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# The low thermal gradient Czochralski crystal growth and microstructural properties of a $Pb_2MoO_5$(20-1) cleaved surface

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**Abstract**

The optical quality $Pb_2MoO_5$ single crystals were grown by the Low Thermal Gradient Czochralski Technique (LTG Cz). As a result, the $Pb_2MoO_5$ crystals with the diameter of 40-50 mm and the length of ~100 mm were grown. The grown crystals phase composition was identified by the X-ray single crystal structure analysis in space group *C*2/*m*, *a* = 14.2221(11), *b* = 5.7852(5), *c* = 7.3262(6) Å, β = 114.168(2)°, *Z* = 4 ($R_1$ = 0.0336). The $Pb_2MoO_5$(20-1) substrates were prepared by cleavage, and the surface properties were evaluated by RHEED and AFM. The superposition of wide Kikuchi lines and crystal reflexes was found by RHEED. The AFM measurements indicate as low surface roughness as ~0.2 nm. Thus, the atom smooth surface of $Pb_2MoO_5$ was formed by cleavage.

**Keywords:** $Pb_2MoO_5$, cleavage, microstructure, RHEED, AFM

## 1. Introduction

Crystals with a layered structure comprise relatively weak chemical bonds in a selected direction, and this results in strong anisotropy of their basic chemical and physical properties, including chemical reactivity, mechanical, thermal, electronic and optical parameters [1-6]. Layered crystals may possess good cleavage properties along the specific crystallographic direction with the formation of a large area cleaved surface showing an excellent structural quality up to the nanometric level. In layered chalcogenides, where metal-chalcogen bonds are long and interlayer links are formed by weak van der Waals bonds, the preparation of an atomic smooth substrate surface by cleavage is widely used in experimental techniques [3,7-9]. As for oxide crystals, the detail studies of man-made crystal cleaved surface, to our best knowledge, are very scarce in the literature and dominantly belong to wolframite-family tungstates. Now, it is clear that bulk crystal quality is a key factor to get the atomic-smooth cleaved surface. In the past, from empirical experience, several other oxide crystals with cleavage properties were discovered, and, commonly, this feature was considered negative in optical and electronic applications because serious problems may appear during a sample's cutting and polishing.

Double lead molybdate $Pb_2MoO_5$, space group *C*2/*m*, belongs to the family of $Pb_2XO_5$ (X = S, Cr, Mo, W) compounds with a framework type structure [10,11]. The $Pb_2MoO_5$ crystal structure is shown in Fig. 1 [11,12]. The structure is formed by corner linked $PbO_9$ polyhedrons and distorted $MoO_4$ tetrahedra and can be classified as a framework without evident layer formation. However, the Pb-O bond lengths in the $PbO_9$ polyhedrons are strongly different and, if to remove the comparatively long bonds Pb1-O2, Pb1-O3, Pb2-O2 and Pb2-O1 in the range of 261.5-381.3 pm [10], as shown in Fig. 1, the layered structure can be found. The complex layers are parallel to (20-1) planes.

Presently, $Pb_2MoO_5$ is considered as one of the best known acousto-optical (AO) materials because of its high AO figure of merit [13-16]. $Pb_2MoO_5$ melts congruently and, respectively, large perfect single crystals can be grown by efficient Czochralski method [17-19]. The mechanical

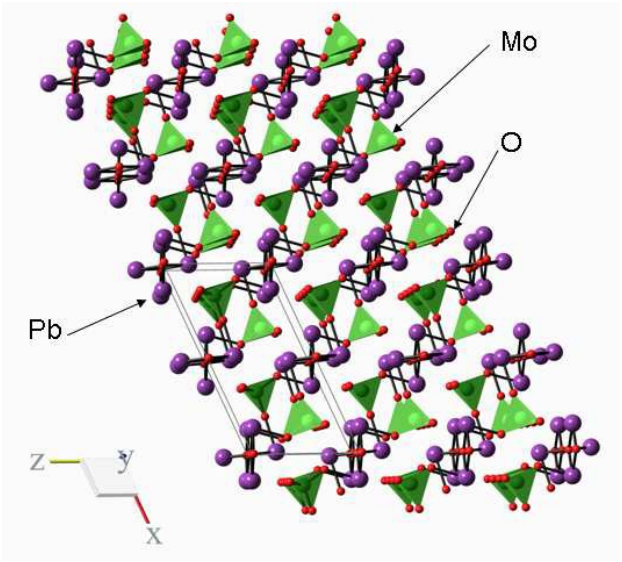


Fig. 1. A fragment of the $Pb_2MoO_5$ crystal structure. The unit cell is outlined. Lone atoms are omitted for clarity. Only comparatively short bonds Pb1-O4, Pb1-O1, Pb2-O4 and Pb2-O3 are shown.

properties of the $Pb_2MoO_5$ crystal permit the boule cutting and preparation of the sample in an arbitrary crystallographic direction needed for physical parameter measurements [13-17,20-23]. Nevertheless, the pronounced cleavage parallel to plane (20-1) was reported in the literature [14,16,20]. The cleavage effect is evidently provided by disruption of comparatively long Pb-O bonds between the layers shown in Fig. 1. The structural and chemical properties of the (20-1) cleaved surface in $Pb_2MoO_5$ remain to be unknown. Thus, the present study is aimed at the $Pb_2MoO_5$ crystal growth under the low thermal gradient conditions and evaluation of cleaved (20-1) surface microstructural properties.

