

# Effects of different potassium salts on the formation of mullite as the only crystal phase in kaolinite

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## Abstract

The phase transition in kaolinite from 1050 °C to 1600 °C without and with different potassium salts (KF, KNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>) as mineralizers and the changes of the composition and morphologies of mullite formed in kaolinite have been investigated. The adding of enough potassium has been found to inhibit the formation of cristobalite in kaolinite. The fluorine is found to be beneficial to increase the reaction activity of aluminium from metakaolinite and so the potassium fluoride has promoted more pseudotetragonal mullite formed at 1100 °C than the other two mineralizers. The influence of potassium salts on the composition and microstructure of mullite formed from kaolinite with increasing the heating temperature has been scrutinized in detail. The formation condition for the only crystal phase of mullite from kaolinite has been shown.  
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## 1. Introduction

Mullite is a kind of favorable material for steel, glass, and petrochemical industries, with its high chemical stability, good thermal shock resistance, superior refractory properties, and its strength retained up to 1300 °C. Mullite is also a main and important component in porcelain, refractory, and porous ceramics,<sup>1–3</sup> while kaolinite is a raw material widely used to prepare porcelain, refractory and porous ceramics.

The forming sequence and the composition of mullite on heating kaolinite without adding mineralizers have been analyzed by many investigators.<sup>4–7</sup> Pask<sup>8</sup> compared the formation of mullite from kaolinite and sol–gel mixtures, and claimed that with an infinitely slow heating rate to heat kaolinite, spinel was the first and the only phase formed from metakaolinite, which then transformed to orthorhombic mullite by reacting with silica. While with an infinitely fast heating rate, pseudotetragonal mullite was the first and the only phase, which converted to orthorhombic mullite at higher temperature. However, with a normal heating rate, the formation of spinel and pseudotetragonal mullite inter-

acted and occurred concurrently. According to Chakravorty,<sup>9</sup> kaolinite formed mullite in two ways: (i) by polymorphic transformation of cubic mullite at 1150 °C to 1250 °C and (ii) by nucleation of mullite in amorphous aluminosilicate phase and subsequent growth above 1250 °C. In addition, the composition of mullite formed from different starting materials is different and Al<sub>2</sub>O<sub>3</sub> mole content of mullite is also various with increasing the heating temperature. Okada<sup>10</sup> has analyzed the data for the changes of Al<sub>2</sub>O<sub>3</sub> mole content of mullite formed in kaolinite, other clays, and various sol–gel mixtures at 950–1500 °C, and has found that Al<sub>2</sub>O<sub>3</sub> mole content of primary mullite (pseudotetragonal mullite) is higher than that of secondary mullite (orthorhombic mullite).

The phase transition sequence and the phase composition during heating kaolinite are intensively affected in the presence of mineralizers. Generally speaking, K<sub>2</sub>O, CaO, MgO, etc. are common crystallographic impurities in kaolinite and are often added to kaolinite as mineralizers, among which K<sub>2</sub>O has an especial effect in the phase transition of kaolinite. The addition of MgO to kaolinite caused mullite formation via spinel or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase and that of CaO caused mullite formation directly from metakaolinite.<sup>11</sup> The influence of K<sub>2</sub>O, added to kaolinite as nitrate, on high temperature reactions of kaolinite was investigated by Johnson, and it was found that K<sub>2</sub>O accelerated the

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Table 1  
Chemical composition of kaolinite powder.

	Constituent								LOI (1000 °C)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	
Amount (wt%)	46.60	35.79	1.20	1.01	0.17	0.07	0.10	0.06	15

formation of mullite and cristobalite.<sup>12</sup> According to Yamuna,<sup>13</sup> however, only mullite was crystallized during heating kaolinite when K<sub>2</sub>CO<sub>3</sub> acts as a mineralizer, and the crystallization of cristobalite was completely inhibited.

In the present work, mullite formation in kaolinite without and with certain potassium salts, namely, KF, KNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> as mineralizers, has been studied at 1050–1600 °C. There has been little report on comparing the influence of the contents of K<sub>2</sub>O and different acid groups in the potassium salts on the phase transition of kaolinite and forming mullite as the only crystal phase in kaolinite. The influence of the potassium salts on the composition and the microstructure of mullite formed from kaolinite with increasing the heating temperature has been discussed.

