

The optical properties of LiNbO₃ single crystals obtained in air atmosphere

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(Received 15 January, revised 28 March 1999)

Single crystals of LiNbO₃ were grown by the Czochralski technique in an air atmosphere. The critical diameter and the critical rate of rotation were calculated. X-Ray measurements of the powder were carried out to obtain the lattice parameters. The optical constants were calculated by Kramers-Kronig analysis of reflectance data. The optical properties of LiNbO₃ single crystals were studied for samples grown in an air atmosphere to investigate the influence of air on the optical properties of the formed crystals. A peak due to OH⁻ groups appears in the transmission spectrum at 3385 cm⁻¹. It was still present after annealing in an air atmosphere at temperature up to 873 K, but it was no longer detectable after annealing at 1473 K in an electric field. Thick films of the high-temperature superconductor YBa₂Cu₃O₇ (Ag) were obtained on plates of LiNbO₃ single crystals. The obtained results are discussed and compared with published data.

Key words: single crystals, Czochralski technique, lithium niobate, critical rotation rate, critical crystal diameter, optical properties.

Lithium niobate is a non-linear crystal that is often employed as a poekel cell for Q-switching applications. It offers excellent transmission properties coupled with a high extinction ratio and low halfwave voltage. A well-developed growth and fabrication process allows for the production of large aperture devices. Other applications of lithium niobate include parametric oscillators, external cavity frequency doubles, and acousto-optic devices. Recently surface wave filters fabricated on lithium niobate have been employed as broadcast IF filters in colour television receivers, the output modulator for video games and computer links, while cable television now utilises a lithium niobate vestigial sideband filter in their modulator.¹⁻³

The crystal structure of LiNbO₃ is rhombohedral (trigonal) (space group R3c, point group 3m). The trigonal lattice constants are $a = 0.54944$ nm and $\alpha = 55^\circ 52'$ with equivalent hexagonal parameters of the unit cell $a = 0.5148$ and $c = 1.3863$ nm,

as determined by Abrahams *et al.*⁴ Lithium niobate is insoluble in water, practically inert to acids at room temperature, has density of 4.64 g cm^{-3} , relative molar mass of 147.85, a Mohs hardness of 5, a melting point of 1523 K, a Curie point of 1423 K, a thermal expansion coefficient $\alpha_a = 15.4 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 7.5 \times 10^{-6} \text{ K}^{-1}$ and a thermal conductivity of $4.186 \times 10^{-2} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$. Well-known members of the R3c space group are CaTiO_3 and SrTiO_3 . As SrTiO_3 has been applied as a substrate for superconducting materials,^{5–7} we wanted to determine if LiNbO_3 grown in air atmosphere could be useful as a substrate for superconducting materials. It has been found that LiNbO_3 single crystals could be grown either in an air^{1–3} or in an oxygen atmosphere^{8–10} by the Czochralski technique. In the present work the optical properties of LiNbO_3 single crystals have been studied for samples grown in an air atmosphere in order to investigate the effect of the air atmosphere on the optical properties. It is the second stage in our investigations to determine whether LiNbO_3 can be used as a substrate. The results of the first stage, the study of non-annealed samples, were published in a previous article.¹¹

EXPERIMENTAL

Single crystals of LiNbO_3 were grown in an air atmosphere by the Czochralski technique using a MSR 2 crystal puller as described in Ref. 11. The pull rates were generally in the range of 5–6 mm h^{-1} , and the best results were obtained with a pull rate of 5 mm h^{-1} . The crystal rotation rates were between 35 and 45 rpm. The best results were obtained with a crystal rotation of 35 rpm. The crucible was not rotated during the growth. After the growth run, the crystal boule was cooled at a rate of about 50 °C h^{-1} down to room temperature.

The crystals were annealed in a horizontal resistance furnace in an air atmosphere.

X-Ray measurements of the LiNbO_3 powders were recorded using a Philips PW 1170 instrument in the 2θ range from 10° to 60° using the Cu anticathode wavelength $\alpha_{\text{CuK}\alpha 1} = 0.154051 \text{ nm}$. The anode load was 40 kV and 30 mA. The diffractograms were recorded in steps of 0.02° , with a recording time of 1.25 s for each step.

