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Preparation and characterization of potassium tetratitanate whiskers

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Potassium tetratitanate ($K_2Ti_4O_9$) whiskers with an average diameter and aspect ratio of 1-3 μm and 20-30 respectively were synthesized by calcinating mixtures of industrial grade potassium carbonate (K_2CO_3), anatase TiO_2 and potassium fluoride (KF). The effects of the titanium compounds, molar ratio of K_2O/TiO_2 and content of KF on the morphology of the whiskers were investigated. The results indicated that the addition of KF improved the growth of potassium tetratinate crystals.

Key words: Potassium tetratitanate, Whiskers, Solid state reaction, KF.

Introduction

Potassium tetratitanate is composed of a layer structure with TiO_6 octahedra units sharing edges at one level that combine with linear groups above and below, to form zigzag ribbons [1]. The narrow-wide regions repeats every *b*, and potassium ions are situated in the wider region [2]. The interlayer distance of 0.85 nm can accommodate almost all of the heavy metal ions. Potassium tetratitanate whiskers are one of the useful ion exchangers for purification of heavy metal ions from industrial waste water [3] and for nuclear waste material treatment [4]. The hydrous crystal represented as (H^+, H_3O^+)Ti_4O_9 is also reported to be useful as an ion exchanger [5, 6].

Potassium titanate whiskers have been synthesized by a solid state reaction, flux growth [7], slow-cooling calcination [8], and a hydrothermal reaction [9, 10]. Bao *et al.* [11] prepared a series of potassium titanates from $TiO_2{\cdot}nH_2O$ hydrates and K_2CO_3 by a solid state reaction. Yokoyama *et al.* [12] obtained fibrous crystals of $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ from the vapor phase by the reaction of K_2TiF_6 or a KF-TiO_2 mixture. Li *et al.* [13] used KF and TiO_2 mixtures as starting materials to synthesize high quality $K_2Ti_6O_{13}$ whiskers.

This paper describes a method synthesizing high quality whiskers by calcinating mixtures of K_2CO_3, TiO_2 and KF. Here KF was used as an accelerant to improve the growth of potassium tetratitanate crystals.

Experimental

Industrial grade K_2CO_3 (Anyang, Henan, China) and TiO_2 (anatase TiO_2 or rutile TiO_2 or H_2TiO_3, Yuxing Chem. Co., Jinan, China) were used as starting materials, which were dried at 40 °C for 24 h. The dried starting materials with K_2O/TiO_2 molar ratios of 1 : 3, 1 : 3.5, 1 : 4 and KF whose content based on the starting material mixtures was 5 wt.%, 6 wt.% and 7 wt.% were mixed homogeneously, respectively. Then the mixtures were put into an alumina crucible and heated at 8 °C min^{-1} to 1000 °C for 6 h. The samples were crushed and ground subsequently.

TG-DTA was performed with an analyzer (FRC/T-1, Beijing optical instrument Co. Ltd). Samples were heated from 20 °C to 1000 °C at a rate of 10 °C min^{-1} in air. The morphology of the samples were characterized by an optical microscope (XSP-18B, Maidisen instrument Co. Ltd, Nanjing). The crystallization of the samples was identified by X-ray diffraction technique (XRD, D/MAX-YA, Rigaku, Japan).

Results and Discussions

TG-DTA analysis

Fig. 1 shows the TG-DTA curves of the mixtures of starting materials with different contents of KF (Fig. 1(a) without KF, Fig. 1(b) with 6 wt.% KF). In Fig. 1(a), peaks around 90 °C and 135 °C on the DTA curve are explained by the evaporation of water and organic reaction residues. An endothermic peak around 840 °C corresponding to 10.8% weight loss may result from the thermal decomposition of K_2CO_3 and the formation of the $K_2Ti_2O_5$ phase, and a small endothermic peak around 930 °C corresponding to no weight loss seems to be due to the transformation of $K_2Ti_2O_5$ into $K_2Ti_4O_9$ [14]. In Fig. 1(b), peaks around 60 °C and 105 °C are explained by evaporation phenomena. An endothermic peak around 660 °C corresponds to the peak around 840 on the DTA curve of Fig. 1(a). Comparing to Fig. 1(a) and Fig. 1(b), it can be found that the addition of KF into the mixture of K_2CO_3 and TiO_2 reduced the decomposition temperature of K_2CO_3 and improved the phase formation of potassium titanates.