## 2. Experimental procedure

A kaolinite powder (Tianjin Guangfu (Group) Co., Ltd., China) was used as the raw material with the chemical composition listed in Table 1. Seven different powder samples were prepared, three of which were added 3 wt% KF, KNO<sub>3</sub> or K<sub>2</sub>SO<sub>4</sub> as mineralizers, named as KF (kaolinite with 3 wt% KF), KN (kaolinite with 3 wt% KNO<sub>3</sub>), and KS (kaolinite with 3 wt% K<sub>2</sub>SO<sub>4</sub>). In addition, the other four samples are named as K (kaolinite without potassium salts), KN4 (containing 3.46 wt% KNO<sub>3</sub>), KN5 (containing 5.11 wt% KNO<sub>3</sub>), and KFA (containing 2.39 wt% AlF<sub>3</sub>·3H<sub>2</sub>O). KN4 contains the same content of K<sub>2</sub>O (1.99 wt% K<sub>2</sub>O) to KS, KN5 contains the same content of K<sub>2</sub>O (2.95 wt% K<sub>2</sub>O) to KF, and KFA contains the same content of fluorine (0.98 wt% fluorine) to KF. The kaolinite powders without and with potassium salts were mixed in a ball milling with alcohol for 72 h, followed by drying at 80 °C for 12 h. The powders were heated at 1050–1600 °C with a heating rate of 5 °C/min and a duration time of 1 h.

The phases of heated powders were identified using an X-ray diffractometer (XRD, D/max-2550, Japan), operated at 200 kV, 45 mA, with experimental condition as follows: a step width 0.02° and a scanning range of 10–80°. The diffraction peaks of mullite in (2 2 0) and (1 1 1) were measured by a step scan with a scanning speed of 0.3°/min and a count time of 4 s.

The morphologies and chemical composition of heated powders were characterized by Scanning Electron Microscope (SEM, LEO-1530, Germany). High temperature differential scanning calorimetry (DSC, NETZSCH STA 409 PC/PG, Germany) investigation was used to characterize the thermal behavior of different samples with and without potassium salts. Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, American), with resolution of 4 cm<sup>-1</sup>, was used to characterize the phase transition of kaolinite at different temperatures.

## 3. Results and discussion

### 3.1. Phase transition without and with different potassium salts

Fig. 1 shows the DSC curves of samples K, KF, KN, KS in the temperature range of room temperature to 1300 °C. There is an endothermic peak at 400–600 °C and an exothermic peak at 990 °C in each curve. The endothermic peak of the sample KN lies at 520 °C, while that of the other samples are approximately at 500 °C. The difference of the endothermic peak temperature is caused by that KNO<sub>3</sub> decomposes into K<sub>2</sub>O and nitrogen oxides which are escaped in gaseous form. Then only K<sub>2</sub>O actually acts as the mineralizer in the sample KN. The appearance of the exothermic peak is attributed to the formation of Al–Si spinel and weakly crystallized pseudotetragonal mullite, which include more Al ions with stable sixfold coordination than metakaolinite. At the process, amorphous silica and amorphous aluminosilicate were also simultaneously formed.<sup>13–15</sup> The exothermic peak of the samples are all at 990 °C, which indicates that potassium salts have no obvious effect on the exothermic reaction, representing the formation of Al–Si spinel and weakly crystallized pseudotetragonal mullite is not related to the presence of potassium salts.

Table 2 shows the phase composition of heated samples with different potassium salts at different heating temperatures, identified by XRD. The amount of liquid phase formed due to the presence of K<sub>2</sub>O from the additional potassium salts is evaluated using the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–K<sub>2</sub>O phase equilibrium diagram<sup>16</sup> as a guide. It can be seen that the liquid phase appears at 1050 °C. Furthermore, the amount of liquid phase increases with increasing the heating temperature (1050–1600 °C) and the amount of

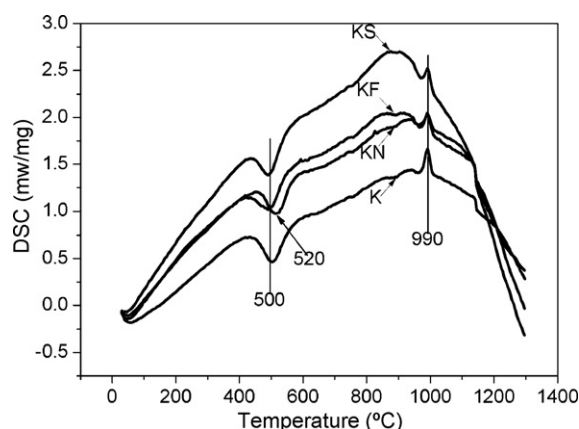


Fig. 1. The DSC curves of samples K, KN, KF and KS from room temperature to 1300 °C.

Table 2  
Batch formulations and phases identified for heated products.

