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Growth, optical and microstructural properties of PbB_4O_7 plate crystals

A.I. Zaitsev [a], A.S. Aleksandrovsky [b], A.S. Kozhukhov [c,f], L.D. Pokrovsky [d], V.V. Atuchin [d,e,f,*]

[a] Laboratory of Crystal Physics, Kirensky Institute of Physics, SB RAS, Akademgorodok, Krasnoyarsk 660036, Russia
[b] Laboratory of Coherent Optics, Kirensky Institute of Physics, SB RAS, Akademgorodok, Krasnoyarsk 660036, Russia
[c] Laboratory of Nanodiagnostics and Nanolithography, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia
[d] Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia
[e] Functional Electronics Laboratory, Tomsk State University, Tomsk 634050, Russia
[f] Novosibirsk State University, Novosibirsk 630090, Russia

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ABSTRACT

Centimeter-sized optical quality plate-like PbB_4O_7 crystals have been grown by Czochralski method. The fundamental absorption edge has been found at 237 nm (corresponding bandgap 5.75 eV) with the distinct sideband protruding up to 300 nm. The crystals are well faceted with the (100), (010) and (101) planes, (100) surfaces being mostly developed. The etching in diluted nitric acid (5 wt.%) at the temperature of 90 °C have been used to reveal the defect structure and remove melt residuals. The (100) surface shows the presence of etching pits and twin boundaries. The Kikuchi line pattern and developed microrelief with the roughness of ~8 nm have been observed by RHEED and AFM, respectively.

1. Introduction

The noncentrosymmetric optical borate crystals are the basic materials of modern high-power laser systems because of appropriate nonlinear optical (NLO) coefficients, a wide transparency window including visible and UV ranges, and high optical damage thresholds [1–19]. Orthorhombic lead tetraborate PbB_4O_7 (PBO) was discovered in binary system $PbO–B_2O_3$ many years ago [20–22]. The PBO crystal is isostructural with SrB_4O_7 (SBO), and its structure belongs to the *mm*2 point group. The space group used throughout the present paper is $Pmn2_1$. The crystal structure of PBO is shown in Fig. 1 [23–25]. The PBO structure is formed by the rigid three-dimensional framework of corner-linked BO_4 tetrahedrons, and lead atoms occupy large cages in the structure and are coordinated by nine oxygen atoms. Such framework structure is common for the MB_4O_7 (M = Sr, Pb, Eu) crystal family and provides a very high hardness up to ~1270 kg/mm^2 and nonhygroscopicity of the borates [14,26]. PBO is a nonlinear crystal with a rather large nonlinearity of the second order, optical transparency over the spectral range of 235–4000 nm and comparatively low birefringence [26–28]. Besides, PBO possesses a large Raman-type nonlinearity of the third order [29,30]. The electrooptic, piezoelectric, acoustic and acoustooptic properties of PBO are among the highest ones for borate crystals [31–34]. Other PBO properties are less studied.

A prominent feature of SBO and PBO crystals is the formation of a strongly pronounced growth faceting even in the case of Czochralski growth from a stoichiometric melt [26,28]. In this context, our objective is to evaluate the microstructural properties of PBO surface and compare them to such borates as LiB_3O_5 (LBO), CsB_3O_5 (CBO) and β-BaB_2O_4 (BBO) widely used in frequency conversion devices. The hardness of these borate crystals is comparatively low and, as it was found in the previous experimental studies, the optical surface of LBO, CBO and BBO prepared by mechanical polishing methods is typically covered by a thick amorphous modified layer with badly controlled parameters, and that is crucial for many effects [35–37]. As for the MB_4O_7 family, previously, high surface chemical stability was found for SrB_4O_7 powder in the air [14], and, respectively, similar properties would be supposed for the PBO surface.

2. Experimental

The PbB_4O_7 single crystal has been grown from the melt by Czochralski method. The charge has been prepared from $2PbCO_3 \cdot Pb(OH)_2$ and H_3BO_3 taken at the stoichiometric ratio. Crystal growth was performed in the air from a platinum crucible 50 mm in diameter and 70 mm high with 300 grams of the charge. The seed oriented in the [100] direction was used. The plate-like

* Corresponding author at: Institute of Semiconductor Physics, Novosibirsk 630090, Russia. Tel.: +7 (383) 3308889; fax: +7 (383) 3332771.
E-mail address: atuchin@isp.nsc.ru (V.V. Atuchin).