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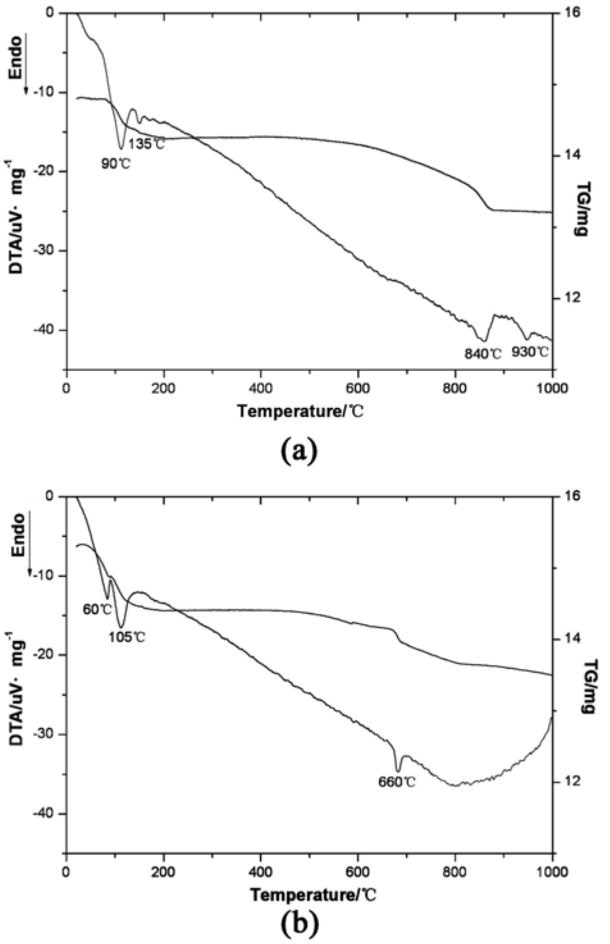

Fig. 1. TG-DTA curves of samples: (a) without KF; (b) 6 wt.% KF.

Effects of titanium compounds on whiskers morphology

Fig. 2 shows optical microscope images of the calcined samples with different titanium compounds at 1000 °C. As shown in Fig. 2(a), the sample with rutile TiO_2 contains some particles and short whiskers with a length of about 1-10 μm, while for the samples with anatase TiO_2 and H_2TiO_3 as titanium compounds, the whiskers grew better with the same experiment conditions (Fig. 2(b) and Fig. 2(c)). However, H_2TiO_3 is a paste intermediate product and it is difficult to mix with the other raw materials. From the viewpoint of production, anatase TiO_2 is a better titanium compound for preparing.

Effects of molar ratio K_2O/TiO_2 on crystallization and morphology

Fig. 3 shows the XRD patterns of the samples with different K_2O/TiO_2 molar ratios. For the samples with K_2O/TiO_2 molar ratios of 1 : 3 and 1 : 3.5, the dominant phase is $K_2Ti_4O_9$ (JCPDS 32-0861). But the intensity of diffraction peaks of the sample with a K_2O/TiO_2 molar ratio 1 : 3.5 (Fig. 3(b)) is higher than that of the sample with a K_2O/TiO_2 molar ratio 1 : 3 (Fig. 3(a)). For the sample with a K_2O/TiO_2 molar ratio 1 : 4, the

