# PREPARATION AND CHARACTERIZATION OF BOEHMITE, CuO, TiO₂ AND Nb₂O₅ BY HYDROTHERMAL ASSISTED SOL-GEL PROCESSING OF METAL ALKOXIDES

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*Conventional and hydrothermally assisted sol-gel processing have been used to synthesis of monodispersed nanosize boehmite, copper, titanium and niobium oxides from their alkoxides. The prepared powders have been characterized by X-ray diffraction (XRD), thermal analysis (TGA/DSC) and scanning electron microscopy (SEM). XRD, infrared spectroscopy (IR) and thermal analysis showed that the degree of crystallization of boehmite, prepared by hydrothermally assisted sol-gel processing from aluminum 2-butoxide, increases by increasing processing temperature. Pure tenorite phase was formed in either conventional or hydrothermally assisted sol-gel processing from copper 2-pyridylethoxide. Conventional sol-gel processing of titanium oxide from titanium 2-ethoxyethoxide resulted to formation of a mixture of rutile and anatase phases, whereas hydrothermally assisted sol-gel processing ends up to formation of pure anatase phase. Single phase Nb₂O₅ is formed in either conventional or hydrothermally assisted sol-gel processing from niobium 2-ethoxyethoxide. Scanning electron microscopy (SEM) revealed spherical, nanosize and homogenous particles for the oxides prepared by hydrothermally assisted sol-gel processing.*

## INTRODUCTION

In recent years, preparation of ceramic powders by sol-gel process and hydrothermal method has attracted a considerable amount of interest [1-5]. Part of this interest was caused by the fact that these methods offer good grip for control of morphology, homogeneity, surface area and pore size distribution in comparison to conventional routes [6]. Although, hydrothermal method is simple, low temperature process and cost effective route for the preparation of crystalline single-phase oxides; sol-gel is expensive route for the preparation of ceramics. However, when certain specifications such as homogeneity, high purity, narrow particle-size distribution and agglomerate free powders are needed in electroceramic industry, the sol-gel process is probably the best approach [7-9]. But in most cases, due to high sensitivity of metal alkoxides to the moisture and inhomogeneous precipitation during conventional sol-gel processing, alkoxides with long-chain alkyl group or internally coordinated alkoxides for reducing rate of hydrolysis is required to prepare precursor materials [10-13]. This approach has successfully been applied to prepare alumina, beohmite and occasionally for other oxides in either classical or hydrothermal methods [14-15]. However, large amount of carbon in the precursor materials, as shown by thermal analysis [16], will prevent complete crystallization of ceramics at lower temperature, and calcination at higher temperature will led to the aggregation or phase transformation. Furthermore, trace amount of carbon residue can have negative impact on quality of powder that would be an obstacle for the preparation of high-quality materials for advanced technology.

The aim of this work was to prepare metal oxide powders from their metal alkoxides by combing hydrothermal and sol-gel process, two powerful ceramic processing methods, in order to decrease the rate of hydrolysis. In this approach by avoiding direct contact of water with metal alkoxide, the hydrolysis rate decreases and allows preparing nanosized spherical powders, not accessible by sol-gel or conventional routes.

## EXPERIMENTAL

### Synthesis

Aluminum 2-butoxide, niobium ethoxide and copper methoxide were synthesized according to literature [17, 18]. The prepared aluminum and niobium alkoxides were doubly distilled in vacuum in order to obtain

high quality metal alkoxide precursors. Titanium isopropoxide was purchased from Fluka and used as received. Niobium and titanium 2-ethoxyethoxides were prepared by reaction of niobium ethoxide and titanium isopropoxide with 2-ethoxyethanol in benzene [17, 19]. Copper 2-pyridylethoxide was prepared by reaction of copper methoxide and 2-pyridylethanol in THF [20]. The mixtures were stirred overnight and then released solvents and alcohols were removed under reduced pressure to obtain viscose products.

### Conventional sol-gel processing

0.25 M solution of metal alkoxide in parent alcohol was prepared and then hydrolyzed with a 10% solution of deionized water in parent alcohol under vigorous stirring at ambient temperature. The product was filtered off and dried overnight at 100°C and stored for analysis.

### Hydrothermally assisted sol-gel processing

For the hydrothermally assisted sol-gel processing, metal alkoxides were diluted to various concentrations with parent alcohol, the mixture was loaded into a glass container and transferred into a 300 ml stainless steel autoclave. Dilution of metal alkoxides was carried out in Schlenk line [21], and their transfer into autoclave was performed in moisture-free atmosphere to prevent their hydrolysis before introducing into a hydrothermal chamber. The gap between glass container and chamber was filled with 50 ml of distilled water and then the autoclave was tightly closed. The chamber was heated at various temperatures. After five to twenty four hours, the autoclave was cooled and the product was filtered off and dried overnight at 100°C. Experimental conditions for the hydrothermally assisted sol-gel processing of various metal alkoxides are given in table 1.

