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Crystallization and phase evolution of potassium titanates from alkoxide derived precipitates

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A series of titanates having general formula $M_2O \cdot nTiO_2$ (where M represents an alkali metal and $n = 2$–9) form two-dimensional layered or tunnel structures of corner, edge or face sharing TiO_6 (or TiO_5) polyhedra, with interlayer cations [1]. Potassium titanates may be fabricated in the form of whiskers and fibers, and have found application as cheap fillers and reinforcements in composites [2, 3] and as ion-exchange materials [4]. The photoactivity of these materials has also been of interest. When noble metals or metal oxides are incorporated into the structure, photocatalytic activity for cleavage of water has been demonstrated, [5] and photoluminescence at room temperature has also been reported from phases in this system [6].

Although most reports of the synthesis of layered titanates have involved solid state reaction (see for example reference [6]), recently a number of wet-chemical processing routes have been examined. Implicit in the utilization of these methods, is an applications driven desire to produce powders of high surface area. Using sol-gel chemistry, Jung and Shul have prepared potassium hexatitanate powders by co-hydrolysis of titanium and potassium alkoxides, followed by supercritical drying [7]. Hydrothermal routes to prepare layered titanates have been reported by Masaki and coworkers, who used a starting mixture of titanium metal and potassium hydroxide [8]. This work included the observation of a novel phase of composition $KTiO_2(OH)$ having a hexagonal tunnel structure. Starting from a titanium alkoxide and potassium hydroxide, Yahya *et al.*, utilized subcritical and supercritical water conditions to synthesise these phases having a fibrous microstructure [9]. In the present work we detail a preliminary investigation of the phase evolution during crystallisation of potassium titanates, following calcination or hydrothermal processing of amorphous precipitates resulting from the hydrolysis of titanium isopropoxide by aqueous KOH. This forms part of an overarching investigation into the optimization of the processing variables for the synthesis of crystalline layered titanates in high yield.

All starting materials were supplied by the Aldrich Chemical Company, and used without further purification. Titanium isopropoxide was dissolved in propan-2-ol, and an aqueous solution of potassium hydroxide was added dropwise with constant stirring (for this investigation a K:Ti, molar ratio of 1:2 was chosen). A colloidal system developed which is consistent with alkali catalyzed hydrolysis and condensation of metal alkoxides [10]. Following filtration and drying, the resulting precipitates were subjected to three methods of heat treatment: calcination in air or a reducing atmosphere (5% H_2 in N_2), or heating as a slurry in water at 220 °C under autogenous pressure. The latter process was carried out in a PTFE lined autoclave. The phase composition was determined by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer employing Cu-K_α radiation, and with reference to the JCPDS (Joint Committee on Powder Diffraction Standards) powder diffraction file. The morphology, size and composition of the titanate particles were determined using a Jeol 820 scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDX) attachment.

The initial precipitates were amorphous as gauged by XRD (Fig. 1a). Following calcination in air at progressively higher temperature, for 12 h, (Fig. 1b–f), XRD revealed weak reflections from the hexatitanate ($K_2Ti_6O_{13}$) present as a small fraction of a predominantly amorphous matrix. Distinct reflections which could be assigned to the tetratitanate ($K_2Ti_4O_9$) were present following firing at 800 °C. The hexatitanate still persisted, although it must be stressed that the amorphous phase was clearly dominant throughout. Bamberger and coworkers, have reported the co-existence of hexatitanate and tetratitanate in materials solidified from molten TiO_2 and K_2CO_3 [11], although this is in contrast to the recent work of Bao *et al.* who reported a phase transformation from the tetratitanate to hexatitanate on heating sintered materials formed from mixtures of K_2CO_3 and TiO_2 to progressively higher temperatures [12]. We tentatively suggest here, that in our route the hexatitanate is a kinetic product. In addition, a progressive reduction in the crystallinity of the system was observed following firing at higher temperature. This is in accord with earlier work where it was reported that the crystalline component is thermally stable up to ca. 1000 °C [8]. We also observed that for samples fired in a reducing atmosphere, the layered KTi_8O_{16} phase formed, again present as a portion of a predominantly amorphous material. The powder XRD pattern from a sample produced following firing at 1150 °C in 5% H_2 in N_2 is shown in Fig. 2. This material is of interest as a potassium ion host in disposal of high-level liquid waste from nuclear fuel reprocessing [13]. The optimum conditions required to produce this phase in high yield, by sol-gel chemistry, have yet to be ascertained.