## 2. Experimental

The $Pb_2MoO_5$ single crystals were grown along the direction orthogonal to the cleavage plane. Initially, the oriented seed was prepared by cleavage of the mm-size $Pb_2MoO_5$ crystals grown by spontaneous crystallization from the stoichiometric melt. The diameter of the cleaved (20-1) seed face was ~10 mm. The seed was clamped onto the Pt rod, and the $Pb_2MoO_5$ single crystals were

grown by the Low Thermal Gradient Czochralski Technique (LTG Cz) [24-27]. The use of LTG Cz decreases the losses of volatile PbO and $MoO_3$ oxides because the significant melt overheating during growth is avoided. The initial charge was prepared using lead(II,IV) oxide $Pb_3O_4$ (reagent grade, Shymkent lead plant, Kazakhstan) and molybdenum oxide $MoO_3$. Previously, the $MoO_3$ oxide was deeply purified by double sublimation with subsequent double recrystallization in aqueous solutions. The purification technology is well developed in NIIC (Novosibirsk, Russia) [28]. The stoichiometric oxide mixture was inserted into a platinum crucible with the diameter of 70 mm and the height of 150 mm. Then, the charge was heated at the rate of 50 grad/h into the growth chamber up to 970–980 °C in the air. Before seeding, the melt was being homogenized during 12 h. The $Pb_2MoO_5$ crystals were grown at the rate of 0.3-2.5 mm/h and at the rotation rate of 12 rpm. The temperature gradient at the growth front was not above 0.1-0.2 grad/mm. As a result, the $Pb_2MoO_5$ crystals with the diameter of 40-50 mm and the length of ~70-100 mm were grown. The crystal weight was up to 800 g. The $Pb_2MoO_5$ crystal grown by the LTG Cz method is shown in Fig. 2.


Fig. 2. A $Pb_2MoO_5$ crystal grown by the LTG Cz technique. The seeding and bottom parts are cut.

The single-crystal X-ray diffraction experiment for compound $Pb_2MoO_5$ was carried out with a Bruker Nonius X8 Apex diffractometer equipped with a 4K CCD detector, using graphite monochromated $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) at ambient temperature. Reflection intensities were integrated using the SAINT software and corrected for absorption by the semi-empirical method (SADABS program) [29]. The structures were solved by the direct method with SIR2004 [30] and refined by the full-matrix least squares method against $F^2$ on all data using the SHELXTL software [31]. All the atoms were refined in the anisotropic approximation. The crystallographic parameters of the studied $Pb_2MoO_5$ crystal are given in Table 1, and the atom coordinates are given in Table 1S (in the supplement). The bond lengths and angles are given in Table 2S (in the supplement). The structural parameters of $Pb_2MoO_5$ defined in the present experiment are in good relation with those obtained by powder methods [11]. CSD 428844 contains supplementary crystallographic data for compound $Pb_2MoO_5$ in ICSD.

Table 1. Crystal data and structure refinement for $Pb_2MoO_5$

| | |
|---|---|
| Empirical formula | $MoO_5Pb_2$ |
| Formula weight | 590.32 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | *C*2/*m* |
| Unit cell dimensions | *a* = 14.2221(11) Å |
| | *b* = 5.7852(5) Å |
| | *c* = 7.3262(6) Å |
| | β= 114.168(2)° |
| Volume | 549.95(8) $Å^3$ |
| Z | 4 |
| Density (calculated) | 7.130 $Mg/m^3$ |
| Absorption coefficient | 63.251 $mm^{-1}$ |
| F(000) | 984 |
| Crystal size | 0.06 x 0.05 x 0.02 mm |

| | |
|---|---|
| Theta range for data collection | 3.05 – 32.57° |
| Reflections collected | 2753 |
| Independent reflections | 1089 ($R_{int}$ = 0.0414) |
| Completeness to theta = 25.00° | 99.8 % |
| Data / restraints / parameters | 1089 / 0 / 52 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final $R$ indices ($I>2\sigma_I$) | $R_1$ = 0.0336, $wR_2$ = 0.0834 |
| $R$ indices (all data) | $R_1$ = 0.0358, $wR_2$ = 0.0851 |
| Largest diff. peak and hole | 5.415 and -6.071 e/Å$^3$ |

The X-ray rocking curves were recorded using a two-crystal diffractometer DSO-1T ($Cu_{K\alpha 1}$ radiation, λ = 1.54056 Å) equipped with the Ge(004) monochromator. Initially, the substrate plane was adjusted to be parallel to the X-ray beam and, then, the angles of possible diffraction reflections were found by symmetrical scanning (ω-scan). In accordance with the calculations, the reflections of 1-4 orders from (20-1) planes should be at 7.31, 14.74, 22.43, 30.58° in reference to the surface normal. In the experiment with a cleaved $Pb_2MoO_5$ surface, all these reflections were observed at the calculated angles, and that verifies the cleaved plane orientation.