### Characterization techniques

X-ray diffraction (XRD) patterns of powder were collected on a Phillips PW-1730 diffractometer with CuKα radiation. Thermal analysis was carried out in a Rheometric Scientific STA-1500 with heating rate of 10°C/min in air. Electron microscopy was performed on a Phillips XL-30 scanning electron microscope (SEM). For observation of morphology by SEM, powders were coated with gold/palladium. Infrared spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer in KBr pellets at a resolution of 4 cm$^{-1}$. Specific surface areas were measured using BET method on a Quantachrome surface area analyzer at -196°C by nitrogen absorption ($S_{BET}$). Samples were degassed at 150°C for several hours prior to analysis.

## RESULT AND DISCUSSION

### Boehmite

Development of boehmite phase was followed by XRD, TGA/DSC, and FTIR. X-ray diffraction shows that the boehmite prepared below 50°C is poorly crystallized, pesudoboehmite develops at 100°C, and well-crystallized boehmite forms above 150°C (figure 1). Furthermore, for the sample processed at 50°C diffraction lines are broad and by increasing processing temperature the line broadening decreased. It is worth to mention that bayerite, Al(OH)$_3$, was the major phase in the preparation of boehmite from precipitated precursor from aluminum nitrate and sodium hydroxide under hydrothermal conditions at 120°C, and pure boehmite is formed only at prolonged heating time at 160°C [22]. However, present study shows no bayerite in the processing temperatures range of 50-200°C. This clearly reveals a significant role of the processing strategy or

Table 1. Experimental conditions.

| sample | metal alkoxide | Solvent | Concentration (mol/l) | Processing temperature (K) | Processing time (h) | Product |
|--------|----------------|---------|------------------------|-----------------------------|----------------------|---------|
| Al-1 | Al(O-$^s$Bu)$_3$ | $^s$BuOH | 2 | 323 | 24 | Boehmite |
| Al-2 | Al(O-$^s$Bu)$_3$ | $^s$BuOH | 2 | 373 | 5 | Boehmite |
| Al-3 | Al(O-$^s$Bu)$_3$ | $^s$BuOH | 2 | 423 | 5 | Boehmite |
| Al-4 | Al(O-$^s$Bu)$_3$ | $^s$BuOH | 2 | 473 | 5 | Boehmite |
| Cu-1 | Cu(OCH$_2$CH$_2$C$_5$NH$_4$)$_2$ | THF | 0.25 | - | - | Tenorite |
| Cu-2 | Cu(OCH$_2$CH$_2$C$_5$NH$_4$)$_2$ | THF | 0.25 | 333 | 7.5 | Tenorite |
| Ti-1 | Ti(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_3$ | Toluene | 0.25 | - | - | Rutile+Anatase |
| Ti-2 | Ti(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_3$ | Toluene | 0.25 | 473 | 5 | Anatase |
| Nb-1 | Nb(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_3$ | Toluene | 0.25 | - | - | Nb$_2$O$_5$ |
| Nb-2 | Nb(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_3$ | Toluene | 0.25 | 473 | 5 | Nb$_2$O$_5$ |

precursor in the preparation of boehmite under hydrothermal conditions. As previously noticed, the broadening of individual diffraction lines for boehmite prepared under hydrothermal conditions are different [22].

Figure 2 shows the TGA and DSC data for a boehmite sample prepared under hydrothermal condition at 150°C. The results are very similar to those reported for the fibrous boehmite [23]. The TGA curve shows 2 % weight loss in the temperature range of 75 to 100°C, this weight loss was accompanied by an endothermic peak centered at 70°C in the DSC curve, suggesting that the weight loss is due to the elimination of physically adsorbed water. For the sample Al-1 processed at 50°C, the intensity of the endothermic peak increases and its center is shifted to ca. 100°C. The distinct endothermic peak in the temperature range of 400 to 700°C in the DSC curve with significant weight loss in the TGA curve is associated with dehydration of boehmite to alumina. Interestingly, the intensity of dehydration peak increases and becomes sharper with increasing processing temperature. The weight loss in the 400-700°C rang in the TGA curve for the boehmite prepared at 200°C reaches 15 %, corresponding approximately to one mole of water. This is in good agreement with the XRD result, which shows boehmite phase well developed at 200°C. Furthermore, the XRD analysis indicates that the boehmite powder converts to $\gamma$-alumina by calcination at 500°C, the well-known process for the preparation of fine alumina from boehmite [24].