It is interesting to note that a precipitate formed by hydrolysis of titanium isopropoxide alone, fired, for 12 h at 1000 °C in air, yields highly crystalline titania

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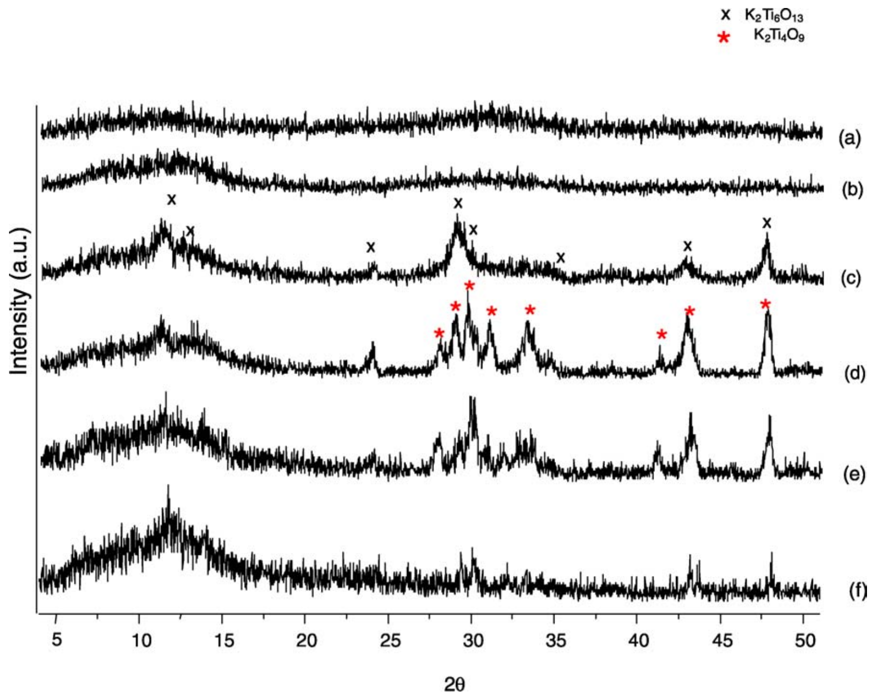

Figure 1 X-ray powder diffraction patterns of materials obtained following calcination of precipitates formed by the hydrolysis of titanium isopropoxide by an aqueous potassium hydroxide solution, in a K:Ti molar ratio of 1:2. (a) Unheated precipitate, and heated for 12 h at (b) 200 °C, (c) 500 °C, (d) 800 °C, (e) 1000 °C, and (f) 1150 °C.

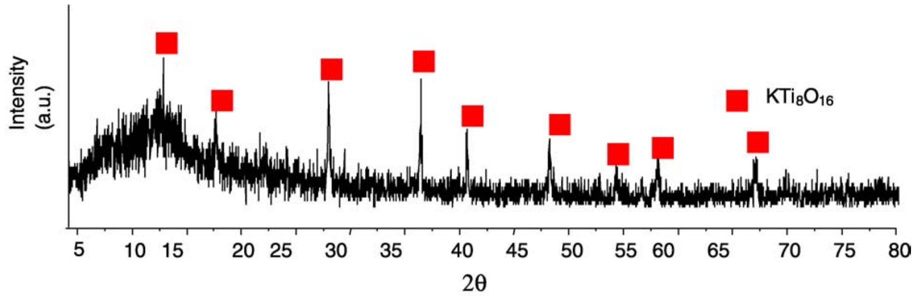

Figure 2 Powder XRD patterns of the product prepared by hydrolysis precipitation of titanium isopropoxide and potassium hydroxide (K:Ti molar ratio = 1:2) followed by calcination of the precipitate in 5% H_2 in N_2 at 1150 °C.