Sample code	KN	KS	KF
K	97% kaolinite + 3% KNO <sub>3</sub> (ρ = 1.72% K <sub>2</sub> O) <sup>a</sup>	97% kaolinite + 3% K <sub>2</sub> SO <sub>4</sub> (ρ = 1.99% K <sub>2</sub> O) <sup>a</sup>	97% kaolinite + 3% KF (ρ = 2.95% K <sub>2</sub> O) <sup>a</sup>
1050 °C	(S* M A L <sup>†</sup> ) L	(S* M A L <sup>†</sup> ) L	(S* M A L <sup>†</sup> ) L
1100 °C	(S* M* A L <sup>†</sup> ) L	(S* M* A L <sup>†</sup> ) L	(S* M* A L <sup>†</sup> ) L
1150 °C	(M* S* A L <sup>†</sup> ) L	(M* A L <sup>†</sup> ) L	(M* A L <sup>†</sup> ) L
1250 °C	(M* C L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L
1350 °C	(M* C L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L
1450 °C	(M* C L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L
1600 °C	(M* L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L	(M* L <sup>†</sup> ) L
Phases formed at various heating temperatures	81.8% 18.2% 79.8% 20.2% 78.3% 21.7% 73.7% 26.3% 64.3% 35.7% 56.5% 43.5% 53.1% 46.9%	77.6% 22.4% 75.4% 24.6% 73.5% 26.5% 67.6% 32.4% 56.3% 43.7% 55.4% 44.6% 52.6% 47.4%	67.5% 32.5% 65.0% 35.0% 61.8% 38.2% 54.8% 45.2% 53.9% 46.1% 52.6% 47.4% 49.1% 50.9%

“\*”: Major crystalline phase; M: mullite; S: Al–Si spinel; C: cristobalite; A: anatase; L: the liquid phase due to the presence of K<sub>2</sub>O from the additional potassium salts; L<sup>†</sup>: the liquid phase due to the presence of fluorine and/or the impurities from kaolinite; ρ: the weight percentage of K<sub>2</sub>O from the additional potassium salts in the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–K<sub>2</sub>O system.  
<sup>a</sup> Batch formulations.

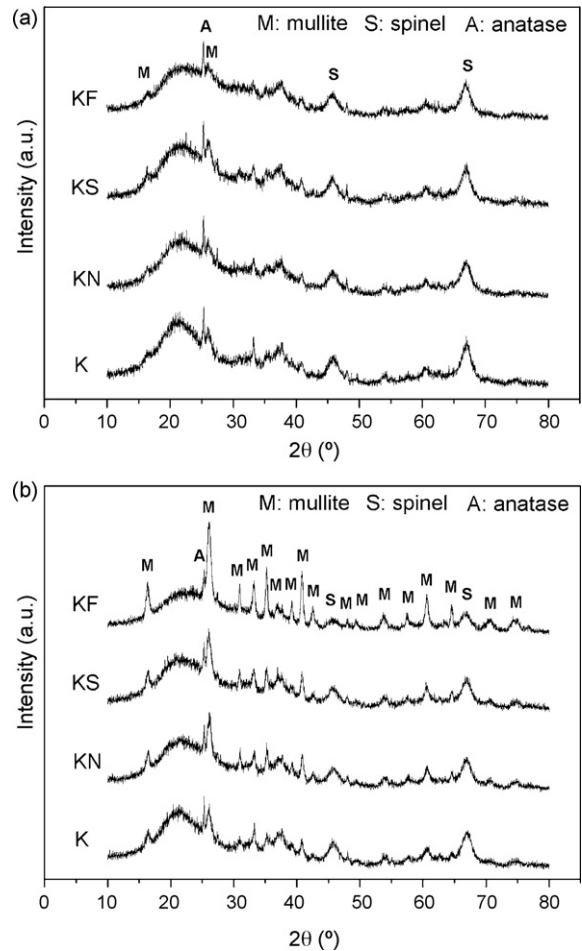


Fig. 2. The XRD patterns of samples K, KN, KS and KF heated (a) at 1050 °C and (b) at 1100 °C.

K<sub>2</sub>O (0–2.95%). Besides the above liquid phase, there are a little other liquid phase formed due to the existence of the crystallographic impurities in kaolinite. The formation of liquid phases is beneficial to the nucleation and growth of mullite.

For the samples heated at 1050 °C (Fig. 2(a)), the diffraction peaks of Al–Si spinel are the major crystal peaks. Small diffraction peaks of mullite began to appear, such as that at 2θ = 16.432° (according to JCPDS 15-0776). In addition, there is a small sharp peak for anatase TiO<sub>2</sub> as impurity.<sup>12</sup> Chen et al.<sup>17</sup> found the similar phenomena with the kaolinite heated at 1050 °C for 24 h. The large diffusion ring at 2θ between 20° and 24° is corresponding to the presence of amorphous aluminosilicate and amorphous silica, which generally formed at the exothermic peak temperature in the DSC curves.<sup>18</sup>

After the samples were heated at 1100 °C, the diffraction peaks of mullite become distinct, whereas the intensities of the spinel diffraction peaks and the diffusion ring decrease. In addition, the sample KF has sharper diffraction peaks of mullite than the others’ (Fig. 2(b)), which is attributed to that both K<sub>2</sub>O and fluorine act as mineralizers.

