

Structure and chemical properties of optical surfaces of LiB_3O_5 , $\beta\text{-BaB}_2\text{O}_4$, and CsB_3O_5 crystals

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Comparative analysis of structure and chemical properties of mechanically polished surfaces of LiB_3O_5 , $\beta\text{-BaB}_2\text{O}_4$, and CsB_3O_5 nonlinear crystals have been conducted by use of RHEED and XPS methods. It is shown that usually optical surfaces of these crystals are covered with a 5-nm and thicker layer of amorphous material. This modified layer can be removed by mechano-chemical aftertreatment without loss of optical quality, which increases chemical stability of the surface in air.

Introduction

Nonlinear-optical borate crystals are typically characterized by a wide range of optical transmission, relatively small nonlinear coefficients, and quite satisfactory mechanical properties.^{1–3} Transparency in the near UV and record high optical damage thresholds of boric-oxide materials, which allow efficient obtaining of UV harmonics of emissions from solid-state near-IR sources, are of principle importance for practical use of these crystals. The crystals like $\beta\text{-BaB}_2\text{O}_4$ (BBO), LiB_3O_5 (LBO), and CsB_3O_5 (CBO) are widely used for manufacturing of nonlinear elements. Required optical quality of these crystals is provided by already developed crystal growing technologies.^{4–8}

In addition to structure perfection of source crystals, the minimum defect level when polishing optical surfaces is the key technological problem in manufacturing elements for the UV range. Usually mechanical polishing in aqueous suspensions of different fine abrasives is used.^{3,9} However, the combination of low borate hardness, low aquation resistance, and easy amorphization seemingly because B_2O_3 is a classical glass former results in a number of effects reducing the quality of the obtained surfaces. In particular, abradant particles trapping, developed amorphized layer formation, as well as fast degradation of the optical surface in contacting with the atmosphere including the mechanical fracture of the crystal may occur.^{3,10–12} All these factors results in degradation with time of the performance characteristics of nonlinear optical elements, including a decrease of the optical damage threshold. Thus, the principal subject of this study was comparative analysis of physicochemical parameters of mechanically polished surfaces of the LBO, BBO, and CBO and development of methods to stabilize their parameters.

1. Research techniques

The optically polished surfaces of LBO (100), BBO (001), and CBO (001) crystals were obtained

by mechanical polishing in aqueous suspensions of nanodiamonds. Crystallographic surface properties were studied by the method of reflection of high-energy electron diffraction (RHEED) at electron energy of 50 keV. Slow electron gun was used to eliminate surface charging in measurements.

Chemistry and electron properties of a surface were controlled by X-ray Photoelectron Spectroscopy (XPS) technique. Photoelectron spectra were obtained with the use of non-monochromatic radiation of the MgK_α -line (1253.6 eV). Spectral resolution was 0.5 eV. Output energy scale was calibrated to the Cu $2p$ (932.7 eV) and Cu $3p$ (75.1 eV) lines, which provides for accuracy ΔE of ± 0.1 eV in determination of the element lines positions throughout the entire energy range accessible. Surface charge effects were considered in relation to the C $1s$ (284.6 eV) or Ar $2p_{3/2}$ (242.3 eV) lines. As a result of ion sputtering, light surface doping with argon was observed.

2. LiB_3O_5

Combination of Kikuchi lines, single-crystal reflexes, and halo with various ratios of the above component intensities is observed in electron-diffraction patterns obtained by the RHEED method for new-prepared LBO surfaces of samples from different lots. According to interpretation, crystal phase fully agrees with the LBO-structure. The presence of Kikuchi lines is an evidence of high structure perfection of the volume, while the intense halo, which is shown in Fig. 1a as an example, is the evidence of the presence of amorphous phase on the surface.

As known from practical experience, earlier invisible small scratches appear on the initially smooth polished LBO-surface on the third day of contact with air under room conditions. Background intensity and halo in RHEED pictures increase during this time interval, which points to increase of amorphous substance fraction within the limits of ~ 50 -Å thickness analyzed.

