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Hydrothermal conversion of Nb-anatase nanoparticles into layered titanates

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Abstract

The formation mechanism of layered titanates is described and Nb incorporation into these layers discussed. Titanate-based structures were obtained in highly alkaline solutions by the hydrothermal synthesis of Nb-anatase powder prepared by a modified sol–gel method. Samples were characterised by XRD, FT-IR and Raman spectroscopy, SEM and TEM (including EDS). The results confirmed the formation of layered trititanates, after 3 h of hydrothermal synthesis. Raman and EDS analyses have shown that Nb ions enter the layered structures. Results suggest the restructuring of the starting powder into individual trititanate nanosheets, as a possible formation mechanism of layered titanates, which proceeds with their roll up into a one-dimensional structure.

Keywords: A. Powders: chemical preparation; B. Spectroscopy; B. Electron microscopy; D. TiO_2; Layered Nb–titanates

1. Introduction

The type and structural characteristics of one-dimensional (1D) materials, as well as their properties are strongly determined by the processing method and the conditions of preparation. In general, there are three main approaches for the preparation of these materials: template methods [1], anodic oxidation [2,3], and wet chemical methods [4–6]. Especially, the synthesis of titanate 1D structures fabricated by the hydrothermal method, proposed by Kasuga et al. [4], has received considerable attention because of its low cost and simplicity.

Besides the growing interest in obtaining one-dimensional titanates, the exact mechanism of hydrothermal titanate nanotube formation is still a controversial topic. Also, the clarification of the individual stages that precede the formation of the 1D structures, is one of the open questions; even the composition of these materials is still a subject of debate [7]. According to the literature, different crystal structures and compositions have been suggested, such as trititanates ($A_2Ti_3O_7$ where A = H or Na), tetratitanate $H_2Ti_4O_9{\cdot}H_2O$, lepidocrocite titanates $H_xTi_{2-x/4}\square_{x/4}O_4$, $H_2Ti_3O_7{\cdot}xH_2O$ ($\square$ – vacancy), $Na_xH_{2-x}Ti_3O_7$ and TiO_2 anatase [5–8]. Some authors have concluded that 1D structures were formed by rolling of single layers peeled from crystal plates possibly due to hydrogen deficiency on the surface [5–11]. On the other hand, some researchers explain this mechanism by the wrapping of multilayer nanosheets [8,12]. However, a completely distinct mechanism of nanotube formation has been proposed [13,14]. Authors have suggested that the rollup theory is only valid when local concentration fluctuations generate extreme conditions (temperature, pH and reaction time) at the surface of the nanoparticles. It was claimed that local concentration fluctuations which appear on the crystallite of the starting material under hydrothermal conditions, initiate the formation of nanoloops from the starting material, which then become seeds for an oriented crystal growth process that leads to titanate nanotubes [15,16]. The shape of the cross-section is determined by the curvature of the seeding nanoloop. Since these are flexible ensembles only a few nanometers in length

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and diameter, they can give rise to spiral, onion, or even multiple-spiral nanotube cross-sections.

In this work, titanate nanotubes were synthesized by a hydrothermal method. The structure and morphology of the synthesized nanotubes depends on the hydrothermal conditions, but are also influenced strongly by the phase composition of the starting powders [17–19]. Therefore we have synthesized anatase particles where an appropriate amount of niobium is introduced in their structure; the obtained powder is then used for the hydrothermal reaction.

The main subject of this work was to elucidate the formation mechanism of layered titanates as a stage which precedes the nanotube formation. The possibility of niobium incorporation into the titanate layered structure, through the starting powder, was also investigated. From that point of view, this research has been focused on the early stages of the one-dimensional titanate formation.

