

Characterization of niobium(v) oxide received from different sources

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Abstract The characterization of three commercial powders of niobium(V) oxide received from two producers was made. The thermal behavior of Nb₂O₅ up to melting point and its microstructure were studied using X-ray powder diffraction, thermoanalytical methods (DSC/TG), infrared spectroscopy (IR) and scanning microscopy. Analysis of the obtained results revealed that the starting structure of niobium(V) oxide and its thermal behavior depend on the origin of niobia. Depending on the origin of the powder and of its thermal treatment, three polymorphs of Nb₂O₅ can be observed. Sintering of powders above 1200 °C results in the formation of single phase, H-Nb₂O₅.

Keywords Niobium(V) oxide · Polymorphism · Microstructure

Introduction

Niobium(V) oxide as one of transition metal oxides (TMOs) has been extensively studied due to its promising properties and applications. There are many reports focusing on its crystal structure [1–12] as well as on its electrical [13, 14], catalytic [15–17], optical [18, 19] and thermal properties [8, 11, 20–22]. There are nine polymorphic forms of Nb₂O₅ that have so far been reported: TT, T, B, M, H, N, P, R and Z [1, 23, 24]. They belong to low-temperature (TT, T), medium-temperature (M, B) and

high-temperature forms (H) [25]. The M-phase (tetragonal structure with I4/mmm space group) was reported to form in the presence of H-Nb₂O₅ [26]. In some cases, N-phase accompanies M-, B- or H-forms and it seems to be metastable. Formation of P-phase is possible only in the presence of a small amount of water. R-form can be obtained by chemical transport of Nb₂O₅ at temperature 600–800 °C. Z-form was reported to be present as a secondary phase with B-Nb₂O₅ and is formed from H-Nb₂O₅ after heat treatment at 800–1100 °C under high pressure [24]. The formation of a selected polymorph and its thermal behavior are dependent on its synthesis route and possible impurities [1]. The most common polymorphs are the T-Nb₂O₅ (orthorhombic form with Pbam space group) [25] and H-Nb₂O₅ (monoclinic form with P2 space group) [27]. The H-phase is the most thermodynamically stable form of Nb₂O₅ and can be obtained from any other polymorph after properly conducting heat treatment.

Commercially available Nb₂O₅ is often multiphase, with one phase dominating [28–30]. The content of the coexisting Nb₂O₅ polymorphs is not specified by providers and differs slightly in each batch, and neither reported in the literature when Nb₂O₅ is used for synthesis. As it is explained in the literature, one of the biggest challenges in the current studies of niobates is the control and reproducibility of their properties, which are typically influenced by synthesis methods and the quality of used niobium(V) oxide. Additionally, it is known that there is a direct structural relationship between the source form of Nb₂O₅ and the obtained binary and ternary oxides [4]. The influence of phase composition of Nb₂O₅ starting powder on the phase equilibria in the Nb₂O₅-based solid solution has been reported in [28]. Hreščak et al. [31, 32] investigated the influence of different polymorphic forms of niobium pentoxide on the solid-state synthesis of potassium

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sodium niobates. They showed that orthorhombic Nb_2O_5 reacts in the presence of carbonates forming stoichiometric $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$, while under the same conditions mixture of $\text{H-Nb}_2\text{O}_5$ and $\text{T-Nb}_2\text{O}_5$ forms an inhomogeneous mixture of solid solutions with various Na/K ratios. The authors suggested that the reason for such behavior is not only polymorphic form of Nb_2O_5 but also the particle size distribution of niobia. These reports indicate that the origin and related specific chemical and physical properties of the niobium oxides can have a decisive influence on the interpretation of phase equilibria in binary and ternary systems with niobium pentoxide as one of independent constituents. Obtaining reliable data on phase equilibria is conditioned by the quality of the pure system components used in investigations. Care should be taken with the possible impact of the quality of Nb_2O_5 on the properties and the quality of the binary oxides, which are not commercially available. In this context, it becomes obvious that characterization of niobia used for further syntheses and investigation of phase equilibria is extremely important. That is why the present study reports the thermal, structural and microstructural characterization of three commercial samples of niobium(V) oxide.

