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HIGH PURITY TUNGSTEN (VI) OXIDE FOR OBTAINING PROMISING LASER MATERIALS

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A method based on two-stage sublimation purification for obtaining high-purity tungsten (VI) oxide was developed. An impurity analysis of a commercial preparation of tungsten (VI) oxide was performed using mass spectrometry with inductively coupled plasma. Potassium-gadolinium-tungstate [KGW] crystals grown using commercial reagents and tungsten (VI) oxide with chemical purity of 99.999 wt.% were obtained. A comparative analysis of crystals grown from different initial tungsten oxides was performed. It is shown that the developed high-purity tungsten (VI) oxide does not reduce the chemical purity of the grown KGW crystals and is a promising raw material for the technology of glass-ceramic optical materials based on tungstates.

Key words: High-purity tungsten oxide, potassium-gadolinium tungstates [KGW], promising laser ceramic

Unalloyed and rare-earth alloyed with tungstates continue to hold an important place in industrial and scientific fields [1 – 4]. The main innovation in the field of laser manufacturing technology is the development of ceramic laser materials [5, 6]. This is exactly the situation in the field of potassium-rare-earth tungstates, when, in addition to the conventional use of laser active media based on monoclinic potassium-rare-earth tungstates in the form of bulk single crystals, researchers took steps to obtain these materials in the form of transparent optical ceramics [7]. Steps have also been taken to obtain thin layers of crystals of this family on glass substrates [8] in order to create waveguide microlasers as part of integrated optics products.

The production of ceramics requires significantly less time than the growth of single crystals of these compounds from a solution in a melt [flux method]. Moreover, the size of monocrystalline optical elements is limited by the cross section of the boule, while the technology for manufacturing glass ceramics makes it possible to obtain large samples with high optical quality. The advantages of ceramics are undeniable: low cost, possibility of scaling up, introduction of a high concentration of alloying additives [6], and high fracture toughness in comparison with single crystals of similar compositions. However, as a rule, when crystals are grown from melt their chemical purity increases. In consequence, for most impurities the distribution factor is greater than 1. In the manufacture of ceramic and glass-ceramic laser elements, the chemical purity remains practically unchanged from the charge to the final product if there is no interaction of the material with the container or mold during the manufacture of samples. The technological hygiene of personnel is not taken into account in this case. Thus, the requirements of chemical purity in the manufacture of laser ceramic and glass-ceramic products are higher than in the growth of single crystals.

To date, high-quality laser single crystals based on oxygen-containing compounds are characterized by chemical purity 99.99 wt.% and higher, while the requirements of modern semiconductor materials start from 99.99999 wt.% for gallium arsenide [9] and end at 99.999999999 wt.% for silicon [10]. All this makes it necessary to develop new high-purity materials that are actual for glass and glass-crystal lasers. One of these materials is tungsten (VI) oxide, which is used as the main (by weight) component of many laser crystals.

PREPARATION OF HIGH-PURITY TUNGSTEN OXIDE

In the literature very little attention is paid to the chemical purity of the starting reagents used for synthesizing tungstate crystals for photonics. In one of the few works [11]

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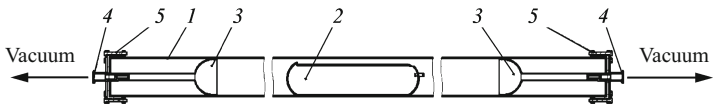

Fig. 1. Diagram of the reactor for purifying substances by means of vacuum sublimation: *1*) reactor vessel in the form of a cylindrical tube; *2*) container for loading the starting material; *3*) collector of volatile impurities; *4*) connection to vacuum system; *5*) fungal seal.

the content of random impurities in $NaBi(WO_4)_2$ crystals was analyzed and it was shown that the purification of the initial reagent WO_3 is a key factor in securing stable growth and high quality of the obtained crystals.

The reason for such sparse attention from researchers of tungstate crystals to the purity of the starting reagents lies in the widespread misconception that the chemical purity of reagents at the level 99.99 wt.% is fully sufficient for synthesizing high-quality oxide optical materials. There exists the opinion that concentrations of residual impurities at the level 10^{-2} wt.% have no appreciable effect on the optical quality of these crystals or their spectral luminescence characteristics or their structure-sensitive properties.