2. Experimental

2.1. Synthesis of starting powder and layered titanates

One-dimensional titanate-based structures were synthesized in highly alkaline solutions using the hydrothermal procedure at 150 °C for different durations, following a procedure reported before [20]. Anatase nanoparticles doped with niobium were used as a starting material; they were synthesized by a modified sol–gel method, from a mixture of an aqueous solution of Ti-butoxide ($Ti(OC_4H_9)_4$ – Fluka, Switzerland) and ethanol solution of $NbCl_5$ (Merck, Germany). The atomic ratio of niobium in respect to titanium was set to 6 at.%. The reaction was carried out at 80 °C in the presence of NH_4OH and a great excess of water. After steaming for several hours, the obtained white powder was washed a number of times until pH = 7 was reached and was then dried at 120 °C for 1 day.

The formed Nb-doped anatase nanoparticles were dispersed in an aqueous solution of 10 M NaOH and stirred for some time. Then, the solution was transferred into a sealed vessel and the hydrothermal reaction was carried out at 150 °C for different times, up to 20 h. After the hydrothermal treatment, the powders were washed with distilled water and absolute ethanol, until a neutral pH was reached. The formed layered titanate-based structures were dried at 120 °C for 1 day. These samples were given the name Ts-*x*/Nb, were *x* stands for the time duration (in hours) of the hydrothermal reaction (3, 10 and 20 h).

2.2. Characterisation techniques

The structural changes caused by the hydrothermal conversion of anatase particles to layered titanates were studied by Raman and FT-IR spectroscopy, as well as electron microscopy. The morphology and the microstructure of the samples before and after the hydrothermal treatment were additionally examined by X-ray powder diffraction (XRD). X-ray diffraction patterns of the as-synthesized structures were collected on a Philips PW 1050 instrument using Cu-Kα radiation of wavelength 1.5404 Å. The XRD data were recorded with a step of 0.02°/s. The microstructure and morphology of the samples were analyzed using a JEOL JSM 6460LV scanning electron microscope (SEM) and the layered structure was revealed by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV, equipped with an energy-dispersive X-ray spectroscopy tool (EDS) and capable of performing the selected area electron diffraction (SAED) required. Fourier-transform infrared spectroscopy measurements were performed using a Nicolet-Nexsus 670 FT-IR. Raman spectra were measured in backscattering geometry using the InVia Renishaw micro-Raman spectrometer operating in normal mode and the 514.5 nm line of an Ar+ laser as the excitation beam. The incident laser power on the sample was 0.4 mW and was applied to a spot diameter of 1.2 μm.

3. Results and discussion

3.1. Characterisation of the starting powder

XRD patterns of powders synthesized with the modified sol–gel method are presented in Fig. 1. These patterns show that samples prepared with and without niobium, Tb–6Nb and Tb powders respectively, consist of the anatase phase with a very small amount of brookite, since a peak at $2\theta = 30.8°$, characteristic for brookite phase, can be identified (ICDD card 29-1360). The patterns are very similar and only a small shift to the higher 2θ can be observed for the Tb–6Nb powder indicating the change in the lattice constant, probably caused by the niobium incorporation. Average crystallite size of the starting powders, estimated by Scherrer's equation [21], is about 4.5 nm. Available data on the solubility of niobium in the lattice of titanium dioxide varies in the literature. Some authors [22] believe that niobium can be introduced into titania structure up to 40 at.%, while some of them [23] consider the formation of a separate phase, $TiNb_2O_7$, at the grain boundary