The infrared spectrum of individual samples is shown in figure 3. Typical bands for well-crystallized boehmite [25], 3075 and 3280 cm$^{-1}$, O-H stretching vibrations; 1075, 1150 cm$^{-1}$, O-H bending vibrations; 740 cm$^{-1}$, Al-O stretching vibration; and strong band at 480 cm$^{-1}$, Al-O bending vibration, are visible in the spectrum. The intensities of the above mentioned bands



Figure 1. XRD pattern of hydrothermal hydrolysis product of aluminum *tris-sec*-butoxide, Al-2) 373 K, Al-3) 423 K and Al-4) 473 K.
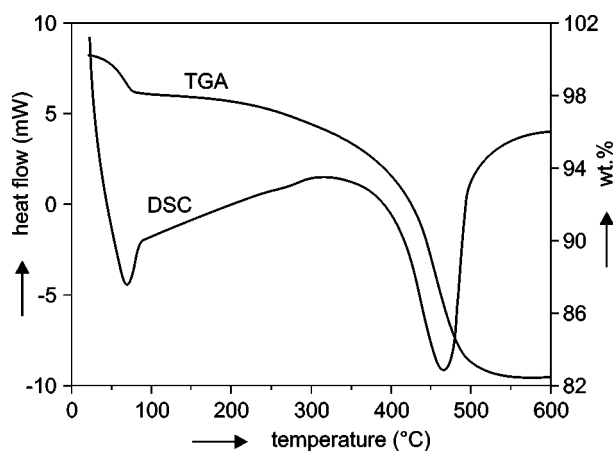


Figure 2. TGA and DSC curves of hydrothermal hydrolysis product of aluminum tris-sec-butoxide at 423 K, Al-3.
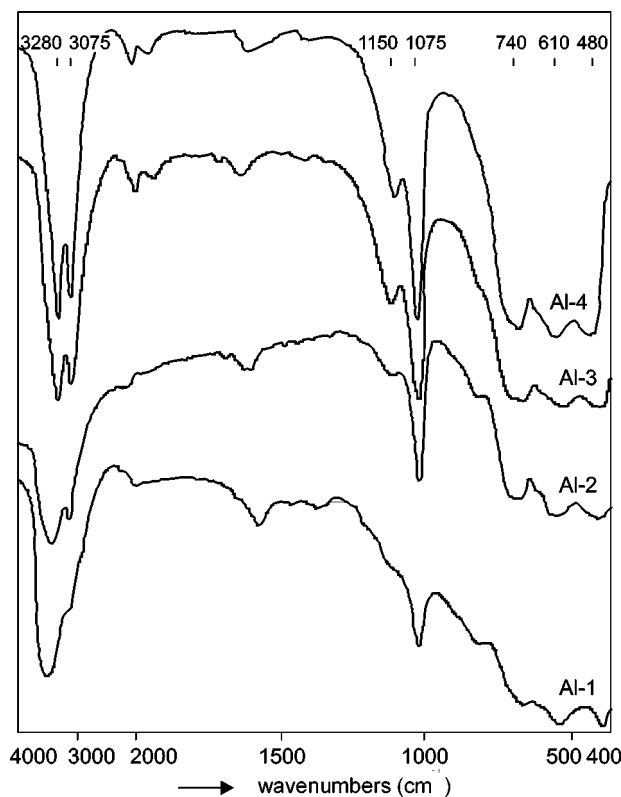


Figure 3. IR spectra of hydrothermal hydrolysis product of aluminum *tris-sec*-butoxide, Al-1) 323 K, Al-2) 373 K, Al-3) 423 K and Al-4) 473 K.

increases from sample Al-1 to Al-4 and it is in good agreement with the XRD results, which indicate that the degree of crystallization increases by increasing processing temperature. Interestingly, the broad hydroxyl and water band at ca. 3500 cm⁻¹ for the sample processed at 50°C splits into two bands at higher processing temperatures and indicates the development of well crystallized boehmite phase. Seemingly, in lower processing temperature the rate of hydrolysis is very slow and water is mostly trapped in particles rather than react with aluminum alkoxide. This argument is consistent with the TGA data indicating that the sample processed at higher temperature contain lower amount of water. Therefore, one may conclude that in the hydrothermal processing of boehmite, processing temperature is more crucial than the other parameters. This could be a reason for the formation of non-boehmite phase in direct hydrolysis of aluminum alkoxides, which provides large amount of water to system during hydrolysis at room temperature [13]. Apparently, hydrolysis mechanism of aluminum alkoxide is differing in hydrothermal assisted sol-gel processing from conventional one. The infrared spectra similar to the XRD results show no formation of bayerite phase, which is typical phase in low temperature hydrothermal processing of boehmite in the conventional hydrothermal processing [22].

