

Structure and chemistry of LiB_3O_5 (LBO) optical surfaces

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The properties of LiB_3O_5 (LBO) surfaces have been studied with reflection high energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). The superstructure ordering with the relations $a=4a_0$, $b=2b_0$ and $c=2c_0$, where a_0 , b_0 and c_0 are the LBO cell parameters, has been detected by RHEED analysis. Depth profiling by XPS shows that the thickness of the top surface layer contaminated by carbon is ~ 20 Å. Electronic parameters of LBO have been defined for the surface cleaned by ion beam sputtering. The ratio of original elements at the surface is in close relation with the formal composition of LBO.

Key words: lithium triborate, surface, superstructure, chemical composition.

Introduction

Lithium triborate LiB_3O_5 (LBO) is an important nonlinear optical crystal widely used for harmonic generation in visible and UV ranges [1]. LBO is characterized by high optical damage threshold, sufficiently high non-linearity, large acceptance angle and low birefringence that makes it most suitable for high intensity harmonic generation [1-3]. The crystals of LBO possess comparatively high spontaneous polarization and moderate piezoelectric coefficients [4, 5]. By using an ion implantation technique, in near surface layers of LBO substrate optical waveguide structures may be produced [6, 7]. During the last few years methods of LBO crystal growth have been actively developed and today optical-quality single crystals a few hundred grams in weight and with dimensions sufficient for the majority of nonlinear optical applications are available [8-13].

Fabrication of nonlinear optical devices includes as a necessary stage the preparation of polished surfaces with high optical quality. The production of such surfaces on LBO substrates, however, is a difficult technological task because of the relatively low hardness and hygroscopicity of this material [14]. Moreover, it is known that LBO surfaces, either as grown at high temperature [8] or prepared by mechanical polishing at room conditions [15, 16], are not chemically inert and react with the atmosphere with the precipitation of new foreign phases. For practical applications in nonlinear devices the relationships between surface optical damage

threshold and adhesion of optical coatings and real properties of LBO surfaces are of great importance. In this respect the crystal structure and chemical composition of mechanically-polished LBO surface are considered in the present study.

Experimental Methods

A crystal of LBO was grown by the top seeded solution growth (TSSG) method from a flux. The substrates were cut from the part of this crystal without any visible defects or inclusions. The planes [100] were hand polished up to an optical grade. Before observation the surface was cleaned chemically to remove residual polishing materials.

Crystallographic surface properties were investigated by RHEED at an electron accelerating voltage 65 kV. To eliminate charging effects a charge-neutralization flood gun was utilized. Surface electronic parameters were defined using the XPS method. X-ray photoemission spectra were obtained with a MAC-2 (RIBER) analyzer using nonmonochromatic Mg K_α radiation (1253.6 eV). The energy resolution of the instrument was 0.5 eV and the measured full width at half maximum (FWHM) of the $\text{Cu } 2p_{3/2}$ line was 1.4 eV. The binding energy scale was calibrated by reference to $\text{Cu } 2p$ (932.7 eV) and $\text{Cu } 3p$ (75.1 eV) lines yielding an accuracy of ± 0.1 eV in any peak position determination in reference to copper Fermi level. The photoelectron energy drift due to charging effects was taken into account in reference to the position of the $\text{C } 1s$ (284.6 eV) line generated by adventitious carbon on the surface as-inserted into the vacuum chamber. Depth profiling has been produced by ion beam sputtering with Ar^+ of 3 keV energy at a sample current of 100

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nA. The ion beam was rastered over an area $8 \times 22 \text{ mm}^2$. Under these conditions the sputtering rate was estimated to be $0.13 \text{ \AA}/\text{min}$. The sputtering has been continued up to stabilization of the C 1s core level intensity. For bombarded surfaces the progressive shift of binding energy of the C 1s core level to lower energies has been revealed with increasing sputtering time. So, to account for the charge accumulation for the surfaces subjected to Ar^+ bombardment the persistence of the B 1s binding energy was postulated. With this calibration the binding energies of O and Li core levels remained unaffected for all the sputtering times achieved in these experiments.

