Acoustic properties of LNM crystal

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Abstract. We report linear acoustic and acousto-optical properties of LiNa₅Mo₉O₃₀ (LNM) single crystal. This relatively new crystal, known for its complex crystallographic structure, is optically biaxial with high birefringence of 0.2545 at 450.2 nm, and crystals that consist of molybdates are widely used in different applications, from scintillators, double β-decay detectors, “dark matter” sensors to electro optics. The lowest measured propagation velocity of shear wave was 1200 m/s, and for the longitudinal mode it was 4100 m/s, which are a relatively low value for crystalline media. The maximum attenuation of the longitudinal wave at a frequency of 180 MHz was moderate and equal 20 dB/cm·GHz². The values of the acousto-optic figure of merit for light diffraction on a longitudinal acoustic wave were also determined, the maximum value of the coefficient was 13 c.u., which exceeds the efficiency of the one used in AO devices material α-SiO₂. Thus, the set of measured acoustic and elastic-optical properties shows a new promising optically biaxial material for acousto-optics, which needs for further researching.

1. About the LiNa₅Mo₉O₃₀ crystal: properties and growth

We report linear acoustic and acousto-optical properties of LiNa₅Mo₉O₃₀ (LNM) single crystal. This relatively new crystal is known for its complex crystallographic structure, it is optically biaxial with high birefringence of 0.2545 at 450.2 nm, and crystals that consist of molybdates are widely used in different applications, from scintillators, double β-decay detectors, “dark matter” sensors to electro optics. The LNM single crystal is characterized by the lowest mm² orthorhombic symmetry, with unit cell parameters a = 7.2265 Å, b = 37.1575 Å, c = 17.9398 Å. The dielectric axis X fits with the crystallographic axis a, the Y axis with the c axis, and the Z axis fits with the b axis. The crystal is not water soluble and has a Mohs hardness of 5. For the first time LiNa₅Mo₉O₃₀ phase was obtained in [1], the LNM single crystal was firstly grown in [2], the crystal density is 4.04 g/sm³ [2]. The scope of complex molybdates crystals is very wide. They are used as scintillators, double β-decay detectors, “dark matter” sensors, as well as acousto-optic modulators of laser radiation, etc. [3, 4].

The crystalline sample provided for the research has dimensions of 4.6x11.5x8.7 mm along the a, b and c crystallographic axes, respectively, and were synthesized at the Dmitry Mendeleev University of Chemical Technology of Russia in Moscow. For the growth of a single crystal, ultrapure reagents,
Li$_2$CO$_3$, Na$_2$CO$_3$ with purity 4N, manufactured by Fox-Chemicals GmbH, and especially pure molybdenum oxide with purity 6N, manufactured by ARMOLED, were used. The quality control of reagents was carried out using ICP-MS. The single crystal of the composition LiNa$_5$Mo$_9$O$_{30}$ has a congruent character of melting and was grown by the low gradient Czochralski method with a temperature gradient in the melt of 1 K/cm. The draw rate was 1 mm/hour, the rotation speed of the crystal ranged from 8 to 25 rpm. The crystal was grown from a stoichiometric composition on the seed, oriented in the direction of the main axis. The control of the stoichiometry of the grown crystal was carried out by the SIMS method, along the entire length of the boule. It was found that 75% of the boules have a stoichiometric composition.

![Figure 1.](image1)

To determine the optimal conditions for growing a single crystal, a numerical simulation of the thermal node was performed. The calculated configuration of the heat node allowed growing a high-quality single crystal with a mass of more than 250 grams.

The material is transparent in the visible range of optical radiation, has a large transmission window (0.357-5.26 μm), is optically biaxial, and has relatively large values of the refractive index, with noticeable anisotropy (1.8266, 2.0123 and 2.0414 at a wavelength of 0.6365 μm) [2].