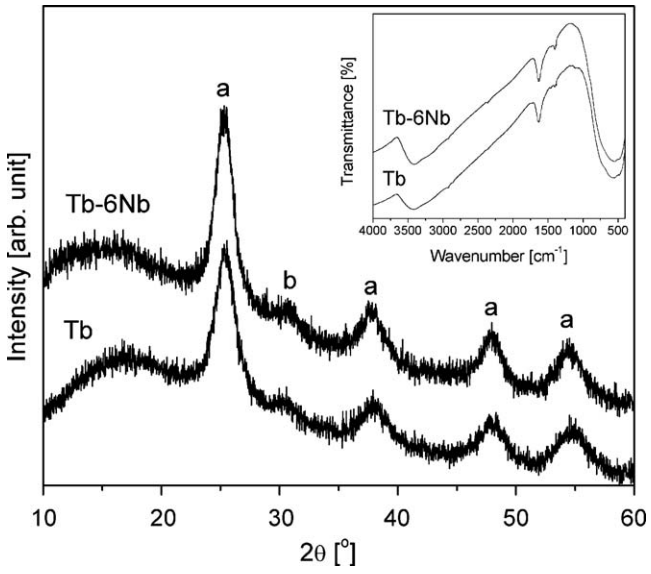

Fig. 1. XRD patterns and FT-IR spectra (inset on the top right) of starting powders, Tb and Tb–6Nb (a: anatase and b: brookite).

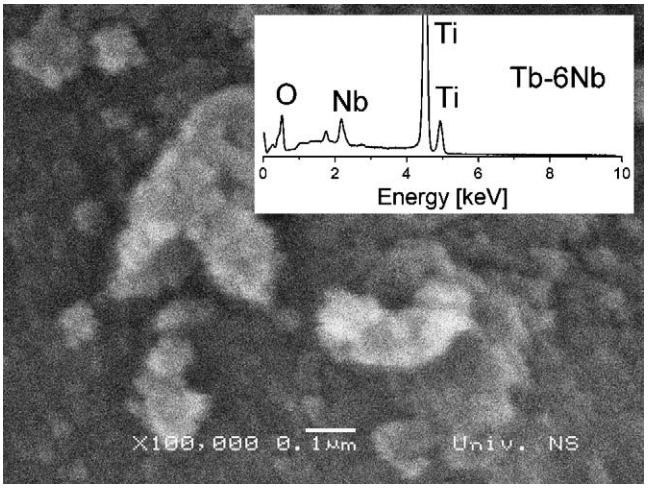

Fig. 2. SEM image of the starting powder, Tb–6Nb and the corresponding EDS spectrum in the top right corner.

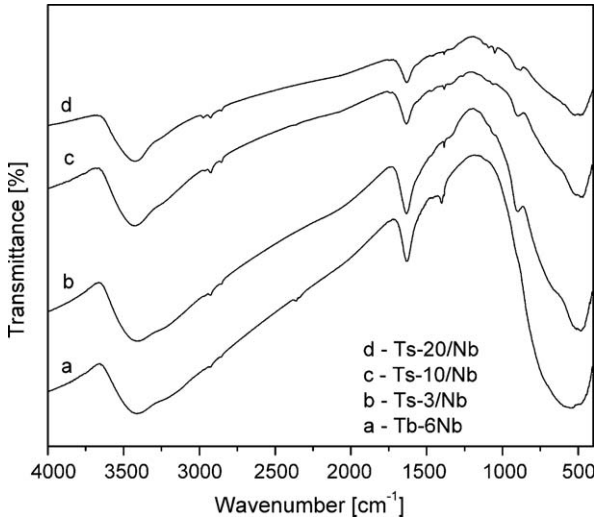

Fig. 4. FT-IR spectra of the starting powder, Tb–6Nb and Nb–titanate layered structures.

of rutile when more than 6.6 at.% of niobium is added into the structure. Since the XRD pattern of Tb–6Nb powder shows only the anatase phase (brookite is present only in traces), it can be assumed that niobium entered the titania lattice. FT-IR spectra presented on the top right of Fig. 1, show only a slight difference in the position and shape of the vibrations characteristic for Ti–O bonds (450–600 cm^{-1}), hydroxyl groups at 3400 cm^{-1} and water molecules at 1650 cm^{-1}. This can be the result of very small amount of niobium introduced in the anatase structure as the ionic radius of niobium is similar to that of titanium [22]. The results imply a very similar structure for the undoped and the doped powders, so in order to investigate the possible formation of Nb-doped one-dimensional titanate structure and how it is influenced by the duration of the hydrothermal reaction, the Tb–6Nb powder was used as a starting powder for further synthesis. The SEM image shown in Fig. 2, indicates a very fine particulate structure of the starting powder with a high degree of agglomeration. The EDS spectrum confirmed the Nb incorporation into the anatase structure.

