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On an increase in the volume concentration of hydrogen in undoped $LiNbO_3$ crystals of congruent composition

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The efficiency of the process of increasing the volume concentration of hydrogen in $LiNbO_3$ crystals of congruent composition by heating in a humid atmosphere has been studied. It is shown that pretreatment of $LiNbO_3$ crystals in adipic acid makes it possible to significantly increase the volume concentration of hydrogen in the sample during subsequent thermochemical treatment in wet air.

Keywords: lithium niobate, hydrogen, electrical conductivity, IR spectroscopy.

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Introduction

One of the applications of lithium niobate (LN) crystals $LiNbO_3$ is the creation of narrow-band holographic interference filters [1]. At the same time, a holographic lattice is recorded in a nominally pure or specially doped LN sample with its subsequent thermal fixation [2]. The diffraction efficiency of the recorded hologram and its lifetime depends on many factors, including the concentration of impurities (including hydrogen) in the crystal [3]. Therefore, it is desirable to optimize the concentration of all impurities in the LN crystals used for these purposes. Note that the problem of introducing a controlled amount of metal ions (Fe, Cu, Mg, Zn, etc.) into the crystal of LN is successfully solved already at the stage of their synthesis [4].

A certain amount of hydrogen ions is introduced into the structure of LN crystals during their growth, which is due to the presence of water vapor in the growth atmosphere [4]. It is believed that the volume concentration of H^+ c_H ions in congruent LN crystals (CLN) grown using the Czochralski method and not subjected to additional thermochemical treatments lies within $(1-10)\cdot 10^{18}\,\mathrm{cm}^{-3}$ [5].

There are two main methods to lower c_H in LN such as high-temperature annealing in vacuum and annealing in dry oxygen atmosphere [6]. This processing allows reducing c_H to $1\cdot 10^{17}\,\mathrm{cm}^{-3}$. One of the most effective ways to increase c_H (over the entire volume of the sample) in LN is considered to be annealing of LN at temperatures $(873-1273)$ K in an atmosphere of wet oxygen or air, which allows to preserve the transparency of the crystal in the optical range [6]. A modification of this method is annealing in a humid atmosphere when a constant electric field with a strength of $E \sim 400$ V/cm is applied to the crystal along any nonpolar direction [7], which increases the efficiency of proton exchange.

Heat treatment of LN crystals in acids with a high boiling point [5,6] is commonly used to create waveguides on the surface of LN crystals. At the same time, in the thin near-surface layers of the processed sample, the ions Li^+ are partially replaced by H^+ with the formation of the compound $Li_{1-x}H_xNbO_3$. This compound is not stable, and when the crystal is heated in air, both partial diffusion of H^+ ions into the sample and the departure of these ions from the crystal, accompanied by the destruction of the modified near-surface layer, occurs.

Interesting results were obtained in [8], where plates x and z of sections of LN crystals underwent double thermochemical treatment. At the first stage, the crystals were in benzoic acid for 70 min at $T = 458$ K. Further, these crystals from 6 to 240 min were heated in a stream of moist oxygen at $T = 673$ K. It turned out that when such samples were heated in moist oxygen, the concentration profile of ions H^+ was significantly eroded, and the total ion content H^+ did not decrease. Thus, there is a probability that during heat treatment of such a crystal in a humid atmosphere at temperatures of the order of $873-1173$ K, the reverse diffusion of hydrogen will also not be observed, and the ions H^+ will be evenly distributed over the sample volume.

The aim of this work was to experimentally verify the possibility of obtaining a uniform (by volume) increase in the volume concentration of H^+ in LN crystals due to the two-stage thermochemical treatment described above and to compare the effectiveness of such a process with the results of other authors.

1. Samples and methods of conducting experiments

6 plates z- of a slice with similar geometric dimensions were used in the experiments. They were made from two nominally undoped monodomenized crystals of congruent LN composition of good optical quality, cut from a single boule synthesized in NPO „Electron–Karat“ (Lviv,

Table 1. Conditions of thermochemical processing of studied samples

№	Treatment mode	
	In adipic acid at $T = 473\,\text{K}$	In a humid atmosphere
1	–	–
2	–	–
3	–	5 h at $T = 973\,\text{K}$
4	5 h	5 h at $T = 973\,\text{K}$
5	–	5 h at $T = 1073\,\text{K}$
6	5 h	5 h at $T = 1073\,\text{K}$

Ukraine). The thickness of all the plates was $\sim 2.7\,\text{mm}$, and the polar axis was directed along this short face. Plates made from the first crystal (samples № 1, 3 and 5) were not pretreated in adipic acid, and those made from the second crystal (samples № 4 and 6) were pretreated.