Indeed, for oxide or fluoride crystalline phases the typical limits of solid-phase solubility of impurities of more or less similar chemical nature start, as a rule, at 10^{-1} wt.% [12], and in tungstates, in some cases, they can reach tens of percent [13]. Accordingly, the risk of precipitation of secondary phases based on contaminants forming scattering centers at impurity concentrations 10^{-2} wt.% should be minimal. However, under certain conditions, the distribution of uncontrolled impurities over the crystal can be very nonuniform, and this can lead to if not the precipitation of a second phase in regions of heightened impurity concentration, then at least to local fluctuations of the refractive indices of the medium. Speaking about the possibility of obtaining glass-ceramic materials, this problem becomes more significant, because during the manufacture of ceramics there is no 'self-cleaning' of the material, which is characteristic of the technology of growing single crystals from melts.

Currently, WO_3 reagents from a relatively small circle of manufacturers can be found on the domestic market. A commercial preparation of tungsten (VI) oxide with qualification 99.97 wt.% for metallic impurities is produced by Lankhit LLC. Also, preparations produced back in the USSR and still available on the market are widely used to grow crystals. In the USSR WO_3 preparations were produced with the following qualifications: for making optical glass, for spectral analysis (analytical grade); high purity (ultrapure grade 11-2), chemically pure (pure grade), etc. The current leader in the production of oxide preparations tungsten (VI) is PRC [14]. Analysis using inductively coupled plasma mass spectrometry ICP-MS (NEXIon 300D, Perkin Elmer, USA) showed that there are no preparations on the market with chemical purity higher than 99.97 wt.% (Table 1). This made it necessary to increase the chemical purity of the initial tungsten oxide by using an additional purification procedure.

One way to obtain high-purity substances is sublimation purification in a controlled atmosphere [15]. Performed in this manner the purification process requires control of the following parameters: temperature of the evaporation zones of the initial substance, condensation temperature of the desired product, and control of the vapor-gas atmosphere in the reactor. Sublimation purification of polycrystalline WO_3 was conducted in two stages by annealing in a temperature gradient at a static pressure of the gas-air mixture 60 mm Hg. The temperatures of the first stage process are: temperature of the evaporation zone of the initial substance — 1150°C, temperature of the condensation zone — 990°C. The second stage temperatures are: temperature of the evaporation zone of the initial substance 1120°C; temperature of the condensation zone 990°C. A reactor with two open ends was manufactured in order to increase the productivity of the purification process (Fig. 1). Sublimation of the preparation in two directions increased the productivity of the process 1.8-fold.

As a result of the sublimation process, a WO_3 preparation was obtained in the form of dark-green crystals up to 1.5 mm in size, which acquired a greenish-yellow color after grinding (Fig. 2).

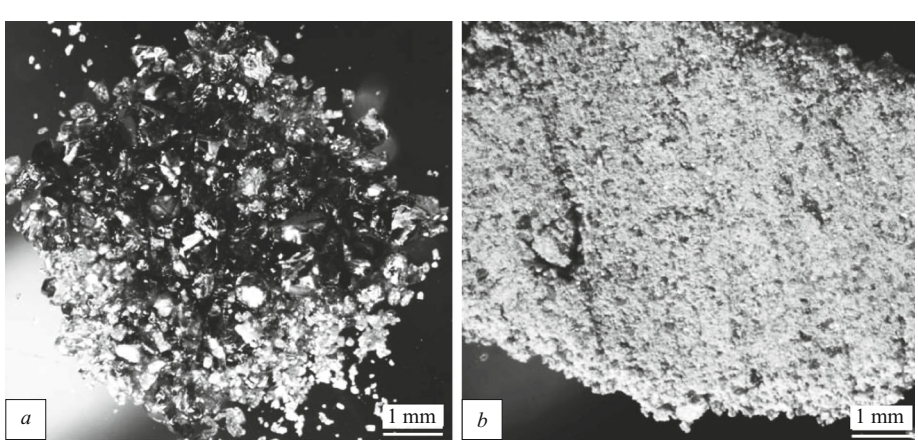

Fig. 2. Photographs of the WO_3 preparation obtained in the process of purification by sublimation: *a*) collected from the walls of the reactor; *b*) after comminution.