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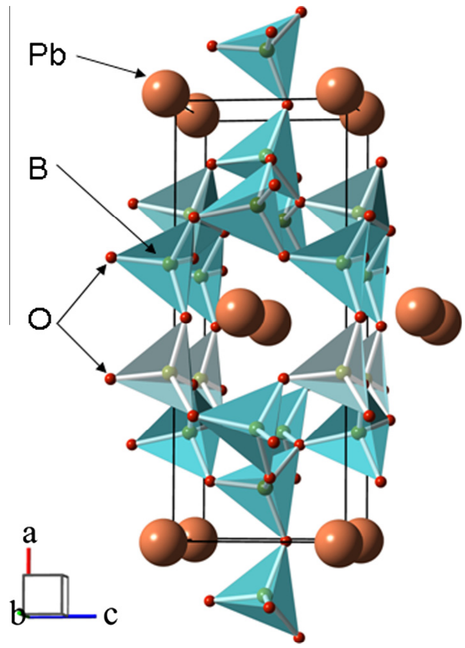

Fig. 1. PbB_4O_7 crystal structure. The unit cell is outlined. Lone boron and oxygen atoms are omitted for clarity.

transparent, colorless PbB_4O_7 single crystal with dimensions $2 \times 22 \times 38$ mm along [100], [010] and [001] directions, correspondingly, was grown in three days. The growth process included starting the growth without pulling (the rotation rate was 8 rpm) for two days and the growth with pulling rate 1.2 mm/day for one day. This crystal had several rather well developed facets; especially pronounced were the facets corresponding to planes (100), (010) and (101). From the as grown crystal, the sample was cut off in order to remove the part near the seed crystal. The (100) facets were not cut or polished during this procedure, and, hence, the top surface layer on these facets is not modified. However, the sample was subjected to etching in diluted nitric acid (5 wt.%) at the temperature of 90 °C for 10 min in order to reveal the defects and remove residual melt species.

The unpolarized transmission spectrum of the unpolished etched crystal was measured in direction (100) with Shimadzu UV-3600 spectrophotometer. The structural properties and micromorphology of the etched PbB_4O_7 (100) surface have been observed by RHEED using EFZ4 device at the electron energy of 50 keV, and AFM measurements were performed with Solver P-47H device in the noncontact mode.

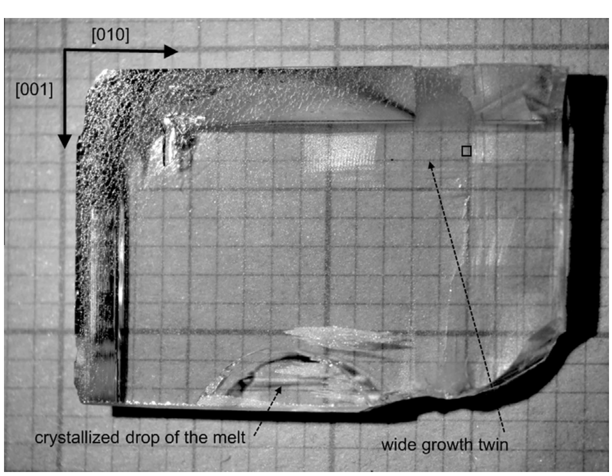

Fig. 2. Bottom growth facet (100) of the PBO crystal after etching.

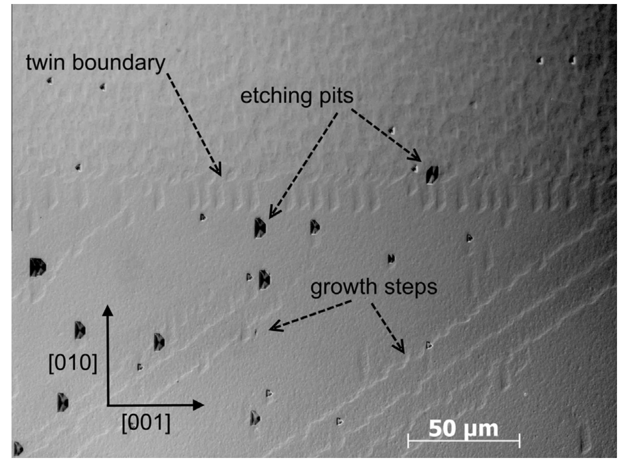

Fig. 3. Etched bottom (100) growth facet of the PBO crystal (square-marked in Fig. 2).