Fig. 3 shows that the sample KFA, which contains the same content of fluorine to KF, has stronger diffraction peaks of spinel and more noticeable diffusion ring at 2θ between 20° and 24°

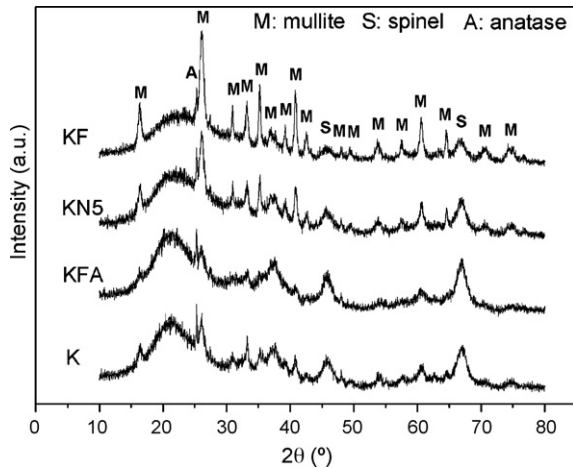


Fig. 3. The XRD patterns of samples K, KFA, KN5 and KF heated at 1100 °C.

than the samples K and KF, whereas the diffraction peak intensities of mullite in the sample KN5, containing the same content of  $K_2O$  to KF, lie between that of mullite in the samples K and KF. According to the above results, it is concluded that the fluorine is able to promote the formation of spinel, whereas the  $K_2O$  is able to promote the formation of mullite. In addition, more mullite is formed when  $K_2O$  and fluorine simultaneously exist in the sample. The reason that fluorine is effectively able to promote the formation of spinel is inferred that F atoms can increase the reaction activity of Al by breaking the Al–O–Si structure in the metakaolinite and can also increase the amount of liquid phases.<sup>19–21</sup> On the other hand, the reason that the  $K_2O$  promotes the formation of mullite is believed that the K atoms are coordinated by non-bridging O (NBO) atoms in liquid phases,<sup>22</sup> which is beneficial to keep the liquid phases in amorphous state and increase the reaction activity of Si–O structure. Therefore, there is more mullite formed at 1100 °C when the potassium fluoride is used as a mineralizer in the sample KF.

FTIR spectra of the samples K and KF heated at 1100 °C is shown in Fig. 4. The absorption bands at 1160  $cm^{-1}$ , 895  $cm^{-1}$ ,

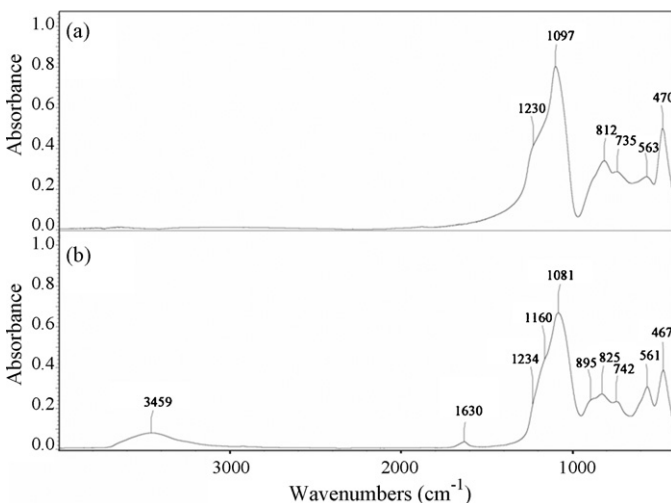


Fig. 4. FTIR spectra of the sample K (a) and the sample KF (b) heated at 1100 °C.

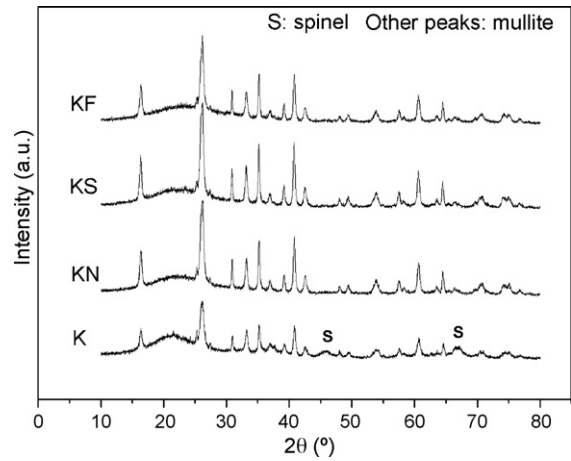


Fig. 5. The XRD patterns of samples K, KN, KS and KF heated at 1150 °C.