Experimental

Following niobium(V) oxides were used in the study: high purity (HP sample, 98.5%, AD4796) and optical grade (OG sample, 99.8%, AD6252), both from CBMM (Companhia Brasileira de Metalurgia e Mineração, Brazil), as well as 99.9% powder (SA sample, Sigma-Aldrich, China).

Structural changes of Nb_2O_5 up to melting temperature were investigated by XRD technique using Siemens D5000 diffractometer equipped with copper radiation tube. The measurements were taken in 2θ angle range of $5\text{--}60^\circ$ with 0.04° step and at 4-s measurement time per step. The high-temperature behavior of niobia was determined by analysis of XRD patterns carried out at ambient temperature on the samples sintered at an appropriate temperature for 10 h and rapidly cooled in mixture of ice and water (supercooled).

Melting points of samples were determined by observation of pelletized powders behavior using pyrometer (Cyclops 100 Ametek Land, Dronfield, U.K.) which was calibrated against melting points of $\text{Ca}_3(\text{PO}_4)_2$ (1810°C), CaKPO_4 (1560°C) and $\text{Ca}_2\text{P}_2\text{O}_7$ (1353°C). The experiments were performed in a horizontal tubular furnace with molybdenum heating wires under argon atmosphere.

Density of powders was determined in argon atmosphere (5 N purity, 1.4 bar) using Ultrapyc 1200e pycnometer (Quantachrome Instruments, USA).

IR spectra of Nb_2O_5 samples were measured in the range of $400\text{--}4000\text{ cm}^{-1}$ using a Thermo Scientific Nicolet

6700 FTIR spectrometer with 2 cm^{-1} resolution. The powders used for measurements were diluted with KBr and pressed in pellets with mass content of $\text{Nb}_2\text{O}_5 < 0.5\%$.

The thermoanalytical study was carried out using a SETSYSTM 1500 (TGA-DSC; SETARAM) calorimeter in the temperature range of $20\text{--}1300^\circ\text{C}$ in argon atmosphere with heating and cooling rates of $10^\circ\text{C min}^{-1}$ (platinum crucibles). The sample weight was $0.040\text{--}0.060\text{ g}$.

Scanning electron microscopy (SEM) was used in order to research the morphology of the studied niobium(V) oxides. SEM micrographs of the samples were registered by a Quanta 250 made by FEI (Japan).

Results and discussion

Figure 1 shows X-ray diffraction patterns of examined Nb_2O_5 powders. Reflections of only one phase can be observed in the patterns of HP and SA samples that correspond to $\text{H-Nb}_2\text{O}_5$ (ICDD card No 37-1468) and $\text{T-Nb}_2\text{O}_5$ (ICDD card No 27-1003), respectively. An analysis of the diffractogram of OG sample revealed a multiphase character of the powder. Reflections of two main phases structurally corresponding to $\text{T-Nb}_2\text{O}_5$ (ICDD card No 27-1003) and $\text{H-Nb}_2\text{O}_5$ (ICDD card No 37-1468) are visible in the pattern. In addition, a third polymorph of niobia, $\text{M-Nb}_2\text{O}_5$ (ICDD card No 32-0711) can be identified in the diffractogram of the OG sample. $\text{M-Nb}_2\text{O}_5$ has been reported to form as a metastable phase during transformation of $\text{T-Nb}_2\text{O}_5$ into $\text{H-Nb}_2\text{O}_5$, which was confirmed by synchrotron radiation high-resolution XRD measurements [26]. It should be mentioned that similar XRD pattern to the M-phase has the $\text{N-Nb}_2\text{O}_5$ (ICDD card No 20-0804, monoclinic structure with C2/m space group).