3.2. Characterisation of Nb–titanate layered structures

XRD patterns of Nb–titanate structures are shown in Fig. 3. In order to follow the structure changes in the powder after hydrothermal reaction, the XRD pattern of the starting material, Tb–6Nb is given in the top right of the image. It is interesting to note that already after 3 h of hydrothermal synthesis, the structure of the starting powder has changed significantly. The peaks characteristic of the anatase phase completely disappeared, favoring the formation of layered titanates. The XRD patterns show mainly four diffraction peaks at $2\theta \sim 9.5^{\circ}$, 24.44°,

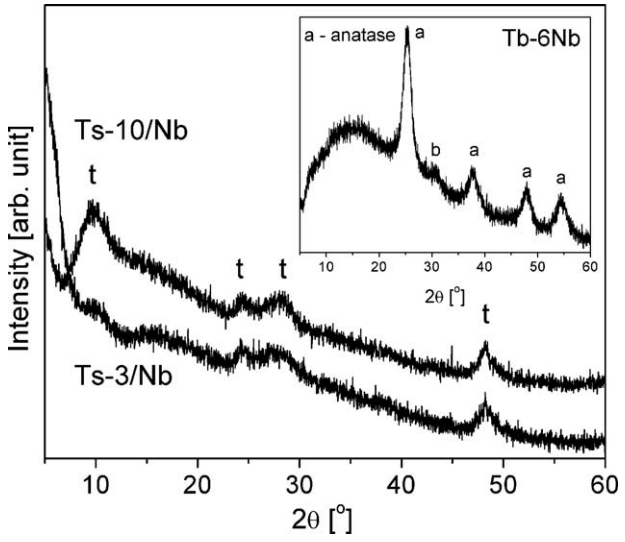

Fig. 3. XRD patterns of the as-prepared Nb–titanate layered structures and starting powder, Tb–6Nb (t: $Na_2Ti_3O_7$ and a: anatase).

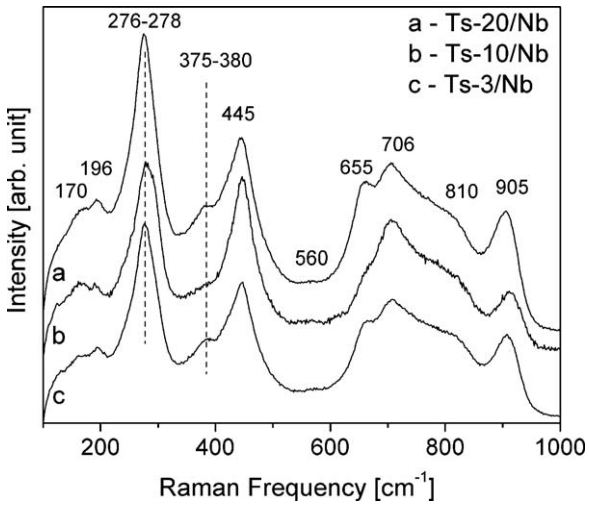

Fig. 5. Raman spectra of Nb–titanate layered structures (Ts-3/Nb, Ts-10/Nb, Ts-20/Nb).