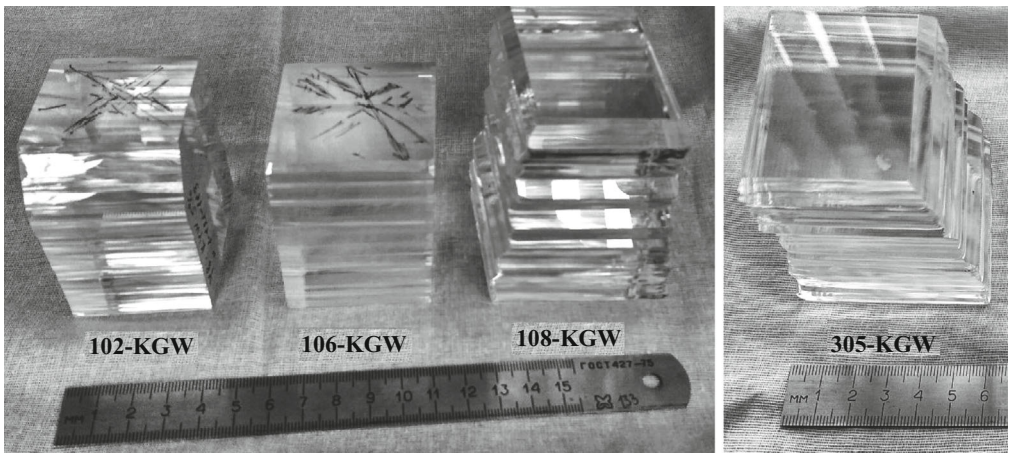

Fig. 3. Photographs of KGW single crystals grown using commercial WO_3 from different manufacturers and a WO_3 preparation obtained by sublimation purification. The designations of crystals correspond to Table 1.

The chemical purity of the tungsten oxide preparation purified in this way was no worse than 99.999 wt.% (for 64 impurity elements, including the limits of determination) (see Fig. 8*a*). The resulting oxide was used to obtain crystals of potassium gadolinium tungstate (KGW).

KGW SINGLE CRYSTALS

Single crystals of KGW were grown from a solution in a melt by the method of Top-Seeded Solution Growth from a cylindrical platinum container onto a single crystal seed cut along the ⟨010⟩ crystallographic direction. Potassium bitungstate $K_2W_2O_7$ was used as a high-temperature solvent. The cultivation process was conducted in a natural atmosphere with no additional sealing of the setup. The initial concentration ratio KGW/$K_2W_2O_7$ was 20/80% by weight. Reagents were used as the initial charge: K_2CO_3, ultrapurity 6-2 produced at the Krasnyi Khimik plant; GdO-G (OST 48-200–81) Gd_2O_3 and WO_3 from different manufacturers, including WO_3 obtained by sublimation purification.

Before weighing, the reagents were calcined in a muffle furnace at 700°C for 3 h to remove moisture and other volatile impurities. Weighed portions were thoroughly mixed in tightly closed polypropylene cans for 2 h. The resulting mixture was loaded into alundum crucibles and calcined at 600°C for 3 h to conduct solid-phase synthesis of the charge. An about 40 mm nominal crystal diagonal is standard for the process developed for growing KGW crystals (Fig. 3). The pulling rate at the nominal growth stage was 1 mm/day.

To study the possibility of impurity elements present in the initial reagents being inherited by KGW crystals the chemical purity of crystals grown using tungsten (VI) oxide preparations from different manufacturers and high-purity tungsten oxide obtained by sublimation purification were investigated (see Table 1). The rest of the reagents used for growth remained unchanged, i.e. the same lots were used.

A comparative analysis of the chemical purity of commercial reagents of tungsten oxide (VI) and the corresponding manufactured crystals (Figs. 4 – 7) allowed the following conclusions to be drawn about the behavior of impurity elements during the growth of potassium-gadolinium tungstate crystals:

– alkali metals present in WO_3 contaminate the potassium-gadolinium-tungstate crystal; the lower the concentra-

TABLE 1. Impurity Purity of Potassium Gadolinium Tungstate Crystals Grown Using Tungsten (VI) Oxide Preparations from Different Manufacturers

