Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth of $CdWO_4$ crystals by the low thermal gradient Czochralski technique and the properties of a (010) cleaved surface

E.N. Galashov [a], V.V. Atuchin [b,c], A.S. Kozhukhov [d], L.D. Pokrovsky [b], V.N. Shlegel [e,*]

[a] *Department of of Applied Physics, Novosibirsk State University, Novosibirsk 630090, Russia*
[b] *Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[c] *Tomsk State University, Tomsk 634050, Russia*
[d] *Laboratory of Nanodiagnostics and Nanolithography, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[e] *Laboratory of Crystal Growth, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russia*

ARTICLE INFO

Keywords:
A1. Atomic force microscopy
A1. Surface structure
A2. Czochralski method
B1. Cadmium compounds
B1. Tungstates

ABSTRACT

The high-quality $CdWO_4$ crystal of 80–90 mm in diameter and 180–200 mm long has been grown by Low Thermal Gradient Czochralski technique (LTG Cz). Large area atomically flat $CdWO_4$(010) substrates have been prepared by cleavage. The $CdWO_4$(010) surface is stable in the air up to 600 °C. At higher temperatures, the precipitation of WO_3 and $W_{19}O_{55}$ oxides has been detected by RHEED.

1. Introduction

Cadmium tungstate, $CdWO_4$, related to the family of wolframite-type crystals $A^{2+}WO_4$ is well-known as one from the best scintillating mediums [1–7]. The potentials of this crystal for Raman laser systems are under considerations because of good spectroscopic parameters [8–10]. Effective luminescent powder samples of $CdWO_4$ were prepared with the help of facile chemical synthesis methods and good photocatalytic properties were found for the tetragonal modification [11–14]. Two polymorph modifications are known for cadmium tungstate where the monoclinic wolframite-type phase is thermodynamically stable at normal conditions and the tetragonal structure is observed at pressures beyond 35 GPa [15,16]. The formation of tetragonal $CdWO_4$, however, is possible at normal conditions under optimal selection of the chemical route [13]. The crystal structure of wolframite-type $CdWO_4$ is illustrated in Fig. 1 [15,17]. The parameters of monoclinic cell of $CdWO_4$ are $a=5.0400(8)$ Å, $b=5.8701(6)$ Å, $c=5.0841(7)$ Å, $\beta=91.476(19)^\circ$, $V=150.36(1)$ Å^3, and $Z=2$, space group $P2/c$. A chain-type structure is formed by parallel zigzag chains of distorted CdO_6 and WO_6 octahedrons spreading along the c axis. Similar to other crystals from wolframite family, the $CdWO_4$ crystals are characterized by good cleavage properties of the (010) planes [8,18–20]. Recently, the microstructural properties of $ZnWO_4$(010) cleaved surface were elucidated in details and it was found that large-area atomically-flat surface formation is possible for high-quality $ZnWO_4$ wolframite crystals [21,22]. The $CdWO_4$ and $ZnWO_4$ are from the wolframite family and similar cleavage properties may be supposed in both materials. Thus, the present study is aimed at the evaluation of morphological and structural properties, and thermal stability of the $CdWO_4$(010) cleaved surface. The $CdWO_4$ crystals grown by Low Thermal Gradient Czochralski technique (LTG Cz) were used for cleaved surface preparation. One of the essential features of the LTG Cz technique is the low thermoelastic stresses in the crystal. Respectively, the crystals are less susceptible to post-growth cracking and the dislocation density is much lower in the crystals grown by the LTG Cz technique. The results of $CdWO_4$ crystal growth along the [010] direction are considered in this report.