742  $cm^{-1}$ , 736  $cm^{-1}$ , 563  $cm^{-1}$  and 561  $cm^{-1}$  are assigned to mullite, that at 1234  $cm^{-1}$  and 1230  $cm^{-1}$  assigned to amorphous silica, that at 3459  $cm^{-1}$  and 1630  $cm^{-1}$  assigned to absorbed water from the environment,<sup>23–25</sup> and that at 1081  $cm^{-1}$  and 1097  $cm^{-1}$  assigned to the hybrid vibrations of  $[SiO_4]$  and  $[AlO_4]$ .<sup>26</sup> The obvious increase of the absorption band at 561  $cm^{-1}$  and the appearance of the absorption bands at 895  $cm^{-1}$  and 1160  $cm^{-1}$ , compared with the sample K heated at 1100 °C, indicate the formation of massive mullite in the sample KF, which is in agreement with the XRD results. In addition, the absorption band at 1234  $cm^{-1}$  becomes smaller in the sample KF than in the sample K, which is due to the reaction between spinel and amorphous silica to form mullite.

At 1150 °C, the diffusion ring at  $2\theta$  between 20° and 24° is more noticeable in the sample K than that in the other three samples. There is still a little Al–Si spinel in the sample K, but none in the other samples (Fig. 5), from which it is concluded that potassium salts have promoted the reaction of Al–Si spinel with liquid phases to form pseudotetragonal mullite.

At 1250 °C, cristobalite diffraction peaks clearly appear at  $2\theta = 21.604^\circ$ ,  $35.626^\circ$ ,  $44.005^\circ$ , and  $56.177^\circ$  (according to JCPDS 27-0605) in the sample K, while only a small diffraction peak of cristobalite,  $2\theta = 21.604^\circ$ , appears in the sample KN. However, there is no any cristobalite diffraction peak in the samples KS and KF (Fig. 6). All the samples except K contain mullite as the only crystal phase after 1350 °C, whereas the cristobalite peaks in the sample K continuously become strong from 1350 °C to 1450 °C and disappear at 1600 °C (Figures not shown. Data see Table 2).

The above results suggest that the differences in the disappeared temperature of the cristobalite are attributed to different contents of the various mineralizers in kaolinite. Potassium salts (KF,  $KNO_3$  and  $K_2SO_4$ ) have effectively inhibited the crystallization of cristobalite though different potassium salts have different effects. The same weight of KF or  $K_2SO_4$  as mineralizers has better effects than that of  $KNO_3$ . The differences of the appearance of cristobalite diffraction peaks between the sample KS and the sample KN are caused by that 3 wt%  $K_2SO_4$  contains more  $K_2O$  (1.99 wt%  $K_2O$ ) than 3 wt%  $KNO_3$  (1.72 wt%  $K_2O$ ). Fig. 7 shows the XRD patterns of the samples KN4 and KS, in



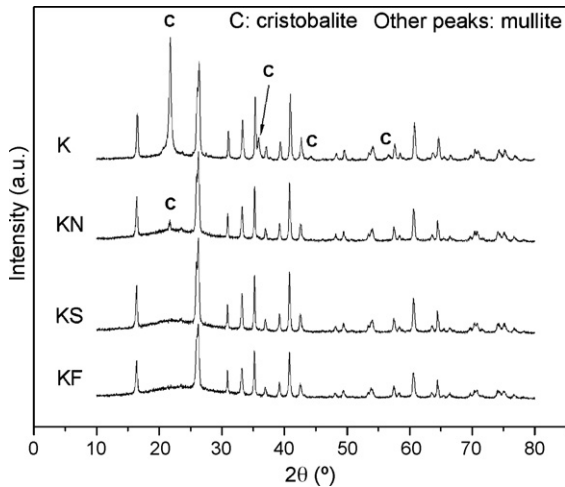


Fig. 6. The XRD patterns of samples K, KN, KS and KF heated at 1250 °C.

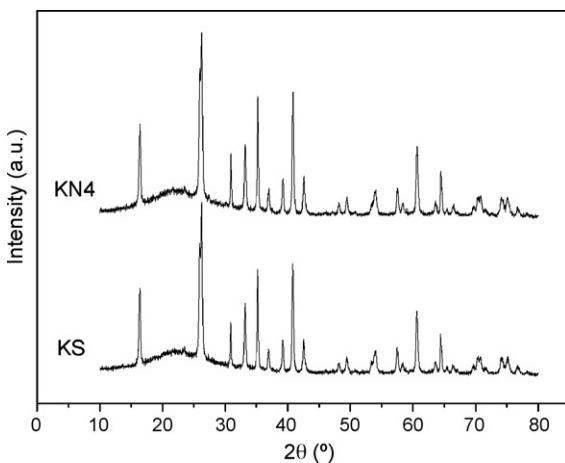


Fig. 7. The XRD patterns of samples KN4 and KS heated at 1250 °C.

