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Molten salt syntheses of alkali metal titanates

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Submicrometer dispersions of rod-like alkali metal titanates were prepared by the flux method, from the reaction of $TiOSO_4$ or TiO_2 precursors in molten alkali metal nitrates, doped with carbonates or hydroxides. Mono-, di-, tetra-, and hexatitanates are formed as a function of the precursor nature and the melt composition. As a rule, in these syntheses poorly crystalline or amorphous solids are obtained, showing the structure of polytitanates on the nanoscopic level. Lamellar potassium hexatitanate can be exchanged by action of a diluted acid, leading to protonic form, free from the alkali metal but retaining initial morphology. Reactivity of $TiOSO_4$ and TiO_2 in molten alkali metal nitrates and their mixtures with the corresponding carbonates was studied by mass spectrometry of the gases evolved during heating of the reaction mixtures. For both pure and doped nitrates it changes in the expected row $Li > Na > K$, following the melts oxobasicity sequence. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Molten salts as reaction media provide an alternative to aqueous chemistry by offering the possibility to change the solubility and/or the reactivity of species [1]. The oxosalts display chemistry of great complexity and include several melts of eminent industrial importance. Alkali metal nitrates are often used as reaction media because of their low cost, and conveniently low melting points. Molten nitrates as applied to the materials synthesis, should be considered as reactive solvents, i.e. they are at once the non aqueous solvents and the sources of active species, providing the precipitation of simple and mixed oxides from the molecular precursors [2]. Nanoscopic dispersions of simple and mixed oxides [3–5], phosphates [6], and other oxosalts were obtained in the molten nitrates. Perovskites, including titanates have been prepared using nitrate fluxes [7–10]. Most recently, preparation of barium titanate by treatment of TiO_2 with molten mixtures of $Ba(NO_3)_2$, KNO_3 and KOH was reported [11].

Alkali metal titanates present interest as ceramics materials [12, 13] or as precursors for the exfoliated lamellar titania [14]. Their preparations in highly anisotropic form are reported, using high temperature melts or hydrothermal conditions [15, 16]. In the present work is reported preparation and characterization of alkali metal titanates using pure and doped molten alkali metal nitrates. Reactivity of pure and carbonate doped melts with titanium (IV) oxide and oxysulfate is also studied.

2. Experimental

Hydrated titanium oxysulfate from Aldrich, or Degussa titanium oxide (specific surface area 100 m^2/g) and alkali metal nitrate in at least 10-fold molar excess relative to the total amount of Ti, were thoroughly mixed and put in a Pyrex reactor. Eventually anhydrous carbonate or hydroxide of the corresponding alkali metal was added. The mixtures were pretreated under a nitrogen flow at 150°C for 2 h to remove water from the precursor salts, then the reaction was carried out at 400–550°C, for 4 h. Note that the sodium and potassium nitrates do not decompose with noticeable velocity up to 550°C therefore they can be safely used as the solvents at these temperatures. After cooling, the solidified melt was washed with distilled water at room temperature then the product was dried overnight in air at 120°C. X-ray diffraction patterns were recorded on a BRUKER diffractometer by using Cu Kα radiation. Identification of phases was made using standard JCPDS files. Surface areas and pore radii distributions were measured by nitrogen adsorption. Chemical analyses of alkali metals and titanium were carried out by using the atomic emission method.

The gaseous products evolved upon heating of the samples were studied using a mass-spectrometer Gas Trace A (Fison Instruments) equipped with a quadrupole analyzer (VG analyser) working in a Faraday mode. The ionization was done by electron impact with an electron energy of 65 eV. The samples (ca 0.1 g) were heated from room temperature to 550°C in a glass cell

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at the heating rate of 1.5° min^{-1}. A silica capillary tube heated at 180°C continuously bled off a proportion of the gaseous reaction products. Several signals were registered, those with $m/e = 18$, 30, 32, 28, 44 and 46, corresponding respectively to ionized species of H_2O, NO, O_2, CO_2 and NO_2. Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 device, at the center of electronic microscopy of Claude Bernard University (Lyon). Transmission electron micrographs were obtained on a JEOL 2010 device with accelerating voltage 200 KeV.

3. Results and discussion

3.1. Characterization of solid products of the molten salt reactions

The results of syntheses carried out in this work are resumed in Table I. It summarizes the properties of solids prepared at different temperatures as a function of the nature of titanium precursor, the nature of the alkali metal cation and that of the doping basic compound, used to increase L-F basicity of the melt.

Preliminary experiments carried out to find the range of the appropriate reaction conditions are not included

TABLE I Reaction conditions and properties of solids obtained in the nitrate melts