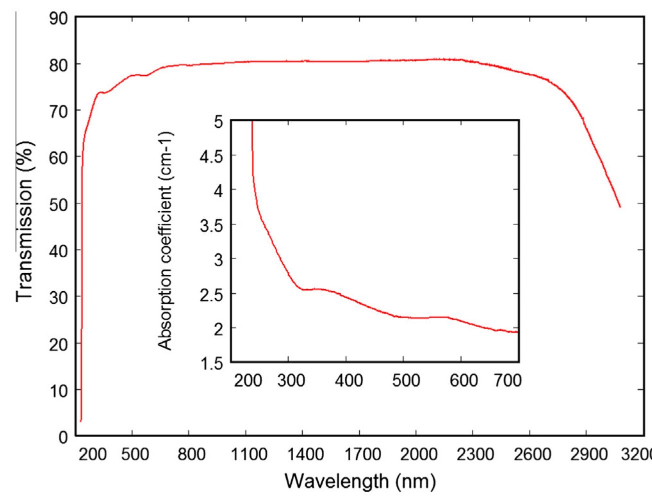

Fig. 4. Unpolarized transmission spectrum of PBO crystal in the direction of (100) axis. Inset: absorption in the UV and visible ranges.

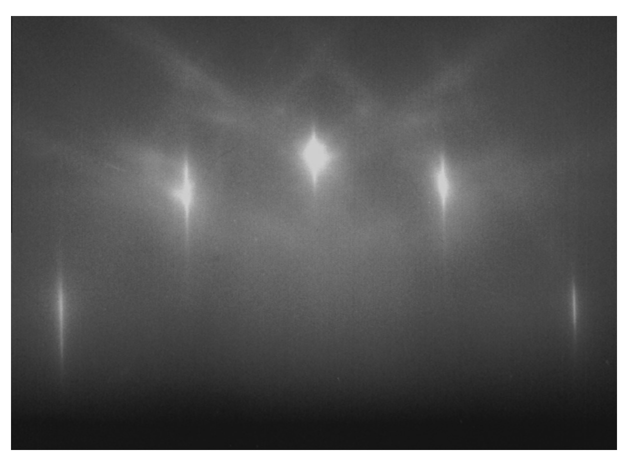

Fig. 5. RHEED pattern recorded from (100).

3. Results and discussion

The PBO sample is shown in Fig. 2. A system of defects has been revealed by optical microscopy. The growth steps and boundaries of polar growth twins can be observed on as-grown surfaces. Etching the as-grown (100) surface revealed etching pits, being the dislocations outcrop onto the surface. The etching patterns observed on this surface reveal the stripes of different etching behavior that means the existence of twins, despite (100) is not a polar surface. Twin boundaries probably correspond to (010) planes, in accordance with the isostructural SBO crystal. The twin boundary nature of the observed stripes is admitted by the difference of etching pits symmetry in twin-free regions and twin boundaries as shown in Fig 3.

The PBO transmission spectrum is presented in Fig. 4. Generally, it is similar to that reported in [26]. The fundamental absorption edge is found at 237 nm (corresponding bandgap 5.75 eV) with the distinct sideband protruding up to 300 nm. Fundamental absorption must be formed mainly by the transitions originating from $^1S_0 \rightarrow {}^3P_1$ transition of free Pb^{2+} ion that is split into two components at least in nine-fold asymmetric crystal field within PBO crystal. Additional band observed in [26] at 350 nm is found in our sample, too; it can be assigned to interband transition originating from weaker transition $^1S_0 \rightarrow {}^3P_0$ of a free ion. In difference from [26], we observe an additional weak absorption band at 550 nm that must be assigned to unidentified impurities.