Results and Discussion

High energy electron diffraction patterns for two mutually perpendicular beam azimuths are shown in Fig. 1(a, b). In intensity the dominant components are monocrystal streaks accompanied by wide Kikuchi lines and a relatively weak diffused background. The crystal phase on the surface was identified as LBO. A background component appeared due to the presence of some surface contaminations. Superstructural ordering has been observed on the surface with the relations $a=4a_0$, $b=2b_0$ and $c=2c_0$. Here a , b and c are the surface ordering lattice parameters and $a_0=8.45 \text{ \AA}$, $b_0=7.38 \text{ \AA}$ and $c_0=5.14 \text{ \AA}$ are the LBO bulk cell constants.

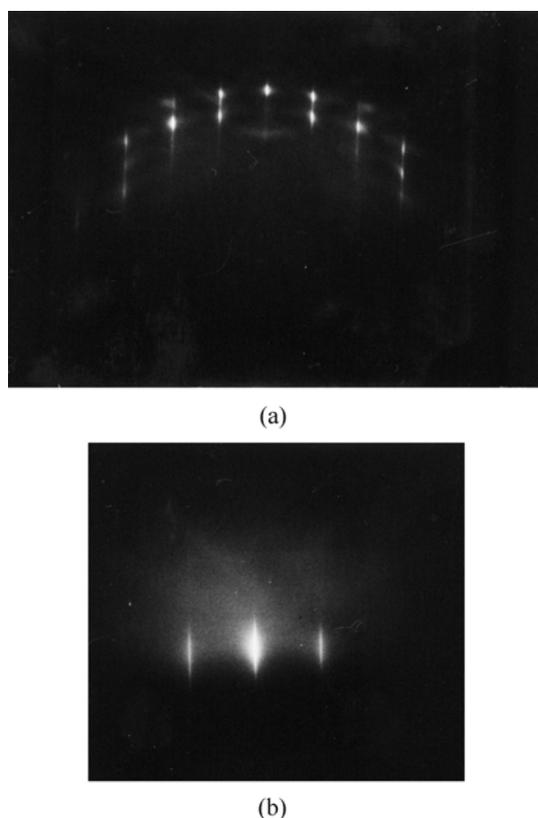


Fig. 1. RHEED patterns of LBO surface. The incident electron beam is parallel to (a) [001] and (b) [010].

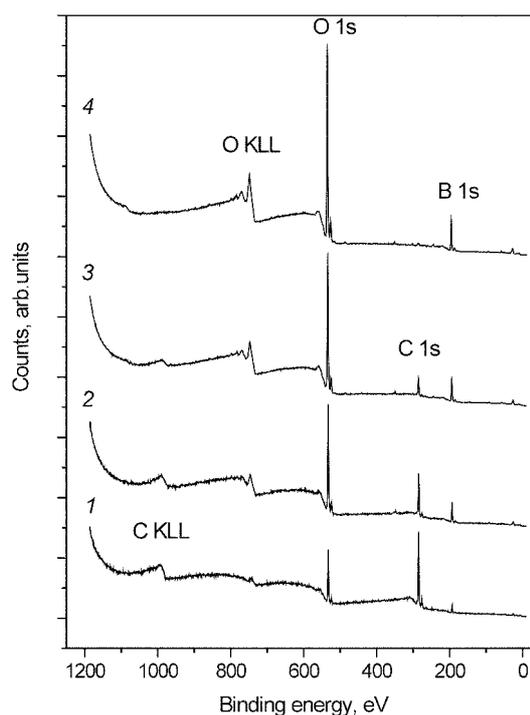


Fig. 2. Survey photoelectron spectra for (1) as-inserted surface and after sputtering for (2) 25 minutes, (3) 80 minutes and (4) 350 minutes.