Sample reference	T °C, time	Reaction mixture	Results : DRX phases observed and morphology description	Ti/Alc at.[a]
LiTi5	500°C, 4 h	11 g $LiNO_3$ 1.6 g $TiOSO_4$	$TiO_2 + Li_2TiO_3$	0.8
LiTiOH5	500°C, 4 h	11 g $LiNO_3$ 1 g LiOH 1.6 g $TiOSO_4$	Li_2TiO_3 Lamellar	0.49
KTiOH51	500°C, 4 h	13 g KNO_3 1 g KOH 2.4 g $TiOSO_4$	TiO_2 Spherical dispersion	47
KTiOH52	500°C, 4 h	13 g KNO_3 1 g KOH 1 g TiO_2	$K_2Ti_4O_9$ Rods	2.28
KTIOH552	550°C, 12 h	13 g KNO_3 1 g KOH 1.6 g $TiOSO_4$	$K_2Ti_6O_{13}$ TiO_2 impurity Needles	3.19
KTIOH58A	500°C, 8 h	13 g KNO_3 2 g KOH 1 g TiO_2	$K_2Ti_4O_9$ $K_2Ti_2O_5$ Rods	1.56
KTIOH58B	500°C, 8 h	13 g KNO_3 1 g KOH 1.6 g $TiOSO_4$	$K_2Ti_6O_{13}$ TiO_2 impurity Rods	4.64
KTIOH58C	500°C, 8 h	13 g KNO_3 2 g KOH 1.6 g $TiOSO_4$	Poorly crystallized $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ Rods	1.90
KTIC5581	550°C, 8 h	13 g KNO_3 1.3 g K_2CO_3 1.6 g $TiOSO_4$	TiO_2	33
KTIC5582	550°C, 8 h	13 g KNO_3 3.9 g K_2CO_3 1.6 g $TiOSO_4$	$K_2Ti_6O_{13}$ Rods	3.17
NaTIC5581	550°C, 8 h	13 g KNO_3 0.8 g Na_2CO_3 1.6 g $TiOSO_4$	TiO_2	26
NaTIC5582	550°C, 8 h	13 g $NaNO_3$ 2.4 g Na_2CO_3 1.6 g $TiOSO_4$	$Na_2Ti_4O_9$ TiO_2 impurity	3.3
NaTIOH58A	500°C, 8 h	13 g $NaNO_3$ 1 g NaOH 1 g TiO_2	$Na_2Ti_4O_9$ Spherical particles	1.97
NaTIOH58B	500°C, 8 h	13 g $NaNO_3$ 1 g NaOH 1.6 g $TiOSO_4$	$Na_2Ti_6O_{13}$ Rods (layers $d = 9.75$; 8.9)	3.13
NaTIOH5BM	500°C, 12 h	13 g $NaNO_3$ 0.92 g NaOH 1.6 g $TiOSO_4$	$Na_2Ti_6O_{13}$ Rods	3.04
NATi5OHC	500°C, 8 h	13 g $NaNO_3$ 2 g NaOH 1.6 g $TiOSO_4$	$Na_2Ti_4O_9$ Spherical dispersion	1.75

[a] Atomic ratio from the data of chemical analysis.

in the Table I. Thus, no products other than titania were obtained in the individual sodium and potassium nitrates. Moreover, the reaction temperatures lower than 500°C (400 and 450°C) as well as short reaction times (1 and 2 h) seem to be insufficient to obtain pure titanates, leading always to titania or its mixtures with target titanates.

Analyzing the data of Table I, qualitative conclusions about the melts reactivity and the synthetic possibilities can be done. A simple rule can be formulated explaining the differences between the reaction products and allowing to predict the results of syntheses in similar reaction mixtures. It is based on the decrease of mean electronegativity (and the increase of oxobasicity) in the sequence of compounds (with Alk staying for an alkali metal):

$$\begin{aligned} &TiOSO_4 - TiO_2 - Alk_2Ti_6O_{13} - Alk_2Ti_4O_9 \\ &- Alk_2Ti_2O_5 - Alk_2TiO_3 \end{aligned}$$

To move from the left to the right of this sequence, oxygen anions O^{2-} should be added to the titanium species. Stronger oxobasicity of the melt (higher temperature or more basic reactants) favors the shift from the right to the left in this row and the increase of Alk/Ti atomic ratio in the product. All the data obtained in this work can be easily realized using this rule. Indeed, the increase of the reaction temperature leads to the increase of alkali metal content in the solids (compare KTiOH552 and KTIOH58B). As concerns the influence of the alkali metal cation, note that the most basic lithium nitrate gives easily simple titanate whereas potassium and sodium produce only titania. The difference between sodium and potassium is also obvious: tetratitanate is more easily obtained in more basic sodium containing melts (compare the solids KTiOH58C and NaTiOH58C). Moreover, using the acid precursor $TiOSO_4$ leads to the solids with systematically lower alkali metal amounts than the same syntheses using an equivalent molar amount of titania. If the amount of base added is not sufficient, it probably neutralized by the oxosulfate precursor giving titania, without possibility to produce titanates, as in the case of specimen KTIOH51. Last, but not least is the fact itself that doping of nitrates with strong oxobases such as alkali metals hydroxides or carbonates allows passing from titania to alkali metal polytitanates.

The morphology and the composition of solid products vary strongly as a function of the reaction conditions. While the solids remain almost XRD amorphous, their particles may have form of rods, whiskers, or lamellae in the case of potassium containing melts (Fig. 1), and fine dispersions for the homologous sodium based preparations (Fig. 2).