The system of Kikuchi lines has been recorded from the (100) surface by RHEED observation as shown in Fig. 5. This indicates a high structural quality of the grown facet (100) etched in dilute nitric acid. Thus, this method can be successfully used for the preparation of PBO (100) surface without an amorphous component that is typically appearing after mechanical polishing of borate crystals, when more complex chemical treatment was needed to remove the modified layer from the surface [35–37]. The topographical $10 \times 10\ \mu m^2$ AFM image and surface profile are shown in Fig. 6. Commonly, the etched (100) surface contains a lot of pits up to several nm deep. Thus, the etching conditions selected were excessively severe and lower temperature and/or shorter time may be used to keep the grown top (100) facet surface. In the future,

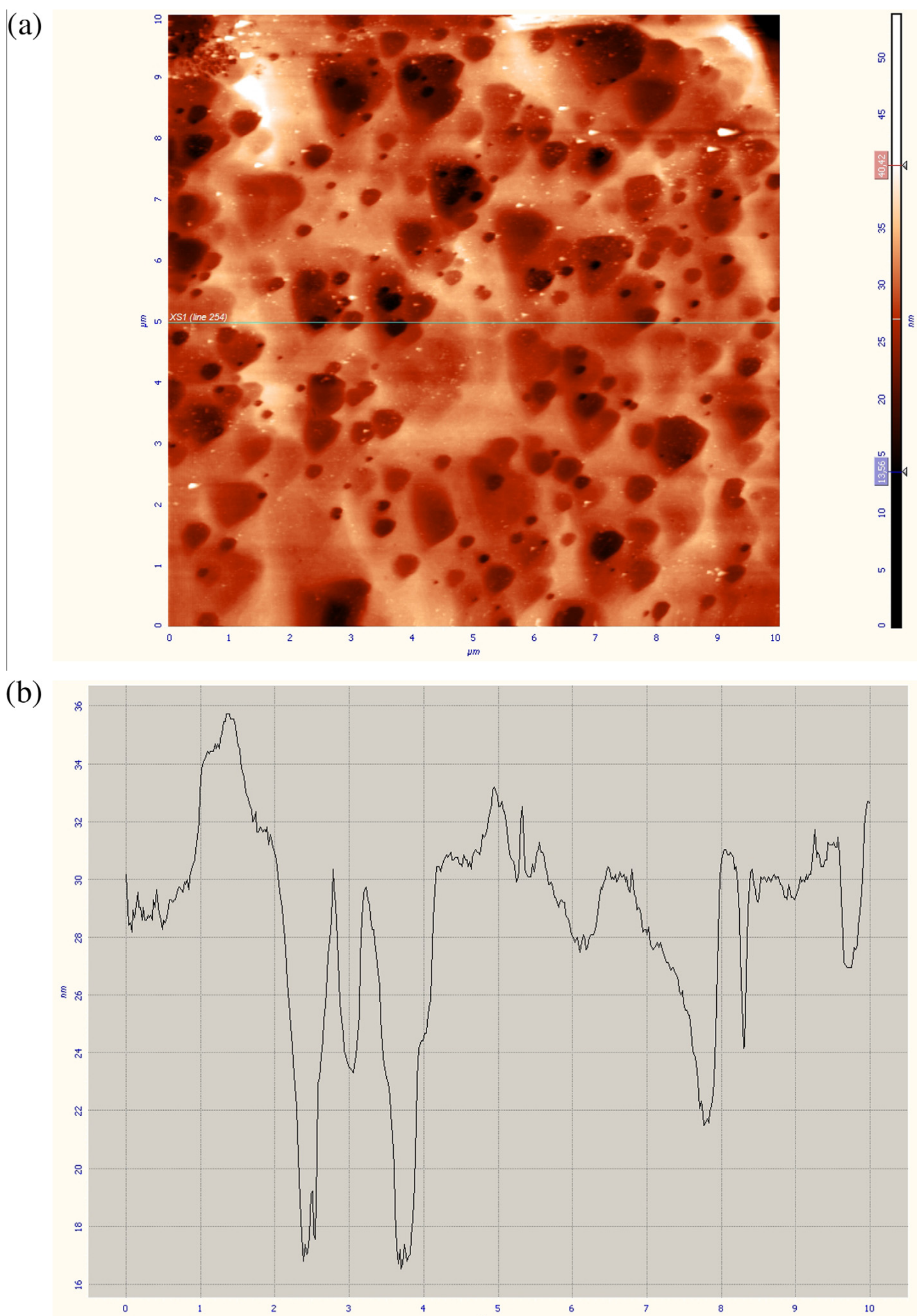

Fig. 6. AFM pattern recorded from (100) etched surface: (a) panoramic view and (b) depth profile.

the PBO (1 0 0) samples can be used for detailed observation of the electronic structure with surface-sensitive techniques, for example, by X-ray photoelectron spectroscopy (XPS). Previously, similar results were found for the LBO growth facet (1 1 0) [38,39]. For the surface, high crystallinity and low contamination level were verified with RHEED and XPS, respectively. Above this, high inertness of LBO (1 1 0) surface to the air agents was found on keeping at ambient conditions [38]. Similar properties can be reasonably supposed for the PBO (1 0 0) surface.