Specific surface areas of samples that prepared by hydrothermal method at 373, 423 and 473 K in 2-butanol are 326, 124, and, 81 m²/g, respectively. The specific surface area decreases with increasing hydrothermal treatment temperature. Those data are consistent with XRD data, that shows the degree of crystallinity increase with increasing processing temperature. The surface area 326 m²/g of the sample processed at 373 K, is very close to the value 322 m²/g recently reported for

the mesoporous boehmite obtained by hydrolysis of aluminum 2-butoxide in mixture of ethanol and water at ambient temperature for 20 hours [26].

Boehmite morphology depends on hydrothermal condition [23]. Formation of rods, fibers, and thin microfoils has been reported [22]. In the present study the morphology of prepared boehmite was observed by scanning electron microscopy and micrographs of boehmite prepared at 423 and 473 K are shown in figure 4. Even at magnification 25000 the primary particles and fine details are not very clear due to the agglomeration and nanometer size of boehmite particles, however, their spherical shape is visible to some extent. Such difficulty for observation of nanosize powders has partially been attributed to the gold coating on the powder required for SEM examination. Effect of hydrothermal treatment temperature on particles size was not noticeable by SEM.

The exact assembly mechanism of boehmite formation in the present work is not known at this time; however, it seems likely that the nanoparticle assembly instead of supramolecular assembly mechanisms, which previously reported for the formation of boehmite and other oxides, is the operating mechanism [26-27]. The broad pore size distribution, 4.2 nm, of the sample processed at 100°C is consistent with the suggested mechanism.

### CuO

Figure 5 shows the XRD pattern of copper oxide obtained from hydrothermal hydrolysis of copper(II) 2-pyridylethoxide after calcination at 500°C. The as prepped material is amorphous and after calcination
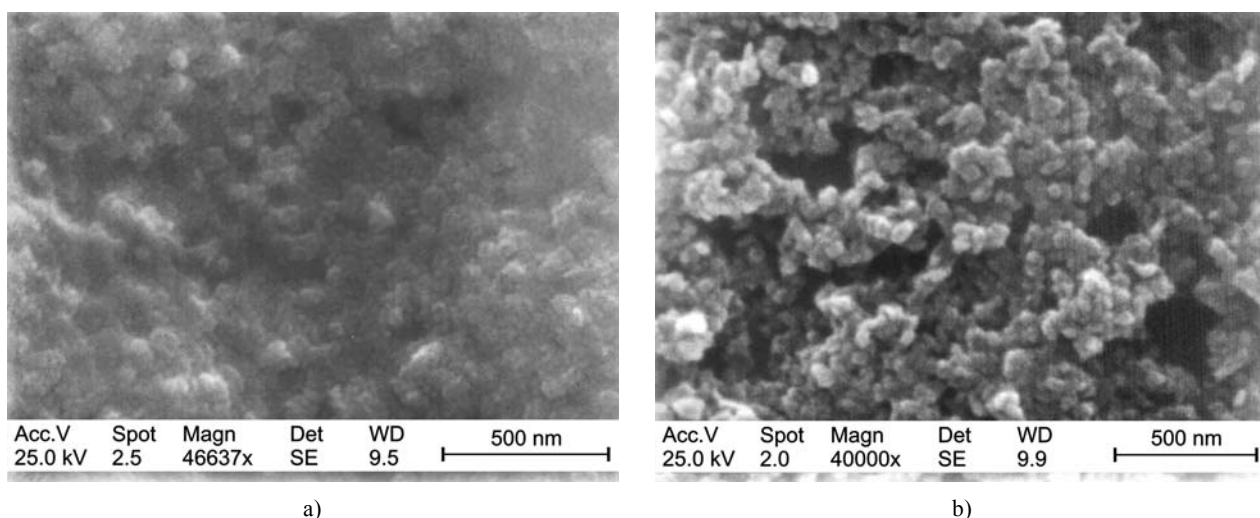


a)



b)

Figure 4. SEM micrograph of hydrothermal hydrolysis of aluminum tris-sec-butoxide, Al-3 (a) 423 K and Al-4 (b) 473 K.