AFM patterns from the cleaved surfaces were recorded using Solver P47-PRO (NT-MDT, Russia) in the semicontact mode. The NSG 11 (NT-MDT, Russia) contilever was installed for the measurements. The top-surface crystallographic properties were evaluated with RHEED using an EFZ4 (Carl Zeiss, Germany) device at electron energy 50 keV.

## 3. Results and discussion

The grown $Pb_2MoO_5$ crystal with the diameter of 40-50 and the length of 70 mm is shown in Fig. 2. The crystal is partly faceted and transparent in the central crystal part. Over the peripheric boule parts, however, the scattering centers were detected under laser beam illumination (λ = 0.6328 μm). The evidence of light-yellow coloration is not clear, and this effect can be supposedly attributed to an admixture of foreign metal ions from the lead oxide. As it is reasonably appeared,

$MoO_3$ can not be a source of coloration because other crystals grown using this starting reagent, for example $ZnMoO_4$, were transparent over visible spectral range [28]. The crystallization front structure is shown in Fig. 3. The central flat part of the crystal is evidently formed due to the layer-

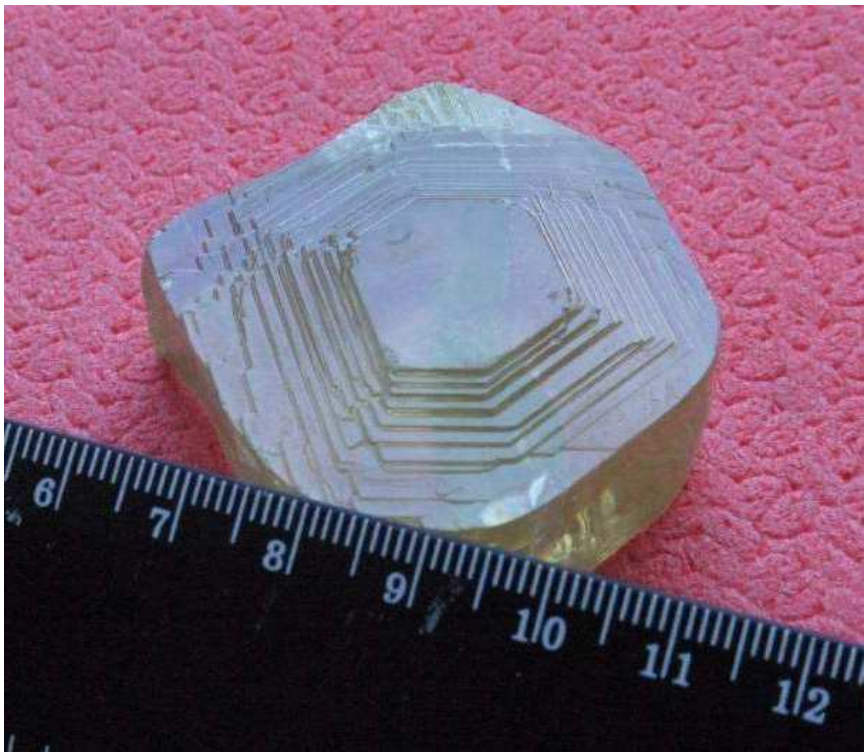


Fig. 3. Bottom part of the $Pb_2MoO_5$ boule.

by-layer growth mechanism starting from the (20-1) seed surface. The area of this flat part is ~230 $mm^2$ onto the crystal bottom that is two times higher than the seed face area. The peripheric crystal part is formed by the macro- and micro-terraces, and they indicate that the block growth mechanism appeared over these regions. Generally, it can be concluded that the internal structure of the $Pb_2MoO_5$ boule is complex. During the LTG Cz growth, two growth mechanisms function in parallel, and the crystal diameter increases dominantly by block growth over the external crystal parts. The central corn crystal part also increases in diameter starting from the seed to the crystal bottom, but the variation is less significant.