2. Experimental

The high-quality inclusion-free $CdWO_4$ crystal of 80–90 mm in diameter and 180–200 mm long was grown by LTG Cz. The special purity WO_3 (NIIC SB RAS, Russia) with Si content <50 ppm and transition metals content <1 ppm was prepared by the original technology [23]. High purity CdO (99.995%, Toho Zinc, Japan) was used without further purification. In the LTG Cz technique, the evaporation and decomposition of the melt is much lower than that in the traditional version of the Cz crystal growth. Therefore, the initial charge was prepared in the stoichiometric composition. $CdWO_4$ synthesis was being carried out in the platinum crucible at the diameter of 100 mm at 1000 °C for 6 h. The melt was kept at the temperature above the melting point by 10–15 °C to homogenize the melt. The crystal growth was carried out at the ratio of

---

[*] Corresponding author. Tel.: +7 383 3308889, fax: +7 383 3332771.
E-mail address: shlegel@niic.nsc.ru (V.N. Shlegel).

0022-0248/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2014.01.029

Please cite this article as: E.N. Galashov, et al., Journal of Crystal Growth (2014), http://dx.doi.org/10.1016/j.jcrysgro.2014.01.029

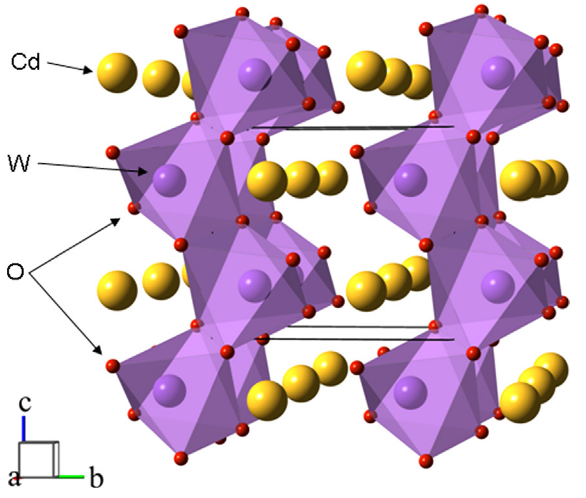

Fig. 1. Crystal structure of $CdWO_4$, wolframite. Unit cell is outlined. Lone atoms are omitted for clarity.

Fig. 2. The $CdWO_4$ crystals grown by LTG Cz method.

crystal diameter to the crucible diameter of 8:10. This diameter relation significantly decreases the open part of the melt surface and, therefore, reduces volatile components evaporation from the melt. The cooling process after the growth was carried out at the rate of 80 °C/h.

The substrates of $CdWO_4$(010) with dimensions $12 \times 0.7 \times 12\ mm^3$ were fabricated by accurate cleaving of a single crystal parallelepiped. The cleavage was produced with a steel knife. After cleaving, the substrates were washed in acetone and distilled water to remove the residual crashed material from the surface. The surface micromorphology was studied by atomic force microscope(AFM) Solver P-47H in the semicontact mode. The top-surface crystallographic properties were evaluated with RHEED using EFZ4 device at the electron energy of 50 keV. To see the thermal stability of the $CdWO_4$(010) surface, a substrate was annealed in the air over the temperature range of 400–700 °C. A platinum box was used as a container to avoid the surface contamination.

3. Results and discussion

The large volume $CdWO_4$ crystal grown by LTG Cz method is shown in Fig. 2. The main problem of $CdWO_4$ crystal growth along the [010] direction is the thermoelastic stresses arising in the crystal due to temperature gradients. Generally, it is particularly difficult to prepare the layered wolframite family crystals with perfect cleavage planes by the crystal growth under high temperature gradients. High radial temperature gradients in combination with the relatively weak (010) interplanar coupling leads to a splitting of the crystal by the cleavage planes. On the other hand, a strong connection in the (010) plane provides the surface stability during crystal growth. When crystals are grown along the [010] direction with a convex shape of the growth front, it is difficult to avoid the so-called “facet effect” [24]. When the crystallization front concaves, this effect appears on the periphery of the crystal. Evidently, the effect generates the inhomogeneity of the crystal bulk properties due to different growth mechanisms at the solidification front and the unstable position of the border coexistence faces and rounded shapes. The problem of thermal stress can be solved by drastic lowering of the temperature gradients down to <1 °C/cm. In parallel, this opens the opportunity to realize the layer-by-layer growth mechanism not only for the (010) plane. When LTG Cz technique is used, the stable coexistence of the (010), (110), (100) planes and a rounded surface is observed at the crystallization front of the $CdWO_4$ crystal. The coexistence of facets and rounded shapes at the solidification front leads to improper result either under high or low temperature gradients. Due to the high stability of the (010) plane at the crystallization front, it is relatively easy to implement the same type of growth mechanism over the crystallization front. Keeping the conditions over the entire length of the growing crystal can get high homogeneity of physical parameters over the crystal bulk in comparison with the crystal grown by the traditional Cz technique.