Thus, PBO possesses good optical properties and high surface stability valuable in many NLO applications. However, in difference to a lot of known NLO borate crystals, PBO lacks large enough birefringence, that hinders obtaining angular phase matching for nonlinear optical conversion processes. Observation of polar growth twins reported in the present paper indicates the possibility to obtain other kinds of phase matching that are already employed in isostructural SBO crystal [40–42].

4. Conclusions

Centimeter-sized plate-like optical quality PbB_4O_7 crystals can be grown from the melt by Czochralski method. The crystals are well faceted with developed (1 0 0) surfaces. The short-duration etching in hot nitric acid is able to remove the residual melt contaminations from the surface and expose the bulk crystallinity. Such prepared (1 0 0) surface possesses the Kikuchi line pattern observed by RHEED analysis. However, the AFM observation reveals a developed microrelief of the etched surface, and the etching conditions used in the present experiment should be further optimized to minimize the microrelief formation.

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References

[1] C. Chen, Z. Lin, Z. Wang, Appl. Phys. B 80 (2005) 1–25.
[2] Feng Chen, Laser Photon. Rev. 6 (5) (2012) 622–640.
[3] A.P. Vasilenko, A.V. Kolesnikov, E.M. Trukhanov, N.A. Pylneva, A.M. Yurkin, V.V. Atuchin, J. Phys.: Condens. Matter 15 (2003) 6801–6808.
[4] A.S. Korotkov, V.V. Atuchin, Proc. SPIE 6258 (2006) 62580B.
[5] A.H. Reshak, S. Auluck, I.V. Kityk, Phys. Rev. B 75 (2007) 245120.
[6] A.H. Reshak, S. Auluck, I.V. Kityk, J. Phys.: Condens. Matter 20 (2008) 145209.
[7] A.S. Aleksandrovsky, A.D. Vasiliev, A.I. Zaitsev, A.V. Zamkov, J. Cryst. Growth 310 (18) (2008) 4027–4030.
[8] A.H. Reshak, X. Chen, S. Auluck, I.V. Kityk, J. Chem. Phys. 129 (2008) 204111.
[9] A.H. Reshak, S. Auluck, I.V. Kityk, Appl. Phys. A 91 (2008) 451–457.
[10] A.H. Reshak, S. Auluck, I.V. Kityk, J. Solid State Chem. 181 (2008) 789–795.
[11] A.H. Reshak, X. Chen, I.V. Kityk, S. Auluck, K. Iliopoulos, S. Courtis, R. Khenata, Curr. Opin. Solid State Mater. Sci. 12 (2008) 26–31.
[12] V.V. Atuchin, B.G. Bazarov, T.A. Gavrilova, V.G. Grossman, M.S. Molokeev, Zh.G. Bazarova, J. Alloys Compd. 515 (2012) 119–122.
[13] X. Yan, S. Luo, Z.S. Lin, Y.C. Yue, X.Y. Wang, L.J. Liu, C.T. Chen, J. Mater. Chem. C 1 (2013) 3616–3622.
[14] V.V. Atuchin, V.G. Kesler, A.I. Zaitsev, M.S. Molokeev, A.S. Aleksandrovsky, A.A. Kuzubov, N.Y. Ignatova, J. Phys.: Condens. Matter 25 (8) (2013) 085503.
[15] R. He, H.W. Huang, L. Kang, W.J. Yao, X.X. Jiang, Z.S. Lin, J.G. Qin, C.T. Chen, Appl. Phys. Lett. 102 (2013) 231904.
[16] K. Li, G.C. Zhang, S. Guo, X. Zhang, R. He, J.X. Zhang, Z.S. Lin, Y.C. Wu, Opt. Laser Technol. 54 (2013) 407–412.