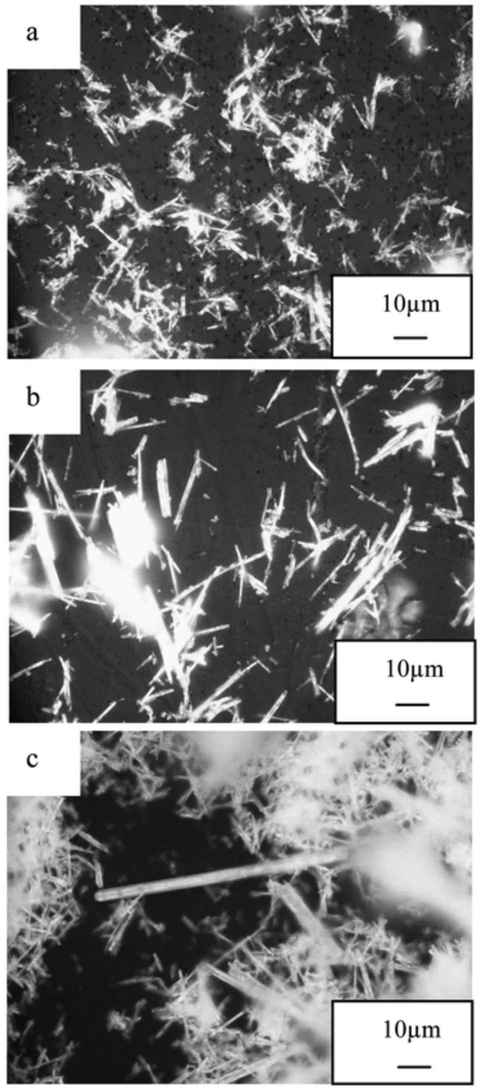

Fig. 2. Optical microscope images of calcined samples with different titanium compounds (a) rutile TiO_2, (b) anatase TiO_2, (c) H_2TiO_3.

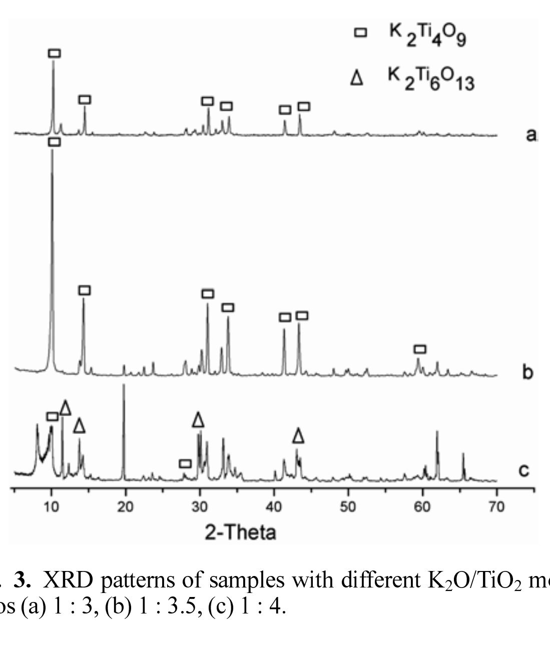

Fig. 3. XRD patterns of samples with different K_2O/TiO_2 molar ratios (a) 1 : 3, (b) 1 : 3.5, (c) 1 : 4.

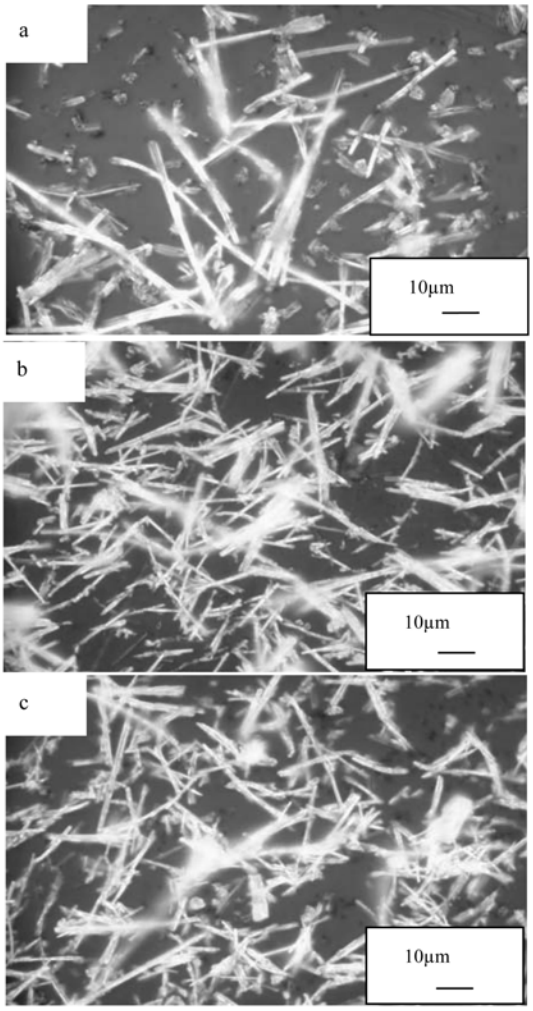

Fig. 4. Optical microscope images of samples with different K_2O/TiO_2 molar ratios (a) 1 : 3, (b) 1 : 3.5, (c) 1 : 4.