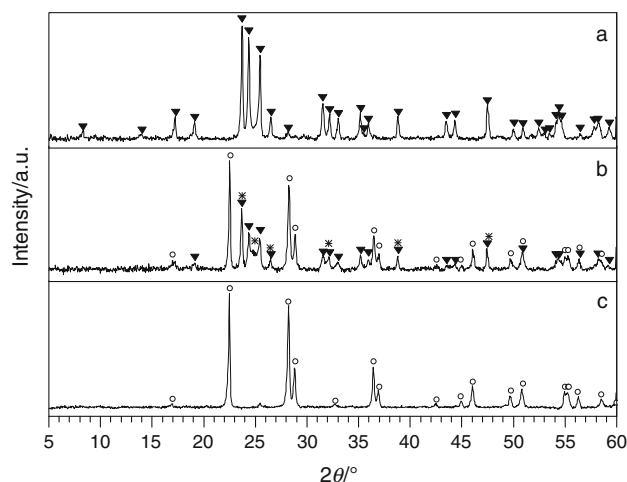


Fig. 1 The XRD patterns of niobium(V) oxide powders: HP (a), OG (b), SA (c) Filled inverted triangle $\text{H-Nb}_2\text{O}_5$, circle $\text{T-Nb}_2\text{O}_5$, asterisk $\text{M-Nb}_2\text{O}_5$

However, the presence of the N-phase was reported only in samples contaminated by F^- or OH^- ions [1, 23, 33, 34], and hence, the presence of M-phase seems to be more justified.

The melting points of Nb_2O_5 samples were determined by pyrometric observations. The values of 1500 ± 20 °C and 1490 ± 20 °C were obtained for powders from CBMM (HP and OG) and SA sample, respectively. The determined melting temperatures are in good agreement with literature data [35, 36].

Structural changes of Nb_2O_5 heated at different temperatures up to melting point were investigated using X-ray powder diffraction and infrared spectroscopy. Figures 2–4 show XRD patterns of samples supercooled from 800 to 1400 °C as well as of molten and next slowly cooled to ambient temperature. The XRD patterns of the HP sample (Fig. 2) sintered at different temperatures evidenced no changes in visible diffraction lines. However, the raised background at $2\theta \sim 25^\circ$ for powders annealed below 1200 °C can suggest the presence of M- Nb_2O_5 . The DSC/TG measurement up to 1300 °C showed no thermal effects on the heating and cooling curves.

In the case of SA sample only T- Nb_2O_5 modification was observed up to 800 °C (Fig. 3). Long-term annealing at 900 °C results in the transition of orthorhombic phase to a mixture of H- Nb_2O_5 and M- Nb_2O_5 . The structural transformation of the niobium pentoxide is accompanied by heat absorption, which is visible on DSC-heating curve of the powder (Fig. 4). The related endothermic effect has the onset temperature of 911 °C. As it has been reported in the previously published literature [37], the phase transition occurs at 900–1100 °C, which is in agreement with the

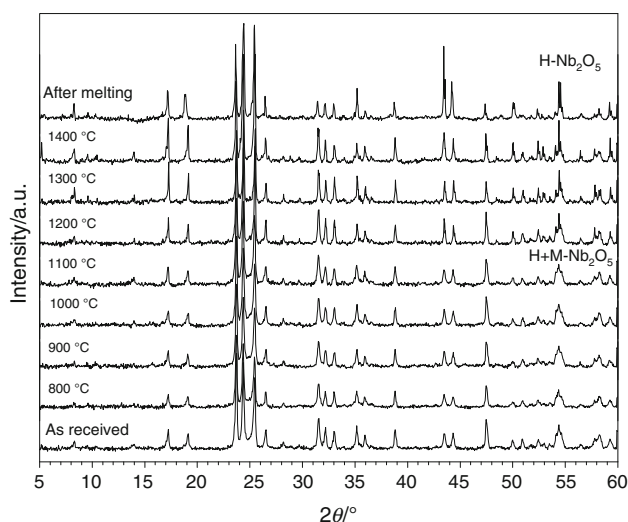


Fig. 2 XRD patterns of HP sample sintered in the 800–1400 °C range for 10 h and after melting