The optical transmission of the samples were recorded with unpolarised light at normal incidence on a Specord IR 75 spectrometer in the wave number range $(5–40) \times 100 \text{ cm}^{-1}$. The recording time for each spectrum was 4.4 min, a grating of 162 furrows mm^{-1} accompanied with an automatic amplifier. The surrounding medium was air, and all measurements were done at room temperature ($T=295 \text{ K}$). The thickness of the polished sample was 3 mm.

Infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. A new hyper splitter was used for the far infrared region – the newest Bomem's beamsplitter for a wider spectral region (from 30–1000 cm^{-1}) and for the infrared region a standard KBr (400–5000 cm^{-1}) beamsplitter. All spectra were obtained for a near normal incidence configuration at the room temperature ($T=295 \text{ K}$). The polarisation was $E||a$. The thickness of the polished sample was 3 mm.

RESULTS AND DISCUSSION

For common usage, the LiNbO_3 single crystals must be homogeneous in the Li/Nb ratio, colourless for optical applications, free from cracks and low-angle grain boundaries. The last two properties are strongly affected by the shape of the crystal/melt interface, as a strongly domed interface induces thermal stresses in the crystal during cooling which might lead to cracks. An inversion from a convex to a concave interface shape is a source of low-angle grain boundary.¹⁰

The inversion is thought to be caused by a transition of the flows in the melt. The onset of inversion is strongly dependent upon the rotation rate of the crystal in such a way that above a critical rotation rate inversion occurs. It was found that the interface shape is strongly affected by the crystal rotation rate, while the crystal orientation and the melt height have little influence on the interface shape.¹⁰

Many authors have attempted to predict the onset of inversion from the results of growth experiment by relating some growth parameters and material constants. As is well known, four different flows can be observed in a pure melt: free convection, surface tension-driven flow, forced convection by crystal rotation, and forces convection by crucible rotation. These flows are satisfactorily expressed by the Navier-Stokes equations. It is convenient to use dimensionless quantities in order to classify the flows in various melts.

When single crystals are grown by the Czochralski technique, two types of convection are usually observed in the melt. The first is free convection due to the difference in temperatures and the second is forced convection, which is a result of crystal rotation. In some papers^{12, 13} some empirical formulas are proposed for the correlation between the parameters ensuring a flat interface. Using an analysis of the hydrodynamics in oxide melts, attempts have been made to suggest more general dependencies describing the conditions under which a flat crystal/melt interface is obtained. Carruthers¹⁴ related buoyancy-driven and forced convection by setting $Gr=Re^2$, where Gr is the dimensionless Grashof number and Re is the Reynolds dimensionless number. Kobayashi¹⁵ did numerical simulations of the hydrodynamics in oxide melts and gave the ratio $Re^{2.5}/Gr=10$ for inversion. Berkowski *et al.*¹⁶ observed flows in simulation experiments with glycerol-water solutions by adding graphite powder to the solutions, while Nikolov *et al.*¹⁷ continued these simulation experiments measuring the flow velocities of the buoyancy-driven down-flow and the forced up-flow under the crystal. Table I summarise the predicted critical rotation rates derived from the different authors.

TABLE I Relations predicting critical rotation rates

| Proposed relations | |
|---------------------------------------|--|
| Carruthers ¹⁴ | $Gr = Re^2$ |
| Kobayashi ¹⁵ | $Re^{2.5}/Gr = 10$ |
| Berkowski <i>et al.</i> ¹⁶ | $\omega_c = (0.37 \pm 0.06)[Gr/dD]^{2.1}]^{0.4}$ |
| Nikolov <i>et al.</i> ¹⁷ | $\omega_c = 3.2 (g \beta \Delta T)^{0.45} D^{0.25} h^{0.16} v^{0.1} d^{-1.06}$ |
| Normalized form of relations | |
| Carruthers ¹⁴ | $\omega_c = 1.312 (g \beta \Delta T)^{0.5} D^{1.5} d^{-2}$ |
| Kobayashi ¹⁵ | $\omega_c = 4.37 (g \beta \Delta T)^{0.4} v^{0.2} d^{-0.8}$ |
| Berkowski <i>et al.</i> ¹⁶ | $\omega_c = 0.37 (g \beta \Delta T)^{0.4} D^{0.36} v^{0.2} d^{-1.16}$ |
| Nikolov <i>et al.</i> ¹⁷ | $\omega_c = 3.2 (g \beta \Delta T)^{0.45} D^{0.25} h^{0.16} v^{0.1} d^{-1.06}$ |