For the preparative goals, the most interesting are off course the syntheses providing homogeneous and single phase solids. The preferred situation is when a reactive solvent present in a large excess provides chemical potential and reactive species appropriate to form a single phase product. This is for example the case of individual K and Na nitrates, which give pure titania in wide range of temperatures, whatever the molar ratio of nitrate to the titanium salt, provided it is high enough for the reaction to occur. However in our preparations using base doped melts, if the large excess of hydroxide or carbonate base was present, single phase polytitanates could be arrested only after proper choice of the reaction conditions. As can be seen from the Table I, the mixtures of titania and titanates or those of different titanates are obtained as a rule. This suggest that the dissolution of titania and the following L-F reactions of different titanates in the melts are parallel and occur with comparable rates. The bases, carbonates or hydroxides, should therefore be considered not just as admixtures changing the melt basicity, but rather as the stoichiometric reagents. Since for the TiO_2 precursor the individual K and Na nitrates are not reactive in the range 400–550°C, the amounts of bases necessary to obtain any titanates can be exactly calculated. By contrast, for the $TiOSO_4$ precursor the problem could be the simultaneous reactivity of both nitrate and basic admixture. However, as suggests the mass spectrometric study (vide infra), at least for the carbonate doped melts, $TiOSO_4$ reacts entirely with the basic admixture and not with the nitrate solvent. Then, providing the appropriate amounts of bases are introduced, nearly single phase products are available.

The single phase products with composition close to the stoichiometry of hexatitanate are KTIOH552 and NaTiOH5BM solids prepared from the titanium oxosulfate precursor in the presence of hydroxides. As inspected by SEM, these specimens consist of homogeneous dispersions of rod like – particles having submicrometer size (Fig. 3). The X-ray diffraction patterns of the non calcined samples are of very poor quality and give just a hint on the compounds present since the lines are very broad. Sintering at 1000°C gives single phase materials, but it does not prove they are formed at lower temperatures. The chemical analysis shows that the solids have compositions close to the stoichiometry of the corresponding trititanates. Some silica impurity (1–2% wt.) was found, probably because of leaching of silicate from the Pyrex reactors.

Transmission electron microscopy with atomic resolution shows that the rods of KTIOH552 and NaTiOH5BM solids are composed by the hexatitanate slabs which are oriented along the rods growth direction (Fig. 4). The layers are more or less disordered according to analysis zone, but the quality of SAED is always poor. The distances between the layers correspond to those of (001) interplane distances in the corresponding hexatanates. EDS analysis showed that the solids are not perfectly homogeneous, with the local Alk/Ti atomic ratio scattering from 0.29 to 0.4. The average values of Alk/Ti atomic ratios were close to those given by chemical analysis.

We see therefore that poorly crystalline rodlike particles of sodium and potassium hexatanates can be easily prepared in the hydroxide doped nitrate fluxes. Further treatment of these solids depends on the application goals. For instance, they can be sintered at higher temperatures to

