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VERSITA

Molten salt synthesis of potassium hexatitanate

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Potassium hexatitanate fibrous crystals have been synthesized by a conventional solid-state reaction and via molten salt process. The molten salt process has been shown to be effective in preparing fine and non-agglomerated $K_2Ti_6O_{13}$ whiskers. The type of molten salt (KCl, NaCl–KCl) has a significant effect on the chemical composition of the whiskers. By using a eutectic mixture of NaCl and KCl, the replacement of potassium ions in solid potassium hexatitanate by smaller sodium ions from the chloride flux can be achieved. The characterization of the samples was carried out by means of XRD, SEM, EDX and WDX.

Keywords: *potassium hexatitanate, synthesis, conventional calcinations, molten salt process, whiskers*

1. Introduction

Potassium titanates ($K_2O \cdot nTiO_2$, $n = 2,4,6,8$) are a family of artificial crystals with unique crystalline structures. They have wide industrial applications as ion exchangers, filters, heat insulators, photocatalysts and as whiskers reinforced plastics, metals and ceramics [1–7]. It is well known that the properties of a material are determined by its structure. Hexatitanate has a tunnel structure and exhibits good thermal insulating properties and high chemical stability [2–4, 8, 9]. Because potassium ions in $K_2Ti_6O_{13}$ are enclosed by the tunnel structure and isolated from the environment, they cannot escape outside and are chemically inert [9].

The control of morphology is a difficult and challenging task in material synthesis and the products with diverse morphologies, such as grains and whiskers may be created under different synthesis conditions [10]. Numerous methods have been developed to synthesize $K_2Ti_6O_{13}$ [11]. Lee *et al.* [12] and Bao *et al.* [10] studied the formation and growth of potassium titanate whiskers and corresponding reactions taking place in the calcination process (including slow-cooling calcination).

Recently, the structure, growth and properties of $K_2Ti_6O_{13}$ whiskers (nanowires) were investigated using hydrothermal methods [3, 13–17]. Moreover, the reported methods to prepare potassium titanate include sol-gel process [2]. Potassium hexatitanate fibres were also synthesized by ion exchange reaction from $K_2Ti_4O_9$ fibres [18] and using fibrous $K_4Ti_3O_8$ as an initial material [4].

The flux growth method has been intensively investigated and various fluxes have also been proposed [19–21]. 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 nitrates doped with carbonates or hydroxides [22]. Gorokhovsky *et al.* [23] reported the possibility to produce potassium titanates by the treatment of TiO_2 powder in molten salt mixtures of different basicity, controlled by admixture of alkali hydroxides. Molten mixtures of KNO_3, K_2CO_3 and KOH were used.

The molten salt synthesis (MSS) seems to be a promising preparation method of complex oxide compounds anisotropic in shape. In this technique the starting materials are mixed together with a salt and then heat treated at a temperature higher than the melting point of the salt (usually alkaline chloride and sulphate). The melting temperature of the salt system can be reduced by using a eutectic mixture of the salts, *e.g.* the use of NaCl/KCl instead of pure NaCl reduces the melting point from 801 °C to 657 °C. The typical starting materials are oxides, but oxalates, nitrates and carbonates can also be used. A reaction between the precursors takes

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place in the molten salt (the flux). The solubilities of starting oxides and reaction products in the salts are usually quite low, so that the liquid and solid phases coexist during the process. The liquid phase accelerates the formation of the complex oxide and its particles growth. The solid product obtained is separated by washing of the final mixture with hot deionized water. MSS has been used to form various ceramic powders such as $BaTiO_3$, $Bi_4Ti_3O_{12}$, ferrites, $Pb(Zr, Ti)O_3$ and niobates relaxors [24–29].

In this paper the preparation of $K_2Ti_6O_{13}$ whiskers by the KCl molten salt method is described. For comparison, the synthesis of $K_2Ti_6O_{13}$ by the calcination method was investigated.

2. Experimental

Chemical grade reagents K_2CO_3 and TiO_2 (anatase) were used as starting materials. They were mixed in appropriate proportion to yield $K_2Ti_6O_{13}$, and ground homogenously in an agate mortar under isopropyl alcohol for 40 min. A conventional calcination method was used: the samples of dry mixture were placed in a platinum crucible, and heated in an electric muffle furnace at different temperatures ranging from 900 °C to 1100 °C for different periods of time, and subsequently naturally cooled down to room temperature. The samples were characterized by XRD and SEM.