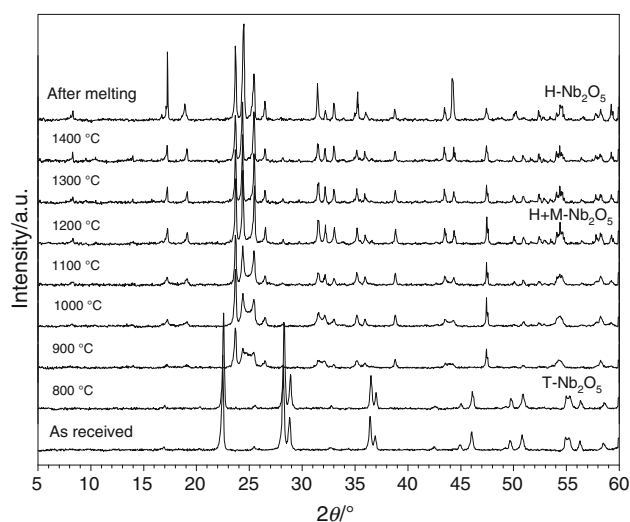


Fig. 3 XRD patterns of SA sample sintered in the 800–1400 °C range for 10 h and after melting

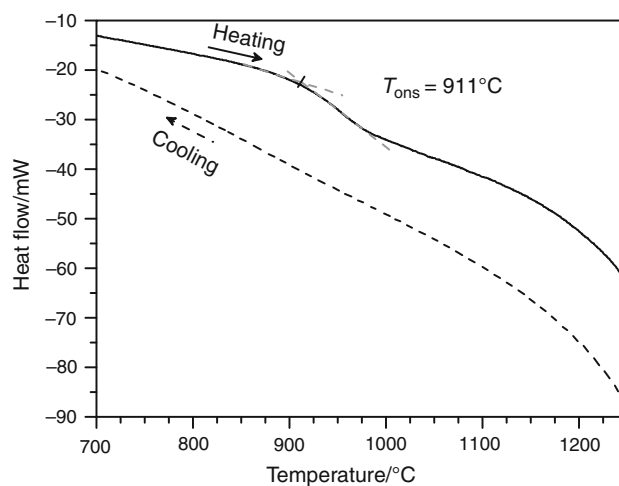


Fig. 4 The heating and cooling DSC curves of SA niobium(V) oxide

results obtained in the current study. Above 1200 °C only H-phase is present in SA powder.

The XRD analysis (Fig. 5) showed that the OG powder is a mixture of T-, M- and H-phases up to 800 °C. Annealing at 900 °C results in the disappearance of T-phase, and at temperature range 900–1200 °C, two polymorphs (M- and H- Nb_2O_5) are observed. Above 1200 °C, only H-phase is present in the powder. No thermal effects and mass changes were visible on DSC/TG-heating curve of the OG sample.

The various Nb_2O_5 polymorphic forms primarily possess NbO_6 coordination which are distorted to an appreciable extent, and some of oxygen atoms are connected to more than one niobium atom. The distortions in the NbO_6 octahedra are caused by the formation of corner- or edge-shared polyhedra [38] and can be identified in the

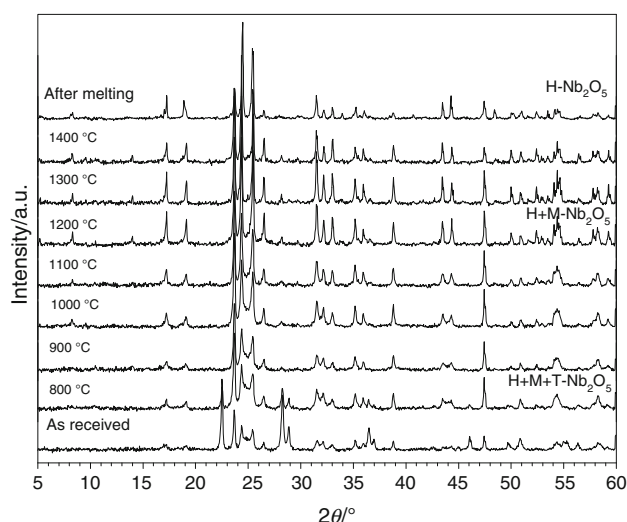


Fig. 5 XRD patterns of OG sample sintered in the 800–1400 °C range for 10 h and after melting