Survey photoelectron spectra measured at different stages of the surface cleaning with Ar ion beam sputtering are shown in Fig. 2. The most intense contamination on the as-inserted surface is carbon. Besides this, weak signals are detected for Ca, Na and Ba core levels. The admixtures, as it seems, may be inserted into the surface during polishing and subsequent chemical cleaning. On sputtering of the surface by ion bombardment the intensities of the original element core levels increase. The dependencies of the magnitudes of signals of C 1s, B 1s and O 1s levels on sputtering time are presented in Fig. 3. It is seen that the magnitudes of these signals stabilize at times greater than 230 minutes

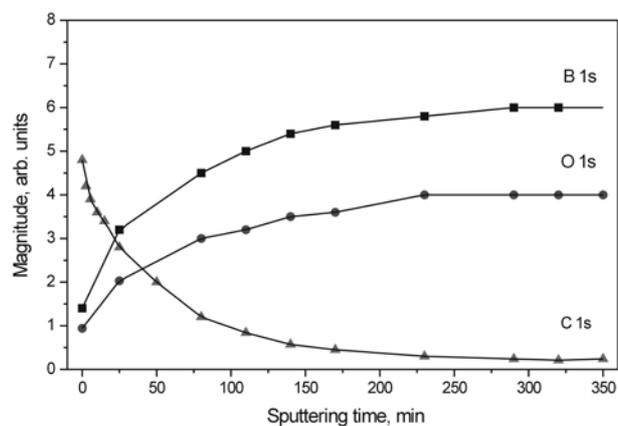


Fig. 3. Dependence of B 1s, C 1s and O 1s level magnitudes on sputtering.

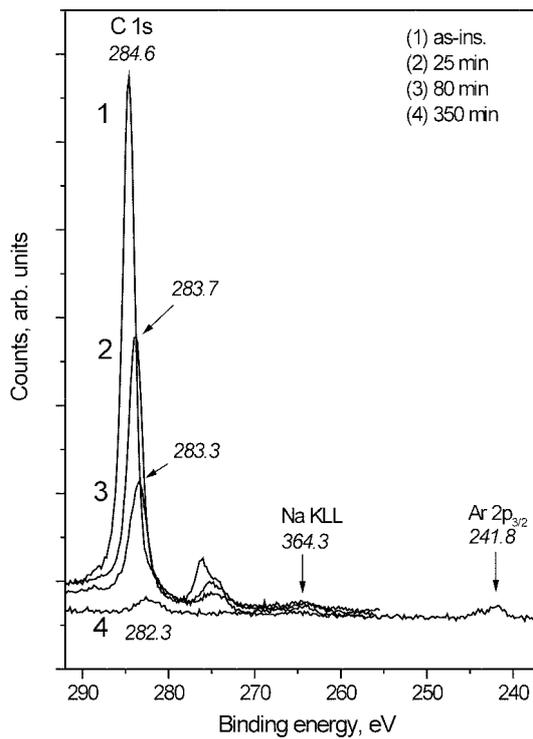


Fig. 4. Detailed spectra for C 1s-Ar 2p range.

but C 1s remains noticeable. Detailed spectra for the photoelectron binding energy range 240-290 eV are shown in Fig. 4. With growth in sputtering time the energy of maximum of C 1s peak shifts to lower energies up to 282.3 finally. Besides the carbon level, the weak signal related to Na KLL Auger-transition proceeds. On sputtering for longer than 80 minutes the 2p-doublet appeared with an Ar 2p_{3/2} binding energy 241.8 eV. Thus on a LBO surface cleaned by sputtering with Ar ion bombardment the relatively intense peak attributed to residual carbon is observed at 282.3 eV. This energy is unusually low for the C 1s core level. Earlier the effect of the gradual shift of the energy of the maximum of the C 1s peak under argon ion bombardment was observed by us during a study of the surface properties of another borate crystal CsB₃O₅ (CBO) and this presumably might be induced by progressive destruction of the skeleton chains of adsorbed hydrocarbons due to interaction with middle energy Ar⁺ ions. However, from the CBO surface the carbon contamination had been removed totally after a relatively short time under similar sputtering conditions. At the