Preliminary proton exchange in adipic acid of samples № 4 and 6 was carried out in a muffle furnace SNOL 58/350 at a temperature of 473 K for 5 h. The heating rate of the furnace was $\sim 200\,\text{K/h}$. The final thermochemical treatment was carried out in a specially designed untight tubular heater, in the working area of which LN plates were placed and preheated water vapor was supplied. After the final thermochemical treatment, the polar surfaces of the samples were polished to optical quality. The modes of thermochemical processing of samples are presented in Table 1.

Measurements of the optical absorption coefficient in the visible region were performed at wavelengths 465, 525 and 635 nm on a photometric device described in [9], and recording of IR absorption spectra in the wavenumber region $(3400-3600)\,\text{cm}^{-1}$ — on the FSM-2202 FTIR spectrometer. IR measurements were performed at unpolarized radiation and room temperature with a resolution of $0.5\,\text{cm}^{-1}$.

An approach based on measuring the integral intensity of IR absorption A_{int} [7] in accordance with the expression $A_{\text{int}}/c_{\text{H}}=(2.1\pm0.32)\cdot10^{-17}$ cm was used to determine the volume concentration of OH^--groups c_{H}. The calculation of c_{H} was also carried out according to the maximum value of the absorption coefficient OH^--groups in the IR range $\alpha_{\max}$, according to the ratio $c_{\text{H}} = \alpha_{\max}(1.67\pm0.09)\cdot10^{18}\,\text{cm}^{-2}$, proposed in [3].

For measurement of electrical conductivity by direct current electrodes made of indium-gallium eutectic were applied to the polar surfaces of the samples which were cauterized at a temperature of about 450 K during the preliminary removal of water molecules adsorbed on the electrode-free surfaces of the samples [10]. Measurements were performed using usual two-electrode method [10].

2. Experimental results

It is known that during high-temperature annealing of LN crystals in a humid atmosphere, their optical absorption in the visible region can change significantly [11]. Table 2 shows the values of the optical absorption coefficients of the studied crystals in the visible region at three wavelength values λ. It can be seen that the samples that have undergone heat treatment in a wet air have an increase in optical absorption at all wavelengths. Visually, this is expressed in the fact that the crystal acquires a gray hue. Usually, this effect is associated with the appearance of additional oxygen vacancies in the crystal [6]. Fundamentally, for any value λ, the values α of the sample № 4 are less than that of the sample № 3, and of the sample № 6 are less than the sample has № 5. In this case, the samples № 3 and № 4 (and also № 5 and № 6) were annealed in a humid atmosphere simultaneously. This may indicate that the pretreatment of LN samples in adipic acid reduces the number of oxygen vacancies V_{O} that occur during subsequent thermochemical treatment in moist air.

The study of IR absorption in the region of valence vibrations of OH^--groups showed that the spectral distribution of $\alpha(\lambda)$ in all samples is almost the same, as illustrated in Fig. 1. This is indirect evidence that as a result of annealing in wet air, a uniform redistribution

Table 2. Optical absorption coefficients of the studied samples

№	$\alpha_{625\,\text{nm}}$, cm^{-1}	$\alpha_{525\,\text{nm}}$, cm^{-1}	$\alpha_{465\,\text{nm}}$, cm^{-1}
1	0.11 ± 0.01	0.16 ± 0.01	0.17 ± 0.01
2	0.09 ± 0.01	0.14 ± 0.01	0.19 ± 0.01
3	0.19 ± 0.01	0.51 ± 0.01	0.61 ± 0.01
4	0.17 ± 0.01	0.33 ± 0.01	0.45 ± 0.01
5	0.21 ± 0.01	0.49 ± 0.01	0.65 ± 0.01
6	0.17 ± 0.01	0.34 ± 0.01	0.46 ± 0.01