converts to tenorite phase [28]. SEM micrograph (figure 6) shows that Cu-2, the copper oxide prepared by hydrothermal hydrolysis of copper(II) 2-pyridyleth-oxide is spherical with high degree of homogeneity, and with average particle size about 150 nm. Interestingly, the same copper oxide phase, tenorite, obtained from conventional hydrolysis, is granular as shown in figure 6, Cu-1. The distinct differences in morphology have been attributed to difference in mechanisms of hydroly-sis-condensation of two processes. As mentioned for the boehmite, nanoparticle assembly mechanisms could be the operating mechanism.
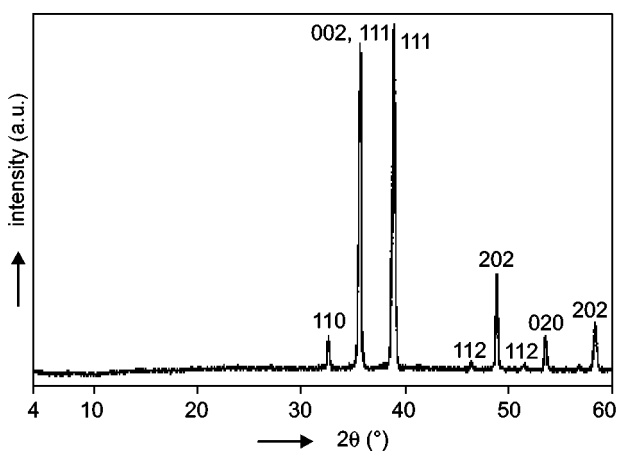


Figure 5. XRD pattern of hydrothermal hydrolysis product of Cu (OCH$_2$CH$_2$C$_5$H$_4$N)$_2$ after calcination at 773 K, Cu-2.

## TiO$_2$

The TGA curve of conventional hydrolysis product of Ti(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_4$ (figure 7, Ti-1) shows about 14 % weight loss in the temperature range of 80 to 110°C, and another 8 % weight loss in the temperature range of 145 to 170°C. Those weight losses are accompanied by endothermic peaks centered at 90 and 160°C in the DSC curve, suggesting that the weight losses is due to the elimination of physically adsorbed water and alcohol, respectively. The exothermic peak in the temperature range about 250-270°C in the DSC curve with about 19 % weight loss in the TGA curve is associated to combustion of organic residues. On the other hand, the TGA curve of the product obtained by hydrothermal hydrolysis of Ti(OCH$_2$CH$_2$OCH$_2$CH$_3$)$_4$ (figure 7, Ti-2) shows 23 % weight loss in the temperature range of 80 to 110°C, and another 23 % weight loss in the temperature range of 130 to 150°C; these weight losses are accompanied by endothermic peaks centered at 90 and 140°C in the DSC curve, suggesting that the weight losses is due to the elimination of physically adsorbed water and alcohol, respectively. The exothermic peak in range 270-350°C in the DSC curve with about 20 % weight loss in the TGA curve is associated with combustion of organic residue. It is interesting to note the similarity between the amounts of the organic residues in two samples obtained by conventional and hydrothermally assisted hydrolysis. Furthermore, thermal analysis indicates that no phase transition or crystallization occurs in the material prepared by hydrothermal hydrolysis of titanium 2-ethoxyethoxide up to 800°C, whereas thermal analysis of conventionally prepared material shows an exothermic peak at 460°C. This peak is attributed to crystallization of rutile phase. XRD revealed
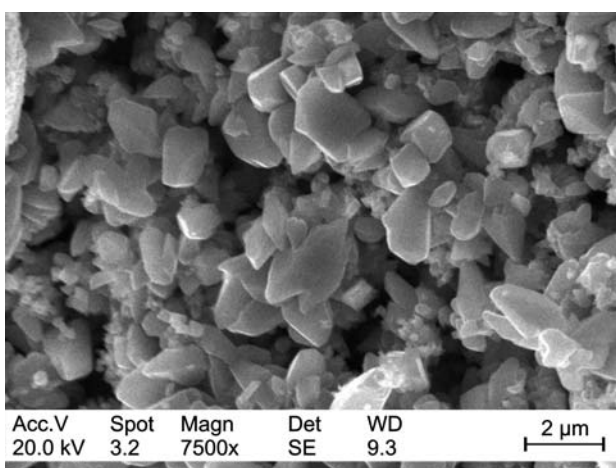


a)
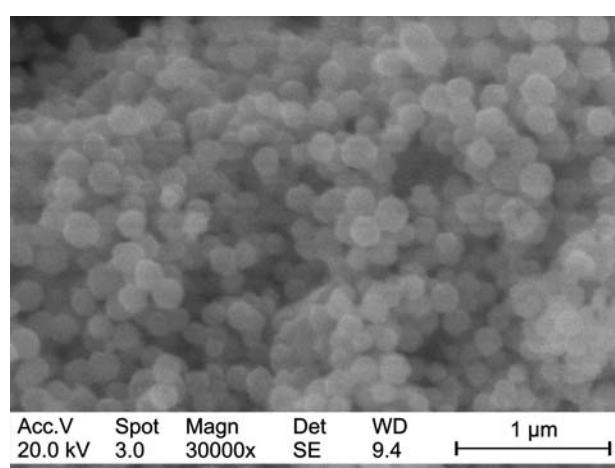


b)

Figure 6. SEM micrograph of conventional Cu-1 (a) and hydrothermal Cu-2 (b) hydrolysis products of copper 2-pyridylethoxide after calcination at 773 K.

pure anatase phase for former and a mixture of anatase and rutile for latter after calcination of materials at 700°C, as shown in figure 8, Ti-2 and Ti-1, respectively.