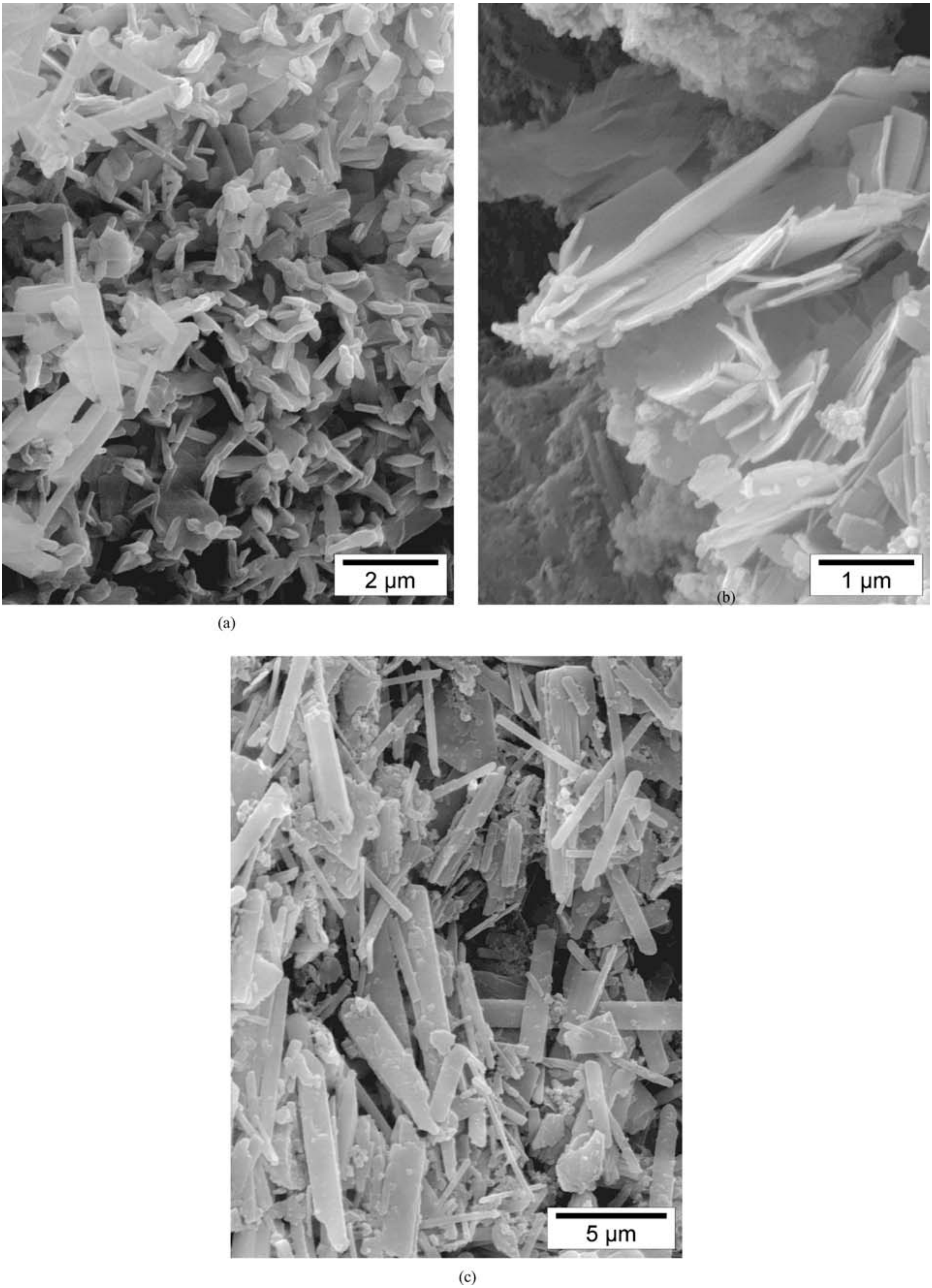
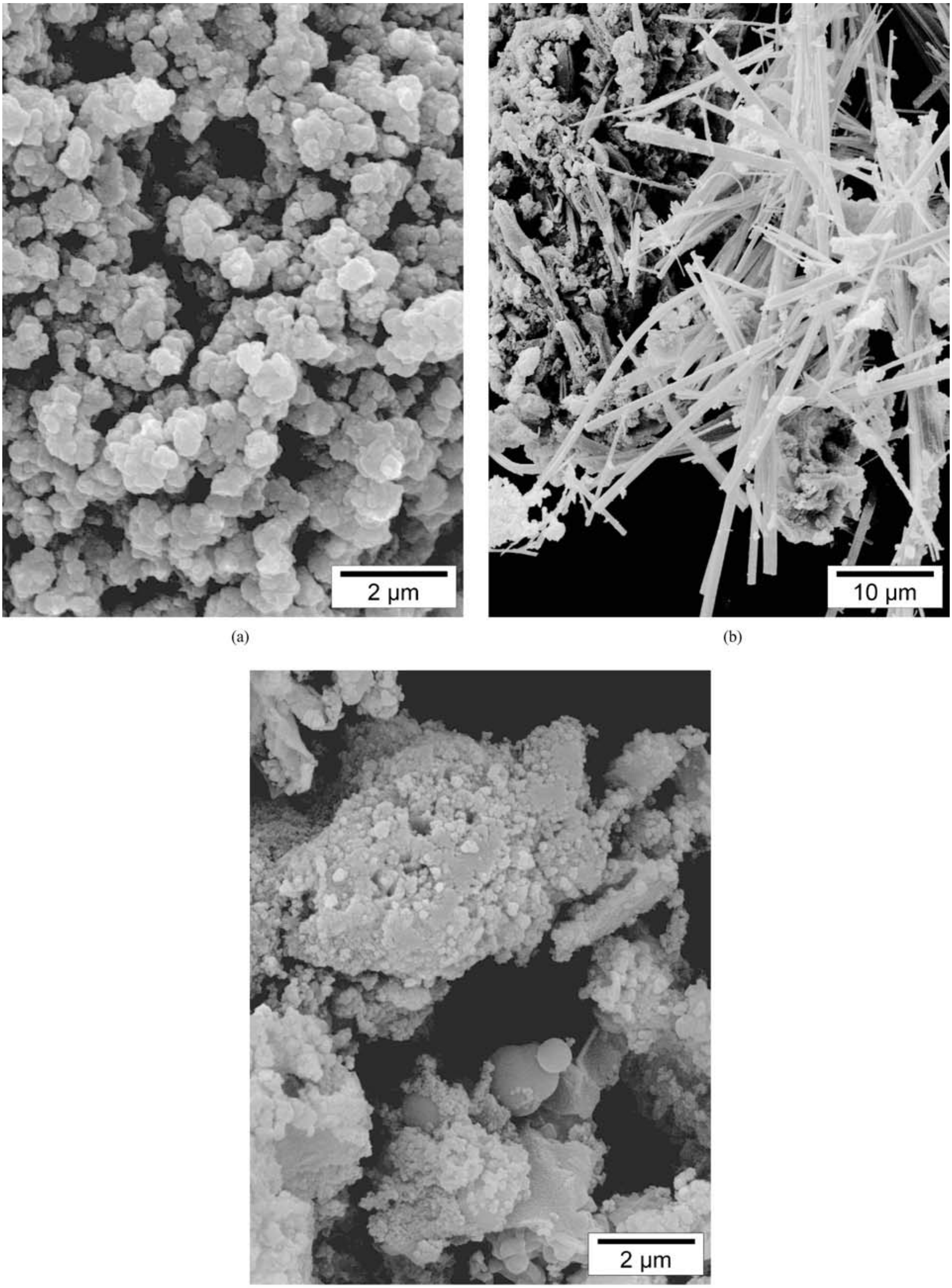


Figure 1 SEM images of the specimens KTiOH58A (a), KTiOH58B(b) and KTiOH58C (c).