[17] R. Möckel, C. Reuther, J. Götze, J. Cryst. Growth 371 (2013) 70–76.
[18] V.V. Atuchin, S.V. Adichtchev, B.G. Bazarov, Zh.G. Bazarova, T.A. Gavrilova, V.G. Grossman, V.G. Kesler, G.S. Meng, Z.S. Lin, N.V. Surovtsev, Mater. Res. Bull. 48 (2013) 929–934.
[19] A.V. Malakhovskii, T.V. Kutsak, A.L. Sukhachev, A.S. Aleksandrovsky, A.S. Krylov, L.A. Gudim, M.S. Molokeev, Chem. Phys. 438 (2014) 137–143.
[20] S. Block, A. Perloff, C.E. Weir, Acta Cryst. 17 (1964) 314–315.
[21] A. Perloff, S. Block, Acta Cryst. 20 (1966) 274–279.
[22] H.S.A. Kumar, C.G. Bergeron, J. Cryst. Growth 22 (1974) 58–60.
[23] D.L. Corker, A.M. Glazer, Acta Cryst. B 52 (1996) 260–265.
[24] W.-D. Stein, J. Liebertz, P. Becker, L. Bohatý, M. Braden, Eur. Phys. J. B 85 (7) (2012) 236.
[25] Tadashi C. Ozawa, Sung J. Kang, J. Appl. Cryst. 37 (2004) 679.
[26] Yu.S. Oseledchik, A.L. Prosvirin, A.I. Pisarevskiy, V.V. Starshenko, V.V. Osadchuk, S.P. Belokrys, N.V. Svitanko, A.S. Korol, S.A. Krikunov, A.F. Selevich, Opt. Mater. 4 (1995) 669–674.
[27] J.F.H. Nicholls, B.H.T. Chai, D. Russell, B. Henderson, Opt. Mater. 8 (1997) 185–191.
[28] K.S. Bartwal, R. Bhatt, S. Kar, V.K. Wadhawan, Mater. Sci. Eng. B 85 (2001) 76–79.
[29] A.A. Kaminskii, L. Bohatý, P. Becker, J. Liebertz, L. Bayarjargal, J. Hanuza, H.J. Eichler, H. Rhee, J. Dong, Laser Phys. Lett. 4 (9) (2007) 660–667.
[30] J. Hanuza, M. Mączka, J. Lorenc, A.A. Kaminskii, P. Becker, L. Bohatý, J. Raman Spectrosc. 39 (2008) 409–414.
[31] L. Bohatý, Z. Kristallog. 164 (1983) 279–283.
[32] X.R. Zhang, Q.L. Zhang, Y.N. Lu, C.M. Gan, P.Z. Fu, H. Yin, J.L. Zhou, Appl. Phys. A 66 (1998) 351–355.
[33] Qing-Biao Zhou, Shu-Yi Zhang, Yue-Kai Lü, Mater. Sci. Eng. B 83 (2001) 249–253.
[34] I. Martynyuk-Lototska, T. Dudok, O. Mys, R. Vlokh, Opt. Mater. 31 (2009) 660–667.
[35] V.V. Atuchin, L.D. Pokrovsky, V.G. Kesler, L.I. Isaenko, L.I. Gubenko, J. Ceram. Proc. Res. 4 (2) (2003) 84–87.
[36] V.V. Atuchin, L.D. Pokrovsky, V.G. Kesler, N.Yu. Maklakova, M. Yoshimura, N. Ushiyama, T. Matsui, K. Kamimura, Y. Mori, T. Sasaki, Opt. Mater. 23 (2003) 377–383.
[37] V.V. Atuchin, V.G. Kesler, A.E. Kokh, L.D. Pokrovsky, Appl. Surf. Sci. 223 (2004) 352–360.
[38] V.V. Atuchin, V.G. Kesler, I.A. Lisova, L.D. Pokrovsky, N.A. Pylneva, A.M. Yurkin, Proc. SPIE 4513 (2001) 107–113.
[39] V.V. Atuchin, V.G. Kesler, I.A. Lisova, L.D. Pokrovsky, N.A. Pylneva, A.M. Yurkin, Cryst. Res. Technol. 38 (10) (2003) 896–902.
[40] A.S. Aleksandrovsky, A.M. Vyunishev, A.I. Zaitsev, V.V. Slabko, Appl. Phys. Lett. 103 (2013) 251104.
[41] A.S. Aleksandrovsky, A.M. Vyunyshev, I.E. Shakhura, A.I. Zaitsev, A.V. Zamkov, Phys. Rev. A 78 (2008) 031802.
[42] A.S. Aleksandrovsky, A.M. Vyunyshev, A.I. Zaitsev, V.V. Slabko, Phys. Rev. A 82 (2010) 055806.