SEM micrographs of titanium oxides prepared by conventional and hydrothermal hydrolysis of titanium alkoxide after calcinations at 700°C are shown in figure 9, Ti-1 and Ti-2, respectively. The plate-like particles are typical for rutile and it is consistent with the X-ray diffraction result. Furthermore, hydrothermal hydrolysis product is homogeneous and monosized similarly as other oxides in the present study.

## Nb₂O₅

The TGA curve of conventional hydrolysis product of $Nb(OCH_2CH_2OCH_2CH_3)_5$ (figure 7, Nb-1) shows about 10 % weight loss in temperature range of 130 to 150°C, and an associated endothermic peak at 140°C in the DSC curve, suggesting that the weight loss is due to the elimination of physically adsorbed water and alcohol. This weight loss for hydrothermal hydrolysis product of $Nb(OCH_2CH_2OCH_2CH_3)_5$ (figure 7, Nb-2) is about 19 % in temperature range of 80 to 140°C. The larger amount of physically adsorbed water in hydrothermally processed sample in comparison with the conventional one is probably due to the larger pore size of former. The 20 % weight loss for conventional product and 24 % weight loss for the hydrothermal product in temperature range of 270 to 310°C in the TGA curve with an exothermic peak centered at 290°C in the DSC curve is associated with the combustion of an organic residue.

The XRD patterns show that the materials prepared by conventional and hydrothermal hydrolysis of niobium 2-ethoxyethoxide converts to single-phase Nb₂O₅ by calcinations at 600°C (figure 8, Nb-1 and Nb-2, respectively).

Figure 9, Nb-1 and Nb-2 show SEM micrographs of conventional and hydrothermal hydrolysis products of niobium alkoxide after calcinations at 700°C. Morphology of the conventional hydrolysis product is granular, whereas hydrothermal hydrolysis product is homogenous and is in nanometer range.
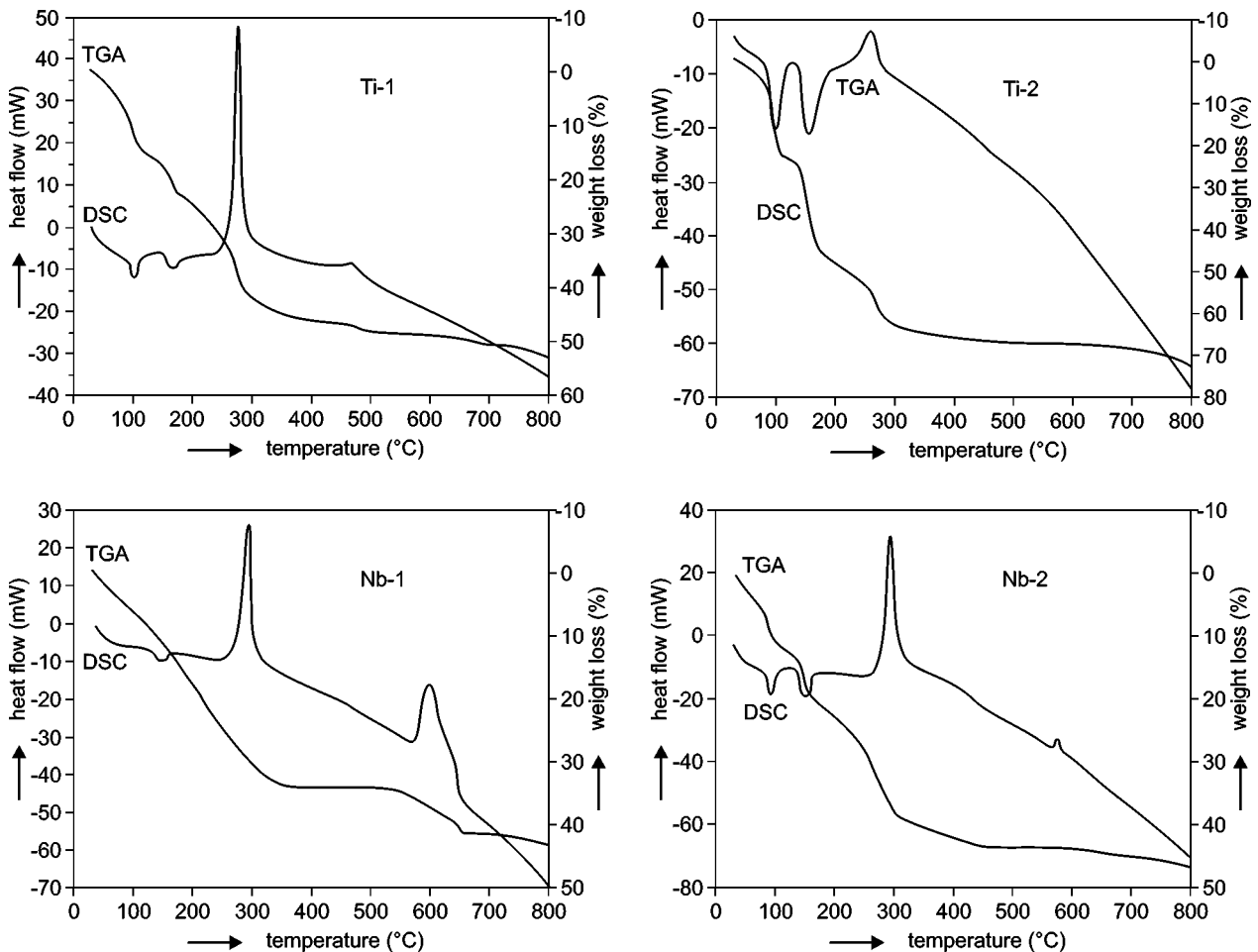