Figure 1 shows the critical rotation rate vs. the critical diameter of LiNbO₃ single crystals obtained using the relations presented in Table I.¹⁰

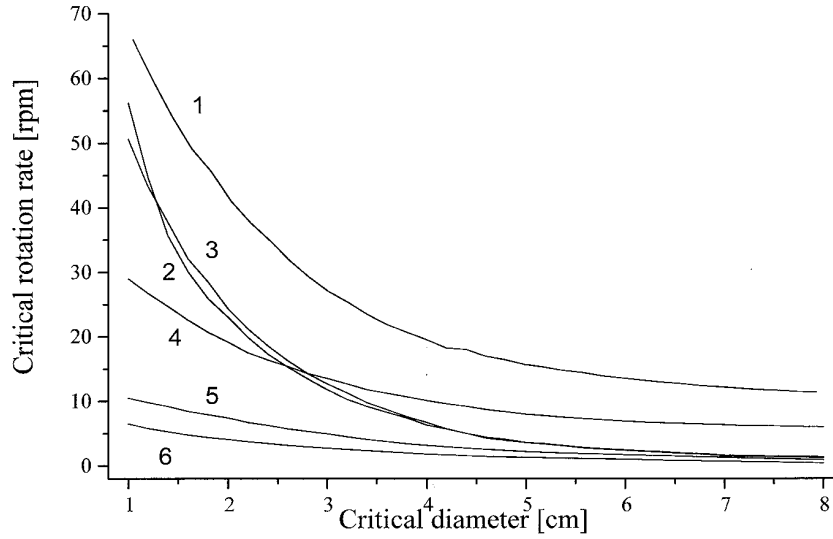


Fig. 1. Plot of the critical rotation rate vs. the critical diameter of LiNbO₃ single crystal derived from Nikolov *et al.*¹⁷ (line 1), Carruthers¹⁴ (line 2), Takagi¹² (line 3), Kobayashi¹⁵ (line 4), Brice *et al.*¹³ (line 5) and Berkowski *et al.*¹⁶ (line 6).

We decided to use the relations derived by Carruthers in calculations for our experimental system. These relations are in a good agreement with the experimental data of many authors^{10–12} and we assumed that it could also be useful in our case.

The critical rotation rate is given¹⁴ by

$$\omega_c = 1.312 (g \beta \Delta T)^{0.5} D^{1.5} d_c^{-2} \quad (1)$$

and the critical crystal diameter

$$d_c = (g \beta \Delta T R^3 \pi^{-2})^{0.25} \omega_c^{-0.5} \quad (2)$$

where ω_c – critical rotation rate, d_c – critical crystal diameter, β – volumetric expansion coefficient of the melt, ΔT – temperature difference, g – acceleration due to gravity, R – crucible radius, and D – crucible diameter.

In our case $\beta = 1.5 \times 10^{-4} \text{ K}^{-1}$, $\Delta T = 30 \text{ K}$, $D = 4 \text{ cm}$, and from Eqs. (1) and (2) the values $\omega_c = 35 \text{ rpm}$ and $d_c = 1.5 \text{ cm}$ are obtained. These results are in a agreement with the published data presented in Fig. 1 and given in the literature.¹⁰ These experimental results explained, (besides the buoyancy-driven convection – Grashof number, and forced convection due to crystal rotation – Reynolds number), the influence of Marangoni flow, which is induced by a temperature variation at the melt-free surface. Marangoni convection (Ma) is given by

$$Ma = -(\partial\gamma/\partial T) \Delta T (R-r) (\rho \nu \alpha)^{-1} \quad (3)$$

where $(\partial\gamma/\partial T)$ – temperature coefficient of surface tension, ΔT – temperature

difference ($T_{\text{crucible}} - T_{\text{mp}}$), R – crucible radius, r – crystal radius, ρ – melt density, ν – kinematic viscosity, and α – thermal diffusivity of the melt.

The conditions for the growth of LiNbO₃ single crystals by the Czochralski technique were optimised. The crystals were pulled at a rate of 5 mm h⁻¹ with a rotation of 35 rpm so that a flat solid/liquid interface was obtained at the required crystal diameter. The obtained crystal boules were colourless and transparent, usually about 15 mm in diameter, and 40 mm long.

