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Studies on the hydrothermal synthesis of niobium oxides

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Abstract

Hydrothermal reactions of commercial Nb_2O_5 with aqueous MOH, M = Na, K, at 200 °C and autogenic pressure provided new routes to different niobium compounds. The reaction of Nb_2O_5 with NaOH was used to synthesize $NaNbO_3$ under mild conditions. The known room-temperature phase was obtained and identified by infrared spectroscopy and X-ray powder diffraction. In similar conditions, reactions of Nb_2O_5 with KOH yielded alkaline aqueous solutions containing soluble potassium hexaniobates. Those solutions were used to prepare $K_6H_2[Nb_6O_{19}]\cdot 13H_2O$ and niobic acid. Hydrothermal reactions of commercial Nb_2O_5 with aqueous MOH, M = Na, K, provided thus a more convenient process of attack to niobium pentoxide than the traditional method of fusion of mixtures of the niobium oxide with alkali metal hydroxides or carbonates. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrothermal syntheses of ceramic powders have interesting potential in view of increasing demand for environmentally benign materials and manufacturing methods. Hydrothermal reactions are usually performed in moderate conditions, do not require expensive precursors or equipment and may yield homogeneous crystalline powders [1,2]. These methods may offer, thus, a low temperature (up to 300 °C) direct route to fine oxide powders.

The commonest and cheapest starting material used in niobium chemistry is niobium(V) oxide, Nb_2O_5. Niobium(V) alkoxides and halides are also commercially available, among other reagents, but they need to be handled in special controlled conditions and some of them are rather expensive. Nb_2O_5 is fairly unreactive. Aqueous solutions of Nb(V) of high pH are usually obtaining by fusing Nb_2O_5 with alkali metal (usually potassium) hydroxides or carbonates followed by dissolution of the melt. Soluble polyoxoniobates are formed in the process [3,4]. Addition of acid to those solutions yields hydrated oxides, $Nb_2O_5\cdot nH_2O$, also called 'niobic acids'. Complexing agents, like oxalate, citrate or tartrate, prevent the precipitation of niobic acids, due to the formation of Nb(V) species soluble in neutral or acid aqueous solution [3].

The hydrated niobium oxides, usually obtained as white precipitates with indeterminate water content [3–5], are more reactive than the anhydrous Nb_2O_5, and they dissolve in aqueous solutions of NaOH, oxalic acid, tartaric acid and others. This could make niobic acids more convenient as Nb(V) starting material for studies or synthesis involving aqueous solutions, but, besides having variable niobium contents, they have the drawback of being unstable and losing reactivity as time passes. They have generally to be freshly prepared prior to use, as they may be kept in reactive conditions only for about a month [6].

A considerable amount of research has been dedicated to the synthesis of a large variety of niobium oxides, either using the conventional ceramic methods or other chemical procedures [1]. Niobium(V) oxide is always the reagent used in high temperature synthesis.

Preparation of the metaniobates $MNbO_3$, M = Li, Na, K, is mostly done by high temperature synthesis, starting with Nb_2O_5 and M_2CO_3 [3,4]. Microwave assisted solid state synthesis of these substances has been reported, with considerably shorter reaction times [7]. In the particular case of $NaNbO_3$, several reports

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could be found that present its synthesis by chemical methods, using different precursors. Niobium ammonium oxalate, $(NH_4)H_2[NbO(C_2O_4)_3]\cdot 3H_2O$, was used in the synthesis of fine $NaNbO_3$ powders by the Pechini method [8,9], and by thermal decomposition of a precursor obtained through solvent evaporation [10]. Kinomura et al. have prepared $NaNbO_3$ by hydrothermal reaction of $Na_8[Nb_6O_{19}]\cdot 13H_2O$ with NaOH and found a new metastable phase with ilmenite-type structure, that was obtained pure in a very narrow temperature and concentration region [11]. Also, $NaNbO_3$ has been obtained by evaporation of a solution of $Na_7H[Nb_6O_{19}]$ under a CO_2 atmosphere [12]. An old report states that crystals of $NaNbO_3$ were obtained by boiling a suspension of Nb_2O_5 in NaOH for about 20 min, but no synthetic details were provided [13]. To our knowledge, no report referring the synthesis of $NaNbO_3$ by hydrothermal reaction of Nb_2O_5 with NaOH has been published.