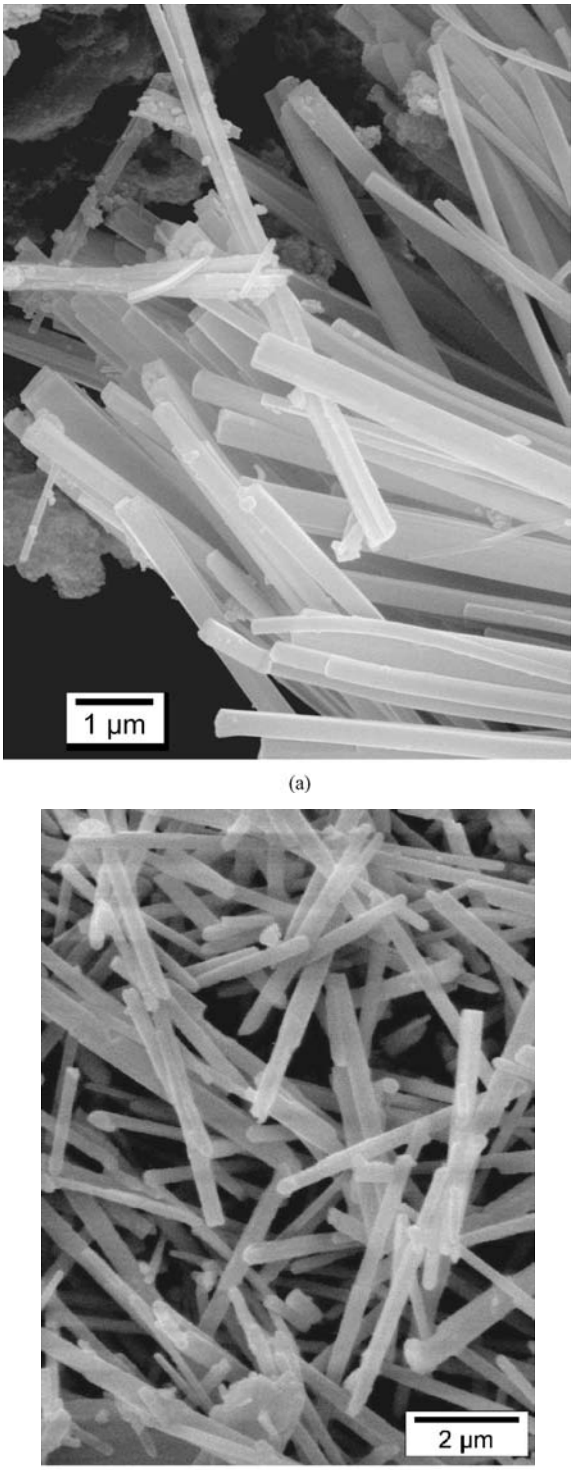


(a)

(b)

(c)

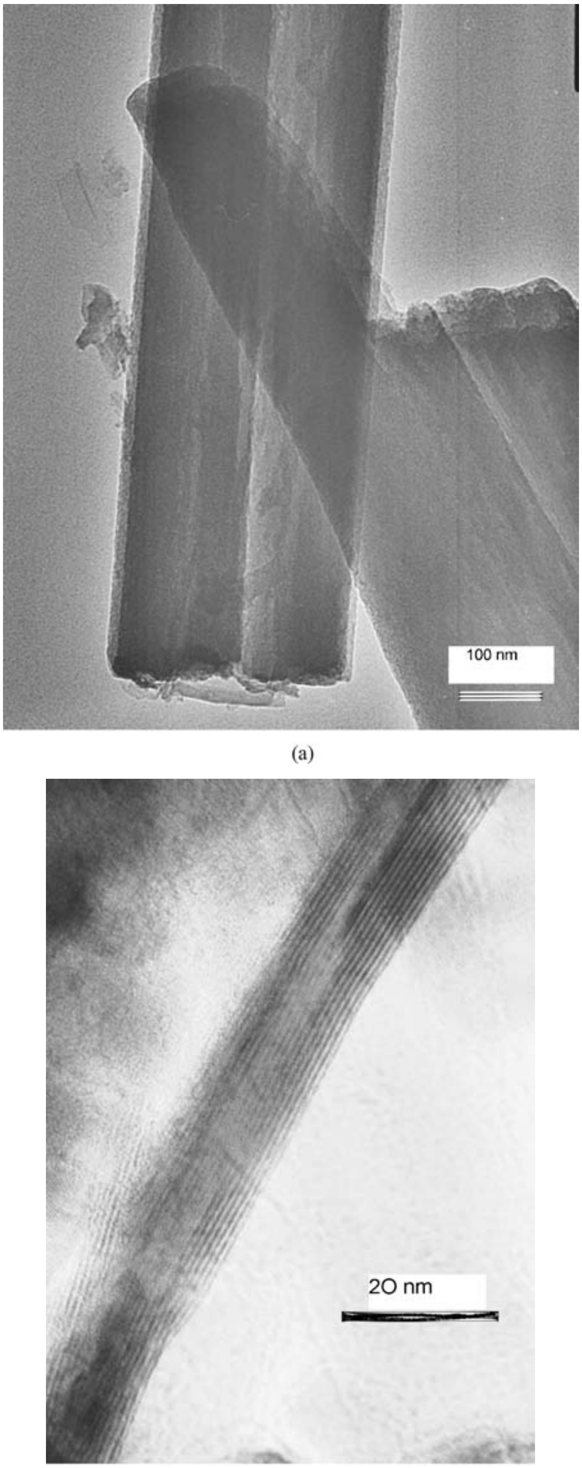
Figure 2 SEM images of the specimens NaTiOH58A (a), NaTiOH58B(b) and NaTiOH58C (c).