As shown earlier, partially crystallized metaboric acid HBO_2 is one of the final product of the reaction

observed at $T = 24^\circ\text{C}$. Surface layer dehydration is observed at $T \sim 300^\circ\text{C}$ with reduction of different lithium borates, other than LiB_3O_5 , at $T \sim 500^\circ\text{C}$.¹³ The above temperature intervals agree with the characteristic temperatures of water-containing borates dehydration with the release of anhydrous amorphous phase.¹⁴

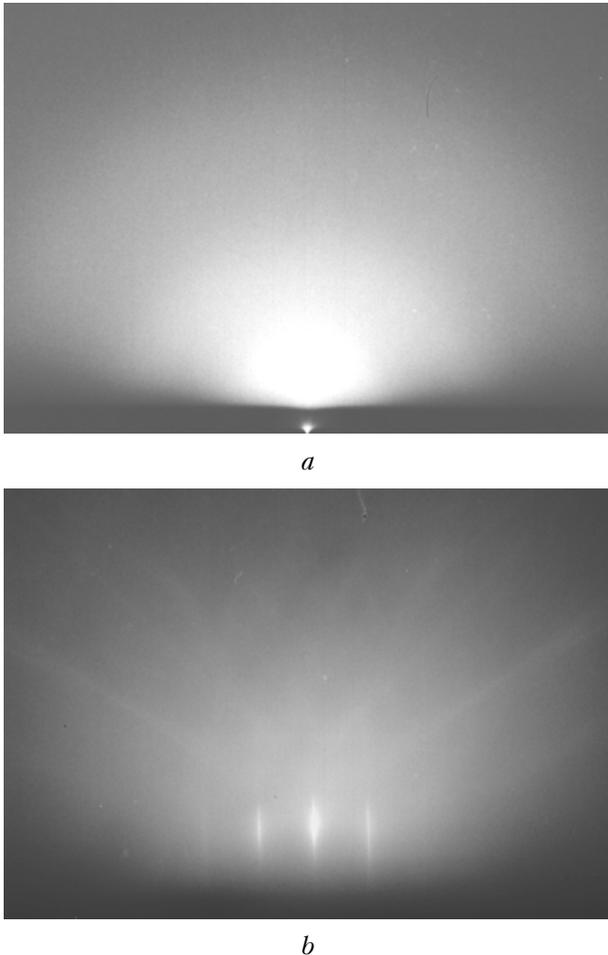


Fig. 1. High-energy (50 keV) electron diffraction from a surface (100) LBO: after mechanical polishing (*a*) and after additional mechanochemical treatment (*b*). Electron beam is directed along [010].

Thus, the following sequence of processes occurring on the LBO-surface can be assumed. Amorphized substance fills small scratches and defects at the final stages of polishing creating illusion of a defect-free flat surface. Precise chemistry of the amorphous phase is uncertain and depends on peculiarities of the polishing process. In contacting with air, the above substance interacts with water vapor and its physical volume increases, which results in flatness distortion of the optical surface of the crystal.

When it is possible to obtain an LBO-surface of optical quality just after mechanical polishing or with the help of additional mechanochemical treatment in glycerinated media, without amorphous phase, the surface lifetime increases; it remains stable

during 1 month.^{15,16} Figure 1*b* shows diffraction from such an LBO-surface. High stability of crystal LBO-surface is indirectly proved by quantum-chemical calculations, which have shown the crystal lattice doesn't catch molecules of adsorbed H_2O .¹²

3. $\beta\text{-BaB}_2\text{O}_4$

In the case of polished BBO surface only background without any sign of diffraction on lattice has been detected by the RHEED method. Typical picture of electron diffraction is virtually the same as in Fig. 1*a*, i.e., the crystal surface is covered with a thick layer of amorphous substance. Estimated by the ellipsometry method, this layer is about 300-nm thick.¹¹ As chemistry analysis by the XPS technique showed, the amorphous phase contains, in addition to basis elements Ba, B, and O, a great deal of carbon, at least in two different states. The detailed XPS spectrum for the C 1s level is shown in Fig. 2. Here the spectral component with the energy of 284.6 eV corresponds to hydrocarbons, adsorbed from the atmosphere, while less intense component with the energy of 288.0 eV is characteristic for carbonate groups CO_3^{2-} .

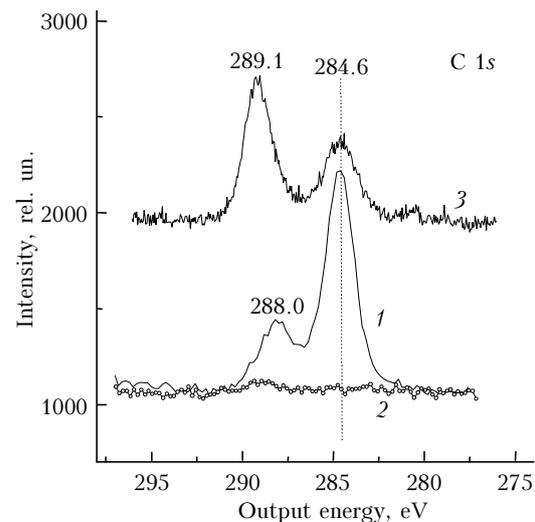


Fig. 2. Detailed XPS-spectrum of the C 1s level: 1 corresponds to polished BBO surface, 2 is to the same surface after ion sputtering during 95 min, and 3 corresponds to BaCO_3 powder.