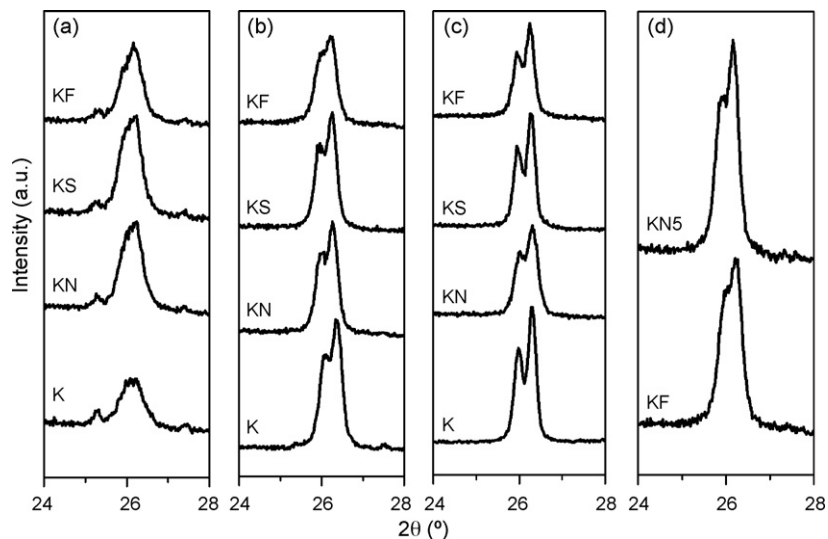


Fig. 8. The (1 2 0) and (2 1 0) diffraction peaks of mullite in samples K, KN, KS, KF and KN5 heated at (a) 1150 °C, (b) 1250 °C, (c) 1350 °C, and (d) 1250 °C.

which the sample KN4, containing the same content of  $K_2O$  to the sample KS, has the same diffraction peaks to the sample KS, which indicates that the formation of cristobalite is determined by the content of  $K_2O$ , whereas the sulfate has little effect on inhibiting the formation of cristobalite.

At 1250 °C, it is found in Fig. 8(a)–(c) that the (1 2 0) and (2 1 0) diffraction peaks of the mullite began to split ( $2\theta = 25.97^\circ$  and  $26.27^\circ$ ), which indicates that pseudotetragonal mullite (primary mullite) starts to transform into orthorhombic mullite (secondary mullite).<sup>27,28</sup> Pseudotetragonal mullite is alumina-rich phase, approximately containing  $\sim 70$  mol%  $Al_2O_3$ , and the length of its  $a$ -axis is close to its  $b$ -axis, while the  $a$ -axis of the orthorhombic mullite is smaller than its  $b$ -axis.<sup>29,30</sup> The splits of the (1 2 0) and (2 1 0) diffraction peaks of samples K, KN, KS, and KF at 1250 °C are given in Fig. 8(b), which shows that the split degree of the sample KF is the smallest, that is to say, the crystallinity of orthorhombic mullite in the sample KF is the lowest, though it contains the most  $K_2O$ . The sample KN5 contains the same content of  $K_2O$  to the sample KF, but the split degree of the sample KN5 shown in Fig. 8(d) is bigger than that of the sample KF at 1250 °C, which indicates that the fluorine has inhibited the crystallization of orthorhombic mullite. This is attributed to fluorine retarding the formation of Al–O–Si chains in orthorhombic mullite. At 1350 °C, the split degree of the (1 2 0) and (2 1 0) diffraction peaks is more noticeable in the samples KS and K than in the samples KF and KN. This is because the sample KS without the inhibition from fluorine like the sample KF contains more  $K_2O$  than the sample KN, and the sample K contains more Al in the liquid phases due to the formation of cristobalite than the samples KF and KN.