400–1200 cm^{-1} wavenumbers range of IR spectra. Bands belonging to each of specific modes will show multiple bands depending on the symmetry of polymorph and the type of interactions, originating from the way in which polyhedra are linked together. They will appear as a broad absorption band if energy of individual vibrations differ slightly or as a series of discrete bands in the case of a larger difference in energy. Furthermore, different niobium–oxygen bond lengths in various polymorphs cause a shift in IR frequency. The infrared absorption spectra of niobia are characterized by bands assigned to the Nb–O vibrations: Nb₃–O (a trigonal pyramidal structure) stretching, Nb–O–Nb bridging and Nb=O terminal modes observed in the ranges of 380–500, 580–850 and 850–910 cm^{-1} , respectively [30, 39–43].

The differences in IR spectra of Nb₂O₅ polymorphs are best demonstrated by comparison of the results obtained for the single-phase SA powders: received from the producer as well as for the sample annealed at 1200 °C (Fig. 6e, f). In the IR spectrum of the not heat-treated SA powder (T-phase), intensive bands at 565, 619, 815 and 850 cm^{-1} are observed. The other weak absorption band at 727 cm^{-1} is also visible in the spectrum. The broadening of bands in the 500–950 cm^{-1} range indicates that the sample possesses a disordered structure [40]. The IR spectrum of SA sample heated at 1200 °C (H-Nb₂O₅) differs from that of T-Nb₂O₅. The lowering of the crystal symmetry (from orthorhombic to monocline) results in splitting of bands in the range of 550–950 cm^{-1} as well as in intensity increase in bands in the range of 700–800 cm^{-1} . Additionally, new bands at 448, 470, 500 and 960 cm^{-1} could be recognized in the spectra of H-phase. Samples HP and OG annealed at 1200 °C

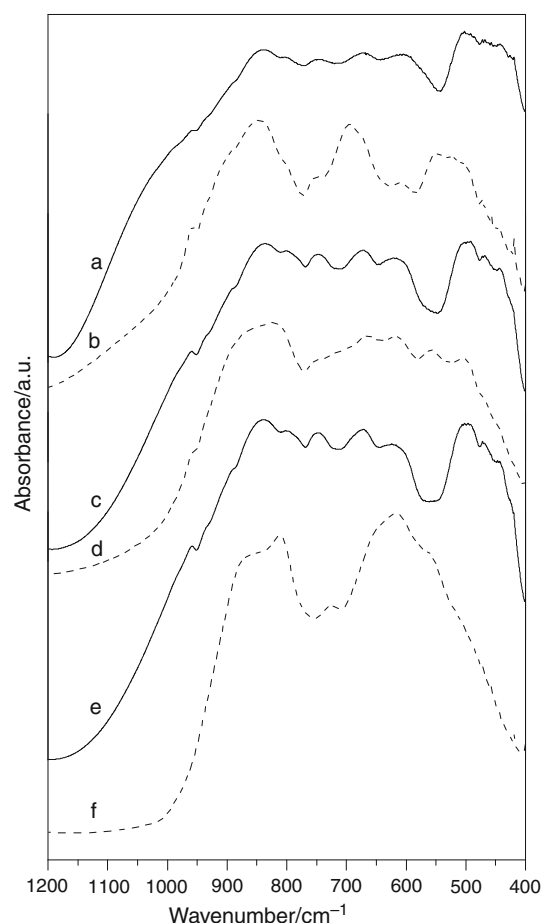


Fig. 6 The IR spectra of niobium(V) oxides: (a, b) high purity, (c, d) optical grade, (e, f) Sigma-Aldrich. Solid line samples obtained by annealing in air at 1200 °C for 10 h and supercooling to ambient temperature, dotted line received powders