(a)

(b)

Figure 3 (a) SEM image showing general morphology of the $K_2Ti_6O_{13}$ nanorods in the KTIOH552 specimen. The average diameter is 200 nm. (b) morphology of poorly crystalline $Na_2Ti_6O_{13}$ in the NaTiOH5BM solid.



(a)

(b)

Figure 4 (a) HRTEM image for 200 nm diameter $Na_2Ti_6O_{13}$ particle. (b) atomic resolved image showing ordered layers of trititanate, $d = 7.7$ A. (c) disordered layers of $K_2Ti_6O_{13}$ keep orientation perpendicular to growth direction.

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obtain the crystalline titanates whiskers used in ceramics. Otherwise they may be treated chemically to extract alkali metals and obtain exfoliated titania, as briefly described below.

The alkali metals hexaitanate materials KTIOH552 and NaTiOH5BM were treated for 12 h by a large excess of 1 M hydrochloric acid, then washed filtered and oven dried. White precipitates collected were analyzed by XRD and TEM. After extraction the KTIOH552 solid become completely amorphous, whereas NaTiOH5BM preserved the same XRD pattern as the initial solid corresponding to poorly crystalline hexatitanate. It appears that potas-

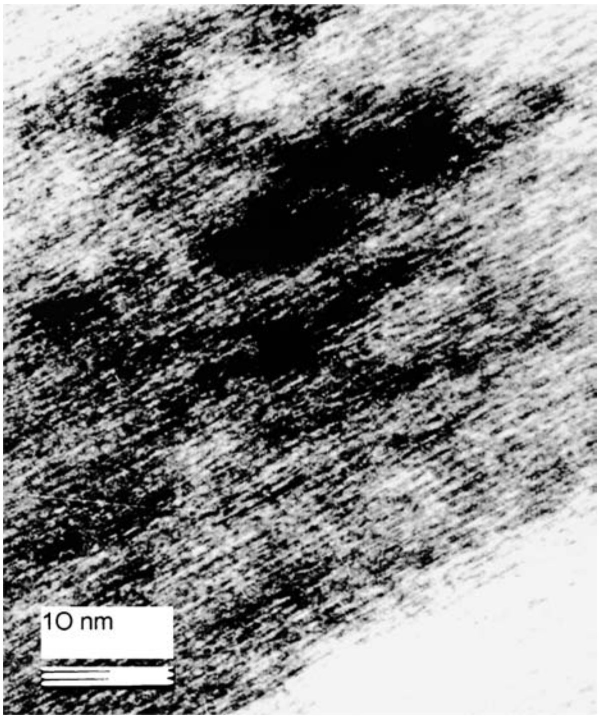

Figure 4 *Continued.*

sium was completely extracted by acid extraction from the KTIOH552 solid, the residual potassium content being less than 0.2% at., as determined by EDS. At the same time the solid kept lamellar morphology at the nanoscopic level (Fig. 5a). The specific surface area as found by low temperature nitrogen adsorption was increased from 5.2 m^2/g in the initial KTIOH552 to 29.8 m^2/g in the HCl- extracted solid. As to the NaTiOH5BM sample, after the extraction by HCl it changed the morphology which becomes cavernous (Fig. 5b). The specific surface area also increased, but not so significantly, progressing from 4.6 m^2/g in the initial solid to 7.8 m^2/g in the extracted one. However the sodium to titanium ratio did not change compared to the initial NATIOH5BM solid, showing that in this case the extraction experiment failed.

3.2. Mass-spectrometric study of $TiOSO_4$ and TiO_2 reactivity in the nitrate melts

The study of reactivity was carried out using SM of evolved gases out in order to establish the reaction equations, and to compare the reactivity of different alkali metal nitrates in a more systematic way than it can be inferred from the data of Table I.

The individual alkali metal nitrates react with $TiOSO_4$ hydrated precursor above their melting points, evolving nitrogen dioxide (seen in the mass spectrometer mostly as NO fragment, (cf. ref [17]) and oxygen, presumably according to the L-F acid–base equations.

$$2NO_3{}^- + TiOSO_4 \Rightarrow TiO_2 + SO_4{}^{2-} + 2NO_2 + \frac{1}{2}O_2 \qquad (1)$$