In MSS method an eutectic equimolar mixture of NaCl (chemical grade) and KCl (chemical grade) with a 657 °C melting point and KCl which melts at 771 °C were used as the molten salts. The reactants (mixture of K_2CO_3 and TiO_2) and salt were mixed completely in the alcohol. The salts were added at 75 vol. %. In addition, the possibility of synthesis of potassium hexatitanate by MSS using a mixture of TiO_2 and KCl (without K_2CO_3) was investigated. The dried mixtures were placed in a platinum crucible and heated in a sealed alumina crucible (to prevent the salt evaporation) in 900 °C -1100 °C for different durations of time. The final products were recovered by washing several times with a hot deionized water until no traces of Cl^- could be detected by $AgNO_3$. The powders were finally dried at 90 °C in a drying oven. The size and shape of the synthesized particles were investigated

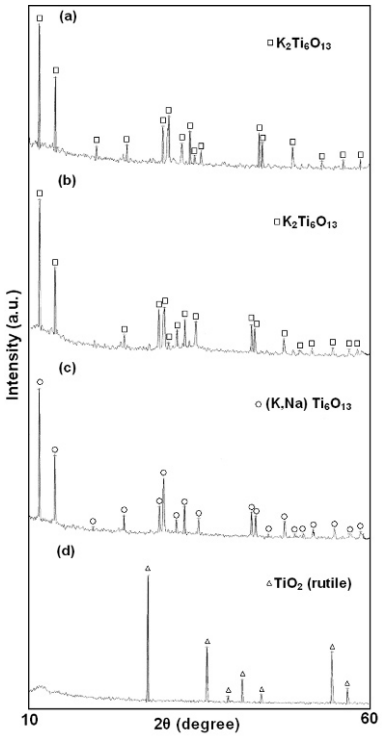


Fig. 1. XRD patterns of the samples synthesized at 1000 °C for 1 h: (a) conventional calcination, (b) MSS, KCl, (c) MSS, NaCl–KCl and (d) MSS, KCl, without K_2CO_3.

with SEM. The phase and chemical compositions of obtained products were determined by XRD, WDX and EDX.

The SEM observations were carried out with a TESLA BS 340 microscope. The XRD patterns were obtained using a SEIFERT XRD 3003 TT diffractometer. The WDX spectra were acquired with an X-ray fluorescence spectrometer PHILIPS PW 2400. The EDX patterns were measured using a HITACHI S-3400N scanning electron microscope with an EDX system THERMO NORAN.

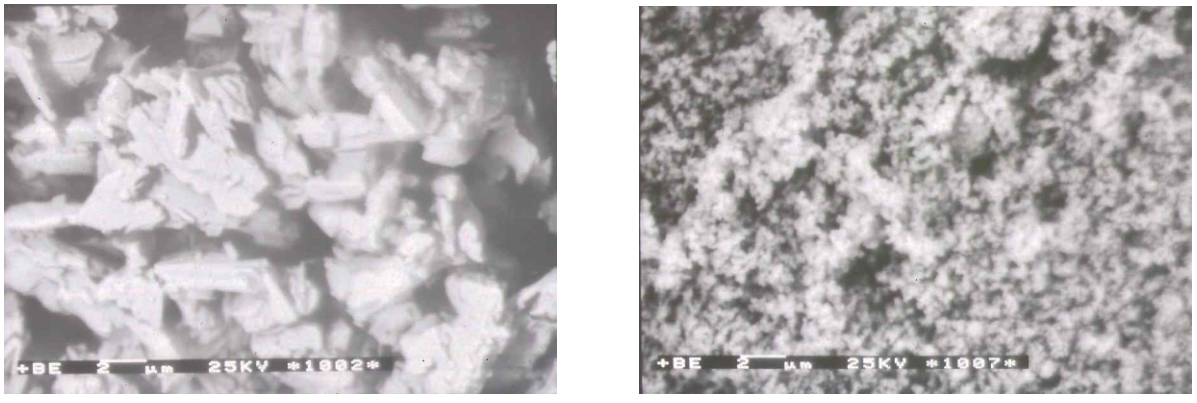
3. Results and discussion

Phase identification of the samples was conducted using the X-ray diffractometry. The XRD data show that the reaction was completed under the synthesis conditions for the mixture: anatase – K_2CO_3 used as precursor (Fig. 1a,b,c). A comparison of interplanar spacings "d" determined from the