28.37° and 48.32°, characteristic of the $Na_2Ti_3O_7$ type of titanates (ICDD card 31-1329). No peaks from niobium compounds are detected, a fact that indicates its incorporation in the layered titanates. The broad peaks are the result of low crystallinity of the as-prepared titanate structures. According to the literature [8,24,25] the peak at $2\theta = 9.5°$ could be ascribed to an interlayer distance which is typical for the trititanate phase. The spacing between layers depends on the content of

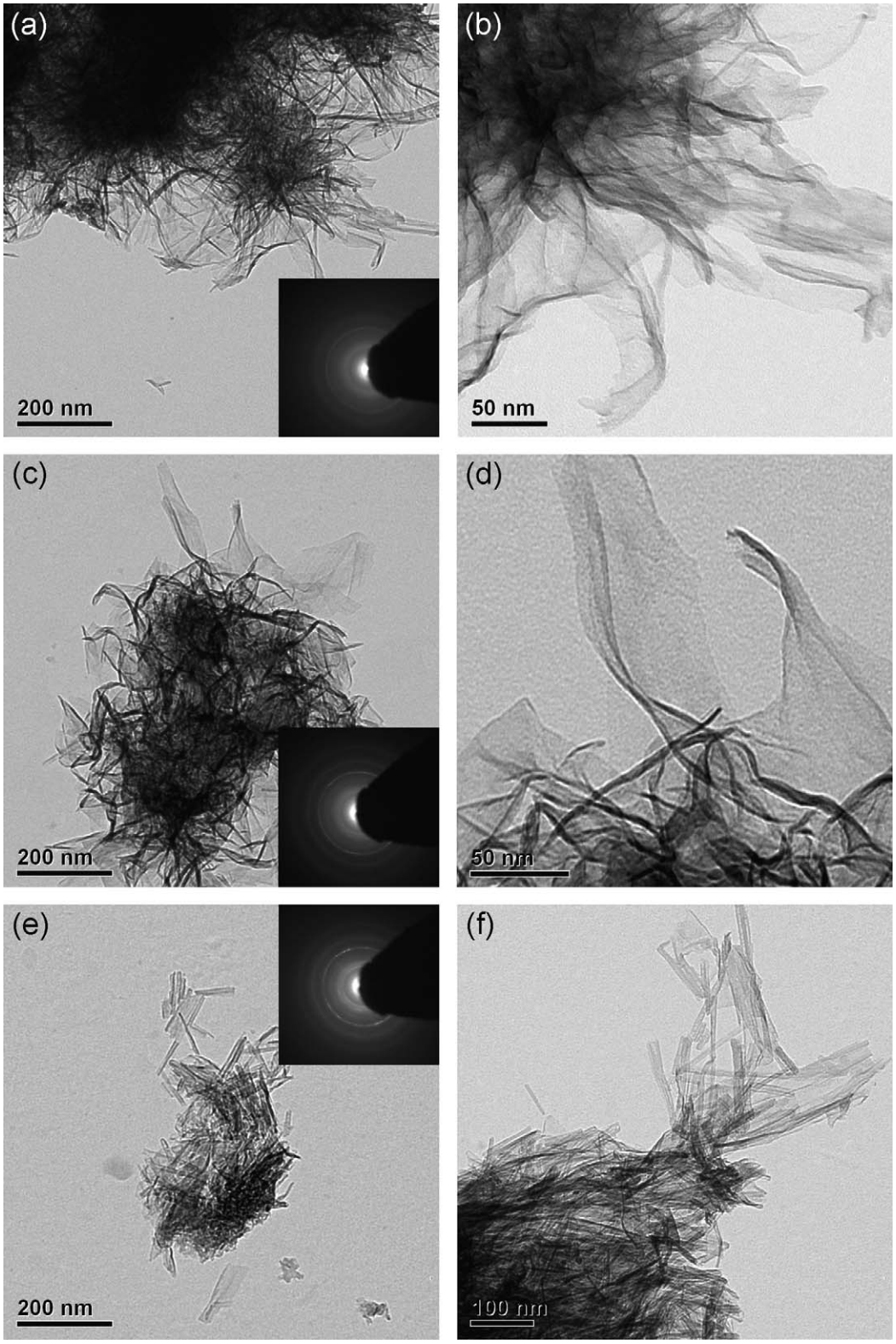

Fig. 6. TEM images of the one-dimensional Nb–titanate layered structures: Ts-3/Nb (a and b), Ts-10/Nb (c and d), Ts-20/Nb (e and f).