same time on the LBO surface the residual carbon with an atomic concentration C/O=0.05 is revealed repeatedly for different polishing conditions [16]. Thus it seems the formation can be thought as a layer containing the carbons chemically bound to the LBO surface. This specific feature of the LBO surface should be accounted for in the complexity of ion beam polishing techniques actively developed in recent years for the surface performance of optical materials [18-20].

Photoelectron binding energies of Li 1s and O 1s levels remain near the same value with sputtering that confirm the persistence of the type of chemical bonds between the original elements with depth from the surface layer. There was no observed additive shoulder on the high energy side of the O 2s peak detected earlier in [17]. It should be noted that this feature of the O 2s core level was also absent in spectra of the LBO valence band measured for a vacuum-fractured surface [21]. A set of binding energies for the original element core levels and the spectral components of the valence band of the LBO measured after sputtering for 350 minutes is shown in Table 1. For comparison, available literature data for this crystal are also presented here. The most interesting of this data to compare with our results are the electronic parameters of LBO defined in [17] for as-grown crystal face with surface charging accounted by reference to the C 1s level. Evidently, there is nearly an exact agreement in energies of the valence band levels and a small difference in binding energy of the Li 1s core level. For B 1s and O 1s core levels, however, the difference is large and far above possible instrumental error. The energy difference (O 1s-B 1s) in both experiments is nearly the same and equal 339.7 eV. A possible reason for this discrepancy is the presence of a foreign phase on the surface of the as-growth crystal face. The surface phase composition was not tested in [17], at the same time the formation of foreign phases on LBO crystal faces, in particular Li₃B₇O₁₂ in

Table 2. Relative atomic concentrations of Li, B and O

Sputtering time, min	O	B	Li
as-inserted	0.55	0.34	0.11
25	0.54	0.35	0.11
80	0.54	0.34	0.12
350	0.58	0.32	0.09
LiB ₃ O ₅	0.56	0.33	0.11

Table 1. Photoelectron binding energies and spectral components of valence band in LBO

Element	O 1s	C 1s	B 1s	Li 1s	O 2s	C	B	A
This study	532.3 (2.06)	284.6	192.6 (1.83)	55.7	25.0	13.8	9.2	6.3
[17]	531.6	284.6	192.0	55.5	25.0	13.4	10.0	6.2
[21]*	533				21	10	6	2

*binding energies are referenced to the valence band maximum

the atmosphere of a growth chamber, has been reported earlier [8, 16].

The chemical composition of the surface was estimated by area analysis of Li 1s, B 1s and O 1s peaks using the coefficients of relative element sensitivities tabulated in [22]. The results of these calculations are presented in Table 2. Evidently, the relative atomic concentrations of the original elements are in good correlations with formal composition of LBO and only slightly vary with depth.

Conclusions

Mechanically polished LBO surfaces have a monocrystal structure with a minor amorphous component. The chemical composition of the surface defined with XPS is in good agreement with the LiB_3O_5 formula. The main surface contamination is carbon. The thickness of the layer strongly enriched by carbon is ~ 20 Å. The presence of carbonate or hydrate groups has not been detected in the surface while these compounds are typical for surfaces of the crystals containing alkali metal oxides.