The topographical $10 \times 10\ \mu m^2$ AFM image and surface profile are shown in Fig. 3. Commonly, the cleaved $CdWO_4$(010) surface is formed by a system of wide plane terraces with as low roughness as ~0.2 nm and the typical area of 3–10 mm^2. The set of terraces is evident in Fig. 3(a). The elementary level step between the terraces is very close to cell parameter *b*, as it is evident from Fig. 3(b). Thus, the cleaved $CdWO_4$(010) surface can be considered as the atomically flat one. However, at the terrace surface, the point defects of 15–30 nm in diameter can be found by wide AFM observation that is typical of the cleaved crystal surface [22,25–27]. The system of Kikuchi lines shown in Fig. 4 was found for the $CdWO_4$(010) substrate by RHEED observation, and that confirms the high crystallographic state of the cleaved surface [28–31].

The thermal stability of the $CdWO_4$(010) surface has been traced by annealing in the air over the temperature range of 400–700 °C followed by RHEED analysis. There was not a foreign phase detected after annealing at 400–600 °C. However, the low-intensity precipitation of WO_3 (PDF 1323P*) and $W_{19}O_{55}$ (PDF 45 0167) oxides was found after annealing at 650–700 °C. The related RHEED pattern is shown in Fig. 5 where the superposition of Kikuchi lines and point reflexes related to $CdWO_4$ and point reflexes related to WO_3 and $W_{19}O_{55}$ oxides appeared. The epitaxial relations obtained for the WO_3 and $W_{19}O_{55}$ precipitates on the $CdWO_4$(010) surface are reported in Tables 1 and 2. As it seems, the precipitation of free tungsten oxides is induced by a CdO loss from the top surface of the $CdWO_4$(010) substrates at high temperatures.

Please cite this article as: E.N. Galashov, et al., Journal of Crystal Growth (2014), http://dx.doi.org/10.1016/j.jcrysgro.2014.01.029