KGW crystal	Initial tungsten oxide (VI)		Chemical purity of the KGW crystal, wt.%
	Manufacturer, qualification, standard	Chemical purity, wt.%	
102-kgv	Lankhit LLC, batch 3, 99.98% in terms of metallic impurities	99.970	99.9980
106-kgv	Stavropol Chemical Reagents and Luminophores Plant dedicated to the 50th Anniversary of the USSR, purity, TU 6-09-397–75 (Batch 1)	99.970	99.9970
107-kgv	Zouping Changshan Town Zefeng Fertilizer Factory (CPR),WO_3-2, 99.90% (Batch 1)	99.970	99.9900
108-kgv	Leningrad Plant Krasnyi Khimik, ultrapurity 11-2, TU 6-09-3796–77 (Batch 1)	99.970	99.9960
305-kgv	After sublimation purification	99.999	99.9987

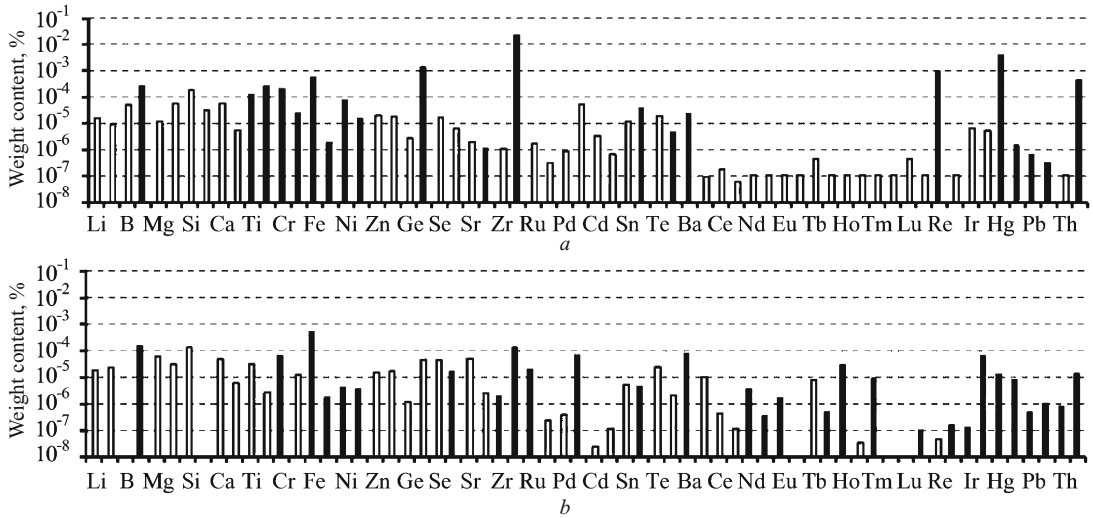

Fig. 4. Impurity composition according to ICP-MS analysis: *a*) WO_3 (Lankhit LLC, batch 3); *b*) KGW crystal 102-kgv.

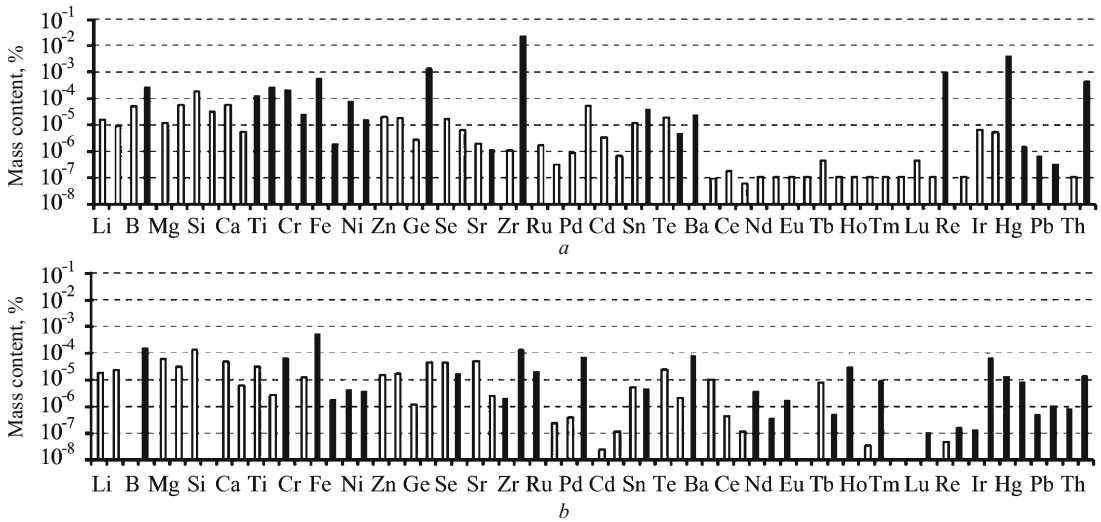

Fig. 5. Impurity composition according ICP-MS analysis: *a*) WO_3 produced by the Stavropol Plant of Chemical Reagents and Luminophores, part, TU 6-09-397–75 (Batch 1); *b*) KGW 106-kgv crystal.