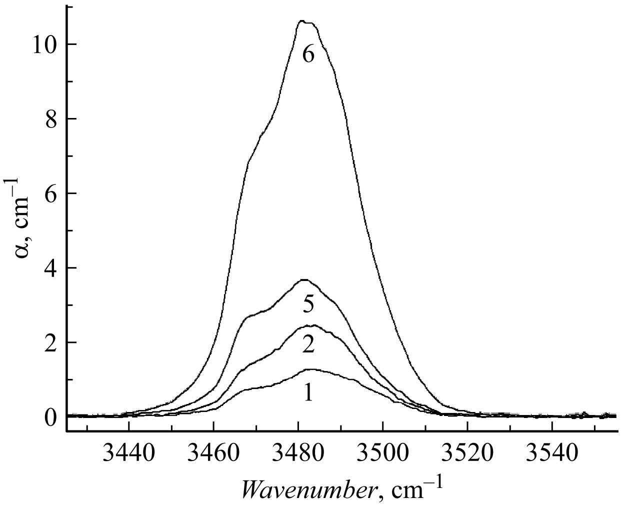

Figure 1. IR absorption spectrum in some studied samples LN.

Table 3. Parameters of the IR absorption spectrum OH^--groups and volume concentration of hydrogen c_H in the studied samples

№	A_{int}, cm^{-2}	c_H, cm^{-3*}	α_{max}, cm^{-1}	c_H, cm^{-3**}
1	72.6	$(3.5 \pm 0.5) \cdot 10^{18}$	2.32	$(3.7 \pm 0.2) \cdot 10^{18}$
2	45.1	$(2.2 \pm 0.3) \cdot 10^{18}$	1.34	$(2.2 \pm 0.2) \cdot 10^{18}$
3	118	$(5.6 \pm 0.7) \cdot 10^{18}$	3.88	$(6.5 \pm 0.3) \cdot 10^{18}$
4	313	$(14.9 \pm 2.0) \cdot 10^{18}$	8.64	$(14.4 \pm 0.8) \cdot 10^{18}$
5	116	$(5.5 \pm 0.7) \cdot 10^{18}$	3.67	$(6.2 \pm 0.3) \cdot 10^{18}$
6	330	$(15.7 \pm 2.1) \cdot 10^{18}$	10.6	$(17.70 \pm 0.95) \cdot 10^{18}$

Note. * calculation according to [7], ** calculation according to [3].

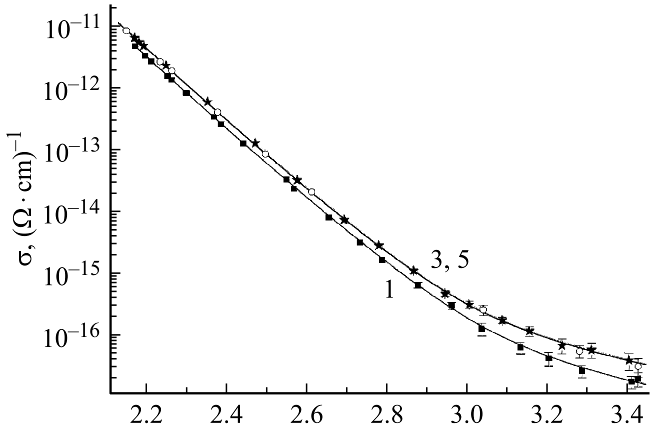

Figure 2. Temperature dependence of the specific electrical conductivity of samples № 1, 3 and 5 (asterisk). Solid lines — optimal approximation by expression (1).

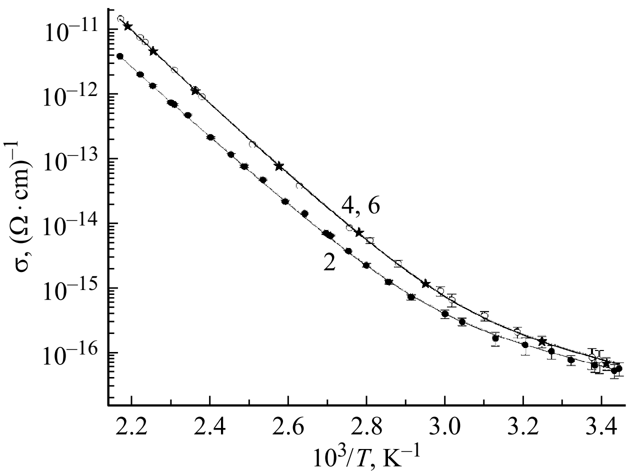

Figure 3. Temperature dependence of the specific electrical conductivity of samples № 2, 4 and 6 (asterisk). Solid lines — optimal approximation by expression (1).