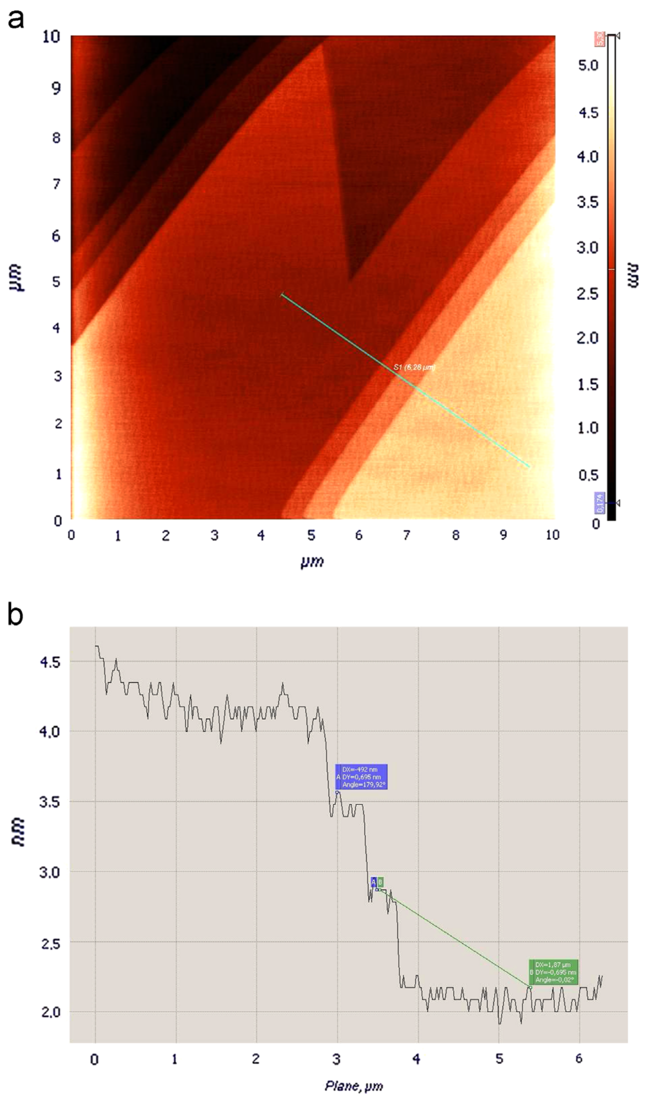

Fig. 3. AFM pattern recorded from (010) cleaved surface: (a) panoramic view and (b) depth profile.

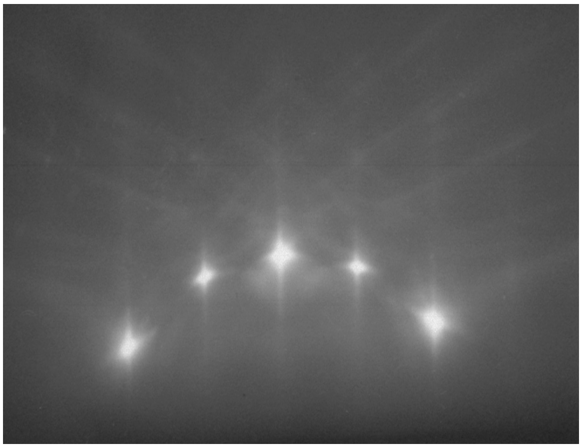

Fig. 4. Kikuchi line pattern recorded from the (010) cleaved surface.

4. Conclusions

The high structural quality of $CdWO_4$ single crystals grown by LTG Cz technique from the melt prepared using high-purity starting reagents permits the formation of large area $CdWO_4(010)$ substrates by a simple cleavage. The cleaved $CdWO_4(010)$ surface is characterized by the presence of atomically flat terraces. High crystallographic quality of the cleaved $CdWO_4(010)$ surface gives an opportunity to consider $CdWO_4$ as a promising substrate material for epitaxial technologies. The $CdWO_4(010)$ surface is stable in the air over the temperatures up to 600 °C.

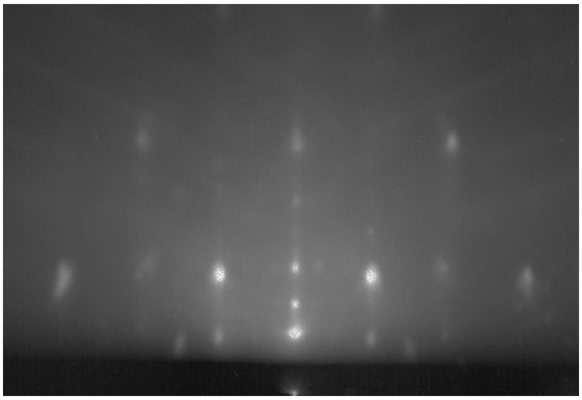

Fig. 5. RHEED pattern recorded after subsequent annealings at 400 °C for 15 h, 500 °C for 1 h, 600 °C for 6 h and 650 °C for 5 h.

Table 1
Epitaxial relations for $WO_3/CdWO_4(010)$ system.

