

Structure and chemical composition of CsB₃O₅ (CBO) optical surface

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Abstract Polished surface of CsB₃O₅ (CBO) has been observed by reflection high energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). For comparison, electronic properties of CBO powder have been studied by XPS. It has been found that the crystal surface is covered by thick amorphous layer with chemical composition closely related to that of CBO. Great enrichment of top surface by cesium, ~30% in reference to the bulk of the modified layer, has been displayed by depth profiling.

Key words Cesium triborate, Surface, XPS, RHEED, Depth profiling

1. Introduction

Cesium triborate CsB₃O₅ (CBO) is a nonlinear optical (NLO) crystal that can be used for deep ultraviolet generation up to 185 nm [1,2]. This crystal is characterized by wide transparency range 167~3000 nm, high bulk optical damage threshold ~26 GW/cm², broad angular acceptance bandwidth, small walk-off angles and large effective NLO coefficient for UV light generation [1-6]. Cesium triborate is a congruent compound and can be grown from both a stoichiometric melt or a solution [7-10]. Present state of CBO crystal growth technique permits to yield large crystals up to 120 g in weight with high optical uniformity [6, 11].

Practical applications of any optical crystal for harmonic generation, besides enough big size in synchronism direction and low level of bulk light scattering, request for creation of high-performance end faces of nonlinear device. At the same time it is known that borate crystals are difficult materials for polishing because of relative softness and hygroscopicity [12]. As a result of interaction with polishing materials crystal surface exhibits great modification. Such effects as strong amorphization of β -BaB₂O₄ [13] and LiB₃O₅ [14], surface contamination of CsLiB₆O₁₀ by ZrO₂ [15] has been reported for borate crystals. As to chemical stability of the surface of borate crystals polished up to optical grade, the

findings are very scare. Moisture induced degradation of CsLiB₆O₁₀ has been studied in [16, 17]. As to CBO, it is only known from practical experience that this material has hygroscopicity like β -BaB₂O₄. So, the main aim of our study is the determination of the real structure and chemical composition of CBO surface mechanically polished to optical grade.

2. Experimental

CBO crystal was grown from a slightly Cs₂O-enriched melt by top seed solution growth (TSSG) method. The commercially available 99.9% purity Cs₂CO₃ and B₂O₃ were used for the charge preparation. The exact saturation point 825.1°C was determined by repeated seeding. The single crystal with the typical dimensions 23×21×11 mm³ was grown for the growth period of five days. The substrate was cut from the crystal part having no visible defects or scattering. The plane (001) was polished to optical grade with water-based suspension of nanodiamonds (0.3 μ m) and cleaned chemically to remove the residuals of polishing materials from the surface.

Crystallographic surface properties were investigated by RHEED at electron accelerating voltage 50 kV. For charging effect elimination the charge-neutralization flood gun was utilized. Element composition and surface electronic parameters were defined with XPS method. X-ray photoemission spectra were obtained with MAC-2 (RIBER) analyzer using nonmonochromatic Mg K α radiation (1253.6 eV). The energy resolution of the instrument was 0.5 eV

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and measured full width at half maximum (FWHM) of Cu $2p_{3/2}$ line was 1.4 eV. Binding energy scale was calibrated in reference to Cu 2p (932.7 eV) and Cu 3p (75.1 eV) lines yielding the accuracy of ± 0.1 eV in any peak position determination in reference to copper Fermi level. Photoelectron energy drift due to charging effects was taken into account in reference to the position of C 1s (284.6 eV) line generated by adventitious carbon on the surface as-inserted into vacuum chamber. Depth profiling has been produced by ion beam sputtering with Ar^+ energy 3 keV at sample current 100 nA. The ion beam was rastered over the area 5×14 mm². Under the conditions the sputtering rate was estimated as 0.25 Å/min. For bombarded surfaces the progressive shift of binding energy of C 1s core level to lower energies has been revealed with increasing sputtering time. So, to account the charge accumulation for the surfaces subjected to Ar^+ bombardment the persistence of Cs 4d binding energy was postulated. This calibration was chosen because the photoelectrons binded from this core level are characterized by highest kinetic energy and, respectively, are excited from deeper layers with minimum influence of very surface layers. It should be pointed that under the convention the binding energies of all other Cs core levels remains unaffected for all sputtering times achieved in experiment. To pick out the effects induced by the surface layer damaged by interaction with ion beam, when the time of sputtering by 3 keV Ar^+ beam achieves 400 min, the energy of ions was changed on 1.5 keV and sputtering was continued for 150 min. After this all element core levels were measured again. As a final step the calibration of energy scale drift was checked. For this the sample was pulled out from vacuum chamber and had been exposed to laboratory air during 2 h for restoring the layer of adsorbed hydrocarbons on the surface. Then the sample was inserted again into XPS chamber and the detailed spectrum was recorded for C 1s-Cs 4s energy interval in one range. Now, if to adjust the maximum of C 1s peak to 284.6 eV, then the Cs 4s core level has the same energy as for bombarded surface. This confirms the validity of current energy calibration in reference to Cs 4d core level.