[14]. In contrast, in the presence of potassium ions, an amorphous product is formed at this temperature. Hence, the degree to which potassium ions are incorporated into the initial sol state and resulting dried precipitate, and the extent of atomic level mixing of reactants, is crucial to the formation of potassium titanates in high yield. Furthermore, the K/Ti ratio has been shown to influence the surface area of gel-derived potassium titanate, and the relative proportion of tetratitanate to hexatitanate [7]. To qualitatively gauge the effectiveness of potassium incorporation in our gels from a practical standpoint, precipitates were washed with 0.1 M HCl, dried and calcined in air at 800 °C. Powder XRD (Fig. 3) revealed the crystallization of anatase, in addition to hexatitanate, indicating some leaching of K^+ from the precipitate had occurred.

Hydrothermal processing, as an alternative to calcination, affords the possibility of crystallization under milder conditions [15]. This was manifest here as products of greater crystallinity and lower amorphous content were formed following hydrothermal treatment of the amorphous precipitates produced by alkoxide hydrolysis. This was evidenced by sharper reflections, and higher signal-to-noise ratio of their diffraction patterns in comparison with the calcined samples. Fig. 4 shows powder XRD patterns for precipitates treated under hydrothermal conditions for progressively increasing duration. The hexatitanate clearly crystallized at a significantly lower temperature than by calcination in air, and there was some evidence for tetratitanate formation following heat treatment for 48 h. A representative SEM image is shown in Fig. 5, which reveals the formation of a fibrous microstructure, with needles between 1–5 μm in length, accompanied by material of indeterminate morphology. EDX analysis revealed a stoichiometry in accord with expectation for potassium hexatitanate, with no evidence for inhomogeneity in the distribution of potassium or titanium. For samples that had been calcined in air, it was found that temperatures in excess of 800 °C were required to create a comparable microstructure. Following an extended heat treatment (500 h) there was a dramatic reduction in the concentration of the crystalline phase following firing for this extended period. To the best of our knowledge,