WO_3	$CdWO_4$
(100)	(001)
(001)	(100)
(010)	(010)

Table 2
Epitaxial relations for $W_{19}O_{55}/CdWO_4(010)$ system.

$W_{19}O_{55}$	$CdWO_4$
(100)	(010)
(001)	(−103)
(010)	(301)

Acknowledgments

This study was partly supported by the programs of Ministry of Education and Science of Russian Federation (contract 16.518. 11.7091).

References

[1] M.J.J. Lammers, G. Blasse, D.S. Robertson, The luminescence of cadmium tungstate ($CdWO_4$), Phys. Status Solidi A 63 (2) (1981) 569–572.
[2] S.L. Fritz, L.T. Cook, High-resolution digital X-ray detector utilizing a discrete array of $CdWO_4$ scintillators and a self-scanned photodiode array, Med. Phys. 14 (2) (1987) 244–248.
[3] H.J. Kim, Hee Dong Kang, H. Park, Shi-hong Doh, Sung Hwan Kim, Sang Jun Kang, Large size $CdWO_4$ crystals for energetic X- and γ-ray detection, J. Nucl. Sci. Technol. S5 (2008) 356–359.
[4] P. Belli, R. Bernabei, R.S. Boiko, V.B. Brudanin, N. Bukilic, R. Cerulli, D.M. Chernyak, F.A. Danevich, S. d'Angelo, V.Ya. Degoda, A.E. Dossovitskiy, E.N. Galashov, Yu.A. Hyzhnyi, S.V. Ildyakov, A. Incicchitti, V.V. Kobychev, O.S. Kolesnyk, G.P. Kovtun, V.M. Kudovbenko, J.R. de Laeter, A.L. Mikhlin, S.S. Nagorny, S.G. Nedilko, A.S. Nukolaiko, S. Nisi, D.V. Poda, R.B. Podviyanuk, O.G. Polischuk, D. Prosperi, A.P. Shcherban, V.P. Shcherbatskyi, V.N. Shlegel, D.A. Solopikhin, Yu.G. Stenin, V.I. Tretyak, Ya.V. Vasiliev, V.D. Virich, Development of enriched $^{106}CdWO_4$ crystal scintillators to search for double β decay processes in ^{106}Cd, Nucl. Instrum. Methods Phys. Res. A 615 (2010) 301–306.
[5] A.S. Barabash, P. Belli, R. Bernabei, R.S. Boiko, F. Cappella, V. Caracciolo, D.M. Chernyak, R. Cerulli, F.A. Danevich, M.L. Di Vacri, A.E. Dossovitskiy,

Please cite this article as: E.N. Galashov, et al., Journal of Crystal Growth (2014), http://dx.doi.org/10.1016/j.jcrysgro.2014.01.029

E.N. Galashov, A. Incicchitti, V.V. Kobychev, S.I. Konovalov, G.P. Kovtun, V.M. Kudovbenko, M. Laubenstein, A.L. Mikhlin, S. Nisi, D.V. Poda, R.B. Podviyanuk, O.G. Polischuk, V.P. Shcherbatskyi, V.N. Shlegel, D.A. Solopikhin, Yu.G. Stenin, V.I. Tretyak, V.I. Umatov, Ya.V. Vasiliev, V.D. Virich, Low background detector with enriched $^{116}CdWO_4$ crystal scintillators to search for double β decay of ^{116}Cd, J. Instrum. 6 (2011) P08011.

[6] W. Klamra, T. Szczesniak, M. Moszynski, J. Iwanowska, L. Swiderski, A. Syntfeld-Kazuch, V.N. Shlegel, Ya.V. Vasiliev, E.N. Galashov, Properties of $CdWO_4$ and $ZnWO_4$ scintillators at liquid nitrogen temperature, J. Instrum. 7 (2012) P03011.