Na^+ ions which remain in the structure after the synthesis, and it can range from 0.8 to 0.95 nm [10,19,26]. The presence of Na^+ ions between the layers can influence the stoichiometry of titanates and lead to lattice deformations, which in turn cause the shift and broadening of the characteristic XRD peaks, observed in Fig. 3. The intensity of the peak around 9.5° is increasing, indicating a rise in crystallinity with the duration of the hydrothermal reaction.

The FT-IR spectra of Nb–titanate structures obtained after different hydrothermal reaction times are shown in Fig. 4. In comparison with the spectrum of the starting powder, there is a significant difference in the shape and position of the characteristic vibrations, especially in the 400–800 cm^{-1} range, implying a structure modification and a possible formation of an one-dimensional titanate-based structure. According to the literature [27], different Ti–O vibrations can be observed in the wavelength range of 450–700 cm^{-1}. The presence of these bands in Fig. 3, indicate both tetrahedral and octahedral coordination of titanium ions. Since these bands are missing in the starting powder, it can be assumed that observed vibrations are a result of the braking the Ti–O bonds and the formation of titanate layers by the intercalation of Na^+ and OH^- ions into the structure. In addition, a new band appears at around 900 cm^{-1}, also observed in Raman spectra (Fig. 5), which corresponds to the vibration of Ti–O non-bridging oxygen bonds, and probably the formation of Ti–O–Na bonds. This band is typical for one-dimensional structures [28], while its small intensity could be explained with the very low concentrations of Na ions (due to extensive ion exchange with H^+ during washing). The shape and intensity of the observed bands are changing with the duration of the hydrothermal reaction. Intense band located around 3400 cm^{-1} is due to OH-stretching vibrations of hydrohyl groups.

Raman spectra of Nb–titanate layered structures are presented in Fig. 5. Raman spectra are rich with many bands in agreement with previous reports on titanates [29–33]. Many factors affect the number of these bands as well as their frequency and width: crystal structure, Na content, H_2O percentage, titanate form (bulky layer form, 2D nanosheets, nanotubes). Raman spectra show the bands that can be attributed to sodium trititanate, $Na_2Ti_3O_7$ [29–31]. Furthermore, the low frequency bands (<600 cm^{-1}) fit better with the Raman modes of titanates with very low Na content [32]. Upon increasing the duration of the hydrothermal reaction minor changes are observed in the Raman modes. The vibrational frequencies at about 195 and 275 cm^{-1} can be assigned to lattice modes and Ti–O–M (M = Nb^{5+} or Na^+) modes [33,34]. The intensive peak at 278 cm^{-1}, which is characteristic for sodium titanates with layer structure [35], shows a small red Raman shift (2 cm^{-1}). Also, a red shift by 5 cm^{-1} was observed for the 380 cm^{-1} mode, while intensities of 560 and 706 cm^{-1} bands, related to the layered structure, marginally decrease. These effects are interpreted as a sign of conversion from a titanate layered structure to a tubular structure [36], by a proton-exchange reaction, which is in good agreement with the structural evolution observed by TEM (Fig. 6). The band at about 445 cm^{-1}, is assigned to the internal vibrations of the robust TiO_6 octahedra [15]. The peak at 905 cm^{-1} is a characteristic band of titanates prepared with hydrothermal synthesis with NaOH, and is assigned to the symmetric stretching mode of a short Ti–O bond of sodium titanate in the layered structure [31]. This implies that sodium titanate with a layered structure is formed and is considered to be the precursor for the nanotube formation. This mode could also come from vibrations in interlayer space or from the surface of the layered titanates [31,33].