The c -axis is perpendicular to the plane of spontaneous cracking and we obtained slices by cutting parallel to the c -axis. The mechanically damaged surface layers were etched off in a hot mixture of two parts HF and one part HNO₃ for about 2 min.¹¹ The [210] or a -axis direction is perpendicular to the direction of spontaneous polarisation, *i.e.*, the [001] direction. All spectra were recorded by polarisation $E \parallel a$ and confirmation for this was the spectrum recorded at the room temperature,¹¹ which is almost identical with the published spectrum.¹⁸

A plot of the spectral transmission of the investigated sample in the wave number range (1500–4000) cm⁻¹ is presented in Fig. 2. It shows that the transmission has an absorption band centred at 3385 cm⁻¹. The cut-off value is at ≈ 1700 cm⁻¹.

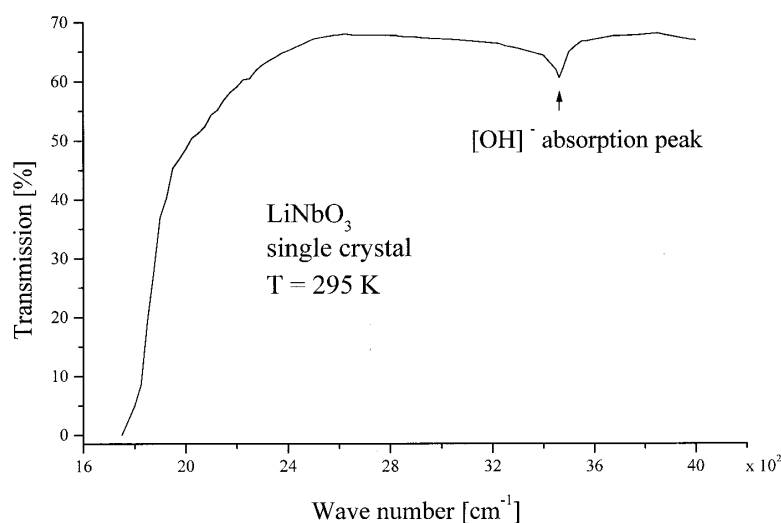


Fig. 2. Plot of the transmission vs. wave number of LiNbO₃ single crystal in the range of 1500–4000 cm⁻¹ at the $T = 295$ K.

This weak absorption band at 3385 cm⁻¹ is caused by OH groups. The origin of its appearance is the air atmosphere used during the process of crystal growth. It is reported in the literature that the OH band can appear between 3700–3200 cm⁻¹ due to hydrogen bonding which extends the OH absorption band and moves it towards lower wave numbers.¹⁹

The usual way of removing OH group from the crystal is by the process of annealing. Annealing was performed in an air atmosphere on polished slices of single crystal of LiNbO_3 first at 373 K to investigate the presence of adhesion-bonded moisture on the surface. The results showed that moisture was not responsible for the peak at 3385 cm^{-1} . Then annealing was performed at 573 K, but with no change. The same results were obtained after annealing at other temperatures up to 873 K. Since temperatures below 873 K are the common annealing temperatures and at higher temperatures oxygen reduction commences, single annealing in an electric field was performed at 1473 K on a sample of a LiNbO_3 single crystal. An air atmosphere was used with an electric field of 3.75 V cm^{-1} , while the process duration was 10 min. After this treatment, the peak at 3385 cm^{-1} disappeared. It should be mentioned that the commonly used LiNbO_3 single crystals are crystals after the process of single domains had been performed, *i.e.*, after annealing.

The polarised infrared reflectance spectra of LiNbO_3 were recorded in the range $30 - 5000\text{ cm}^{-1}$. The range $100 - 2000\text{ cm}^{-1}$ was used for Kramers–Kronig (KK) analysis and the transverse (TO) and longitudinal (LO) frequencies of the optical phonons were obtained. These results were published in our previous article¹¹ and they are almost identical with the parameters published for LiNbO_3 samples grown in an oxygen atmosphere.¹⁸

The structure properties were obtained using X-ray analysis of powdered samples. The diffractometer PW 1710 was used in the 2θ range from 10° to 60° . The unit cell of LiNbO_3 was calculated by the least square method using all 11 reflections including more K_{02} for 5 reflections. The X-ray diffractogram for powdered LiNbO_3 is given in Fig. 3.