2. Acoustic properties

2.1. Measurement of the bulk speed and attenuation of ultrasonic longitudinal waves by acousto-optic methods

The propagation velocities of longitudinal acoustic waves are determined by the acousto-optic (AO) method by comparing the angle between +1 and -1 diffraction orders arising from the diffraction of light by a sound wave propagating in a reference (SiO$_2$) and probe (LNM) materials. The diffraction pattern was taken on the screen, equally distant from the acoustic column in both materials. Thus, to restore the speed of sound in the material under study, it is sufficient to compare the ratio of the distances between the diffraction orders and the speed of ultrasonic in fused quartz. The measured propagation velocities of the longitudinal mode in the LNM crystal were $V_X = 4100$ m/s, $V_Z = 5235$ m/s and $V_Y = 4780$ m/s.

Measurements of the attenuation of ultrasound in a single crystal LNM were carried out by an acousto-optic method. It is known that the intensity of diffracted light with an acousto-optic effect depends on many factors [5]. As for the dependence of the intensity of the diffracted light on the intensity of the ultrasonic wave in the region of acousto-optic interaction, with a low diffraction
efficiency, it is almost linear. This circumstance allows us to measure the attenuation of ultrasound [5]. The ultrasonic wave is launched into the crystal in a pulsed mode. The pulse duration must be sufficiently short, and the pulse repetition period must be much longer than the pulse duration. The diameter of the laser beam passing through the medium must be substantially smaller than the dimensions of the sample under study. An ultrasound pulse, launched into the test medium through the entrance face, propagates in it along the test direction, passes through the laser beam, and, after being reflected from the face opposite to the input edge, goes back and passes through the laser beam again.

Due to the attenuation of the ultrasonic wave, the intensity of the diffracted light $I_2$ on the pulse going back will be less than the intensity $I_1$. The diffracted beams fall on the photodetector, which is synchronized with the master pulse generator. The recording of the intensity of each pulse is carried out after the angle of incidence of the light on the ultrasound corresponds to the fulfillment of the Bragg phase matching condition [6]. The distance $L$, that the acoustic wave passed in the medium between these two scattering events, can easily be defined as the product of the ultrasonic wave propagation velocity along the selected direction in the medium $v$ and the time delay between the first and second diffracted light pulse $L = v \tau$. The ratio $a = I_2/I_1$ gives us the absolute value of the attenuation of ultrasound in intensity in the case of an ultrasonic wave with frequency $f$ passing a distance $L$ in the medium. The value

$$
\Gamma = \frac{10 \cdot \lg(I_2/I_1)}{(10^{-9} \cdot f)^2 \cdot 10^{-2} \cdot L}
$$

gives the attenuation in units of dB/sm·GHz$^2$.

This approach to measuring the attenuation of ultrasound avoids the need to pass a laser beam through different areas of the sample under study and, as a result, does not require normalization of the intensity of the diffracted light to the intensity of the transmitted beam $I_0$. Such a normalization introduces an additional error if the optical faces of the crystal are not processed well enough and have a profile that is different from the planar one. It should also be noted that attenuation measurements should be carried out at such high frequencies at which it begins to manifest itself.

This method has some of the following limitations: the implementation of acousto-optical scattering and registration of the two pulses mentioned above is important in the medium under study, the divergence of ultrasound should be small, and the ultrasonic wave should propagate along those directions of the medium where there is no significant acoustic demolition.

Single crystal LNM, belongs to the orthorhombic system. The calculated crystal density is 4.0 g/cm$^3$ [1]. Crystalline sample was oriented its faces orthogonal to the crystallographic axes. The sample has the following dimensions: 4.6 mm along the crystallographic axis $a$, 11.5 mm along the axis $b$ and 8.7 mm along the axis $c$. The velocities of longitudinal ultrasonic waves along these axes, measured in operation, are $V_a = 4100$ m/s, $V_b = 5235$ m/s, and $V_c = 4780$ m/s (table 1).