Table 1. The strong and medium lines of XRD patterns

hkl	$K_2Ti_6O_{13}$ PDF No. 74-0275	$K_2Ti_6O_{13}$ PDF No. 40-0403	$Na_2Ti_6O_{13}$ PDF No. 73-1398	$Na_2Ti_6O_{13}$ PDF No. 37-0951	Precursor: anatase – K_2CO_3 mixture		
					Hexatitanate CMO[a], 1000 °C, 1 h	Hexatitanate MSS (KCl flux), 1000 °C, 1 h	Hexatitanate MSS (NaCl–KCl flux), 1000 °C, 1 h
200	7.6781	7.699	7.4660	7.468	7.6731	7.7179	7.5423
201	6.3961	6.401	6.2757	6.292	6.3916	6.4248	6.3036
110	3.7070	3.688	3.6325	3.629	3.6827	3.6922	3.6547
310	3.0614	3.050	2.9925	2.981	3.0468	3.0546	3.0148
203	2.9642	2.964	2.9651	–	2.9621	2.9709	2.9541
112	2.8028	2.795	2.7784	–	2.7939	2.7989	2.7829
402	2.7004	–	2.6737	2.671	2.6982	2.7037	2.6865
403	2.5793	2.581	2.5550	2.546	2.5786	2.5824	2.5311
404	2.0993	2.099	2.0883	2.085	2.0977	2.1011	2.0876
602	2.0771	2.078	2.0448	2.043	2.0766	2.0794	2.0601
020	1.9100	1.898	1.8725	1.868	1.8982	1.9007	1.8847
514	1.7574	1.755	1.7371	1.732	1.7542	1.7567	1.7421
712	1.6658	1.664	1.6361	–	1.6637	1.6649	1.6501
223	1.6055	1.598	1.5832	–	1.5986	1.6000	1.5912

[a]Conventional Mixed Oxides

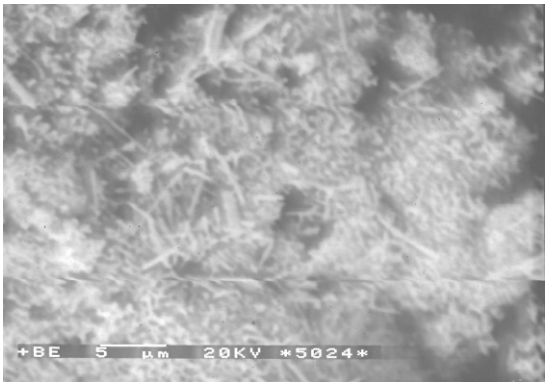


(a) (b)

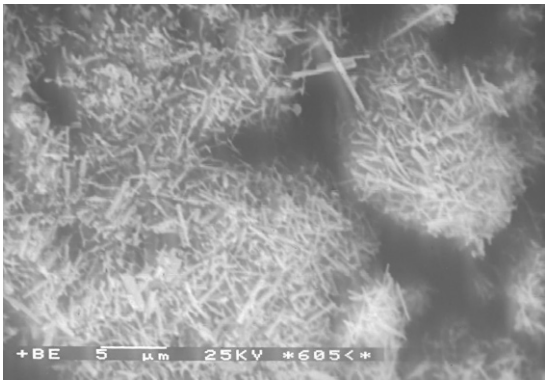
Fig. 2. SEM micrographs of the starting materials: (a) K_2CO_3 and (b) TiO_2 anatase.

XRD patterns of the samples prepared by a conventional solid state reaction and via MSS (use of pure potassium chloride as the molten salt), is shown in Table 1. It should be noted that the agreement is satisfactory.