For reference, the X-ray photoelectron spectra were measured also for CBO powder. For this purpose CBO crystal piece was grinded and pressed into freshly prepared indium foil. The over-all contact time of the powder with air from grinding to insertion into vacuum chamber was not above 10 min. The C 1s level of hydrocarbons adsorbed at the surface was taken as the

internal reference at 284.6 eV.

3. Results and Discussion

For polished CBO surface RHEED patterns displays the background signal and Kikuchi lines in far zone. So, thick amorphous layer of modified material covers the surface. The survey XPS spectra for as-inserted substrate surface and CBO powder are shown in Fig. 1. Only the signals of original elements Cs, B, O and adventitious carbon are visible. Detailed spectra for C 1s-Cs 4s binding energy range are presented in Fig. 2. The basic features of the spectra from powder and polished surface are nearly the same. Two foreign components have been detected on the substrate surface. The Mo 3d doublet at ~ 222 eV is evidently related to sample holder. Also the weak feature is prominent at ~ 263.5 eV in the substrate spectra. This level was attributed to Na KLL signal revealing some contamination of the surface by sodium during polishing or chemical cleaning. The O 1s core levels corresponding to CBO substrate and powder are shown in Fig. 3. Comparing the shape of the lines, one can see the similarity of the spectra, so the chemical state of oxygen in CBO crystal and amorphous phase covering polished crystal surface is the same. The spectral range B 1s-Cs 4p is shown in Fig. 4.

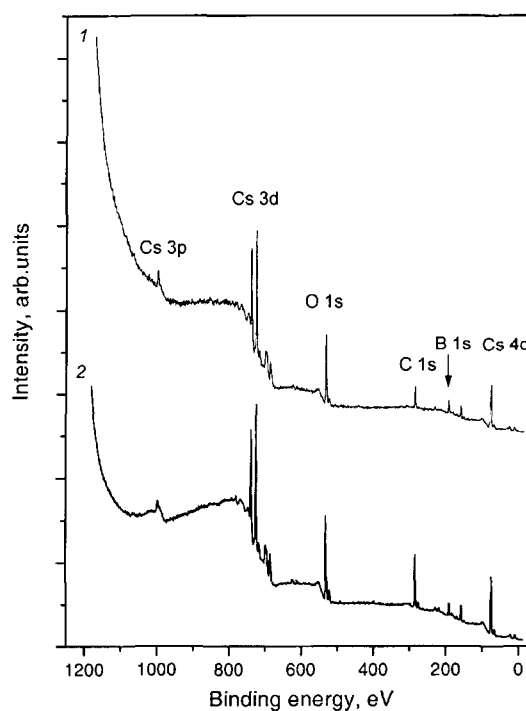


Fig. 1. Survey X-ray photoelectron spectra for CBO (1) crystal surface and (2) powder.

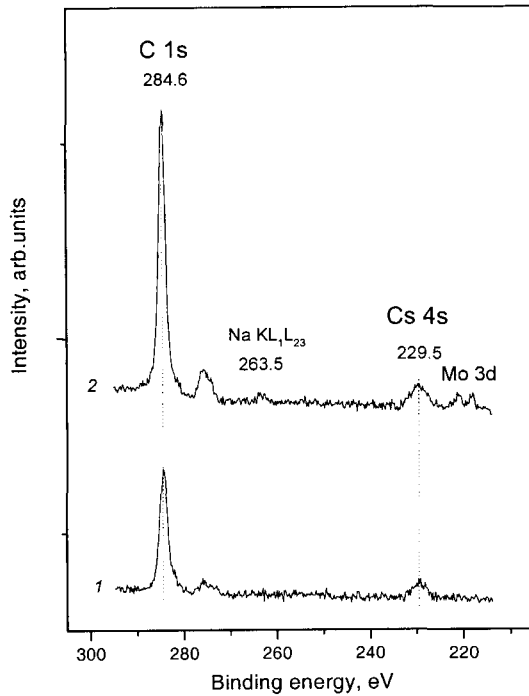


Fig. 2. C 1s-Cs 4s photoelectron binding energy range: (1) powder and (2) crystal surface.