To evaluate the internal crystal quality, the $Pb_2MoO_5$(20-1) substrates with the diameter of ~24 mm and thicknesses in the range of 1.5-2.5 mm were prepared by cleaving the crystal with a steel

knife in the air. The bulk structural quality can be estimated by the rocking curve comparison, as shown in Fig. 4. The full width at a half maximum (FWHM) of the diffraction peak measured from

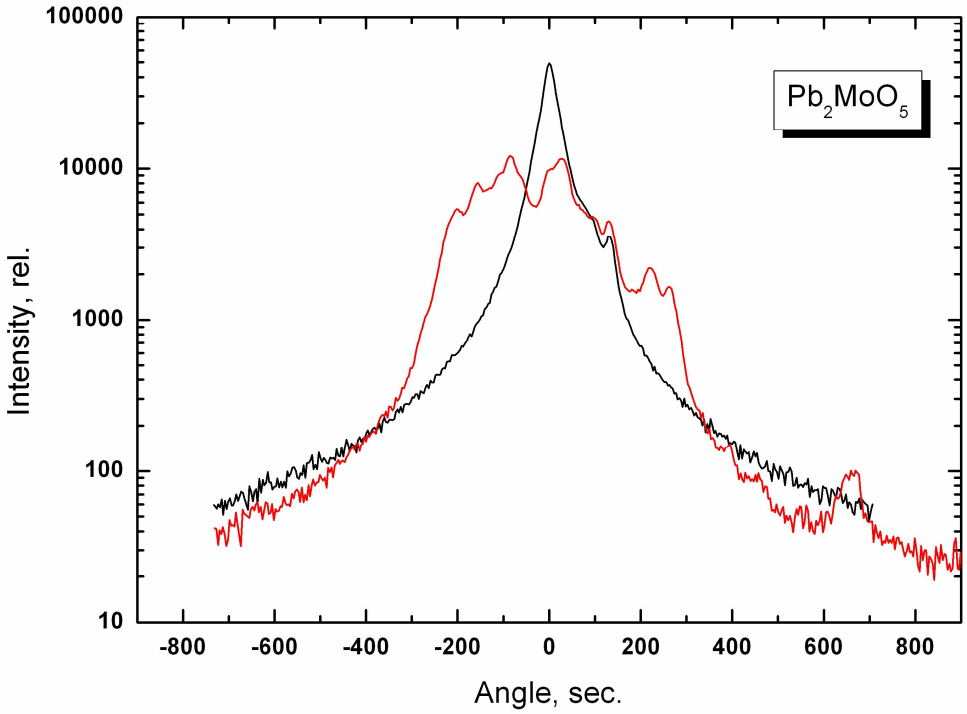


Fig. 4. Rocking curves recorded for reflex (40-2) from the (black) central and (red) peripheric parts of cleaved $Pb_2MoO_5$(20-1) substrate.

the central part of the substrate is ~ 30″. Comparatively, at the periphery of the substrate, the FWHM parameter is ~300″ high due to the blocked type structure. The RHEED pattern recorded from a cleaved crystal surface is shown in Fig. 5. The superposition of wide Kikuchi lines and crystal reflexes is evident, and that verifies an excellent surface structural quality. There is no amorphous component detected at the cleaved surface that is similar to the cleaved surface state previously observed in $AWO_4$ (A = Zn, Cd) tungstates [25-26].

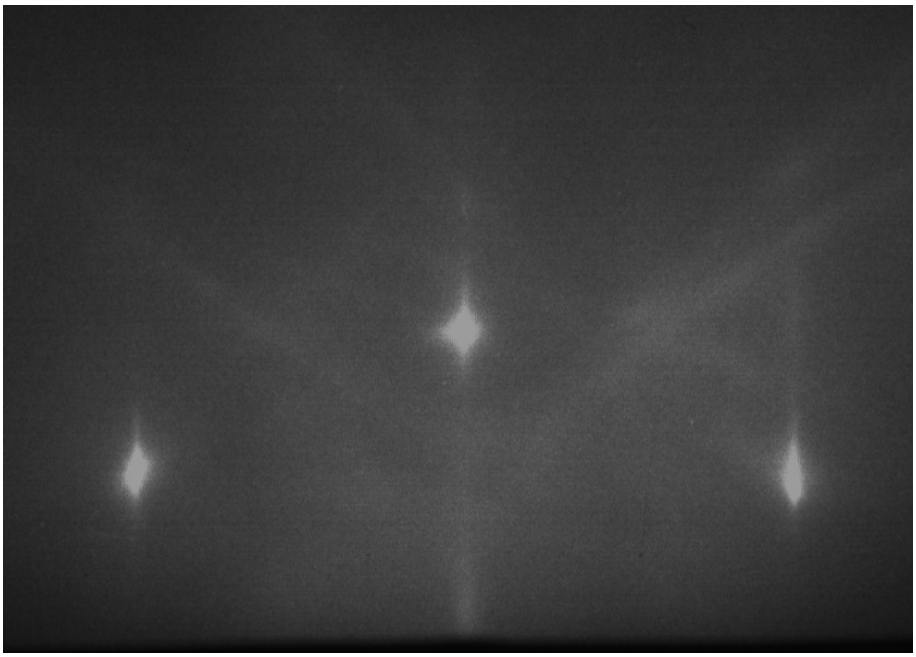

Fig. 5. A Kikuchi lines pattern recorded by RHEED for the cleaved $Pb_2MoO_5$(20-1) surface. The electron beam is along [212].