tion of, for example, Na or Cs, in the tungsten (VI) oxide, the less WO_3 enters the crystal;

– the source of metal impurities (Fe, Cr, V, Mn, Co, Ni) in KGW crystals is the original tungsten (VI) oxide or uncontrolled contaminants;

– all analyzed crystals contained impurity platinum with content 5×10^{-5} to 7×10^{-7} wt.%, the source is platinum growing crucible;

– the mercury weight content in the crystals is 1×10^{-5} wt.%, while its weight content in the initial oxide is 4×10^{-3} wt.%.

Previously, the authors of [11, 16] suggested that Fe, Cr, and other *d*-elements (possessing chromophore centers) are responsible for the color of the tungsten crystals. In a KGW single crystal obtained from high-purity WO_3 (99.999 wt.%) the weight content of these impurities did not exceed 5×10^{-5} wt.%, and the crystal was colorless, while the crystals obtained from commercial preparations of tungsten oxide sometimes had light-green tint.

It should be especially noted that the use of a sublimation purified WO_3 preparation did not lead to noticeable contamination of the grown crystal with platinum (Fig. 8). This can be explained by the fact that the sublimation process was conducted at a controlled partial pressure of oxygen, thus fixing the concentration of superstoichiometric oxygen in the resulting polycrystalline WO_3.

In summary, the method developed for obtaining high-purity polycrystalline WO_3 makes it possible to manu-

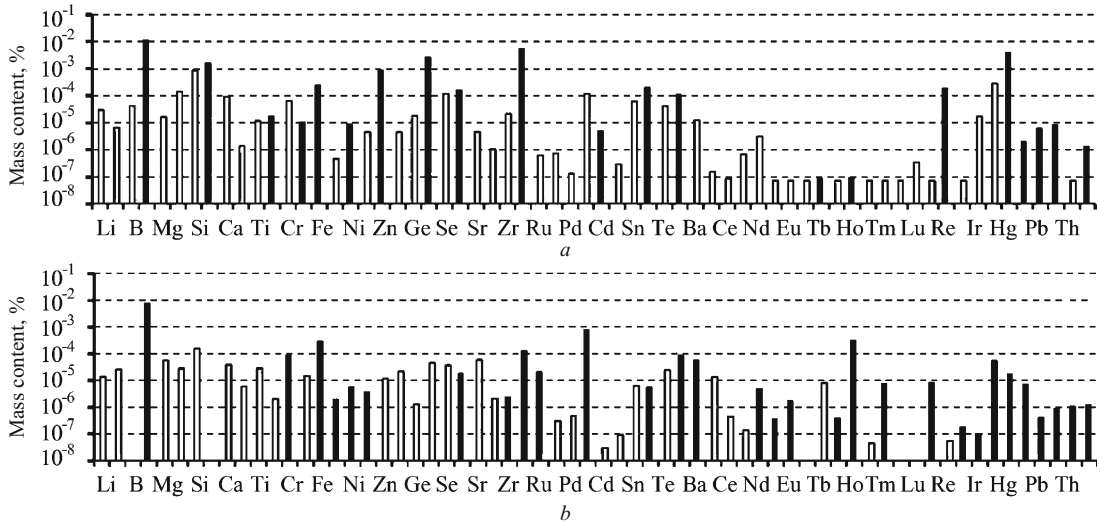

Fig. 6. Impurity composition according to ICP-MS analysis: *a*) WO_3 manufactured by Zouping Changshan Town Zefeng Fertilizer Factory (CPR) WO_3-2, (Batch 1); *b*) KGW crystal 107-kg.