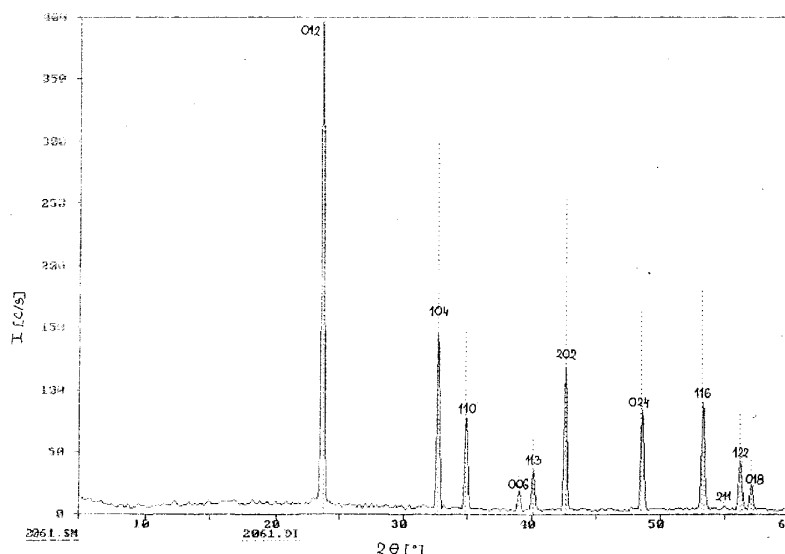


Fig. 3. X-Ray pattern of powdered LiNbO_3 single crystals.

The intensities of the reflections for some crystal planes, together with their Miller indexes and distances between the planes of the reflections are given in Table II. The intensities of the reflections from Fig. 2 are given together with published intensities for the same planes in JCPDS ("Joint Committee on Powder Diffraction Standards").

Table II. The spacing of the lattice planes, Miller indices and intensities for LiNbO₃ given in comparison with the literature data⁸

| d_{exp}/nm | d_{lit}/nm | (hkl) | I/I_{max} | $(I/I_{\text{max}})_{\text{lit}}$ |
|----------------------------|----------------------------|---------|--------------------|-----------------------------------|
| 0.3746 | 0.3754 | 012 | 100 | 100 |
| 0.2735 | 0.2739 | 104 | 36 | 40 |
| 0.2574 | 0.2576 | 110 | 18 | 20 |
| 0.2309 | 0.2311 | 006 | 4 | 4 |
| 0.2248 | 0.2249 | 113 | 7 | 10 |
| 0.2242 | | | 4 | |
| 0.2121 | 0.2124 | 202 | 26 | 10 |
| 0.2115 | | | 12 | |
| 0.1874 | 0.1876 | 024 | 20 | 16 |
| 0.1719 | 0.1720 | 116 | 22 | 20 |
| 0.1714 | | | 10 | |
| 0.1671 | 0.1674 | 211 | 2 | 2 |
| 0.1638 | 0.1638 | 122 | 10 | 12 |
| 0.1633 | | | 5 | |
| 0.1615 | 0.1615 | 018 | 6 | 6 |
| 0.1611 | | | 3 | |

It can be seen from Table II that many of the reflections correspond to LiNbO₃ crystal with the parameter of the hexagonal unit cell $a = 0.5148$ nm and $c = 1.3863$ nm.⁴ Some divergence from compared results can be explained by the fact that X-ray powder diffraction analysis gives statistics result, where, in some case, some reflections can be absent, and the other can appear with higher intensities than they really have.²⁰ Our calculated results for the lattice parameters are $a = 0.51494$ nm and $c = 1.38620$ nm, which are in good agreement with published data. It also has to be said that doublets were found for (hkl) : 113, 202, 116, 122 and 018 which correspond to X-ray reflections of $K_{\alpha 1}$ and $K_{\alpha 2}$, present in the ratio 2:1.²⁰ It has been reported that only almost perfect single crystals can split X-ray reflections into $K_{\alpha 1}$ and $K_{\alpha 2}$ and the presence of doublets is one more confirmation about the quality of the produced crystals.

LiNbO₃ single crystals are a very valuable material as parts of electro-optic devices. The usual method of crystal growth consists of two steps where the first step concerns any method of crystals growth and the second annealing the grown crystal near the Curie temperature in an electric field. It is known that SrTiO₃ is a very suitable material as a thin or thick superconducting substrate. As LiNbO₃ belongs the same group as SrTiO₃ (perovskite structure), it was of great interest to

see if LiNbO_3 could also be used as a substrate. So far we have not found any information on this in the literature. In the present work, the optical properties of LiNbO_3 single crystals, grown and post-annealed in air, have been studied to investigate the influence of air on the crystal quality. It is a continuation of our study of LiNbO_3 as high-temperature superconducting substrate.¹¹

The thick film of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ag) was obtained on a $600\text{ }\mu\text{m}$ thin single crystal of LiNbO_3 by the screen printing technique followed by sintering at 1173 K in oxygen and then slowly cooling to room temperature.²¹ The resistivity curve of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ag) is presented in Fig. 4.

