy absorption band is present) or from 800°C (when the high-energy absorption band dominates), the absorption spectrum at room temperature is characterized only by the high-energy band. When $\text{LiNbO}_3\text{:Fe}$ crystal is heated up to 655°C in reducing atmosphere, the absorption of Fe^{2+} -ions is so intensive that it is hard to talk about possible band realignment during cooling the crystal from this temperature. The spectrum of $\text{LiNbO}_3\text{:Fe}$ crystal is characterized by wide absorption band with the maximum at $20\,000\text{ cm}^{-1}$ both at 655°C and at room temperature (fig. 5). Some decreasing of the absorption at the low-energy region can be caused either by the temperature shift of band maximum or by possible realignment of bands, as it is observed in nominally pure LiNbO_3 [12].

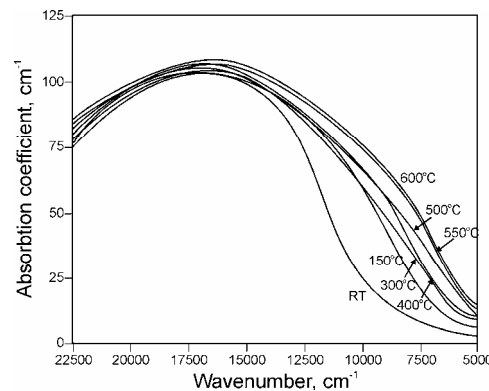


Fig. 5. Optical absorption spectra of $\text{LiNbO}_3\text{:Fe}$ crystal registered during cooling from 600°C to room temperature in reducing atmosphere

Thus we have determined two main peculiarities in behavior of LN crystals, doped with Fe-ions in comparison with pure LiNbO_3 during their high-temperature annealing.

Firstly, coloration processes of $\text{LiNbO}_3\text{:Fe}$ crystals during their high-temperature treatments in reducing atmosphere start in the visible spectral range at noticeably lower temperatures (300°C). Obviously, it is caused by recharging processes of iron ions $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$.

Secondly, on reduction kinetics both in visible (to a lesser extent) and in infrared spectral region (to a greater extent) one can observe their significant deviation from monotony when annealing atmosphere is changed from oxidizing to reducing. At the initial stages the speed of band formation is decreasing, but after some time the dependencies becomes monotonous again that is explained by the redistribution of electrons from polarons to Fe-ions.

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ОСОБЛИВОСТІ ПРОЦЕСІВ ЗАБАРВЛЕННЯ КРИСТАЛІВ LiNbO₃:Fe ПІД ЧАС ВИСОКОТЕМПЕРАТУРНИХ ОКИСНО-ВІДНОВНИХ ОБРОБОК У РЕЖИМІ *IN SITU*

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У роботі досліджено вплив високотемпературних відпалів (20–800°C) в окиснювальній (O₂) та відновлювальній (Ar + H₂) атмосферах на оптичні властивості кристалів LiNbO₃, легованих іонами Fe у режимі *in situ*.

Проаналізовано отримані спектри поглинання і кінетичні залежності. Зроблені припущення про можливу природу змін оптичного поглинання, спричинених високотемпературними окисно-відновними відпалами. Визначено особливості процесів забарвлення кристалів $\text{LiNbO}_3:\text{Fe}$ порівняно із номінально бездомішковими кристалами LiNbO_3 .

Ключові слова: ніобіт літію, термомеханічна обробка, оптична спектроскопія, точкові дефекти.

ОСОБЕННОСТИ ПРОЦЕССОВ ОКРАСКИ КРИСТАЛЛОВ $\text{LiNbO}_3:\text{Fe}$ ВО ВРЕМЯ ВЫСОКОТЕМПЕРАТУРНЫХ ОКИСЛИТЕЛЬНО- ВОССТАНАВЛИВАЮЩИХ ОБРАБОТОК В РЕЖИМЕ *IN SITU*

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В работе проведены исследования влияния высокотемпературных отжигов (20–800°C) в окислительной (O_2) и восстанавливающей ($\text{Ar} + \text{H}_2$) атмосферах на оптические свойства кристаллов LiNbO_3 , легированных ионами Fe в режиме *in situ*. Проведен анализ полученных спектров поглощения и кинетических зависимостей. Сделаны предположения о возможной природе изменений оптического поглощения, вызванных высокотемпературными окислительно-восстанавливающими отжигами. Определены особенности процессов окраски кристаллов $\text{LiNbO}_3:\text{Fe}$ в сравнении с номинально беспримесными кристаллами LiNbO_3 .

Ключевые слова: ниобат лития, термомеханическая обработка, оптическая спектроскопия, точечные дефекты.

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