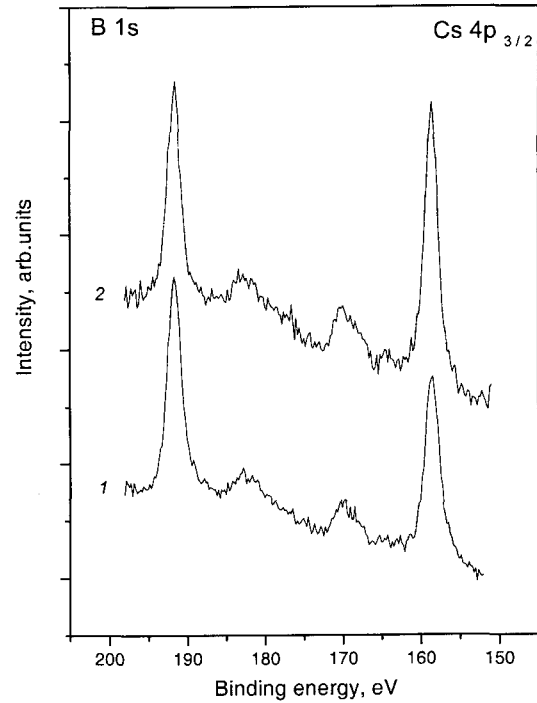


Fig. 4. B 1s-Cs 4p binding energy range: (1) powder and (2) crystal surface.

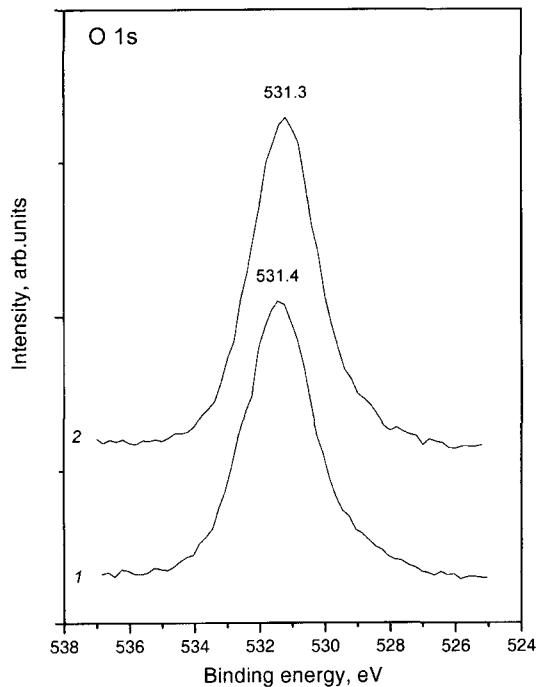


Fig. 3. O 1s core level for CBO (1) powder and (2) crystal surface.

The spectrum from the substrate surface is essentially identical to the B 1s and Cs 4p doublet of CBO powder exhibiting the same chemical state of boron and cesium ions in the both cases. It should be noted that complex structure of Cs 4p_{1/2} component at 170 eV appeared due

Table 1
Binding energies (eV) and FWHM of original element core levels in CBO

Core level	CBO powder	Polished surface
O 2s	23.7	23.7
B 1s	191.7 (1.83)	191.7 (1.80)
Cs 4s	229.5	229.5
O 1s	531.4 (2.19)	531.3 (2.09)
Cs 3d _{5/2}	724.3 (1.95)	724.3 (1.94)
Cs 3p _{3/2}		997.6
Cs 3p _{1/2}		1064.7

to Coster-Kronig fluctuation effect. The binding energies of the original elements and half-widths (FWHM) of the core levels measured for as-inserted substrate surface and CBO powder are presented in Table 1. The Auger parameter of Cs is 1293.0 eV that is very close to the value 1292.8 eV measured in CBO powder.