of ions occurred H^+ from surface layers over the entire volume of samples. Parameters of IR absorption spectra and calculation results c_H, according to [3,7], are given in Table 3. Attention is drawn to the difference in the values of c_H in samples № 1 and № 2, but this is consistent with the fact that samples of LN cut from different parts of the same boule can be characterized by significantly different volume concentrations of hydrogen [12]. As can be seen from Table 3, the results of the calculation of c_H by [3,7] for each of the samples overlap within the margin of error.

It is well known that the volume concentration of H^+ or D^+ ions strongly affects the electrical conductivity $\sigma(T)$ of LN crystals in the temperature range 348–571 K [7]. Therefore, we conducted a study of the dependence of $\sigma(T)$ on the direct current of this series of samples in the temperature range 295–453 K. The results are shown in Fig. 2 and 3.

It has recently been shown [13] that the dependence of $\sigma(T)$ LN crystals of different compositions that have not undergone reductive thermochemical treatment can be correctly described within the framework of the presence of three types of mobile carriers with the following activation energies: $E_1 \cong 1.33$ eV, $E_2 \cong 1.03$ eV and $E_3 \cong 0.29$ eV. It was assumed that E_1 and E_2 are responsible for the activation energies of ions Li^+ and H^+ respectively, and E_3 — for electronic (polaron) conductivity. Thus:

$$\sigma(T) = \frac{A_1}{T}\exp\left(-\frac{E_1}{k_0 T}\right) + \frac{A_2}{T}\exp\left(-\frac{E_2}{k_0 T}\right) + A_3 \exp\left(-\frac{E_3}{k_0 T}\right), \quad (1)$$

where k_0 — Boltzmann constant, T — temperature. The coefficients A_1, A_2 and A_3 are proportional to the volume concentration of lithium vacancies, the volume concentration of hydrogen ions c_H, as well as electron capture centers.

The results of calculating the coefficients A_1, A_2 and A_3 for the studied samples obtained from the optimal approximation of experimental results by the expression (1) are given in Table 4.

Figure 4 shows the dependence of the value of the coefficient A_2, responsible for the proton contribution to electrical conductivity, on A_{int}. It can be seen that within the margin of error, this dependence is — linear, and this result is quite expected.

It is noteworthy that the coefficients of A_1 in crystals after thermochemical treatment are noticeably greater than before it. In accordance with the standard description of ionic conductivity in dielectrics, the coefficient A_1 can be expressed as $A_1 = qn\mu_0$, where n — the volume concentration of vacancies, q — ion charge, and μ_0 — pre-exponential multiplier in the expression describing the temperature dependence of the mobility of this ion:

$$\mu(T) = \mu_0 \exp\left(-\frac{E_a}{k_0 T}\right), \quad (2)$$

where $E_a = E_1$ is activation energy.

Table 4. Coefficients of expression (1), obtained from optimal approximation of experimental results on electrical conductivity

№	A_1 $(\Omega\cdot\text{cm})^{-1}\cdot\text{K}$	A_2 $(\Omega\cdot\text{cm})^{-1}\cdot\text{K}$	A_3 $(\Omega\cdot\text{cm})^{-1}\cdot\text{K}$	c_H, cm^{-3}
1	$(505\pm50)\cdot10^{-3}$	$(1.9\pm0.4)\cdot10^{-4}$	$(1.7\pm0.4)\cdot10^{-12}$	$(3.6\pm0.3)\cdot10^{18}$
2	$(305\pm20)\cdot10^{-3}$	$(1.2\pm0.3)\cdot10^{-4}$	$(3.4\pm1.5)\cdot10^{-12}$	$(2.2\pm0.5)\cdot10^{18}$
3	$\sim655\cdot10^{-3}$	$\sim2.8\cdot10^{-4}$	$\sim3.5\cdot10^{-12}$	$(5.6\pm0.7)\cdot10^{18}$
4	$\sim1205\cdot10^{-3}$	$\sim7.5\cdot10^{-4}$	$\sim7\cdot10^{-12}$	$(14.9\pm2.0)\cdot10^{18}$
5	$(655\pm70)\cdot10^{-3}$	$(2.8\pm0.3)\cdot10^{-4}$	$(3.5\pm0.8)\cdot10^{-12}$	$(5.5\pm0.7)\cdot10^{18}$
6	$(1205\pm120)\cdot10^{-3}$	$(7.5\pm0.7)\cdot10^{-4}$	$(7\pm2)\cdot10^{-12}$	$(15.7\pm2.1)\cdot10^{18}$