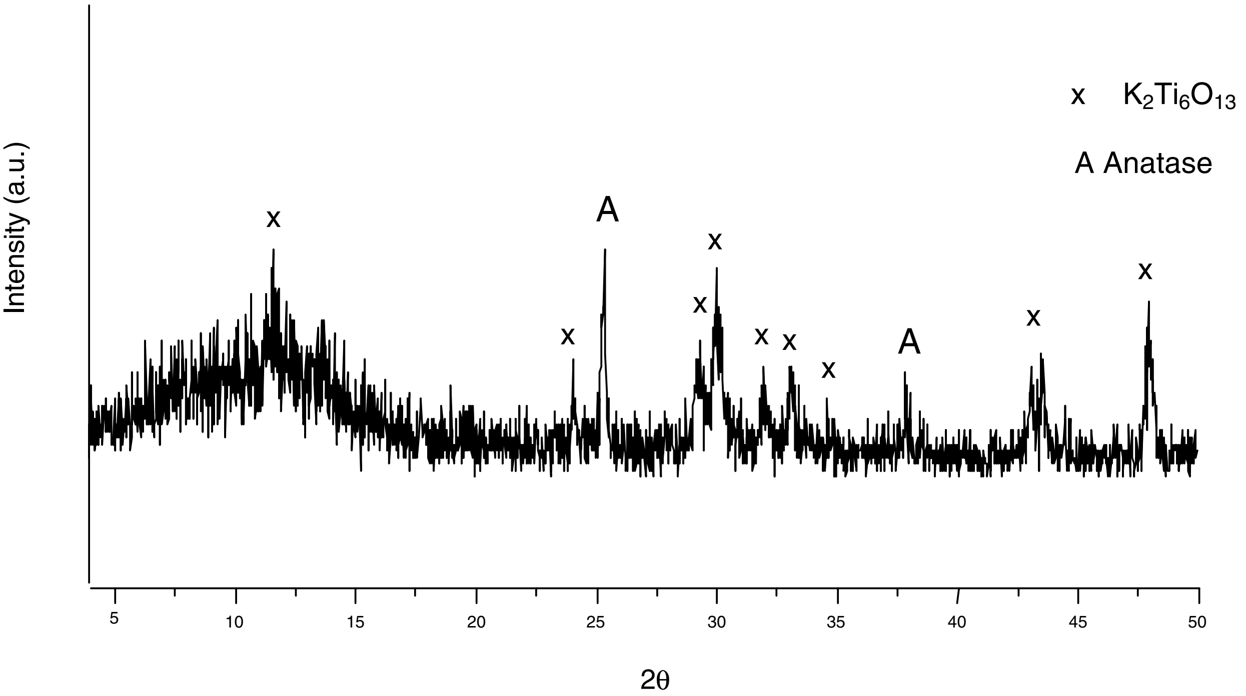

Figure 3 Powder XRD patterns of the product prepared by hydrolysis precipitation of titanium isopropoxide and potassium hydroxide (K:Ti molar ratio = 1:2) followed by acid treatment of the precipitate followed by heating at 800 °C for 12 h.

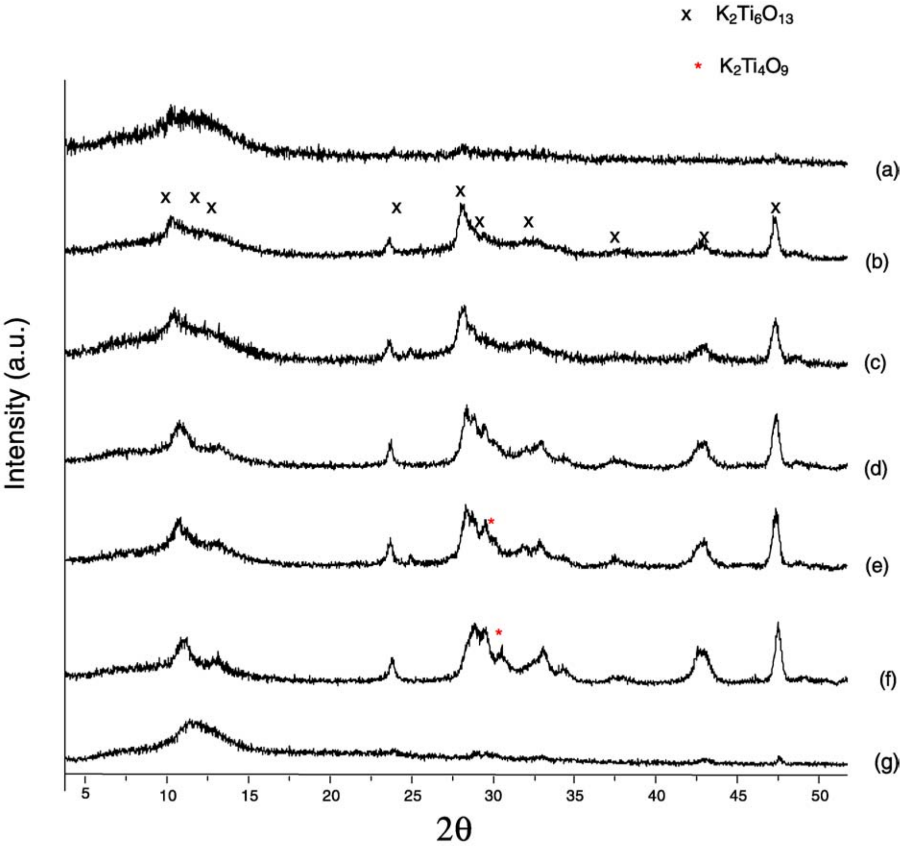

Figure 4 Powder XRD patterns of the product prepared by hydrolysis precipitation of titanium isopropoxide and potassium hydroxide (K:Ti molar ratio = 1:2) followed by hydrothermal processing of the precipitate for: (a) 2 h, (b) 4 h, (c) 10 h, (d) 24 h, (e) 48 h, (f) 72 h, and (g) 500 h.