(Fig. 6a, c) showed spectra similar to SA sample calcined at 1200 °C (Fig. 6e), as they correspond to pure H-phase. The complexity of IR spectra related to the mixture of three polymorphs (sample OG, Fig. 6d) makes it difficult to analyze. The IR spectrum of as-received HP powder (Fig. 6b) slightly differs from the H-Nb₂O₅ spectrum. Instead of a series of discrete bands, the three intensive bands at 845, 694 and 540 cm^{-1} and other two with lower intensity at 749 and 620 cm^{-1} are visible. The band at 960 cm^{-1} characteristic for monoclinic phase also appears. This suggests that HP sample contains more than one polymorphic form. Similar IR spectra for Nb₂O₅ were previously reported and interpreted as spectra of H-Nb₂O₅, although presented XRD patterns indicated that the samples also included M-Nb₂O₅ [41–43]. In order to confirm the presence of the M-form in HP powder, IR spectrum was registered for the SA powder annealed at 900 °C, which contains a significant amount of M-form. The compared IR spectra of the as-received HP powders and SA sample calcined at 900 °C show the same intensive and weak

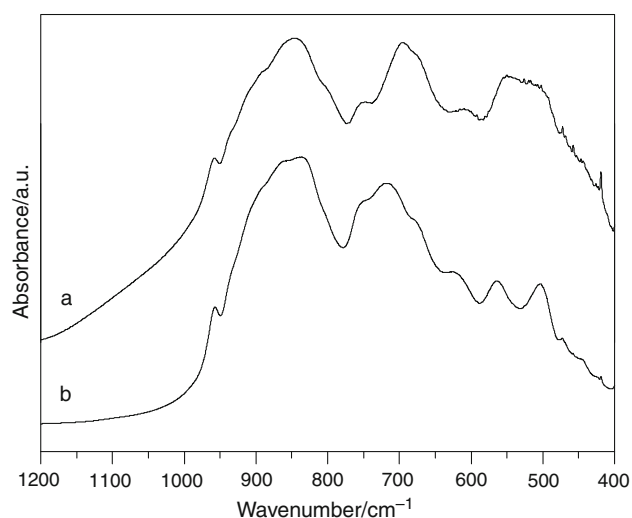


Fig. 7 The IR spectra of *a* as-received HP powder and *b* SA sample calcined at 900 °C

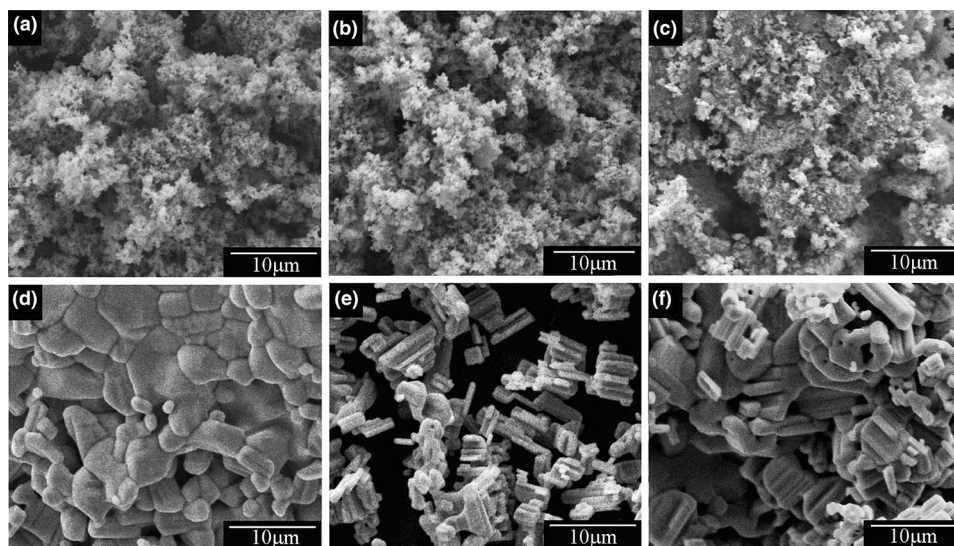
bands at 845 cm^{-1} and 749 and 620 cm^{-1} , respectively (Fig. 7). Absorption band observed at 694 cm^{-1} for HP powder is slightly shifted toward higher wavenumbers (720 cm^{-1}), while the one at 545 cm^{-1} is split into two bands (465 and 504 cm^{-1}). Shifting and splitting of bands are probably due to different contents of $\text{H-Nb}_2\text{O}_5$ and $\text{M-Nb}_2\text{O}_5$ in investigated samples. As the XRD diffraction lines for H- and $\text{M-Nb}_2\text{O}_5$ occur at similar 2θ values, the presence of M-phase can be established on the basis of raised background between two diffraction lines at $\sim 25^\circ$. For the SA powder annealed at 900 °C, it is clearly visible (Fig. 3), while for HP powder it is not obvious and only comparison of the XRD patterns of samples sintered at temperature above 1200 °C reveals discrete increase in background. Based on obtained results, it can be concluded

that the as-received HP sample is also a mixture of polymorphs and contains a small amount of M-phase.