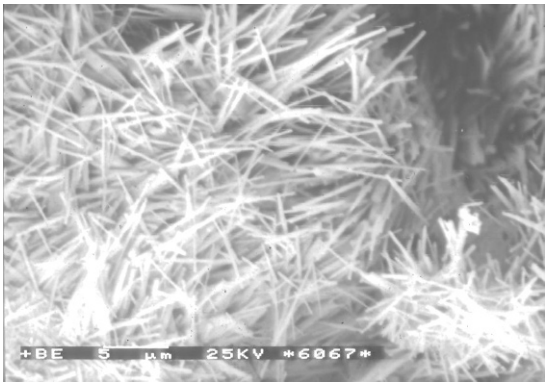
It has been found that potassium hexatitanate is formed as a result of thermal treatment of the stoichiometric mixture of the starting materials (K_2CO_3 and TiO_2), however, the method of synthesis plays a key role in the creation of $K_2Ti_6O_{13}$ whiskers. The particle morphology of the starting materials and synthesized samples is shown in Figs. 2–5. The fibrous crystals of $K_2Ti_6O_{13}$ obtained using conventional method were short and closely packed (Fig. 3). For the sample synthesized at 900 °C the platelet and blocky grains were partly observed, but most grains appeared to form irregular shapes of different sizes, as seen in Fig. 3a. The discrete whiskers were formed using molten salt process (Figs. 4 and 5). These results suggest that the molten salt method is



(a)

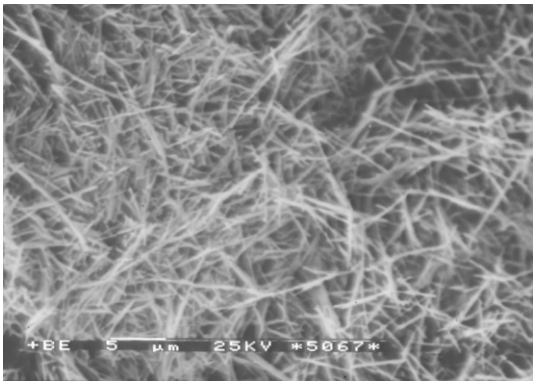


(b)

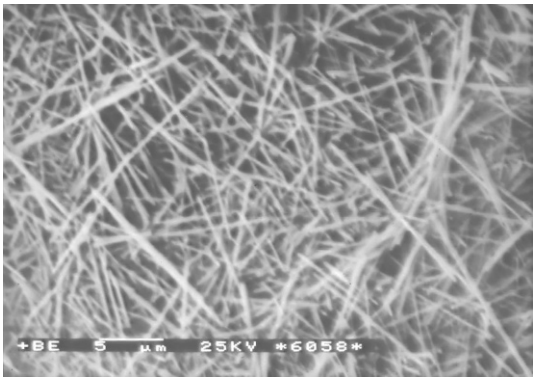


(c)

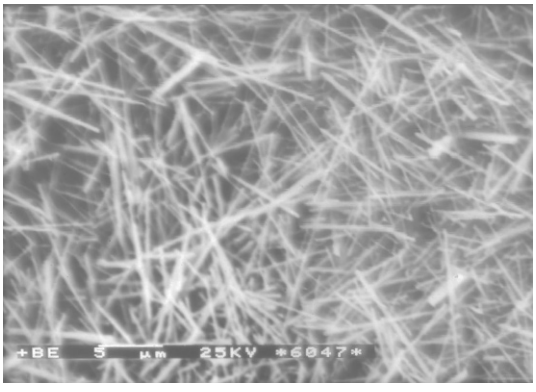
Fig. 3. SEM micrographs of the samples synthesized by the conventional calcination at the temperature of (a) 950 °C for 6 h, (b) 1000 °C for 1 h and (c) 1100 °C for 1 h.



(a)



(b)