The results of AFM measurements are shown in Figs. 6 and 7. A typical topographic AFM image and surface profile are shown in Fig. 6 (a) and (b), respectively. Commonly, the surface is formed by a system of wide plane regions with as low roughness as ~0.2 nm. As shown in Fig. 7, the elementary level step ~0.65 nm between the terraces is in reasonable relation with the *d*-spacing of 0.61 nm estimated by RHEED. Thus, the cleaved $Pb_2MoO_5$(20-1) surface can be classified as the atomically smooth one. Besides, a very interesting example of occasional formations onto the surface is shown in Fig. 1S (in the supplement). One can see the strip-shape elementary layer terrace crossed by a low-level terrace boundary. The height of the low-level step is as low as ~0.1 nm, and, as it seems, this formation appeared due to an incomplete layer step. It is not clear, however, either this incomplete atom layer is on the elementary layer terrace surface or barred in the crystal bulk. This AFM pattern may indicate the possibility of the presence of an incomplete layer defect in the $Pb_2MoO_5$ crystal bulk.

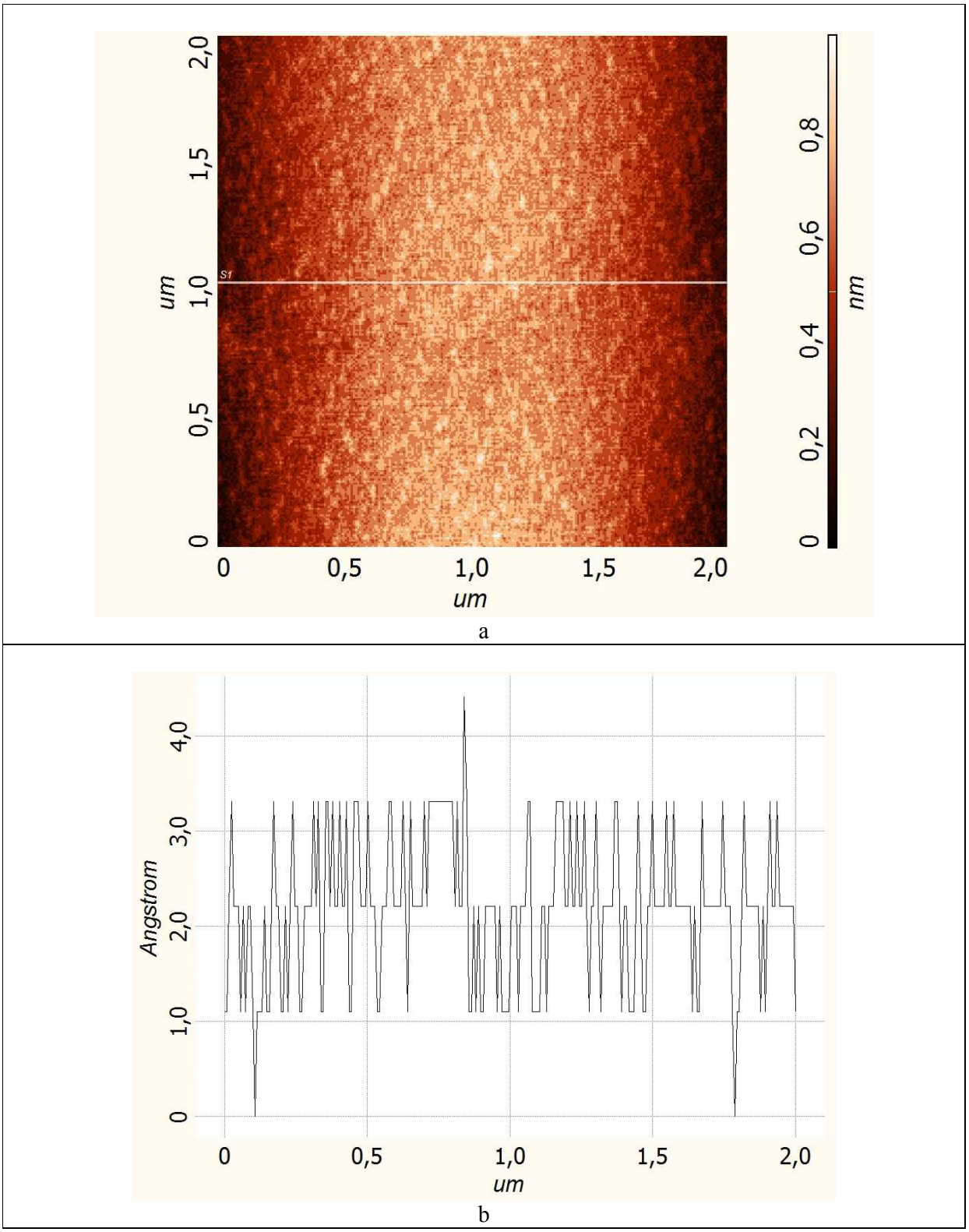


Fig. 6. An AFM pattern recorded from the $Pb_2MoO_5$(20-1) cleaved surface: (a) panoramic view and (b) depth profile.