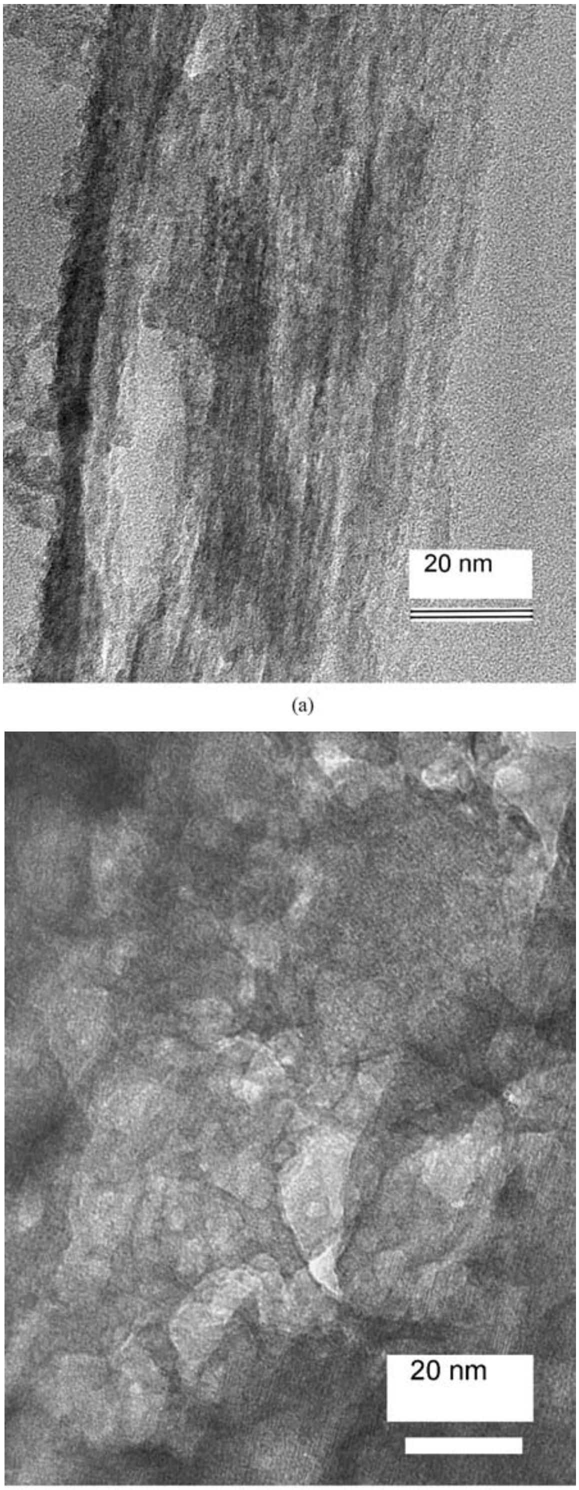

Figure 5 HRTEM photos of the solids treated with diluted HCl:KTIOH552 (a) and NaTIOH5BM (b).

The reactivity of melts changes in the sequence Li > Na > K, in agreement with the sequence of the L-F basicity of the corresponding nitrates (Fig. 6). For lithium and sodium nitrates, the reaction maxima are placed near the corresponding melting points, indicating that the salt and the precursor are potentially highly reactive, but just a good physical contact is lacking in

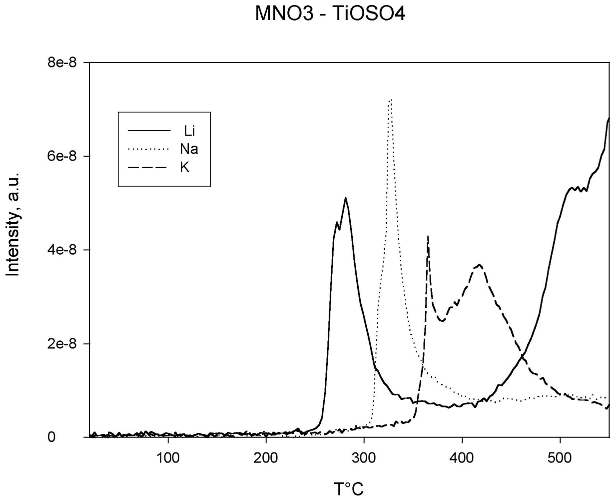

Figure 6 Mass spectra of NO evolved upon linear heating of $LiNO_3$-$TiOSO_4$ (a), $NaNO_3$-$TiOSO_4$ (b) and KNO_3-$TiOSO_4$ (c) mixtures. The molar ratio nitrate to $TiOSO_4$ is 10. Other gaseous products (not shown) are molecular oxygen and NO_2 which follow in step the curves of NO signal.

the solid state for the reactions to occur. When intimate contact of the reactants is provided by the salt fusion, reaction occurs rapidly and no diffusion limitation probably exist in the reaction mixture. In the case of potassium, narrow reaction maximum is observed near the salt fusion point, contributing less than 10% to the total gases production. After this first maximum, the true reaction zone follows, smeared over temperature range almost to 550°C. Sodium and potassium nitrates give only reaction maximum, which corresponds to the transformation of the oxysulfate precursor into TiO_2, whereas $LiNO_3$ continues to react after 400°C producing the simple lithium titanate:

$$TiO_2 + 2LiNO_3 \Rightarrow Li_2TiO_3 + 2NO_2 + \frac{1}{2}O_2 \quad (2)$$

There is no separate reaction maximum corresponding to this reaction, because lithium nitrate begins to decompose not far above 500°C, overlapping with reaction 2 in the temperature range. Moreover, we can not be sure whether titania reacts directly with lithium nitrate or rather with its decomposition product lithium oxide. This mechanistic point seems really difficult since the reaction products are the same in both cases. Anyways, the overall reaction Equation 2 can be written surely. As can be expected from the above described results, dispersed TiO_2 if taken as a precursor, does not react with pure K and Na molten nitrates up to 550°C.

When doped with carbonate, the melts react at lower temperatures and the main gaseous product in all cases is not NO but CO_2 (Fig. 7). Moreover carbon dioxide becomes virtually the only gaseous product, beside water produced due to the salts dehydration. The first CO_2 production peak is observed below the melting points of the corresponding nitrates. In the case of $TiOSO_4$ reaction, the peak of CO_2 peak is much more intense, than for TiO_2 precursor. The blank experiments in the mixtures of nitrates and carbonates in the absence of Ti precursor still show this low temperature CO_2 production, the same as in the case of reaction mixtures containing TiO_2. Therefore this peak is first of all due to solid state $TiOSO_4$ reaction with carbonates and partially due to the decomposition of hydrocarbonates, which are often present in the carbonates because of contact with ambient air and humidity.