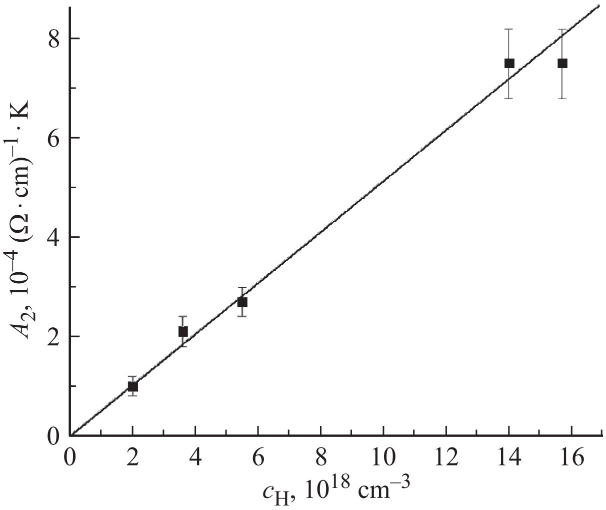

Figure 4. The dependence of the coefficient A_2 on the volume concentration of hydrogen in sample.

As previously assumed [13], the ion of the first type is Li$^+$, and then an increase in A_1 means either a significant increase in the amount of V_Li, which is impossible, or a corresponding increase of μ_0. The second reason is also extremely unlikely. However, another explanation for this effect is possible. It was found [9] in the study of the oxidation of pre-reduced crystals of LN that the activation energy of the mobility of ions O^{2-} is the value of $E_\text{O}=(1.31\pm0.05)$ eV, which within the margin of error coincides with the value of E_1. As follows from Table 2, samples № 3–6 have an absorption coefficient of α_{465} increased, which indicates the possible appearance of V_O. Since $E_1\cong E_\text{O}$, the equation (1) can be adjusted as follows:

$$\sigma(T)=\frac{A_1+A_\text{O}}{T}\exp\left(-\frac{E_1}{k_0T}\right)+\frac{A_2}{T}\exp\left(-\frac{E_2}{k_0T}\right)+A_3\exp\left(-\frac{E_3}{k_0T}\right). \quad (3)$$

Obviously, in any case, the volume concentration of V_Li is much greater than V_O, so we can conclude that in the studied temperature range, the mobility of V_O is several orders of magnitude greater than at V_Li.

3. Results and discussion

As can be seen from Table 3, the change of the content of the volume concentration of ions H$^+$ in the sample № 3, is $(\Delta c_\text{H})_3=(2.1\pm0.7)\cdot10^{18}\,\text{cm}^{-3}$, and $(\Delta c_\text{H})_4=(12.7\pm2.3)\cdot10^{18}\,\text{cm}^{-3}$ in the sample № 4 compared to the samples № 1 and № 2 respectively. Using known data on the depth of the chemically modified layer $\text{H}_x\text{Li}_{1-x}\text{NbO}_3$ when processing plates z-NL slice in adipic acid at a temperature of $T=473\,\text{K}$ [14,15], it is possible to estimate the additional change $(\Delta c_\text{H})'$ at $x=0.5$ and the conditions for the subsequent uniform redistribution of hydrogen over the sample volume. With a plate thickness of $d=2.7\,\text{mm}$, this value is $(\Delta c_\text{H})'\sim9\cdot10^{18}\,\text{cm}^{-3}$. Thus, $(\Delta c_\text{H})'+(\Delta c_\text{H})_3\cong(\Delta c_\text{H})_4$. This confirms the assumption that when conducting high-temperature annealing in a wet air, the reverse diffusion of hydrogen from the surface-modified layers does not occur.