The analysis of SEM micrographs showed that all of the niobium(V) oxide powders, received from producers, were composed of agglomerates built of grains with submicron size (Fig. 8a–c). Heating of the powders at 1200 °C results in strong increase of grains (Fig. 8d–f). The HP sample sintered at high temperature is composed of agglomerated particles with irregular shape and size ranging from 1 to 8 μm (Fig. 8d). The heat-treated SA sample contains well-developed polyhedral grains with an elongated shape and $0.5\text{--}1\text{ }\mu\text{m} \times 2\text{--}6\text{ }\mu\text{m}$ size (Fig. 8e). A small degree of the particles agglomeration is also visible in the SEM image. The microstructure of the OG sample sintered at 1200 °C is similar to the both above discussed powders. Both the small, polyhedral particles and the grains of an irregular shape are present in the powder (Fig. 8f).

Density of the SA sample sintered at 1200 °C has been determined by pycnometric measurements. The mean density of the powder amounted to $d = 5.260 \pm 0.027\text{ g cm}^{-3}$, which is a much higher value than the theoretical density reported for H-phase. The densities of the other samples could not be determined, due to the inability of applied in the measurement gas (argon) to penetrate small pores present in agglomerate samples (Fig. 8d, f). According to the literature, experimentally determined densities of H-phase equal 4.55 [8] and 4.46 g cm^{-3} [1], whereas X-ray densities are: 4.52 [8], 4.54 [9] and 4.55 g cm^{-3} [10]. The reported [8] experimental density was measured using liquid pycnometer on sample that was not verified to be pore-free, so these value should not be considered as true density. There are no details of determination method of the second reported experimental value [1]. The verification of theoretical densities requires re-determination of the exact $\text{H-Nb}_2\text{O}_5$

Fig. 8 SEM images of the commercial powders: *a* $\text{HP-Nb}_2\text{O}_5$, *b* $\text{SA-Nb}_2\text{O}_5$, *c* $\text{OG-Nb}_2\text{O}_5$, and the powders after annealing in air at 1200 °C for 10 h and next supercooling: *d* $\text{HP-Nb}_2\text{O}_5$, *e* $\text{SA-Nb}_2\text{O}_5$, *f* $\text{OG-Nb}_2\text{O}_5$. Magnification $\times 4000$



structure. Further studies of the H-Nb₂O₅ structure re-determination are planned in order to explain the divergence of the density values of H-phase.

Conclusions

1. The crystalline structure of niobia is dependent on the powder origin. The powders were found to be single phase (SA samples) or multiphase (OG and HP samples). Three different polymorphs were identified in investigated powders: T-Nb₂O₅ (SA and OG sample), H-Nb₂O₅ (HP and OG powders) and M-Nb₂O₅ (HP and OG powders).
2. T-Nb₂O₅ exists up to 800 °C as a single phase or in a mixture with H-Nb₂O₅ and M-Nb₂O₅ phases.
3. The phase transition from T-Nb₂O₅ to H-Nb₂O₅ is accompanied by the formation of tetragonal M-Nb₂O₅ and takes place at 911 °C.
4. The pure H-Nb₂O₅ polymorph is observed above 1200 °C, regardless of the initial phase composition of powder.
5. The interpretation of Nb₂O₅ XRD patterns should be made with care because of similarity of H- and M-phases diffractograms. The use of IR technique for the phase purity check seems to be reasonable, while even a small amount of M-Nb₂O₅ results in the presence of characteristic intensive absorption bands in IR spectra of niobia.

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