Figure 7. TGA and DSC curves of conventional (Ti-1 and Nb-1) and hydrothermal (Ti-2 and Nb-2) hydrolysis products of titanium and niobium 2-ethoxyethoxides.
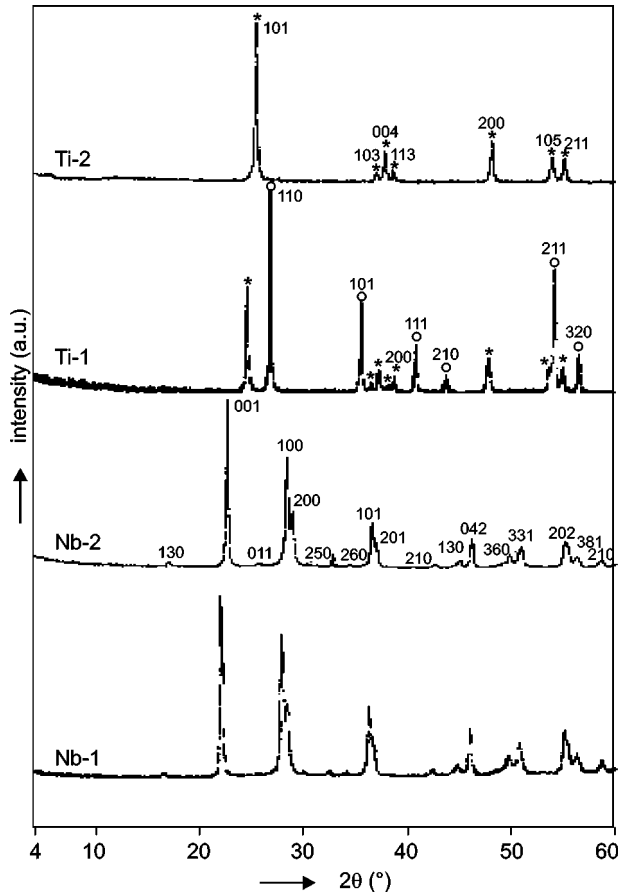
Figure 8. XRD patterns of conventional (Ti-1 and Nb-1) and hydrothermal (Ti-2 and Nb-2) hydrolysis products of titanium and niobium 2-ethoxyethoxides after calcinations at 973 K. (*) rutile (o) anatase.