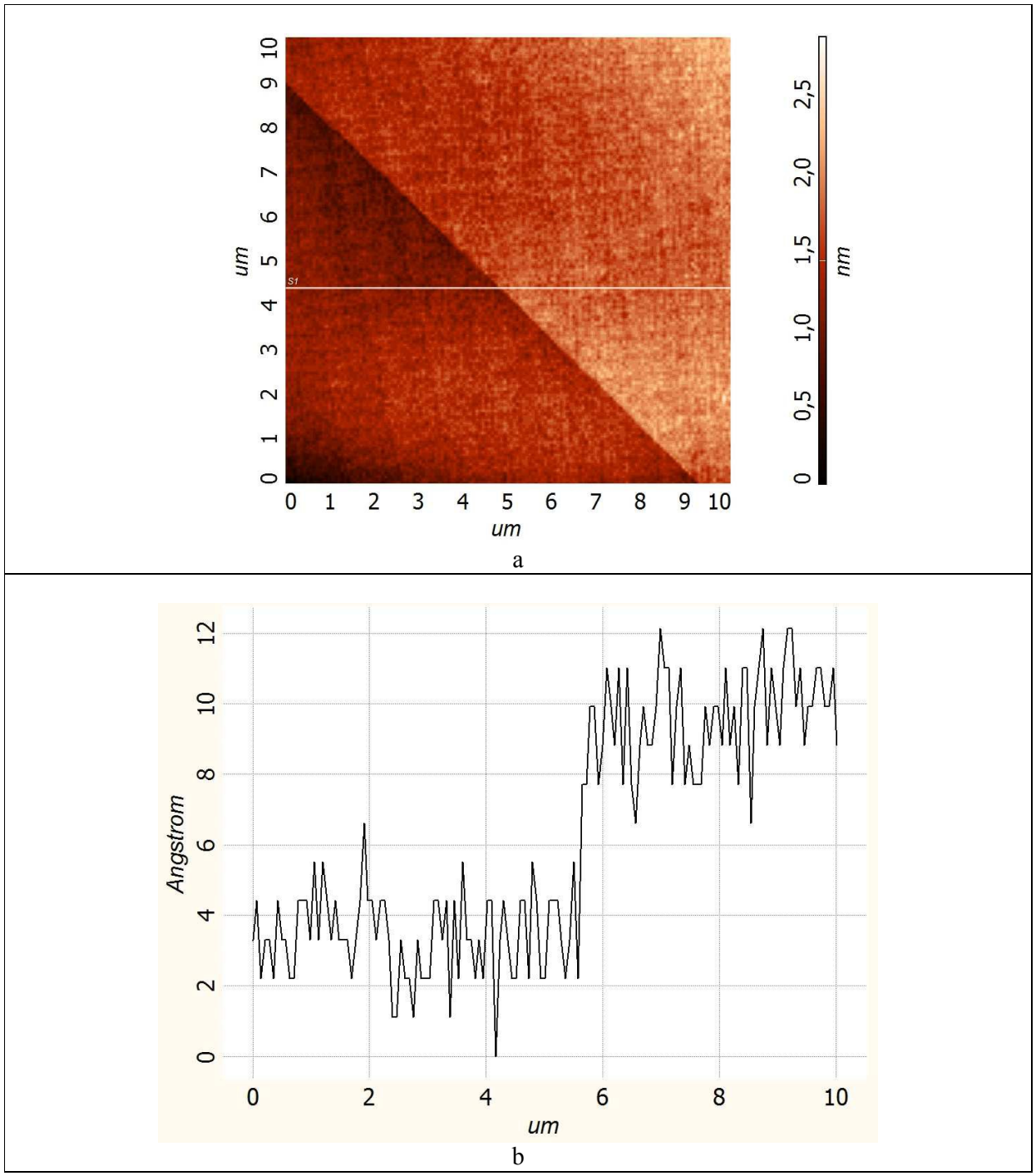


Fig. 7. An AFM pattern recorded from the region of the $Pb_2MoO_5$(20-1) cleaved surface with the elementary step: (a) panoramic view and (b) depth profile.