kinetic instability of this nature at elevated pressure has not previously been reported although Endo *et al.* have demonstrated that leaching by water can convert layered titanates to amorphous structures [16], and Masaki has identified two amorphous phases (fibrous and non-fibrous) within the Ti-KOH-H_2O system following hydrothermal treatment [8].

In summary, crystalline potassium titanates, $K_2Ti_6O_{13}$ and $K_2Ti_4O_9$ within a predominantly amorphous matrix, have been prepared by hydrolysis

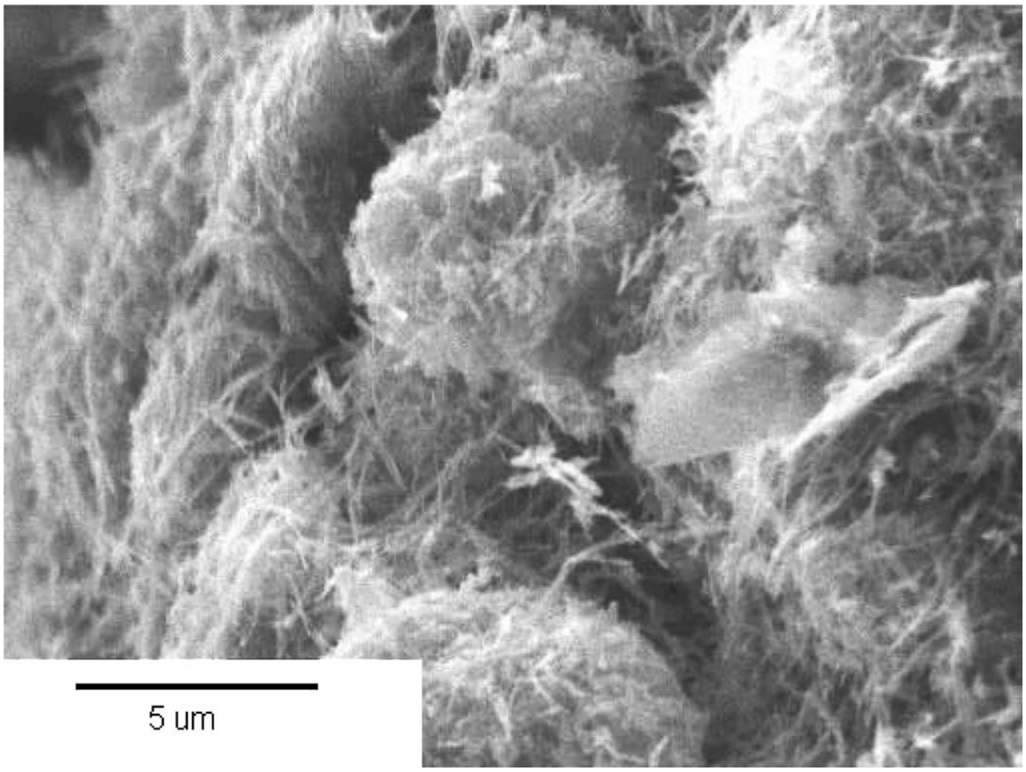

Figure 5 SEM image of the product prepared by hydrolysis precipitation of titanium isopropoxide and potassium hydroxide (K:Ti molar ratio = 1:2) followed by hydrothermal processing for 24 h.

of titanium isopropoxide by an aqueous solution of potassium hydroxide, followed by calcination in air of the resulting precipitates. We also report the novel observation of KTi_8O_{16} on heating the precipitates in a reducing atmosphere. More extensive crystallization was evident following treatment of the precipitates under hydrothermal conditions, although crystallinity was destroyed following processing over an extended period.

Acknowledgments

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