Morphology of synthesized titanates depends on reaction time. TEM images of Nb–titanate structures are presented in Fig. 6. According to these images it can be concluded that already after 3 h of hydrothermal synthesis, anatase completely transforms into the layered titanates, which is in good agreement with previously presented results. In addition, the particle-like morphology of the precursor does not exist any more despite the short reaction time, a fact that implies that the rate of hydrothermal reaction is very high in the early stages of layer formation. Above results confirmed that the formation mechanism of titania nanotubes is a transformation of titania nanoparticles into nanosheets due to the attack of sodium hydroxide during the hydrothermal reaction. As the reaction proceeds, formed nanosheets grow together with a tendency to curl at their edges, leading to the formation of short nanotubes, which is clearly evidenced in Ts-20/Nb sample (Fig. 6e and f). The crystallinity of the layers is increasing with time during the reaction, which is confirmed by the SAED patterns, included in Fig. 6. These results strongly confirm that the one-dimensional titanate structures can be obtained with unexpectedly short durations of the hydrothermal reaction, shorter than stated in the literature [9,37].

In order to confirm the composition of Nb–titanate structures, EDS analyses have been carried on. The EDS spectrum given in Fig. 7 is typical for all investigated samples. EDS pattern of Ts-20/Nb clearly shows the presence of Na, Ti, O and Nb elements, which confirms that Nb–titanates have been formed. EDS spectra were taken from both the centre of the sample (i.e. probing a large volume) and from its side (i.e. probing only the thin layers) to see how Nb is distributed in the

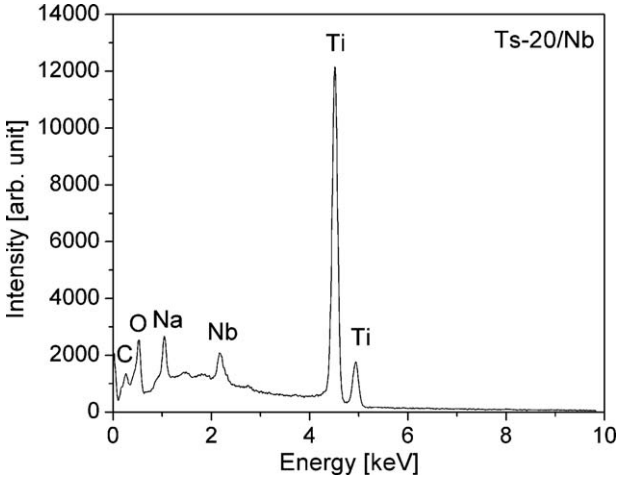

Fig. 7. EDS spectrum of the Ts-20/Nb–titanate structure.

samples. Since the results showed Nb signal on both cases, uniform distribution of Nb ions can be assumed.

4. Conclusions

We have successfully synthesized layered Nb–titanates through a simple hydrothermal procedure. The XRD patterns have shown that hydrothermal treatment at 150 °C at very short reaction times (up to 20 h) results in the disappearance of the anatase peaks (present in starting powder) and new peaks arising, corresponding to the trititanate structure. The FT-IR spectra confirmed that octahedral Ti–O building blocks (around 600 cm^{-1}), the main polyhedrons in the structure of anatase, were broken, and a new peak is starting to appear at around 900 cm^{-1}, which corresponds to the vibration of $Ti–O^-$ non-bridging oxygen bonds, but also could point out a bonding of Na^+ ions to Ti^{4+} ions through oxygen. The change in the shape and position of the band characteristic for octahedral building blocks could indicate that niobium is introduced into the titanate structure. The EDS analyses confirmed the presence of Nb in the powders. Raman spectra suggest the formation of layered Nb–titanates and TEM results confirm the conversion from anatase particles to Nb–titanate layers and even nanotubes. From the above it is inferred that the formation mechanism is the transformation of titania nanoparticles into nanosheets due to the attack of sodium hydroxide in the early stage of the hydrothermal reaction. With the increase of the time of the hydrothermal reaction, the nanosheets grow together with a tendency of curling at theirs edges that leads to the formation of the nanotubes.

Acknowledgments

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