## 4. Conclusions

As it is shown in the present study, the atomic smooth crystal surface of $Pb_2MoO_5$ can be prepared by cleavage. The structural quality of the $Pb_2MoO_5$ crystals grown by LTG Cz is good enough for the preparation of large area substrate suitable for physical parameter measurements. As it was found in the present study, the bulk structure of the $Pb_2MoO_5$ boule is complex. The central part is formed by a tapered corn with the diameter increasing from seed to bottom. The corn is surrounded by the blocked crystal material with a lower structural quality. Further LTG Cz growth technology optimization is evidently topical to increase the corn diameter more. Due to structural similarity, good cleavage properties can also be supposed for other crystals related to the $Pb_2XO_5$ (X = S, Cr, Mo, W) family.

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## References

1. J. Čejka, R. E. Morris, P. Nachtigall and W. J. Roth, *Dalton Trans.*, 2014, **43**, 10274-10275.
2. S. A. Magarill, N. V. Pervukhina, S. V. Borisov and N. A. Pal'chik, *Uspekhi Khimii*, 2007, **76**, 115-146.
3. 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 and O. E. Tereshchenko, *Cryst. Growth Des.*, 2011, **11**, 5507-5514.
4. S. V. Krivovichev, R. S. Bubnova, S. N. Volkov, M. G. Krzhizhanovskaya, A. V. Egorysheva and S. K. Filatov, *J. Solid State Chem.*, 2012, **196**, 11-16.
5. V. V. Atuchin, N. F. Beisel, K. A. Kokh, V. N. Kruchinin, I. V. Korolkov, L. D. Pokrovsky, A. R. Tsygankova and A. E. Kokh, *CrystEngComm*, 2013, **15**, 1365-1369.

6. K. A. Kokh, V. V. Atuchin, T. A. Gavrilova, N. V. Kuratieva and N. V. Pervukhina, *Solid State Commun.*, 2014, **177**, 16-19.
7. Z.-S. Feng, Z.-H. Kang, F.-G. Wu, J.-Y. Gao, Y. Jiang, H.-Z. Zhang, Yu. M. Andreev, G. V. Lanskii, V. V. Atuchin and T. A. Gavrilova, *Opt. Express*, 2008, **16**, 9978-9985.
8. S. Yu. Sarkisov, V. V. Atuchin, T. A. Gavrilova, V. N. Kruchinin, S. A. Bereznaya, Z. V. Korotchenko, O. P. Tolbanov and A. I. Chernyshev, *Russ. Phys. J.*, 2010, **53**, 346-352.
9. S. Fielder, L. El-Kareh, S. V. Eremeev, O. E. Tereshenko, C. Seibel, P. Lutz, K. A. Kokh, E. V. Chulkov, T. V. Kuznetsova, V. I. Grebennikov, H. Bentmann, M. Bode and F. Reinert, *New J. Phys.*, 2014, **16**, 075013.
10. B. F. Mentzen, A. Latrach, J. Bouix and A. W. Hewat, *Mater. Res. Bull.*, 1984, **19**, 549-554.
11. F. Bosselet, B. F. Mentzen and J. Bouix, *Mater. Res. Bull.*, 1985, **20**, 1329-1337.
12. Tadashi C. Ozawa, Sung J. Kang, *J. Appl. Cryst.* 2004, **37**, 679.
13. A. A. Blistanov, V. S. Bondarenko, N. V. Perelomova, F. N. Strizhevskaia, V. V. Chkalova and M. P. Shakovskaia, *Acoustic crystals*, Nauka, Moscow, 1982 (in Russian).
14. Y. Ohmachi and N. Uchida, *J. Appl. Phys.*, 1971, **42**, 521-524.
15. A. Tchernyatin and E. Nazarova, *Eur. Phys. J. Special Topics*, 2008, **154**, 217-220.
16. M. G. Mil'kov, M. D. Volnyanskii, A. M. Antonenko and V. B. Voloshinov, *Acoust. Phys.*, 2012, **58**, 172-179.
17. S. Miyazawa and H. Iwasaki, *J. Cryst. Growth*, 1971, **8**, 359-362.
18. Z. G. Bazarova, M. V. Mokhosoev and E .A. Kirillov, *Inorg. Mater.*, 1980, **16**, 499-500.
19. K. N. Fedorov, Z. G. Bazarova, M. V. Mokhosoev, E. G. Khaikina, F. P. Alekseev and R. P. Shulunov, *Inorg. Mater.*, 1985, **21**, 740-743.
20. N. Uchida and S. Miyazawa, *J. Opt. Soc. Am.*, 1970, **60**, 1375-1377.
21. D. D. Nihtianova, S. S. Angelova, L. K. Djonev, Ts. S. Zheleva, E. A. Tsukeva and K. P. Petrov, *J. Cryst. Growth*, 1995, **148**, 148-154.
22. S. Nedilko, V. Chornii, Yu. Hizhnyi, M. Trubitsyn and I. Volnyanskaya, *Opt. Mater.*, 2014, **36**,

1754-1759.