[7] D.V. Poda, A.S. Barabash, P. Belli, R. Bernabei, R.S. Boiko, V.B. Brudanin, F. Cappella, V. Caracciolo, R. Cerulli, D.M. Chernyak, F.A. Danevich, S. d'Angelo, V.Ya. Degoda, M.L. Di Vacri, A.E. Dossovitskiy, E.N. Galashov, A. Incicchitti, V.V. Kobychev, S.I. Konovalov, G.P. Kovtun, M. Laubenstein, A.L. Mikhlin, V.M. Mokina, A.S. Nikolaiko, S. Nisi, R.B. Podviyanuk, O.G. Polischuk, A.P. Shcherban, V.N. Shlegel, D.A. Solopikhin, V.I. Tretyak, V.I. Umatov, Ya. V. Vasiliev, V.D. Virich, $CdWO_4$ crystal scintillators from enriched isotopes for beta decay experiments, Radiation Meas. 56 (2013) 66–69.

[8] Z. Burshtein, S. Morgan, D.O. Henderson, E. Silberman, Spatial dispersion in polariton spectra of cadmium tungstate ($CdWO_4$) single crystals, J. Phys. Chem. Solids 49 (11) (1988) 1295–1302.

[9] A.A. Kaminskii, H.J. Eichler, Ken-ichi Ueda, N.V. Klassen, B.S. Redkin, L.E. Li, J. Findeisen, D. Jaque, J. Gascía-Sole, J. Fernández, R. Balda, Properties of Nd^{3+}-doped and undoped $PbWO_4$, $NaY(WO_4)_2$, $CaWO_4$, and undoped monoclinic $ZnWO_4$ and $CdWO_4$ as laser-active and stimulated Raman scattering-active crystals, Appl. Opt. 38 (21) (1999) 4533–4547.

[10] H.J. Eichler, G.M.A. Gad, A.A. Kaminskii, H. Rhee, Raman crystal lasers in the visible and near-infrared, J. Zhejiang Univ. Sci. 4 (3) (2003) 241–253.

[11] Hong-Wei Liao, Yan-fei Wang, Xian-Min Liu, Ya-Dong Li, Yi-Tai Qian, Hydrothermal preparation and characterization of luminescent $CdWO_4$ nanorods, Chem. Mater. 12 (10) (2000) 2819–2821.

[12] Yichuan Ling, Liang Zhou, Lei Tan, Yunhua Wang, Chengzhong Yu, Synthesis of urchin-like $CdWO_4$ microspheres via a facile template free hydrothermal method, CrystEngComm 12 (2010) 3019–3026.

[13] Tingjiang Yan, Liping Li, Wenming Tong, Jing Zheng, Yunjian Wang, Guangshe Li, $CdWO_4$ polymorphs: Selective preparation, electronic structures and photocatalytic activities, J. Solid State Chem. 184 (2011) 357–364.

[14] Chang Sung Lim, Microwave-assisted synthesis of $CdWO_4$ by solid-state metathetic reaction, Mater. Chem. Phys. 131 (2012) 714–718.

[15] M.A. Dahlborg, G. Svensson, Structural changes in the system $Zn_{1-x}Cd_xWO_4$, determined from single crystal data, Acta Chem. Scand. 53 (1999) 1103–1109.

[16] R. Lacomba-Perales, D. Errandonea, D. Martinez-Garcia, O. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, J.C. Chervin, A. Polian, Phase transitions in wolframite-type $CdWO_4$ at high pressure studied by Raman spectroscopy and density-functional theory, Phys. Rev. B 79 (2009) 094105.

[17] Tadashi C. Ozawa, Sung J. Kang, Balls&Sticks: easy-to-use structure visualization and animation program, J. Appl. Crystallogr. 37 (2004) 679.

[18] B.P. Nazarenko, V.N. Baumer, E.F. Dolzhenkova, M.B. Kosmyna, Structural defects in Czochralski-grown $CdWO_4$ single crystals, Inorg. Mater. 41 (10) (2005) 1114–1117.