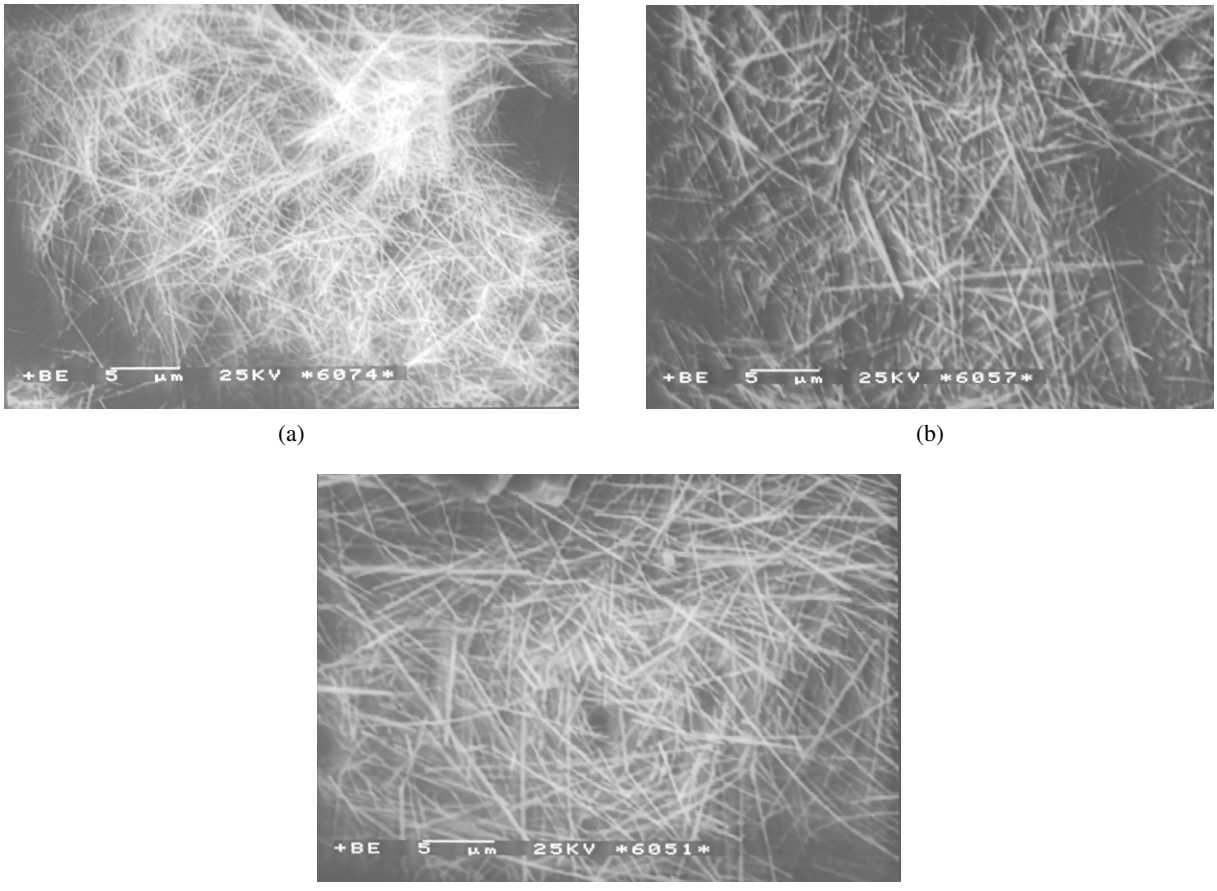


(c)

Fig. 4. SEM micrographs of the samples synthesized via MSS (NaCl–KCl flux) at temperature of (a) 1000 °C for 1 h, (b) 1000 °C for 6 h and (c) 1100 °C for 1 h.

useful for controlling the aggregation state of the fibrous powders. The size of whiskers increased with the temperature of thermal treatment, and the particle size distribution in the samples became more uniform. The length of $K_2Ti_6O_{13}$ whiskers synthesized via MSS was larger as compared to the samples synthesized by a conventional solid state reaction.

When the constituent oxides were heated in the molten salt, the complex oxide particles developed in two processes including the formation of com-



(a) (b) (c)

Fig. 5. SEM micrographs of the samples synthesized via MSS (KCl flux) at temperature of (a) 1000 °C for 1 h, (b) 1000 °C for 6 h and (c) 1100 °C for 1 h.

plex oxide particles and particle growth. The shape and size of the complex oxide powders are determined by the formation mechanism which depends on the relative dissolution rates of the reacting components in the molten salt. When one component dissolves faster than another, the reaction product is formed on the surface of the slower dissolving component, and the complex oxide with the same shape as that of the slower dissolving component is obtained. The dissolution rate of the reacting component depends on the particle size and solubility in the molten salt [24]. $K_2Ti_6O_{13}$ whiskers were not formed by this mechanism, because isometric particles of starting materials were used (Fig. 2). According to [24], when two reactants have comparable dissolution rates in a molten salt, the complex oxide formation takes place somewhere in the molten salt. If this mechanism dominates during the formation process, the complex oxide powder with a characteristic (platelike, needlelike) or lumpy shape is formed. The shape of the product has no connection with the shape of the starting material. During the growth process even the lumpy particles grow to develop a characteristic shape (plate- or needle-like). The cause of the characteristic shape formation is the anisotropy in growth rate. If the growth anisotropy is large, plate- or needle-like particles are formed. The fibrous particles of $K_2Ti_6O_{13}$ were formed by this mechanism. Heating of samples of $K_2Ti_6O_{13}$ at higher temperatures caused the particle growth by Ostwald ripening [30], resulting in elongated particles of high length to diameter ratio, exceeding the minimum value required for whiskers, *i.e.* 20–25 [31].