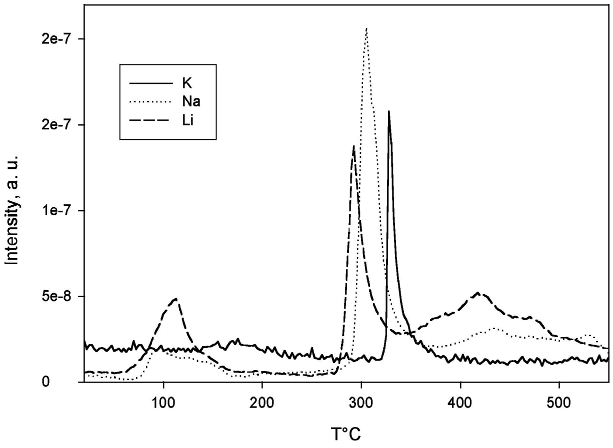

Figure 7 Mass spectra of CO_2 evolved upon linear heating of the mixtures $LiNO_3$-Li_2CO_3- $TiOSO_4$ (a), $NaNO_3$-Na_2CO_3- $TiOSO_4$ (b) and KNO_3-K_2CO_3-$TiOSO_4$ (c). The molar ratio of nitrate to carbonate to oxysulfate is 10:3:1.

From the observed MS curves and characterizations of the solid products the following sequence of reactions can be inferred for the carbonate doped melts:

$$CO_3{}^{2-} + TiOSO_4 \Rightarrow TiO_2 + CO_2 + SO_4{}^{2-} \quad (3)$$

$$6TiO_2 + CO_3{}^{2-} \Rightarrow Ti_6O_{13}{}^{2-} + CO_2 \quad (4)$$

$$4TiO_2 + CO_3{}^{2-} \Rightarrow Ti_4O_9{}^{2-} + CO_2 \quad (5)$$

$$2TiO_2 + CO_3{}^{2-} \Rightarrow Ti_2O_5{}^{2-} + CO_2 \quad (6)$$

$$TiO_2 + CO_3{}^{2-} \Rightarrow TiO_3{}^{2-} + CO_2 \quad (7)$$

Quantitative analysis of MS curves allows to get an idea about the stoichiometry of the reaction stages. Thus, the amount of CO_2 produced per titanium atom is equal in the reactions (3) and (7). Indeed, for the reaction of Li containing flux with $TiOSO_4$ (Fig. 7a) the sum of the areas of two first peaks is equal to the area of the broad reaction maximum observed after 350°C. By contrast for Na containing flux the amount of carbon dioxide emitted in the first two peaks is 71% of the total production, in agreement with the difference in CO_2 production in the reactions (3) and (4, 5).

In the $TiOSO_4$ reactions, sharp CO_2 peaks at the corresponding nitrates melting points were observed for all three alkali metals studied. Is seems that $TiOSO_4$ is highly reactive at these temperatures towards carbonate dissolved in the nitrate melts. When $TiOSO_4$ particles are wetted with the melt it is rapidly transformed into titania. Further reactivity strongly depends on the nature of the alkali metal cations and changes in the expected sequence Li > Na > K. The reactivity decreases drastically in this row. Indeed, if for Li – containing flux a clear reaction maximum is observed, whereas for potassium the CO_2 signal is only slightly higher than background level. Some small amount of oxygen is evolved above 500°C in all carbonate doped reaction mixtures (not shown). As follows from the experiments with pure K and Na nitrates, this oxygen is not due to the L-F reactions of TiO_2, but it might be due to the side L-F reaction of dissolved species of polytitanates with nitrate.

Pure titania taken as a reactant does not show any strong reaction peaks at the Na and K nitrates melting points, neither at higher temperatures. It slowly reacts above 400°C, repeating the reactivity sequence observed in the high temperature part for the $TiOSO_4$ precursor.

As concerns the reaction mixtures doped with alkali metal hydroxides, no easily detectable gases were produced. The dominating reactions are obviously those of titanium precursors with alkali metal hydroxide because only water formation is observed. However, water signal in these experiments was very broad and not convenient to compare the melts reactivity at the conditions applied.

4. Conclusion

Rod-like and lamellar submicrometer dispersions of alkali metal titanates were obtained in the nitrate melts doped with hydroxides or carbonates. In this work only mono, di- tetra- and hexatitanates are obtained, but it seems probable that other lamellar titanates with lower alkali metal amounts might be obtained by thorough control of the reaction conditions. Otherwise, doping of the reaction mixtures described here with other metals in the form stable cations or soluble oxoanions can be proposed as a way to prepare new lamellar titanates, with potential applications in catalysis, electro- and photochemistry.

Rod like and lamellar morphology is often observed in the molten salt preparations. Thus, nanorods of $LiFeO_2$ [18] and Ba titanate [11] were obtained recently using molten nitrates. Earlier, rodlike Ce-Zr oxide particles were prepared in the fluoride doped nitrate flux [19]. The list of examples can be continued.

Two reasons might be suggested as explanation of the particular morphology of solids grown in the melts. First, a precursor or an intermediate phase might occasionally have rodlike particles, which are not dissolved in the melt but undergo further pseudomorphic transformation to the final product. Second, more fundamental property of ionic solvents is promotion of the selective growth of certain crystallographic planes which leads to the systematic appearance of highly anisotropic particles in the reaction products.

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