It is interesting to compare the boron and oxygen binding energies with available data for another borate crystal LiB₃O₅ (LBO) [14, 18]. From X-ray structure data it is known that both CBO and LBO are constructed from a continuous network of (B₃O₇)⁵⁻ groups with interstitial cesium and lithium cations, respectively [19]. Both lithium and cesium in oxide compounds are in the highest oxidation state and minor influence of alkali ion type on chemical bonding in (B₃O₇)⁵⁻ group may be supposed. In this case the binding energies of

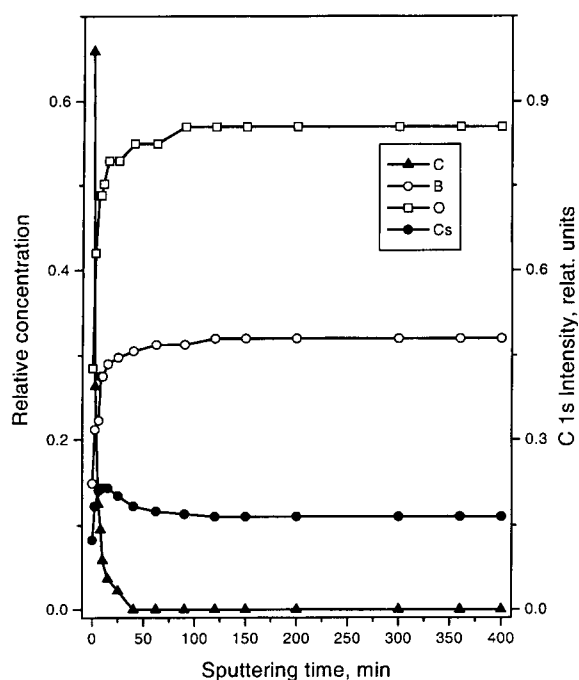


Fig. 5. Chemical composition of CBO polished surface as a function of sputtering time.

boron and oxygen should be the same in both CBO and LBO. To avoid the problems induced by the variations in absolute calibration of binding energy scale, the differences of core level binding energies (O 1s-B 1s) are compare for characterizing the B-O bonding. In CBO the value of (O 1s-B 1s) is 339.7 eV and in LBO 339.7 eV [14] and 339.6 eV [18]. Evident coincidence of the parameter in both materials verifies the identity of boron oxidation state in $(B_3O_7)^{5-}$ cluster in CBO and LBO.

To check the chemical composition of the amorphous layer, depth profiling for the original elements and carbon has been produced with bombardment by Ar^+ , 3 keV ions. The intensities of the lines C 1s, Cs $3d_{5/2}$, B 1s and O 1s are shown in Fig. 5 as a function of sputtering time. Surface carbon contamination has been removed completely after 40 min sputtering. Coincidentally the synchronous increase of the magnitudes of B 1s and O 1s lines has been observed up to saturation. A very unusual dependence of Cs $3d_{5/2}$ line intensity has been detected with depth. There is a pronounced bulge at short sputtering times that reveals the increased Cs content in top surface layer in reference to the bulk. Calculations give 33 % Cs surface enrichment comparing with saturation level in the depth. After first bombardment cycle the sample was kept in high vacuum chamber for 5 h. Next profiling confirms the restoration of Cs enriched top surface layer but with few lower cesium level. So, the segregation of cesium ions to surface occurs

even in vacuum and at 20°C. Similar effect was also detected after 2 h keeping in air. In the latter case the surface cesium content was 6 % higher than that in the depth.

Chemical composition of the layer has been calculated by area analysis of Cs $3d_{5/2}$, B 1s and O 1s core levels. Regrettably, the relative element sensitivities Cs : B : O reported in available literature are very diverse [20-22]. Relative sensitivity Cs : B = 24.3 used in further calculations was, however, determined by us specifically for CBO crystal powder taking the chemical composition Cs : B = 1 : 3 as a basis. The relative sensitivity B : O = 4.0 reasonable, as it seems, for borate crystals was determined previously by us with using LBO crystal sample. The composition calculated from the element peak areas, measured immediately after 400 min of the first sputtering cycle, was Cs : B : O = 0.36 : 1 : 1.80 that is in close relation with CBO nominal composition Cs : B : O = 0.33 : 1 : 1.67. So, in the depth of modified layer the amorphous compound created by polishing is characterized by nearly the same chemical composition as original CBO. Top surface layer composition is another matter; this region is strongly enriched by Cs and, probably, is unstable in time when contacts with air.

4. Conclusions

Thus, polished CBO surface has a very complex, multilayer structure. The CBO crystal is covered by a layer of amorphous material with chemical composition varied through the depth. Far from the surface the amorphous compound has a composition similar to that of CBO but the top surface layers are strongly enriched by Cs. The cesium redistribution over depth is observed experimentally in real time scale and at room temperature. It may be supposed that this factor governs the stability of optical properties of polished CBO surface. Evidently, it is reasonable to test the element distribution over depth in another nonlinear borate materials, LBO for example, searching for similar effects.

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