180 MHz longitudinal ultrasonic wave was generated in an acousto-optic cell (buffer) based on fused silica and launched into the LNM sample alternately along each of the three axes — $a$, $b$, and $c$. Acoustic contact of the ultrasound input face of the sample and the output face of the buffer was carried out through a layer of glycerin. The sample face opposite to the input face (reflecting face) did not have acoustic contact with any solid or liquid body so that the reflection coefficient of the ultrasonic pulse from this face could be considered equal to unity. The crystal was illuminated by a laser beam from a He-Ne laser with a wavelength of 633 nm and aperture 0.8 mm. Ultrasound attenuation measurements were performed as described above, namely by measuring the intensity ratio $I_2$ of diffracted light on an acoustic pulse after it was reflected from the corresponding face with its intensity $I_1$ as a result of diffraction on the same pulse going in the direction of the reflecting face. The beam of light passed through the sample at two different distances from the reflecting face, which gave 2 different values of the absolute attenuation $a$ ($a < 1$) for two different distances (wavelengths), passed by ultrasound. The attenuation values $\Gamma$ were also calculated in units of dB/sm·GHz$^2$. The uncertainty in determining the speed of ultrasound is 0.5%, the uncertainty in determining the time interval $\tau$, and,
consequently, the path length \( L \) is about 5%. The uncertainty in determining the intensity of an ultrasonic wave (the intensity of diffracted light) is about 10%. The attenuation of ultrasound in all three directions is not significant.

2.2. Measurement of propagation velocity of shear ultrasonic waves by pulse method

The harmonic wave velocity may be found by measuring the wave phase. The phase of a plane wave that propagates in the direction of increase of \( x \) is written as \( \varphi(x, t) = \omega t - kx + \varphi \). In the source at \( x = 0 \), the wave phase equals to \( \varphi(0, t) = \omega t + \varphi \). As is evident, the difference of phases \( \Phi \) between the signals of source and receiver is not dependent on time and appears to be a rather simple distance and frequency function:

\[
\Phi(x, f) = \varphi(0, t) - \varphi(x, t) = kx = \frac{2\pi}{c} \cdot f \cdot x
\]

According to the equation, the difference of phases \( \Phi \) is in linear dependence on both distance \( x \) and frequency \( f \), with phase increase rate inversely proportional to wave velocity \( c \). Thus since we know the distance \( x \) between the source and receiver it is possible to measure the ratio of phases \( \Phi \) displacement to frequency \( f \) and from the resulting line slope (\( \frac{\partial \Phi}{\partial f} = \frac{2\pi}{c} \cdot x \)) finally find the velocity \( c \) value.

![Figure 2. Phase versus frequency ratio with linear approximation.](image_url)

The measurement of shear acoustic waves velocity in the orthorhombic crystal sample was carried out by phase method. On the opposing sides of the sample, two transducers were attached. Then one of the transducers excited a shear wave pulse in the sample, and the other one detected it. In the course of measurement for each direction and orientation of shear waves approximately 30 000 ultrasonic pulses in the series of 50 were send. Within each series, the properties of the pulses were uniform therefore they were averaged to provide more accurate results. Various pulse series had different frequency, as it changed linearly from 1.4 MHz to 7.2 MHz. The changes in the phase of the signal were also linear.
Table 1. Propagation velocity of longitudinal and transverse ultrasonic modes along axial directions of LNM crystal, and attenuation of longitudinal ultrasonic waves on a frequency of 180 MHz.

| Polarization | $C_\perp$ [m/sec] | L [mm]                  |
|--------------|-------------------|-------------------------|
| ab           | 1279±3            | 4,64±0,1                |
| XZ           |                   |                         |
| ac           | 1187±3            |                         |
| XY           |                   |                         |
| aa           | 4100±10           |                         |
| XX           |                   |                         |
| ba           | 1283±2            | 8,74±0,1                |
| ZX           |                   |                         |
| bc           | 1796±2            |                         |
| ZY           |                   |                         |
| bb           | 5235±10           |                         |
| ZZ           |                   |                         |
| ca           | 1192±2            | 11,53±0,1               |
| YX           |                   |                         |
| cb           | 1801±2            |                         |
| YZ           |                   |                         |
| cc           | 4780±10           |                         |
| YY           |                   |                         |

Attenuation:

- $a=I_2/I_1 = 0.94$;
- $\Gamma = 20±2$ dB/sm·GHz$^2$;
- $a=I_2/I_1 = 0.94$;
- $\Gamma = 9±1$ dB/sm·GHz$^2$;
- $a=I_2/I_1 = 0.92$;
- $\Gamma = 11±1$ dB/sm·GHz$^2$
If we know a simple equation for wave phase \( \phi(x, t) = \omega t - kx + \phi_0 \), it is possible to combine the changes in signal frequency with changes of phases difference in the source and receiver \( \frac{\partial \phi}{\partial f} = \frac{2\pi}{c} \).