### 3.2. Changes of the composition and morphologies of mullite

The theoretical formula of mullite is  $3Al_2O_3 \cdot 2SiO_2$ , which contains 60 mol% alumina. The mullite formed from kaolinite at different heating temperatures, however, actually contains various contents of alumina. Ban<sup>27</sup> proposed a method by deter-

mining the integral intensities of the (2 2 0) and (1 1 1) diffraction peaks to calculate the alumina mole content of mullite, using the linear relationship:  $\text{Al}_2\text{O}_3 \text{ (mol\%)} = 41.77(I_{220}/I_{111}) + 27.6$ . Fig. 9 shows the variation of  $\text{Al}_2\text{O}_3$  mole content of mullite versus the heating temperatures in the samples K, KS, KN and KF. The  $\text{Al}_2\text{O}_3$  mole content of mullite formed in these samples firstly decreases from 1150 °C to 1350 °C and then increases until 1600 °C. The above changing trend of  $\text{Al}_2\text{O}_3$  mole content of mullite is similar to that formed in kaolinite at temperatures of 950–1500 °C, which Okada have assembled.<sup>10</sup> It is known from the above results that the composition changes of mullite formed and grown up in kaolinite are generally divided into two stages: (i) in the decreasing process of  $\text{Al}_2\text{O}_3$  mole content, it is dominant that the process of pseudotetragonal mullite continuously reacting with liquid phases; (ii) the increasing process is mainly corresponding to the process of orthorhombic mullite nucleating and subsequently growing in liquid phases at higher temperatures.

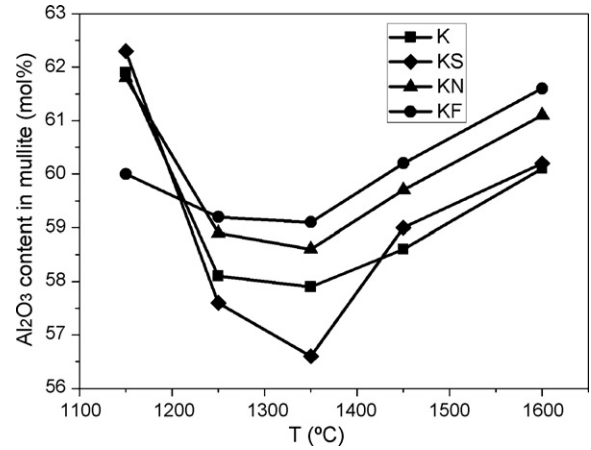


Fig. 9. The changes of the  $\text{Al}_2\text{O}_3$  mole content in mullite versus the heating temperatures in samples K, KN, KS and KF.