## CONCLUSIONS

Hydrothermally assisted sol-gel processing has been used as a new approach for the preparation of several metal oxides. Boehmite, copper, niobium, and titanium oxides are prepared by hydrothermal hydrolysis from corresponding metal alkoxides. All metal oxides prepared by the above mentioned method are spherical and monosize to some extent, in contrast to agglomerate powders obtained from conventional sol-gel processing. The spherical morphology and phase composition of prepared oxides, which arise from hydrothermal hydrolysis of metal alkoxides, can be attributed to a distinct mechanism; however, further work is needed to understand it.
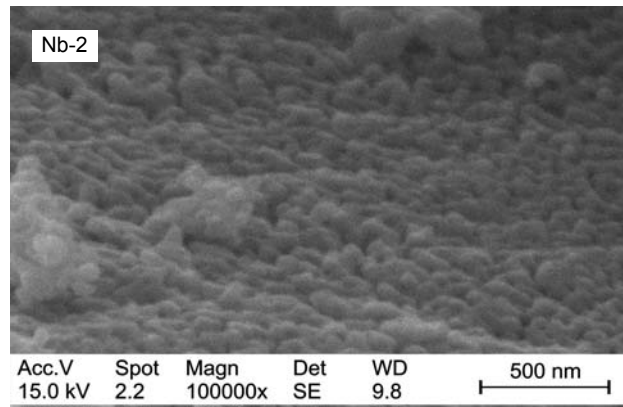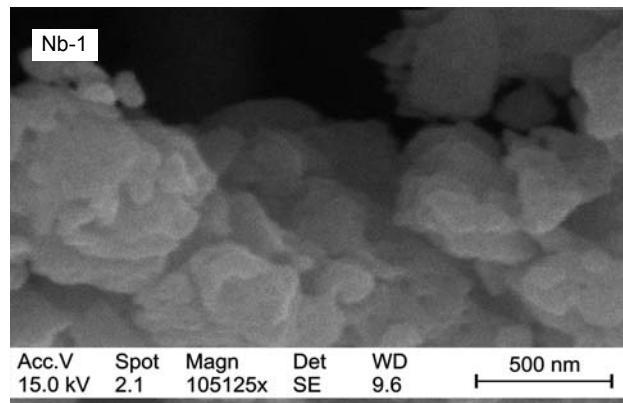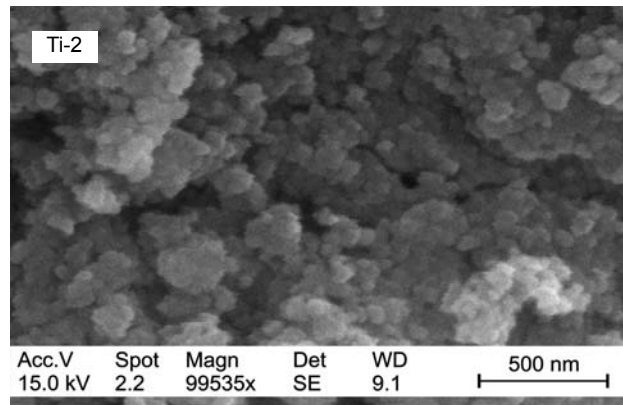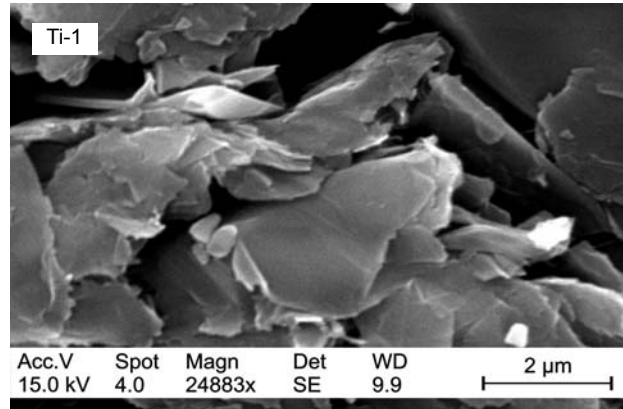
## Acknowledgement

Figure 9. SEM micrographs of conventional (Ti-1 and Nb-1) and hydrothermal (Ti-2 and Nb-2) hydrolysis products of titanium and niobium 2-ethoxyethoxide after calcination at 973K.

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PŘÍPRAVA A CHARAKTERIZACE BOEHMITU, CuO, TiO$_2$ A Nb$_2$O$_5$ ZÍSKANÝCH HYDROTERMÁLNÍ METODOU SOL-GEL Z ALKOXIDŮ KOVŮ

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Konvenční a hydrotermálně asistovaná sol-gel metoda byla použita pro přípravu uniformních nanočástic boehmitu a oxidů měďnatého, titaničitého a niobičného z příslušných alkoxidů. Připravené prášky byly charakterizovány rtg difrakcí (XRD), termální analýzou (TGA/DSC) a řádkovací elektronovou mikroskopií (SEM). XRD, infračervená spektroskopie (IR) a termální analýza ukázaly, že stupeň krystalinity boehmitu, připraveného hydrotermální sol-gel metodou z 2-butoxidu hlinitého, se zlepšuje s rostoucí teplotou zpracování. Čistý tenorit vznikl jak konvenční tak hydrotermální sol-gel metodou z 2-pyridylethoxidu měďnatého. Konvenční sol-gel příprava oxidu titaničitého z 2-ethoxyethanolátu titaničitého vedla ke směsi rutilu a anatasu, ale hydrotermální metoda končila tvorbou čistého anatasu. Jednofázový Nb$_2$O$_5$ vznikl jak konvenční tak hydrotermální sol-gel metodou z 2-ethoxyethanolátu niobičného. SEM odhalil kulovité homogenní nanočástice oxidů připravených hydrotermální sol-gel metodou.