Consequently, with the help of values of the sample length along the propagation direction of the wave \( L \) and the angle of the graph of phase versus frequency ratio, it is possible to estimate wave velocity \( c \).

### 2.3. The coefficient of AO figure of merit of crystal LNM

The values of the acousto-optics figure of merit \( M_2 \) for LNM crystal were measured by the Dixon-Cohen method [7]. These measurements taken on a longitudinal ultrasonic wave with a frequency of 80 MHz. Liquid glycerol gluing was used for acoustic contact of the sample and reference AO cell. The reference AO cell (buffer) based on fused silica also used. Research was carried out for three different directions of propagation of longitudinal ultrasound wave (along the axes \( a, b, \) and \( c \)). Each direction of the ultrasound corresponds to two directions of propagation of light with a wavelength of \( \lambda = 633 \) nm and each of the beams had two polarizations corresponds to the intrinsic optical modes of the sample. The results of measuring the \( M_2 \) listed at the table 2. The absolute accuracy of the method is approximately 20%.

**Table 2.** The values of the coefficients of AO figure of merit \( M_2 \) for LNM crystal under isotropic diffraction on a longitudinal wave.

| Direction of propagation of the ultrasound wave | Direction of propagation of the light | Polarization (\( \text{E vector along axis} \)) | Value of the Acousto-optic figure of merit \( M_2 \), \( \times 10^{-18} \text{s}^3/\text{g} \) |
|-----------------------------------------------|--------------------------------------|-----------------------------------------------|-----------------------------------------------------------------|
| a (X)                                        | b (Z), c (Y)                         | a (X)                                         | 10,2±2,0                                                        |
| a (X)                                        | b (Z)                                | c (Y)                                         | 13,1±2,6                                                       |
| a (X)                                        | c (Y)                                | b (Z)                                         | 10,9±2,2                                                       |
| b (Z)                                        | a (X), c (Y)                         | b (Z)                                         | 0,9±0,2                                                        |
| b (Z)                                        | a (X)                                | c (Y)                                         | 1,9±0,4                                                        |
| b (Z)                                        | c (Y)                                | a (X)                                         | 5,6±1,2                                                        |
| c (Y)                                        | a (X), b (Z)                         | c (Y)                                         | 8,1±1,6                                                        |
| c (Y)                                        | a (X)                                | b (Z)                                         | 5,5±1,1                                                        |
| c (Y)                                        | b (Z)                                | a (X)                                         |                                                                  |

Measurements show that the elastic-optical effect in the LNM crystal is relatively good, but the AO figure of merit \( M_2 \) of the LNM crystal in case of diffraction of light at longitudinal ultrasound waves has relatively small values. The maximum value of the measured figure of merit was 15 a.u.. So the maximum value of \( M_2 \) is many time more than \( M_2 \) of the crystalline \( \alpha-\text{SiO}_2 \) and as well as the KGW crystal [8].

It would be better to combine measurements of AO figure of merit on a new specimen larger than in present measurements. It is necessary to use another AO buffer to excite shear acoustic wave to make a research of the AO properties of LNM on shear waves.

### 3. Conclusion

A new optically biaxial crystal LiNa\(_5\)Mo\(_9\)O\(_{30}\) was under research. In such a media, it is possible to create new configurations of AO interaction, which provides new types of electro-optical devices [9, 10]. The maximum received coefficient of AO figure of merit was \( 15 \times 10^{-18} \text{s}^3/\text{g} \). The minimum propagation velocity of ultrasound was 1200 m/s for the shear mode and 4100 m/s for the longitudinal mode. The attenuation of ultrasound in all three directions at a frequency of 180 MHz is not significant, attenuates less or substantially less than 3 dB/cm (\(< < 2 \) times per 1 cm of the wave propagation). All this speaks of the great promise of the LNM crystal for the purposes and tasks of acousto-optic.
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