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To cite this article: Mikhail Grishechkin *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **613** 012021

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Extra pure tellurium oxide for the growth of high quality paratellurite crystals

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Abstract. Tellurium oxide (IV) single crystals are in demand materials for manufacturing acousto-optical devices optical fibers for IR wavelength range. The initial material for production of active and passive optical materials must have purity better than 99.999 wt% and extremely low concentration of the residual water. The main method of synthesis of TeO_2 is oxidation in nitric acid followed by recrystallization from HCl is complicated, also amount of used high purity acids and waste are very high. Besides the residual water content is no less than 10 ppm. In the research we have developed the procedure for the synthesis of high-purity tellurium (IV) oxide without the usage of liquid oxidants. The process of oxidation of elementary Te was carried out in a flowing quartz glass reactor. Air oxygen was used as an oxidizing agent. The oxidation was conducted at 600-670°C during 24 hours. The produced material was a fine crystalline powder of acicular dendritic crystals of bright white color, identified as $\beta\text{-TeO}_2$ due to X-ray. It was as pure as 5N7 due to ICP-MS. The $\beta\text{-TeO}_2$ crystal grown from the synthesized water-free preparation has demonstrated better optical properties towards the crystals grown from commercial TeO_2 , produced by the «wet» technology.

1. Introduction

Paratellurite crystal ($\beta\text{-TeO}_2$) is a demanded material in the technology of optoelectronics, acousto-optical and electro-optical converters [1,2]. TeO_2 also used as a component of promising glass-fibers transparent in IR wavelength region [3]. Both technologies need the use of high-purity TeO_2 (as pure as 99.999 wt% and better).

To the date the most widely used technology of high-purity TeO_2 based on an oxidation of elemental high-purity tellurium by nitric acid, and subsequent solution recrystallization from hydrochloric acid. This method is laborious and involves the consumption of a large number of high-purity mineral acids and the formation of equivalent amounts of liquid waste that require disposal. Besides, the produced crystalline product contains residual water or OH-groups which drastically influence on the optical properties of the paratellurite crystal and TeO_2 based glass fibers.

The goal of the research was the development of a methodology for the synthesis of high-purity TeO_2 without the use of liquid oxidants and the exclusive stage of recrystallization.

2. Experimental techniques

2.1. Method of TeO_2 synthesis

The concept of the proposed technique consists in oxidation of elementary tellurium by air oxygen under controlled conditions of heat and mass transfer. The oxidation process was carried out in a quartz reactor, sealed from one end, placed in a two-zone resistive furnace. The scheme of the setup is presented in Figure 1.

The preparation of the quartz parts of the setup was reduced to etching sequentially in nitric and hydrofluoric acids and subsequent repeated rinsing with bidistilled water. Liquid TeO_2 easily interacts



with quartz glass forming the complex glass. But when solid TeO is inert to the quartz glass material which is known as a good and high-purity construction material for high temperature vacuum systems [4].

The original tellurium (99.9992 wt%, Figure 2), previously subjected to vacuum sublimation [5], was placed in a boat (5), which was then installed in a reactor (3). A quartz receiver tube – a condenser (6) was placed close to the boat to collect the synthesis product. A fungal seal (7) with a porous filter (4) was placed on the open end of the reactor. The filter (4) controlled the flow rate of oxygen entering the reaction zone and purified the entering gas from suspended solids.

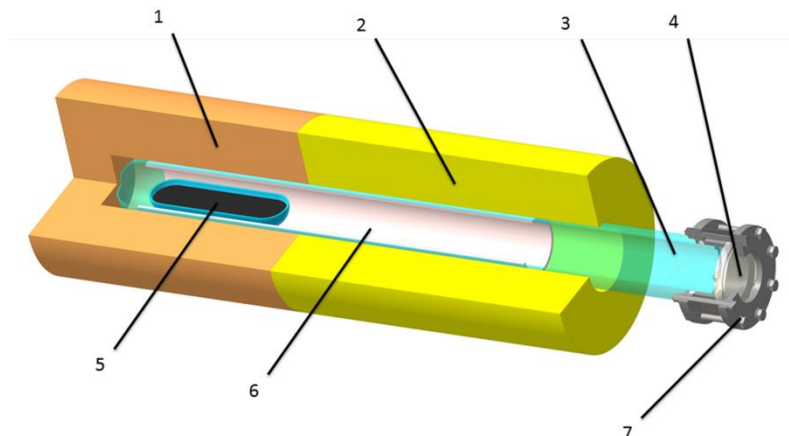


Figure 1. Scheme of the setup for direct synthesis of crystalline TeO_2 :
1 – source heater, 2 – reaction zone heater, 3 – reactor, 4 – porous filter,
5 – boat with source tellurium, 6 – condenser, 7 – fungal seal.