References

1. D.N. Nikogosyan, *Appl. Phys.* A58 (1994) 181-190.
2. D.E. Withers, G. Robertson, A.J. Henderson, Yan Tang, Yong Cui, W. Sibbett, B.D. Sinclair and M.H. Dunn, *J. Opt. Soc. Am. B*10[9] (1993) 1737-1743.
3. Yasunori Furukawa, S.A. Markgraf, Masayoshi Sato, Hodetsugu Yoshida, Takatomo Sasaki, Tatsuhiko Yamanaka and Sadao Nakai, *Appl. Phys. Lett.* 65[12] (1994) 1480-1482.
4. S. Matyiasik and Yu.V. Shaldin, *Solid State Physics* 43[8] (2001) 1405-1408 (in Russian).
5. Y. Wang, Y.J. Jiang, Y.L. Liu, F.Y. Cai and L.Z. Zeng, *Appl. Phys. Lett.* 67[17] (1995) 2462-2464.
6. G.M. Davis, L. Zhang, P.J. Chandler and P.D. Townsend, *IEEE Phot. Techn. Lett.* 4[4] (1993) 430-432.
7. G.M. Davis, L. Zhang, P.J. Chandler and P.D. Townsend, *J. Appl. Phys.* 79[6] (1996) 2863-2867.
8. E. Brück, R.J. Raymakers, R.K. Route and R.S. Feigelson, *J. Cryst. Growth* 128 (1993) 933-937.
9. Hah Gyun Kim, Jin Ki Kang, Soon Ja Park and Su Jin Chung, *Opt. Mater.* 9 (1998) 356-360.
10. N.A. Pylneva, N.G. Kononova, A.M. Yurkin, G.G. Bazarova and V.I. Danilov, *J. Cryst. Growth* 198/199 (1999) 546-550.
11. A.B. Kaplun and A.B. Meshalkin, *J. Cryst. Growth* 209 (2000) 890-894.
12. Ji Won Kim, Choon Sup Yoon and H.G. Gallagher, *J. Cryst. Growth* 222 (2001) 760-766.
13. N. Pylneva, V. Kosyakov, A. Yurkin, G. Bazarova, V. Atuchin, A. Kolesnikov, E. Trukhanov and C. Ziling, *Cryst. Res. Technol.* 36[12] (2001) 1377-1384.
14. E. Prochnow and D.F. Edwards, *Appl. Optics* 37[34] (1998) 8130-8131.
15. T.I. Grigorieva, C.C. Ziling, L.I. Isaenko, L.D. Pokrovsky and L.I. Gubenko, *Proc. of IV Int. Conf. "Crystals: Growth, Properties, Real Structure, Applications"*, Alexandrov, Oct. 18-22, 1999, Russia, V.2, p. 57-63.
16. V.V. Atuchin, V.G. Kesler, I.A. Lisova, L.D. Pokrovsky, N.A. Pylneva and A.M. Yurkin, *Proc. SPIE* 4513 (2001) 107-113.
17. A. Yu. Kuznetsov, M.V. Kuznetsov, I.N. Ogorodnikov, A.V. Kruzhalov and V.A. Maslov, *Solid State Physics* 36[3] (1994) 845-848 (in Russian).
18. Tomosumi Kamimura, Yusuke Mori, Takatomo Sasaki, Hidetsugu Yoshida, Takayuki Okamoto and Kunio Yoshida, *Jpn. J. Appl. Phys.* 37[9A] (1998) 4840-4841.
19. Tomosumi Kamimura, Masashi Yoshimura, Yusuke Mori, Takatomo Sasaki and Kunio Yoshida, *Jpn. J. Appl. Phys.* 38[2B] (1999) L181-L183.
20. Yukihiro Morimoto, Shintaro Miyazawa, Yoshio Kagebayashi, Naoki Kitatochi, Toshio Yokota and Jun Sakuma, *J. Mater. Res.* 16[7] (2001) 2082-2090.
21. R.H. French, J.W. Ling, F.S. Ohuchi and C.T. Chen, *Phys. Rev. B*44[16] (1991) 8496-8502.
22. *Handbook of X-Ray Photoelectron Spectroscopy*, by C.D. Wagner, W.M. Riggs, L.E. Devis, J.F. Moulder, G.E. Muilenberg (Ed.), Publ. By Perkin-Elmer Corp. Phys. Elect. Div., 1979, Eden Prairie, Minnesota, USA.