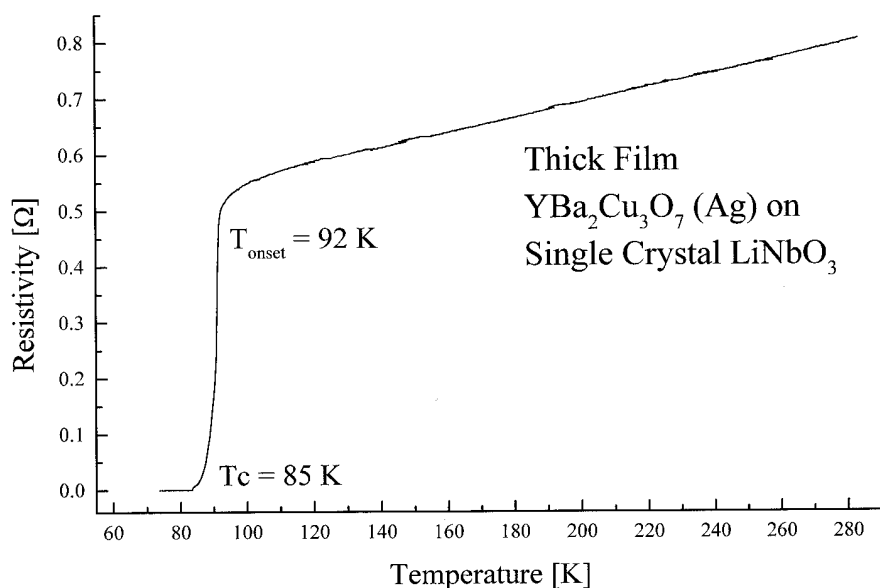


Fig. 4. Resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ag) grown on LiNbO_3 single crystal vs. temperature.

The critical temperature was around 85 K , whereas the superconducting onset was at 92 K . An article about the properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ag) grown on LiNbO_3 substrates will be published.

CONCLUSION

The conditions for growing single crystals of LiNbO_3 were calculated by using a combination of Reynolds and Grashof numbers.

Comparing the optical properties of LiNbO_3 single crystals studied in this paper with the published data for samples grown in an oxygen atmosphere, it can be concluded that the atmosphere generally does not influence the optical properties. The weak absorption band caused by the OH group can be removed during annealing at 1473 K in an electric field of 3.75 V/cm in an air atmosphere. Annealing in an air atmosphere up to 873 K had no influence on the peak in the optical spectrum caused by OH groups.

The first attempt to produce good quality high-temperature superconducting thick films on the new substrate (LiNbO₃ single crystal) proved to be very successful. The critical temperature was around 85 K. With improved sintering conditions we expect to be able to raise the critical temperature up to 90 K.

ИЗВОД

ОПТИЧКЕ ОСОБИНЕ МОНОКРИСТАЛА ЛИТИЈУМ-НИОБАТА ДОБИЈЕНОГ У АТМОСФЕРИ ВАЗДУХА

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Монокристали LiNbO₃ су добијени помоћу технике Чохралског у атмосфери ваздуха. Израчунати су критични пречник и критична брзина ротације. Рендгенска мерења спрашеног узорка су извршена да би се добили параметри решетке. Проучавање су оптичке особине монокристала LiNbO₃ да би се испитао утицај коришћене атмосфере. Из рефлексионих спектра су применом Kramers–Kronig анализе одређене оптичке константе. Пик у трансмисионом спектру на 3385 cm⁻¹ не може да се уклони уобичајеним одгревањима до 873 K у атмосфери ваздуха, али је после монодоменизације на 1473 K уклоњен. Плочице монокристала LiNbO₃ су коришћене као подлога за nanoшење дебелог филма високо температурног суперпроводног YBa₂Cu₃O₇ (Ag). Добијени резултати су дискутовани и поређени са литературним подацима.

(Примљено 15. јануара, ревидирано 28. марта 1999)

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