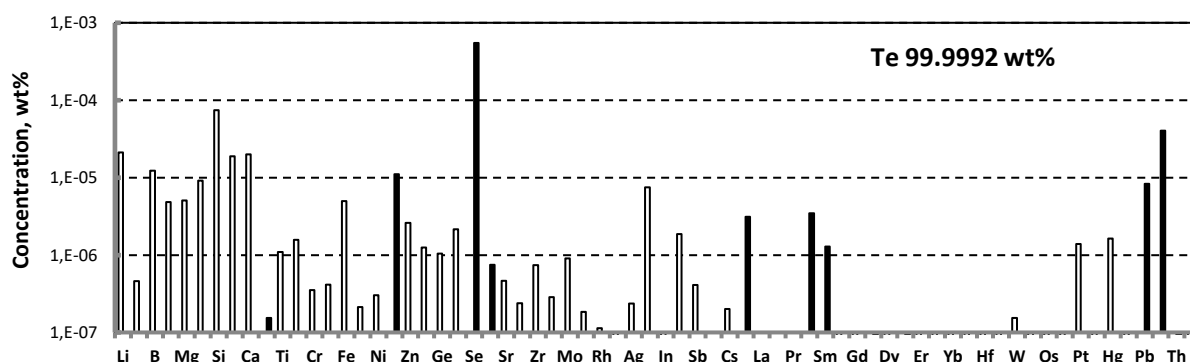


Figure 2. Impurity content in sublimated metal tellurium. The empty bars indicate the limit of detection (LD) of ICP-MS analysis. The concentrations of the non-presented elements were less 10^{-7} wt%

The reactor was heated and held for the time required to evaporate 90% of the loaded tellurium. The temperatures of the heaters (1) and (2) were selected in this way, on the one hand, to ensure the highest evaporation rate of the original tellurium, on the other hand, to prevent the interaction of TeO_2 with the material of the reactor walls and the internal quartz glass rigging.

After the end of the oxidation process, the reactor was cooled down to RT. The condenser (6) with the synthesized preparation was pulled out and the samples of the preparation were taken for the investigation of impurity and phase purity.

2.2. Impurity analysis technique

Samples of the tellurium (IV) oxide preparations were prepared for ICP-MS analysis in a laboratory room that met the ISO 6 cleanroom requirements.

Nitric (HNO_3) and hydrochloric (HCl) acids of 99.9999% purity (based on 68 elements) were produced by the surface distillation (BSB-929-IR, Berghof, Germany) of the respective pure-grade acids. The deionized water (H_2O) was produced by an Aqua-MAX-Ultra 370 Series setup (Young Lin

Instruments, South Korea) and had 18.2 M Ω cm electrical resistance and 99.9999 wt% purity (based on 68 elements).

TeO₂ samples (250 mg) were dissolved in a mixture of nitric (HNO₃) and hydrochloric (HCl) acids at a HNO₃:HCl volume ratio of 1:3 in polytetrafluoroethylene (DAP-100, PTFE, Berghof, Germany) autoclaves using a SpeedWave Four microwave decomposition system (Berghof, Germany). The dissolution process was run for 40 min, and the temperature in the autoclave was maintained at 170°C. The dissolution product was transferred to a polypropylene (PP) test tube. A 1-mL aliquot taken from the resultant solution was transferred to a PP test tube, and then the solution was brought to 10 ml by water. The solution thus prepared was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

The measurements were performed using a NexION 300D ICP-MS system (PerkinElmer, USA) in collision mode (kinetic energy discrimination, KED) [7]. The measurement conditions are summarized in Table 1.

Table 1. ICP-MS analysis conditions and instrumental parameters

Nebulizer type	Concentric (Meinhard), PFA
Spray chamber	Scott double-pass chamber, PFA
Argon flow rate, L/min through the nebulizer	0.96
plasma-forming auxiliary	15
	1.2
Generator power, W	1450
Collision gas (He) flow rate, L/min	14.6
Number of scan cycles	10

2.3. PXRD analysis

To confirm the phase of paratellurite crystal (β -TeO₂) powder X-ray diffraction analysis was carried out using an EQUINOX 2000 (INEL Corp., France). It is known that β -TeO₂ is tetragonal crystal system, space group P41212, cell parameters $a = 4.812(5)$ Å, $c = 7.615(9)$ Å. The X-ray diffraction analysis revealed no extraneous phases in the sample of the produced tellurium dioxide, except the β -TeO₂ phase (Figure 3), despite the fact that the zone of tellurium dioxide formation was close to the boat with the initial substance.