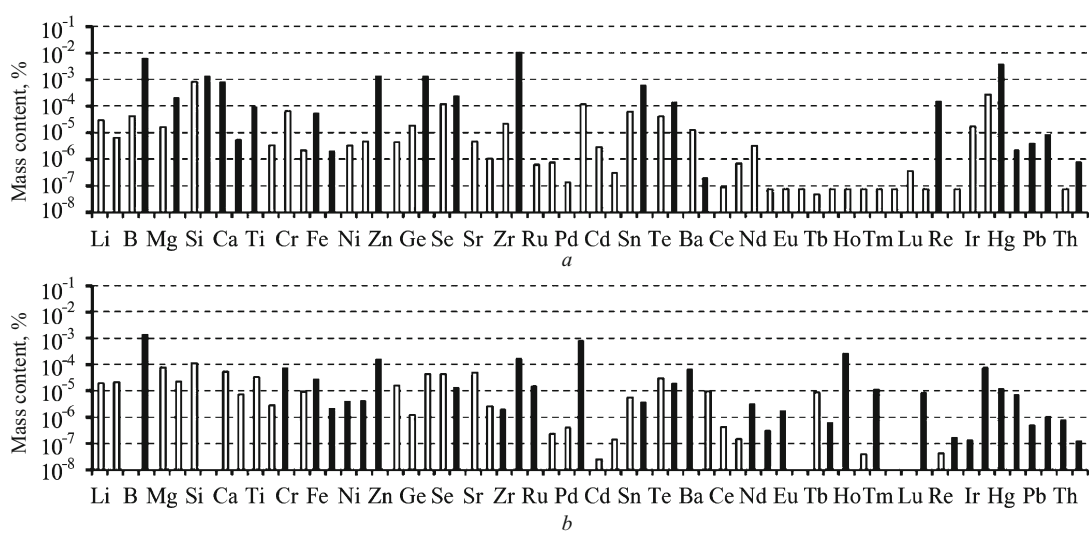

Fig. 7. Impurity composition according to ICP-MS analysis: *a*) WO_3 produced at the Leningrad Plant Krasnyi Khimik, ultrapurity 11-2 TU 6-09-3796–77 (Batch 1); *b*) KGW crystal 108-kgv.

facture a preparation that is suitable for growing high-purity KGW crystals and optical elements from them. The KGW crystals obtained with its help had the highest chemical purity, which was limited only by the impurities inherited from the original K_2CO_3 and Gd_2O_3 preparations. Thus, in terms of the chemical purity of the starting materials, good prerequisites have been created for the development of a technology of glass-crystalline optical and laser elements based on KGW.

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REFERENCES

1. J. Chen, Y. Peng, H. Su, et al., "Studying on the KGd $(WO_4)_2$ crystal based Raman laser with output energy reaching 800 mJ," in: *Advanced Solid State Lasers – Optical Society of America*, Paper ATh2A.28 (2018).
2. A. A. Kaminskii, H. J. Eichler, K. Ueda, et al., "Properties of Nd^{3+}-doped and undoped tetragonal $PbWO_4$, $NaY(WO_4)_2$, $CaWO_4$, and undoped monoclinic $ZnWO_4$ and $CdWO_4$ as laser-active and stimulated Raman scattering-active crystals," *Appl. Optics*, **38**(21), 4533 – 4547 (1999).
3. L. F. Johnson, D. Boyd, K. Nassau, and R. R. Soden, "Continuous operation of a solid-state optical maser," *Phys. Rev.*, **126**, 1406 (1962).