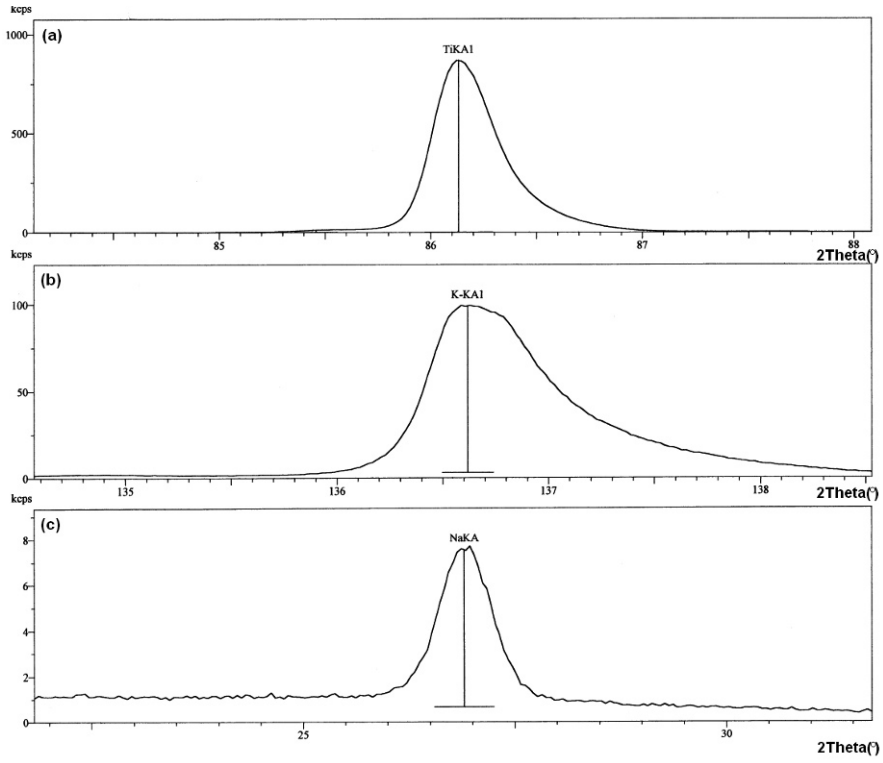


Fig. 6. WDX spectrum of the sample synthesized via MSS (NaCl–KCl flux) at 1000 °C for 1 h: (a) signal of titanium, (b) signal of potassium and (c) signal of sodium.

For the sample obtained via MSS using NaCl–KCl as the salt, the XRD analysis showed that the product was not pure $K_2Ti_6O_{13}$. It can be seen that the diffraction peaks are shifted toward higher angles (Fig. 1). In order to determine the composition of the obtained whiskers, wave-length dispersive X-ray fluorescence analysis (WDX) and energy dispersive X-ray spectroscopy (EDX) examinations were carried out. The data (Figs. 6 and 7) of a sample after synthesis show that the whiskers are composed of the elements K, Na, Ti, and O. These results indicate that a replacement of potassium ions in the solid potassium hexatitanate by smaller sodium ions from the chloride flux can be achieved. K^+ has a larger ionic radius than Na^+ (1.64 Å vs. 1.39 Å). On the other hand, Na^+ has a higher diffusion rate than K^+ even though NaCl has a higher melting point than KCl (801 °C vs. 776 °C) [32].