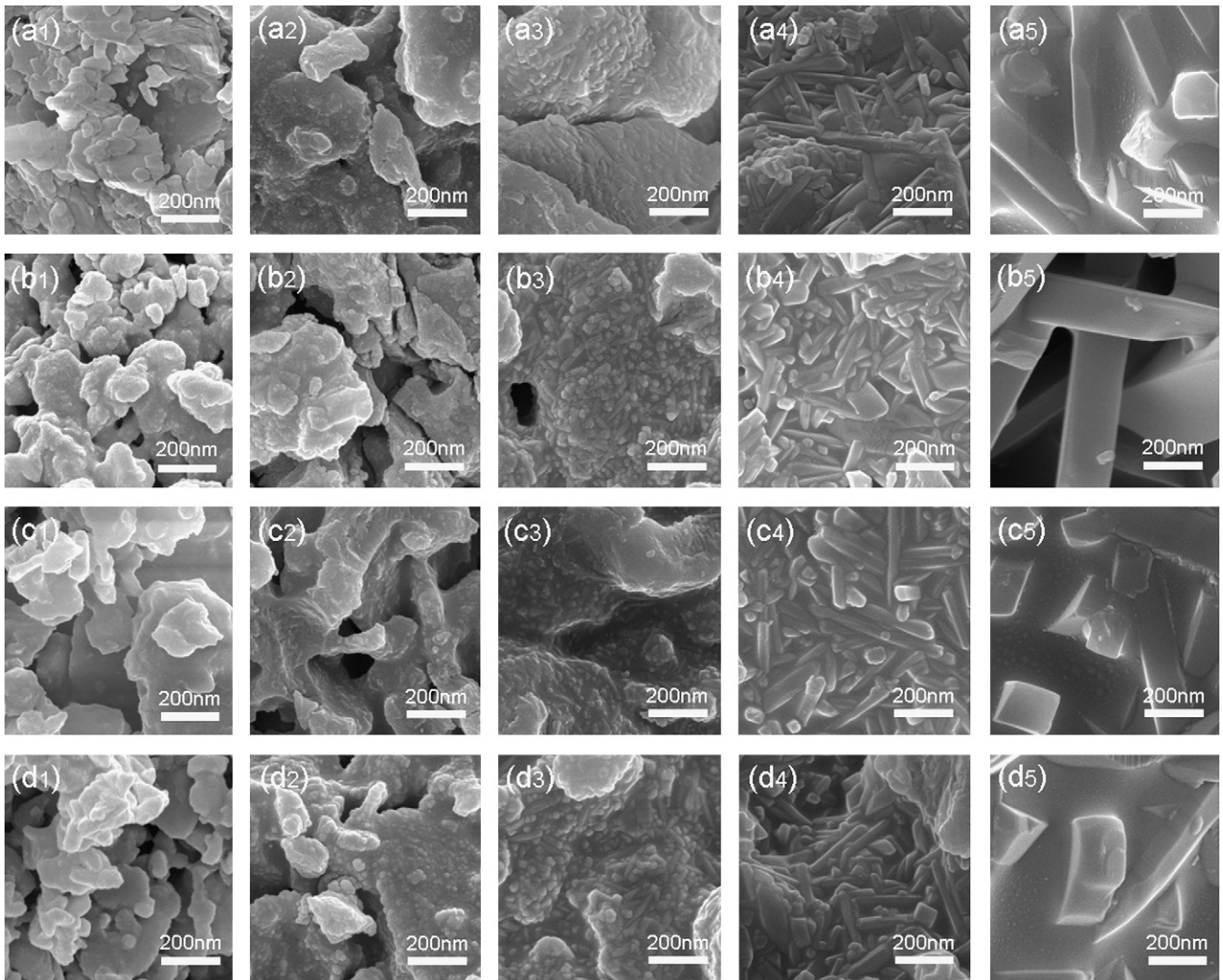


Fig. 10. The sample morphologies of (a) K, (b) KF, (c) KN, and (d) KS at different heating temperatures of (1) 1150 °C, (2) 1250 °C, (3) 1350 °C, (4) 1450 °C, and (5) 1600 °C.

The change ranges of  $\text{Al}_2\text{O}_3$  mole content in mullite are closely related to  $\text{K}_2\text{O}$  content and the properties of anion in potassium salts. The sample KS has a bigger change range than the sample KN because it contains more  $\text{K}_2\text{O}$  than the sample KN. The change range of the decreasing process is smaller in the sample KF than that in the other samples, which is due to fluorine retarding the formation of Al–O–Si chains in mullite.

Fig. 10 shows the morphologies of samples K, KF, KN and KS heated at 1150 °C, 1250 °C, 1350 °C, 1450 °C, and 1600 °C. It shows that the morphologies of samples at 1150 °C are mainly the morphologies of starting materials particles. However, the XRD results in Fig. 4 show that the pseudotetragonal mullite has been largely formed at 1150 °C, which suggest that the crystal grains of pseudotetragonal mullite are much smaller than 200 nm, the bar length in the figure. When increasing the heating temperature to 1450 °C, the smaller particles at 1150 °C have gradually coalesced into bigger particles. In addition, plenty of rod-like orthorhombic mullite and liquid phases are simultaneously formed, which support that the increase of  $\text{Al}_2\text{O}_3$  mole content of mullite is attributed to massive orthorhombic mullite growth in the liquid phases. At 1600 °C, the smaller rod-like orthorhombic mullite grains formed at 1450 °C coalesce into bigger grains by grain boundary reaction.

According to the morphologies of samples K, KF, KN and KS in Fig. 10, a complete morphology evolution of mullite formed in kaolinite for the heating temperatures from 1150 °C to 1600 °C is shown that the small starting material particles containing pseudotetragonal mullite gradually coalesce together and the orthorhombic mullite gradually grows up in liquid phases with increasing the heating temperature. The smaller rod-like crystal grains of orthorhombic mullite are able to be found at 1350 °C, largely grow up at 1450 °C and coalesce into bigger ones at 1600 °C.

#### 4. Conclusions

The same weight of different potassium salts, namely, KF,  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  has different effects on the formation of mullite from kaolinite, which is closely associated with the content of  $\text{K}_2\text{O}$  and the properties of anions in the potassium salts. The KF has been able to promote the massive formation of mullite at 1100 °C than  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$ , while the formation of orthorhombic mullite at 1250 °C and 1350 °C is retarded by the presence of fluorine. The  $\text{K}_2\text{O}$  has been identified as the major composition that inhibits the formation of cristobalite in kaolinite at 1250 °C, while the sulfate in the sample KS has little effect on that. The only crystal phase of mullite in kaolinite can be formed when the content of  $\text{K}_2\text{O}$  is more than 1.99 wt%.

The composition of mullite formed from kaolinite changes in two stages: alumina-rich pseudotetragonal mullite firstly reacts with the amorphous phases, which results in the decrease of  $\text{Al}_2\text{O}_3$  mole content of mullite, and then with increasing the heating temperature, the liquid phases gradually increase and the orthorhombic mullite forms and grows up, resulting in the increase of  $\text{Al}_2\text{O}_3$  mole content of mullite. The rod-like orthorhombic mullite begins to appear and gradually grow up with the liquid phases increasing until 1450 °C, and then the

smaller rod-like mullite grains coalesce into bigger ones by grain boundary reaction at 1600 °C.

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