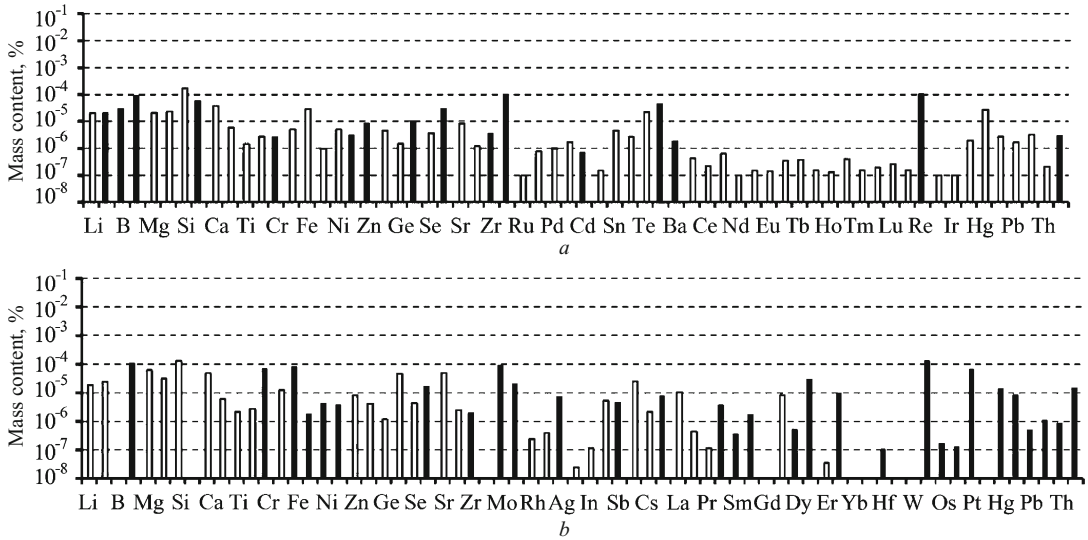

Fig. 8. Impurity composition according to ICP-MS analysis: *a*) WO_3 after sublimation purification; *b*) KGW 305-kgv crystal.

4. A. Schmidt, S. Rivier, V. Petrov, et al., "Continuous-wave tunable and femtosecond mode-locked laser operation of Yb:NaY$(MoO_4)_2$," *J. Opt. Soc. Am. B*, **25**(8), 1341 – 1349 (2008).
5. G. Boulon, "Fifty years of advances in solid-state laser materials," *Opt. Mater.*, **34**(3), 499 – 512 (2012).
6. J. Sanghera, "Ceramic laser materials," *Materials*, **5**(2), 258 – 277 (2012).
7. D. Thangaraju, A. Durairajan, D. Balaji, and Babu S. Moorthy, "Synthesis and characterization of monoclinic $KGd(WO_4)_2$ particles for non-cubic transparent ceramics," *Opt. Mater.*, **35**(4), 753 – 756 (2013).
8. Carlijn I. van Emmerik, R. Frentrop, M. Dijkstra, et al., "Heterogeneous integration of $KY(WO_4)_2$-on-glass: a bonding study," *OSA Continuum*, **2**(6), 2065 – 2076 (2019).
9. G. Ding, Tu Hanlin, Su Xuanyuan, et al., "Growth rate optimization of 6″ GaAs single crystal grown by VGF process, Xiyou Jinshu," *Chinese J. Rare Met.*, **35**, 42 – 46 (2011).
10. F. Shimura, "Single-crystal silicon: growth and properties," in: S. Kasap and P. Capper (eds.), *Springer Handbook of Electronic and Photonic Materials*, Springer Handbooks, Springer (2017); URL: https://doi.org/10.1007/978-3-319-48933-9_13
11. V. Volkov, M. Rico, A. Mendez-Blas, and C. Zaldo, "Preparation and properties of disordered $NaBi(XO_4)_2$, X = W or Mo, crystals doped with rare earths," *J. Phys. Chem. Solids* **63**, 95 – 105 (2002).
12. I. I. Buchinskaya and P. P. Fedorov, "Lead difluoride and related systems," *Rus. Chem. Rev.*, **73**(4), 371 – 400 (2004).
13. E. N. Galashov, V. A. Gusev, V. N. Shlegel, et al., "The growth of $ZnWO_4$ and $CdWO_4$ single crystals from melt by the low thermal gradient Czochralski technique," *Crystallogr. Rep.*, **54**, 689 – 691 (2009).
14. S. S. Belskii and O. E. Belskaya, "Tungsten – production and consumption," in: *Proc. 3rd Inter. Sci.-Tech. Conf. on the Metallurgy of Light and Refractory Metals, Ekaterinburg, October 10 – 11, 2014* [in Russian], UrFU, Ekaterinburg (2014), pp. 162 – 166.
15. I. Kh. Avetisov, A. V. Khomyakov, E. N. Mozhevitina, and A. P. Sadovsky, *Method of Purification of Molybdenum Trioxide, RF Pat. RU2610494C1* [in Russian], applicant and patentee Mendeleev University of Chemical Technology; publ. November 16, 2015.
16. M. Zykova, K. Subbotin, S. Pavlov, et al., "Effect of the accidental impurities onto the absorption spectrum of $NaGd(WO_4)_2$ laser crystal," in: *IEEE. 8th Intern. Conf. on Advanced Optoelectronics and Lasers (CAOL)* (2019), pp. 461 – 464.