XRD pattern reveals the coexistence of $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ (JCPDS 40-0403). This result indicates that a sample with perfect crystallization of $K_2Ti_4O_9$ can be obtained if the K_2O/TiO_2 molar ratio is 1 : 3.5.

The optical microscope images in Fig. 4 reveal the morphology of samples with different K_2O/TiO_2 molar ratios. For the sample with a K_2O/TiO_2 molar ratio 1 : 3 (Fig. 4(a)), some rod-like particles and whiskers 10-50 μm in length and 2-4 μm in diameter were observed. From Fig. 4(b) and Fig. 4(c), we can see that the samples with K_2O/TiO_2 molar ratios 1 : 3.5 and 1 : 4 were mainly composed of whiskers 10-30 μm in length and 1-3 μm in diameter. But for the latter sample, a few grains could be observed. This result indicates that a higher or lower K_2O/TiO_2 molar ratio is not helpful in obtaining perfect whiskers.

Effects of content of KF on whiskers morphology

Fig. 5 shows optical microscope images of samples as the KF content ranges from 5 wt.% to 7 wt.%. From the images, we can see that the dimension of the whiskers increased obviously with an increase of the KF content with the same firing conditions. This result indicates that the addition of KF improved the growth of $K_2Ti_4O_9$ whiskers. However, the addition of more KF would reduce the calcining temperature and make whiskers conglomerate seriously. Under our experimental conditions, the addition of 6 wt.% KF is preferable.

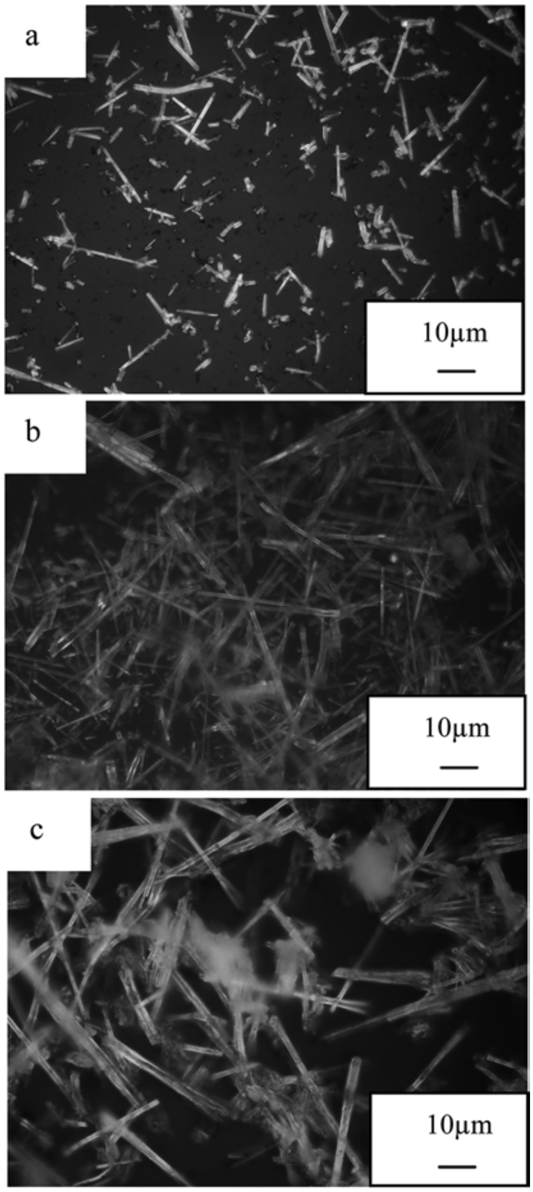

Fig. 5. Optical microscope images of samples with different contents of KF (a) 5 wt.%, (b) 6 wt.%, (c) 7 wt.%.

Conclusions

In this paper, $K_2Ti_4O_9$ whiskers were prepared using industrial grade K_2CO_3, anatase TiO_2 and KF as raw materials at 1000 °C by a solid state reaction. The addition of KF into the mixture of TiO_2 and K_2CO_3 improved the growth of $K_2Ti_4O_9$ crystals. Using anatase TiO_2 as the titanium compound, a K_2O/TiO_2 molar ratio 1 : 3.5 and the addition of 6 wt.% KF gave perfect $K_2Ti_4O_9$ whiskers.

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