[19] J. Johnson, K.O. Findley, F.P. Doty, The deformation and fracture behavior of the scintillating crystal cadmium tungstate, JOM 60 (4) (2008) 56–58.

[20] J. Ruiz-Fuertes, S. López-Moreno, J. López-Solano, D. Errandonea, A. Segura, R. Lacomba-Perales, A. Muñoz, S. Radescu, O. Rodríguez-Hernández, M. Gospodinov, L.L. Nagornaya, C.Y. Tu, Pressure effects on the electronic and optical properties of AWO_4 wolframites (A=Cd, Mg, Mn, and Zn): The distinctive behavior of multiferroic $MnWO_4$, Phys. Rev. B 86 (2012) 125202.

[21] V.V. Atuchin, E.N. Galashov, A.S. Kozhukhov, L.D. Pokrovsky, V.N. Shlegel, Epitaxial growth of ZnO nanocrystals at $ZnWO_4$(010) cleaved surface, J. Cryst. Growth 318 (1) (2011) 1147–1150.

[22] V.V. Atuchin, E.A. Galashov, O.Yu. Khyzhun, A.S. Kozhukhov, L.D. Pokrovsky, V.N. Shlegel, Structural and electronic properties of $ZnWO_4$(010) cleaved surface, Cryst. Growth Des. 11 (2011) 2479–2484.

[23] I.M. Ivanov, Y.G. Stenin, V.N. Shlegel, E.P. Makarov, T.N. Denisova, A.R. Tsygankova, Extrapure WO_3 for the preparation of $CdWO_4$ single crystals, Inorg. Mater. 44 (12) (2008) 1330–1333.

[24] D.T.J. Hurle, B. Cockayne, Handbook of crystal growth, Vol. 2a: bulk crystal growth, in: D.T.J. Hurle (Ed.), Basic Techniques, North-Holland, Amsterdam, 1994.

[25] O.E. Tereshchenko, K.A. Kokh, V.V. Atuchin, K.N. Romanyuk, S.V. Makarenko, V.A. Golyashov, A.S. Kozhukhov, I.P. Prosvirin, A.A. Shklyaev, Stability of the (0001) surface of the Bi_2Se_3 topological insulator, JETP Lett. 94 (6) (2011) 465–468.

[26] V.V. Atuchin, V.A. Golyashov, K.A. Kokh, I.V. Korolkov, A.S. Kozhukhov, V.N. Kruchinin, S.V. Makarenko, L.D. Pokrovsky, I.P. Prosvirin, K.N. Romanyuk, O.E. Tereshchenko, Formation of inert Bi_2Se_3(0001) cleaved surface, Cryst. Growth Des. 11 (2011) 5507–5514.

[27] Yu.M. Andreev, V.V. Atuchin, G.V. Lanskii, A.N. Morozov, L.D. Pokrovsky, S.Yu. Sarkisov, O.V. Voevodina, Growth, real structure and applications of GaSe1-xSx crystals, Mater. Sci. Eng. B 128 (2006) 205–210.

[28] E. Levine, W.L. Bell, G. Thomas, Further applications of Kikuchi diffraction patterns; Kikuchi maps, J. Appl. Phys. 37 (1966) 2141–2148.

[29] J.C.H. Spence, J. Zuo, Electron Microdiffraction, Plenum, New York, 1992.

[30] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, L.D. Pokrovsky, Core level spectroscopy and RHEED analysis of $KGd(WO_4)_2$ surface, Solid State Commun. 133 (2005) 347–351.

[31] V.V. Atuchin, L.D. Pokrovsky, O.Yu Khyzhun, A.K. Sinelnichenko, C.V. Ramana, Surface crystallography and electronic structure of potassium yttrium tungstate, J. Appl. Phys. 104 (2008) 033518.

Please cite this article as: E.N. Galashov, et al., Journal of Crystal Growth (2014), http://dx.doi.org/10.1016/j.jcrysgro.2014.01.029