The synthesis of $KNbO_3$ through the hydrothermal reaction of Nb_2O_5 with KOH has already been reported [14,15]. Depending on the KOH concentration and temperature, that reaction may provide $KNbO_3$, $K_4Nb_{16}O_{17}\cdot 3H_2O$ or complete dissolution of the initial niobium oxide [14,15]. These studies were mainly concerned with the synthesis of the oxides and the dissolution of Nb_2O_5 in the alkaline solutions was only briefly mentioned.

Potassium hexaniobates of general formula $K_{8-x}H_x[Nb_6O_{19}]\cdot nH_2O$, $x = 0$–3, have been prepared before and some spectroscopic data has been published [6,16]. They are usually obtained by crystallization or precipitation from aqueous alkaline solutions of Nb(V) with pH 9–14 [16–19].

We report here the hydrothermal synthesis of microcrystalline, single phase $NaNbO_3$ through the reaction of commercial Nb_2O_5 with NaOH, at 200 °C. Different concentrations and $NaOH:Nb_2O_5$ molar relations were examined. In the conditions used for the synthesis of $NaNbO_3$, the use of KOH in place of NaOH leads to solubilization of the initial Nb_2O_5. From these solutions, solids like $K_6H_2[Nb_6O_{19}]\cdot 13H_2O$ or niobic acid were obtained. This procedure allows, thus, preparation of alkaline solutions of Nb(V) without need of the cumbersome technique of fusion of mixtures of Nb_2O_5 with alkali.

2. Experimental

2.1. Reagents and methods

All chemicals and solvents were used as received. Decarbonated water was used. Nb_2O_5 (99.5%) was purchased from Aldrich. NaOH and KOH were pro analysi grade.

Elemental analysis for Nb, Na and K were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis). Thermogravimetric analyses were carried out in air between 25 and 800 °C at a heating rate of 5 °C min^{-1}, on a Mettler M3 thermobalance equipped with a TC 10A microprocessor.

Infrared absorption spectra were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. Raman measurements were performed with solid samples in a Bruker RFS 100/S FT-Raman spectrometer, equipped with a Nd:YAG laser emitting at 1064 nm. The spectra were obtained in the 200–1200 cm^{-1} range, using the following settings: power at the sample, 50 mW; resolution, 4 cm^{-1}. X-ray powder diffraction patterns were measured on a RigakuD–Max III instrument, using Cu Kα, radiation in the range $2\theta = 3°–130°$. Powder X-ray diffraction patterns were indexed with the POWDERX package [20] and the unit cells were indicated by the TREOR90 indexing program [21]. Cell parameters were refined using the program RIETICA 1.6.7A, by B.A. Hunter. Scanning electron microscope images (SEM) were recorded on a Hitachi S-4100 microscope.

2.2. General procedure for hydrothermal reaction of Nb_2O_5 with MOH, M = K, Na

Nb_2O_5 (0.1 or 0.2 g) and an aqueous solution of MOH (20 cm^3) with concentration corresponding to molar ratio $MOH:Nb_2O_5$ between 2 and 75 were placed in a Teflon lined cylindrical autoclave (60 cm^3 capacity), and introduced in an oven pre-heated to 200 °C for a predetermined period of time. After cooling down (under running cold water), any solid residue was separated by filtration or centrifugation, washed with water and ethanol and dried in a desiccator under vacuum. To the filtrate, absolute ethanol was added and any precipitated solid was filtered, washed with very cold ethanol–water (50%) and ethanol and dried under vacuum. Care should be taken to prevent contamination with carbonates.

2.3. Specific synthetic procedures

2.3.1. $NaNbO_3$

The reaction of Nb_2O_5 and NaOH was performed as described in 2.2, using molar ratios $NaOH:Nb_2O_5$ between 35 and 67 and 6–24 h reaction time. After cooling down, the obtained solid was separated by filtration, washed and dried as described above. *Anal.* Found: (Calc.): Nb, 56.2 (56.7); K, 14.2 (14.0)%.

2.3.2. $K_6H_2[Nb_6O_{19}]\cdot 13H_2O$

The reaction of Nb_2O_5 (0.2 g) and KOH was performed as described in Section 2.2, with a molar ratio $KOH:Nb_2O_5 = 60$ and 24 h reaction time. After cooling down, any insoluble residue was eliminated by