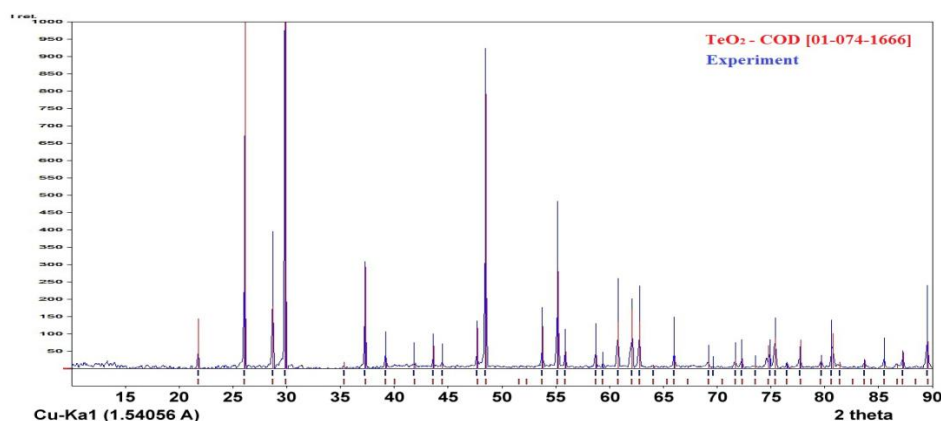


Figure 3. XRD pattern of polycrystalline β -TeO₂ produced by direct synthesis

2.4. IR transmission analysis

A comparative analysis of the IR absorption spectra of samples of a commercial preparation of tellurium oxide obtained by «wet» synthesis and a sample obtained by direct synthesis was carried out. To measure the absorption spectrum, the samples were crushed in an inert atmosphere and compressed into a tablet. Fourier transform infrared spectroscopy (FTIR) was performed on a Tensor 27 FT-IR spectrophotometer

(Bruker, Germany) in the wavelength range $6000\text{--}400\text{ cm}^{-1}$. The FT-IR absorption spectra of samples TeO_2 demonstrated two recent absorption bands around 775 and 656 cm^{-1} , which related to the vibration of the Te-O bond [6]. It was found that an absorption in the IR region of the ($\beta\text{-TeO}_2$ preparation which we made by the direct synthesis was two times less comparing to those for the commercial sample produced by the wet technique. In the case of the commercial sample we also observed vibrational peaks around 3500 cm^{-1} which are attributed to OH-group of the water (Figure 4).

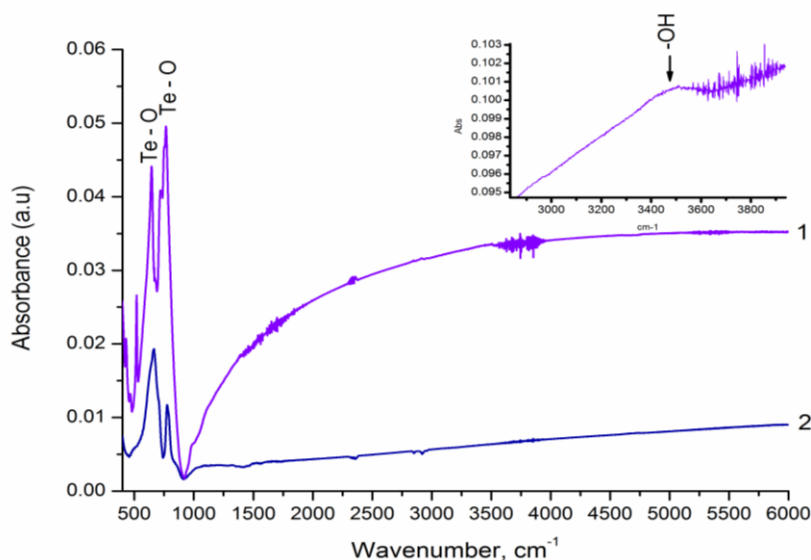


Figure 4. Normalize FT-IR absorption spectra of samples: 1 - commercial preparation («wet» synthesis); 2 – crystalline $\beta\text{-TeO}_2$ produced by direct synthesis

3. Results and discussions

3.1. TeO_2 purification

It has been experimentally established that when the synthesis is carried out at a temperature exceeding 690°C , the TeO_2 formed begins to interact with quartz glass, which leads to product contamination with silicon and rapid destruction of the reactor. Therefore, in the future, the synthesis process was carried out at a reaction zone temperature not exceeding 650°C . The resulting tellurium (IV) oxide was a mixture of fine powder and larger dendritic crystals (Figure 5).