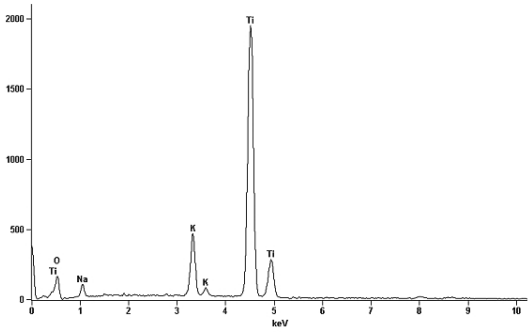
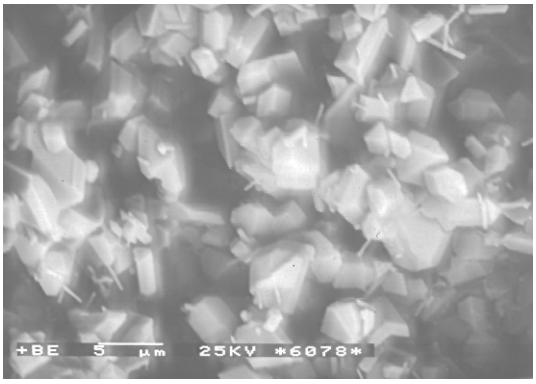
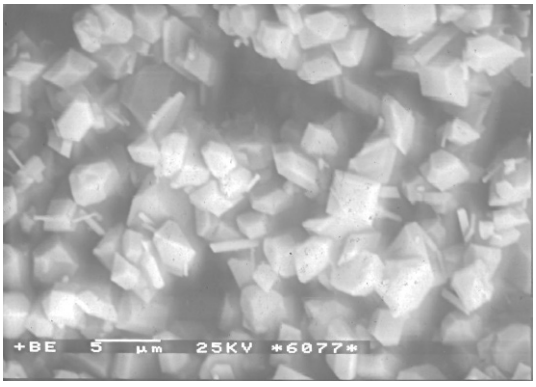


Fig. 7. EDX spectrum of the sample synthesized via MSS (NaCl–KCl flux) at 1000 °C for 1 h.

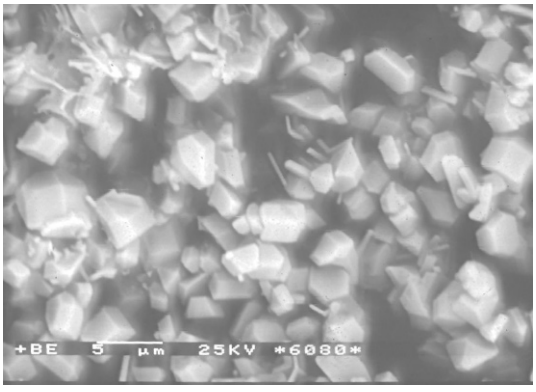
In our experiments, we did not manage to obtain potassium titanate, using the mixture of TiO_2 and KCl as starting materials (without K_2CO_3). The crystals of rutile formed from anatase occurred in the sample after the thermal treatment and washing with deionized water to remove the residual KCl (Fig. 1d). SEM micrographs of the sample exhibit a grained microstructure (Fig. 8). EDX analyses showed the chemical composition of TiO_2 (Fig. 9b), even for a few elongated crystals (Fig. 10).



(a)



(b)



(c)

Fig. 8. SEM micrographs of the sample synthesized via MSS (KCl flux, without K_2CO_3) at 1000 °C for 1 h (different places).

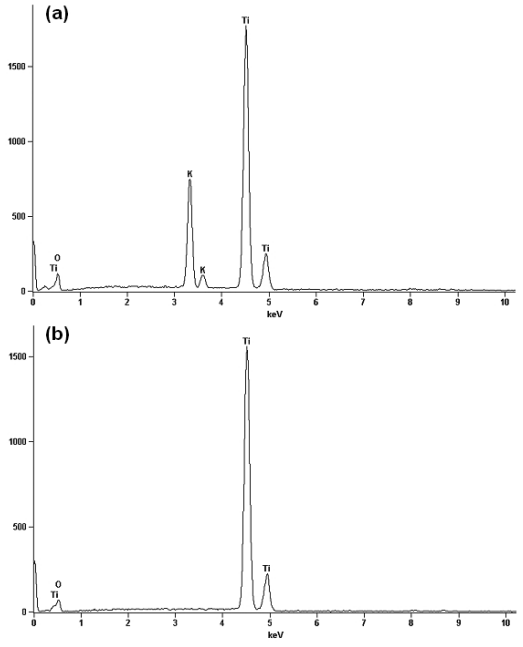


Fig. 9. EDX spectra of the samples synthesized via MSS (KCl flux): (a) with K_2CO_3 as precursor and (b) without K_2CO_3.