23. L.-J. Liao, Q.-N. Zhang, P.-X. Zhang, Y.-L. Liu and A. Tu, *J. Raman Spectr.*, 1984, **15**, 377-379.
24. Y. A. Borovlev, N. V. Ivannikova, V. N. Shlegel, Y. V. Vasiliev and V. A. Gusev, *J. Cryst. Growth*, 2001, **229**, 305-311.
25. V. V. Atuchin, E. N. Galashov, A. S. Kozhukhov, L. D. Pokrovsky and V. N. Shlegel, *J. Cryst. Growth*, 2011, **318**, 1147-1150.
26. V. V. Atuchin, E. A. Galashov, O. Yu. Khyzhun, A. S. Kozhukhov, L. D. Pokrovsky and V. N. Shlegel, *Cryst. Growth Des.*, 2011, **11**, 2479-2484.
27. E. N. Galashov, V. V. Atuchin, A. S. Kozhukhov, L. D. Pokrovsky and V. N. Shlegel, *J. Cryst. Growth*, 2014, **401**, 156-159.
28. L. Berge, R. S. Boiko, M. Chapellier, D. M. Chernyak, N. Coron, F. A. Danevich, R. Decourt, V. Y. Degoda, L. Devoyon, A. Drillien, L. Dumoulin, C. Enss, A. Fleischmann, L. Gastaldo, A. Giuliani, M. Gros, S. Herve, V. Humbert, I. M. Ivanov, V. V. Kobychev, Ya. P. Kogut, F. Koskas, M. Loidl, P. Magnier, E. P. Makarov, M. Mancuso, P. de Marcillac, S. Marnieros, C. Marrache-Kikuchi, S. G. Nasonov, X. F. Navick, C. Nones, E. Olivieri, B. Paul, Y. Penichot, G. Pessina, O. Plantevin, D. V. Poda, T. Redon, M. Rodrigues, V. N. Shlegel, O. Strazzer, M. Tenconi, L. Torres, V. I. Tretyak, Y. V. Vasiliev, M. Velazquez, O. Viraphong and V. N. Zhdankov, *J. Instrum.*, 2014, **9**, P06004.
29. Bruker AXS Inc. (2004). APEX2 (Version 1.08), SAINT (Version 7.03) and SADABS (Version 2.11). Bruker Advanced X-ray Solutions, Madison, Wisconsin, USA.
30. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.
31. G. M. Sheldrick, (1997). SHELXS97 and SHELXL97. Programs for the Refinement of Crystal Structures. University of Göttingen, Germany.

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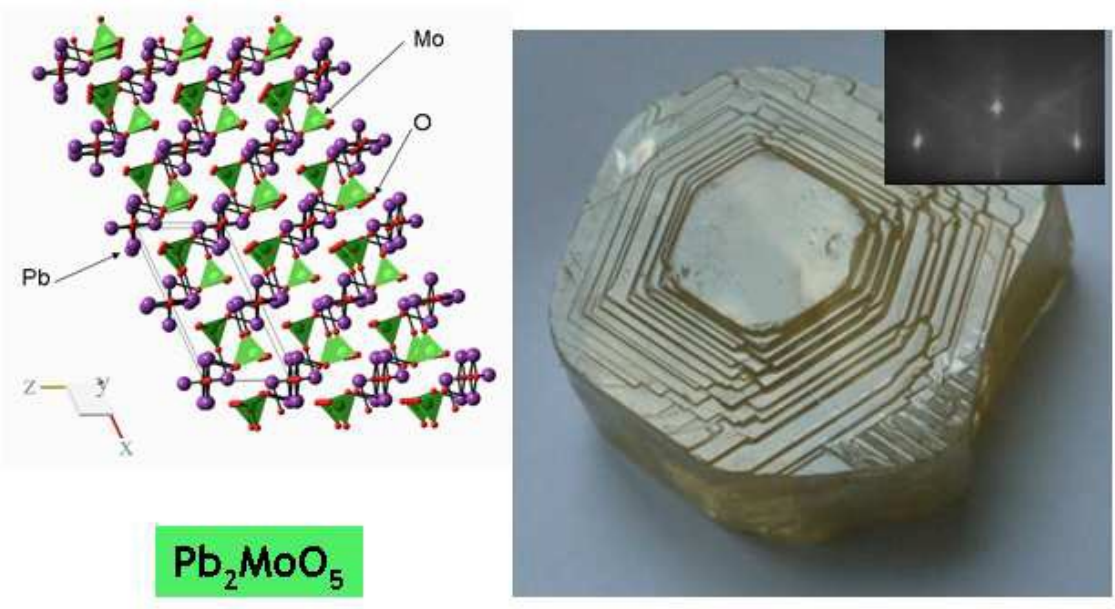


The high-quality $Pb_2MoO_5$ crystal has been grown by LTG Cz method.