According to X-ray phase analysis (Fig. 4), the content of the elemental tellurium phase in samples of tellurium (IV) oxide was below the detection limit (0.5 wt%). The cell parameters of the produced $\beta\text{-TeO}_2$ was slightly different from the reference value: $a = 4.813(4)\text{ \AA}$, $c = 7.617(5)\text{ \AA}$. We explained this difference by the deviation from stoichiometry in our preparation because during the synthesis we optimized the oxygen partial pressure to increase the yield of the final product which was 97%.

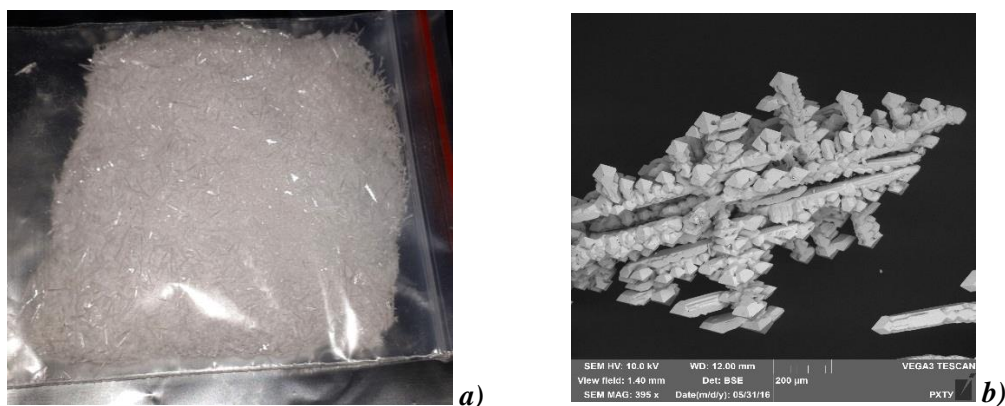


Figure 5. Habitus of the produced crystalline high-purity tellurium (IV) oxide: general image (a) and SEM image (b)

Analysis of the impurity content in the as-synthesized TeO_2 (Figure 6) showed that during the synthesis, the concentration of selenium impurity strongly decreases, while a slight contamination of the preparation with impurities of iron, cobalt, and nickel was observed.

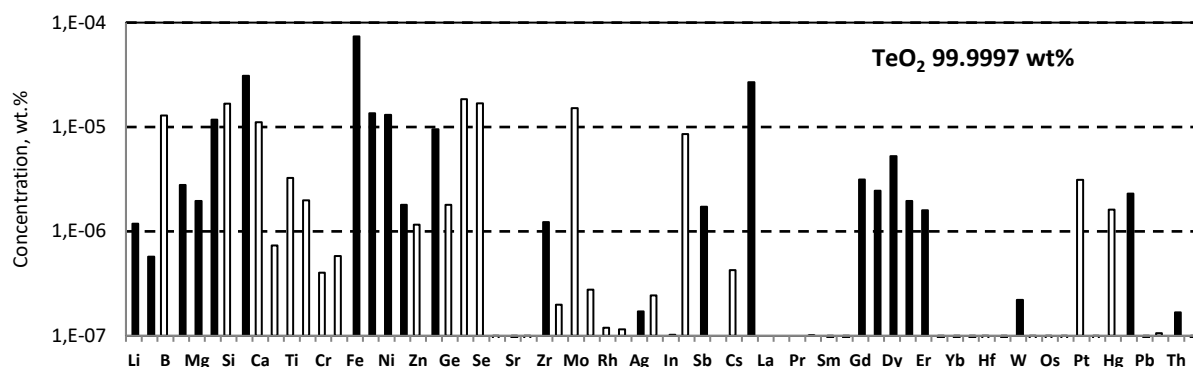


Figure 6. Impurity content in polycrystalline $\beta\text{-TeO}_2$ produced by direct synthesis. The empty bars indicate the limit of detection (LD) of ICP-MC analysis. The concentrations of the non-presented elements were less 10^{-7} wt%

The latter can be explained by secondary contamination during unloading of the preparation. The usage of Teflon devices for unloading improved the purity of the preparation. Finally, the total purity of the obtained polycrystalline $\beta\text{-TeO}_2$ preparation was 99.9997 wt%.