According to [7], in the procedure of fabricating potassium hexatitanate nanobelts via MSS, KCl and TiO_2 were used as starting materials. The authors found that the weight ratio of TiO_2 to KCl had an important influence on the formation of $K_2Ti_6O_{13}$. For the mixture with the TiO_2 content of 1 %, the final product consisted of $K_2Ti_6O_{13}$, rutile and anatase. However, when the TiO_2 content was reduced to 0.2 % or even less (0.05 %), the reaction between TiO_2 and KCl could proceed entirely. The ratio of TiO_2 to KCl must be reduced to some extent in order to attain simple-phase potassium titanate.

The toxicity of fibrous particles depends both on their chemical composition and their dimensions. Potassium titanate fibres and whiskers are respirable materials. The fibre diameter is a critical determinant of respirability. A respirable fibre is a particle with a diameter less than 3 micrometers and a length greater than 5 micrometers and a length to width ratio greater than 3:1. These fibres can reach the deepest part of the lung. Experts at the International Agency for Research on Cancer (IARC) maintain that there is a documentary evidence of the results of experimental research, showing that synthetic ceramic fibres do have a carcinogenic influence on animals. However, there is no information about the carcinogenic influence of ceramic fibres on humans. Thus, according to the IARC, they have been classified to group 2B, as possibly carcinogenic to humans [11].

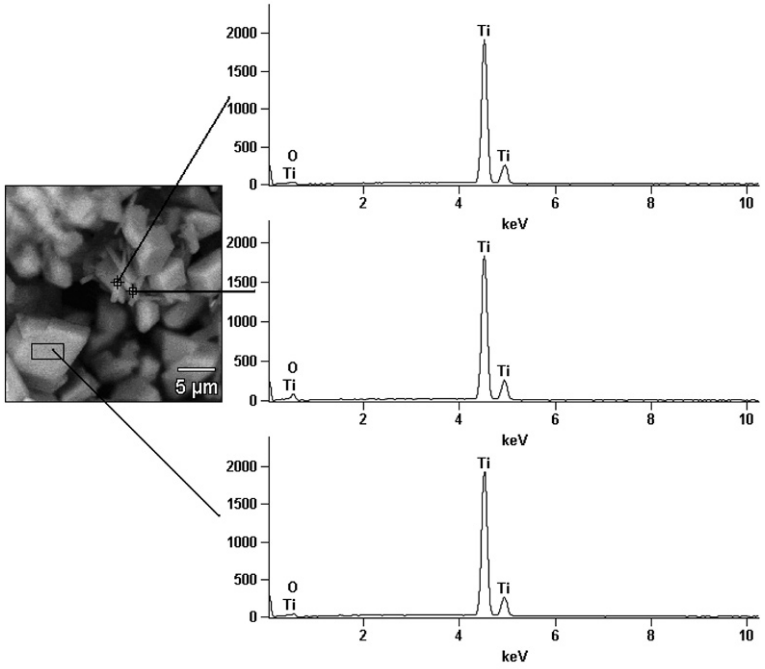


Fig. 10. SEM image and EDX spectra of the sample synthesized via MSS (KCl flux) without K_2CO_3.

4. Conclusions

Potassium hexatitanate fibrous crystals have been obtained as a result of thermal treatment of the stoichiometric mixture of starting materials (K_2CO_3 and TiO_2). Aggregated fibrous particles consisting of numerous smaller fibrous crystals were formed when the $K_2Ti_6O_{13}$ was prepared by a conventional solid-state reaction. The $K_2Ti_6O_{13}$ whiskers were obtained by the molten salt synthesis (MSS) method in chloride salts. Little agglomeration was observed in the powders prepared via MSS. The type of salt has a significant effect on the chemical composition of the whiskers. By using a eutectic mixture of NaCl and KCl, a replacement of potassium ions in solid potassium hexatitanate by smaller sodium ions from a chloride flux was achieved. KCl was used for obtaining pure $K_2Ti_6O_{13}$ whiskers, because NaCl tended to form $Na_2Ti_6O_{13}$. In summary, molten salt process has been shown to be effective in preparing fine and non-agglomerated $K_2Ti_6O_{13}$ whiskers whereas the conventional solid-state reaction resulted in high agglomeration and inhomogeneity of the fibrous powders.

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