Regarding the value of the proportionality coefficient s, there are very significant differences in the literature between the maximum value of the absorption coefficient in the IR range α_max and c_H [3,16–19], which is reflected in the calculation results c_H according to IR spectroscopy data. Therefore, the known data on the efficiency of proton exchange obtained by different authors can be compared only when using the same value s. Table 5 shows the known measurement results of c_H before and after proton exchange in LN and their recalculation either in accordance with [3], or in accordance with [7] — by the values given in the original works are α_max or A_int.

A comparison of the recalculated values of c_H unambiguously shows that the maximum value of $c_\text{H}\sim15\cdot10^{18}\,\text{cm}^{-3}$ achieved by us is close to the value of c_H obtained in [11], but at significantly lower temperature and annealing time.

The maximum of the known values c_H was obtained in [7], however, a fairly thin (0.5mm) sample was used in the experiment. If the number of ions H$^+$ entering the sample during heat treatment depends only on its conditions

Table 5. Known results of the effect of crystal annealing LN in humid atmosphere by volume concentration of OH^--groups

Sample	Dimensions $x \times y \times z$, mm	Processing conditions			$\alpha_{\max}$, cm^{-1}	c_H, $10^{18}\,cm^{-3}$	Ref	c_H** $10^{18}\,cm^{-3}$
		Medium	T, K	t, h				
CLN	$10.0 \times 9.0 \times 1.3$	As grown			1.6	17	[20]	2.67
	$10.0 \times 9.0 \times 1.3$	O_2/H_2O	1193	3	2.94	31		4.91
CLN	$7 \times 10 \times 2$	$(O_2+N_2)/H_2O$	1173	2	3.5		[21]	5.85
CLN	$5 \times 5 \times 5$	As grown					[11]	~ 3.33
		O_2/H_2O	1173	20				~ 14.3
NSLN	$15 \times 15 \times 0.5$	$(O_2+N_2)/H_2O$	1253	20	2.42		[22]	~ 4.04
CLN	$0.5 \times 10 \times 11$	As grown				5.65	[7]	5.65
		O_2/H_2O*	873	?		43		43

Note. CLN — crystal of congruent composition, NSLN — composition is close to stoichiometric; * — processing was carried out when a constant electric field was applied to the sample; ** — evaluation of the corresponding data on $\alpha_{\max}$ or A_{int} in accordance with [3,7].

and its surface area, then such a value would be obtained $c_H \sim 1 \cdot 10^{19}\,cm^{-3}$ with a sample thickness of 2.7mm based on the technology used in [7]. Also note that the process used in [7] requires applying conductive electrodes to the processed crystal and applying a sufficiently high voltage to it, which from a technological point of view is significantly more difficult than pretreatment of the sample in adipic acid.

The results of our additional experiments on the study of the electrical impedance of the sample № 6 in the frequency range $10^{-3}-10^4$ Hz at $T \geq 370$ K qualitatively correspond to those obtained earlier for „as grown" LN samples, which indicates the absence of surface layers with electrical properties that differ from the volume. This indicates the uniformity of the electrical properties of the sample in the polar direction and, consequently, the uniform distribution of ions H^+ and V_O over the sample volume.

Conclusion

It was found that the pretreatment of LN crystals in adipic acid at $T \cong 473$ K allows for a significant increase of the volume concentration of hydrogen in the sample during subsequent thermochemical treatment in moist air compared with untreated crystals. In this case, the ions H^+ are distributed evenly over the sample volume.

Note that none of the papers [7,11,20–22] provide the value of the partial pressure P_{H_2O} of H_2O vapors of the crystal annealing atmosphere. However, this parameter should definitively influence the results of thermochemical treatment, since annealing of LN in pure vapors H_2O or D_2O already at 773 K leads to a strong reducing effect and a sharp increase of the optical density of LN in the visible range [23,24], but does not affect the value of c_H [11].

Therefore, the study of thermochemical processing of LN crystals in a gas medium with a known value of P_{H_2O} is undoubtedly of particular interest — both from the point of view of optimizing proton exchange and minimizing changes in the optical properties of LN in the visible range.

Conflict of interest

The authors declare that they have no conflict of interest.

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