3.2. Paratellurite crystal growth

$\beta\text{-TeO}_2$ single crystal was grown in Czochralski configuration using a growth setup with controlled Ar-O atmosphere. P_{O_2} pressure during the growth process was maintained at the level which had been found during the experiments for direct synthesis of $\beta\text{-TeO}_2$ from vapor. The pulling rate of the cylindrical part was 1 mm/h at 40 mm crystal diameter. The grown crystal demonstrated better optical properties towards the crystals grown from commercial TeO_2 , produced by the «wet» technology (Table 2).

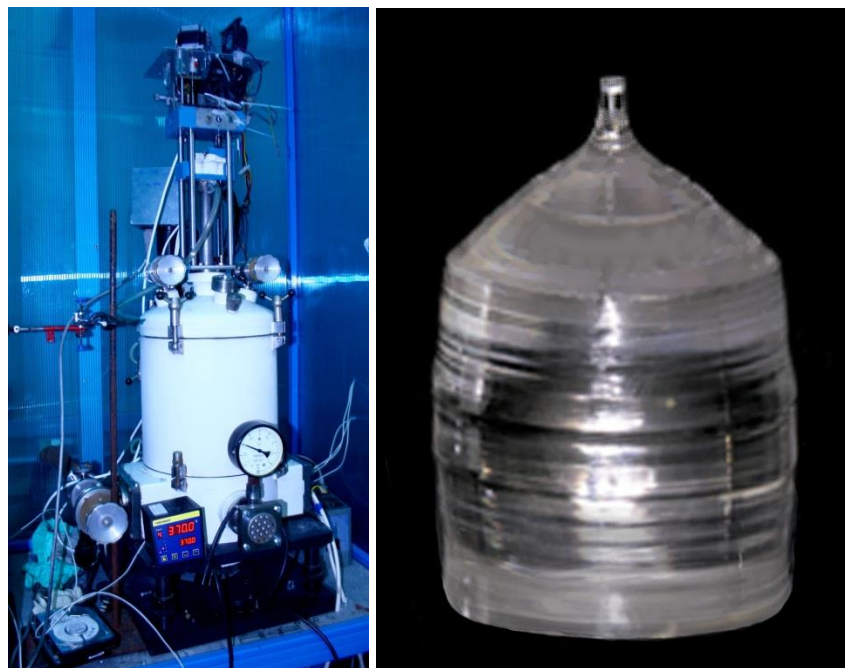


Figure 7. Impurity content in polycrystalline $\beta\text{-TeO}_2$ produced by direct synthesis. The empty bars indicate the limit of detection (LD) of ICP-MC analysis. The concentrations of the non-presented elements were less 10^{-7} wt%

Table 2. Values of specific optical rotation and Verdet constant of paratellurite crystals

λ , nm	Ref. [8]	Ref. [9]	Our crystal
ρ (633 nm), deg/mm	87	84.7±0.3	84.7±0.2
ρ (531 nm), deg/mm	143	146.0±0.3	147.2±0.2
ρ (488 nm), deg/mm	184	186.0±0.3	188.1±0.2
V (355 nm), red A ⁻¹		1.7×10 ⁻⁴	1.9×10 ⁻⁴
Acoustic velocity [001] m/s (633 nm)	4260		4310
Figure of merit [010]>[100] 10 ⁻¹⁵ s ₃ /kg	34.5		34.8

4. Conclusions

The developed technique makes it possible to produce high-purity (99.9997 wt%) polycrystalline β -TeO₂ with lowered residual water content. The preliminary crystal growth experiments showed that the usage of as-synthesized β -TeO₂ allowed decreasing the crystal adsorption in near IR region in about 30 rel.%. This is very promising result for both transmission IR devices (optical fibers) and high power acousto-optical and electro-optical converters. The β -TeO₂ crystal grown from the synthesized 5N7 water free preparation has demonstrated better optical properties towards the crystals grown from commercial TeO₂, produced by the «wet» technology.

Acknowledgement

The research was supported by the Russian Federation Ministry of Education and Science by the agreement with the unique identification code RFMEFI577716X0218.

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