The close to it line at 289.1 eV is observed for BaCO_3 powder. Analysis of detailed spectra of other element lines and the valence band has shown the amorphized BBO, $\text{Ba}(\text{OH})_2$, and carbonates to be the principal chemical components of the amorphous layer obtained as a result of polishing.¹¹ This amorphous layer can be skinned by means of bombardment of a surface by Ar^+ ions with the energy of 3 keV. Thus skinned surface is totally amorphous though it has electron parameters which are characteristic of pure crystal BBO.¹⁷ Hence, BBO can easily be amorphized by means of ion bombardment; chemical stability of such a surface exposed to air needs in an additional

study. The mechano-chemical polishing method is seemingly more promising for producing chemically clean surface of the BBO crystals.¹⁷

4. CsB₃O₅

Pictures obtained by RHEED method for polished surface have shown only diffuse background accompanied by Kikuchi lines at a high diffraction angle.¹⁸ Thus, relatively thick amorphous layer (about 5 nm) covers structure-perfect substrate material in this case as well. Lines of the principal elements Cs, B, and O prevail in XPS spectra for the initial surface.¹⁹ Carbon, which relates to adsorbed hydrocarbons, is the main foreign impurity on the surface. The presence of carbonate groups and some amount of Na inside the amorphous layer is also seen in XPS spectra, recorded consecutively for the above-listed elements at depth profiling by the method of surface ion sputtering. The obtained depth profiles of the line intensities of the principal elements and carbon are shown in Fig. 3.

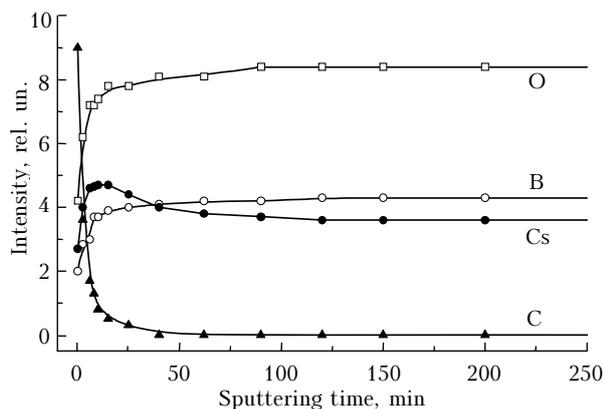


Fig. 3. Intensity profiles of Cs $3d_{5/2}$, B $1s$, O $1s$, and C $1s$ lines as functions of time of CBO surface ion sputtering.

As is seen from Fig. 3, carbon impurity is localized in the surface layer while XPS spectra after 50 min of sputtering are completely free of this impurity. Intensities of lines of the principal element stabilize after about 100 min of bombardment on the level close to indicated chemistry of CsB₃O₅. Long bombardment obviously causes sputtering of the substrate material. Maximum signal from Cs is observed at the initial stages of the sputtering; this points to significant (~25%) enrichment of the surface layer with caesium. It is especially interesting, that after sputtering the signal intensity of a sample gradually rises from the Cs $3d_{5/2}$ in storing in an ultrahigh-vacuum chamber or in room-temperature air, i.e., the enrichment of the surface layer with caesium gradually restores due to Cs diffusion from the substrate at $T = 22^\circ\text{C}$. The nature of increased caesium content on the CBO surface is not yet clarified, but it can be assumed that the effect is associated with the initial stages of forming the phase, more rich in caesium than CBO.

Conclusion

The performed analysis of physicochemical characteristics of polished surfaces of three borate crystals, which are commonly used in nonlinear optics, allow us to elicit some effects determined by specific features of the materials. As could be expected, virtually complete amorphization of the substrate surface layer of these relatively soft materials is the most characteristic feature for mechanically polished borate crystals. The above-mentioned modified layer determines chemical stability of optical LBO, BBO, and CBO surfaces in air. The amorphized layer can be practically completely removed by applying an additional mechanical treatment in special media without any loss of the optical quality of the crystals. The surface of an LBO crystal obtained by this method is relatively stable at room temperature in air while degradation of an CBO-crystal continues due to uptake of water vapor from the atmosphere, as it follows from calculations.¹²

The most important parameter of nonlinear optical elements is optical damage resistance of a crystal surface and antireflection coatings. According to data from Refs. 3 and 20, this parameter, especially for CsLiB₆O₁₀ crystal, significantly increases after skinning of the upper layer of a polished surface by ion bombardment. Similar improvement of the optical stability can be expected for surfaces of the LBO, BBO, and CBO crystals obtained by means of mechano-chemical treatment. However this hypothesis requires experimental validation.

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