



# Controllable preparation and synthetic mechanism of mullite from the bauxite with Fe-rich oxide content



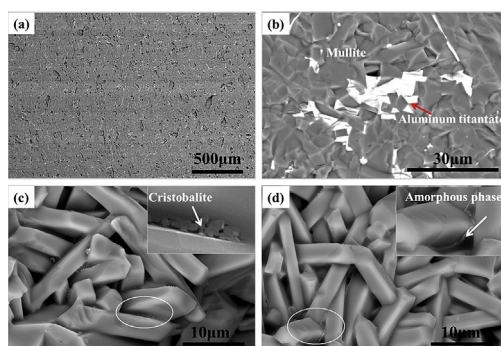
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## HIGHLIGHTS

- Mullite was successfully prepared using the bauxite with Fe-rich oxide content.
- Mullite content in the sintered bauxite reached up to 93 wt%.
- $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  ions entered into mullite and aluminum titanium.
- Synthetic mechanism for mullite was analyzed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To realize reuse of the bauxite with Fe-rich oxide content ( $w(\text{Fe}_2\text{O}_3) \geq 5.0\%$ ), ferric oxide in the bauxite must enter into some phases with high melting point such as mullite and aluminium titanium, avoiding its enrichment and transformation into phases with low melting point. In this paper, controllable preparation of mullite was attained using the bauxite with Fe-rich oxide content as raw materials, by adjusting its mass ratio of  $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)/\text{SiO}_2$  to about 2.57 based on the theoretical design of  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  binary diagram and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{TiO}_2$  ternary diagram. Phase and synthetic mechanism of mullite from the Fe-rich bauxite have been characterized and analyzed by XRD, SEM, EDS and TOPASS refinement software. The results show that  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  ions enter into aluminum titanate and mullite in the form of solid solution. Crystal phases of the bauxite with Fe-rich oxide content after sintering are composed of mullite solid solution, aluminum titanate solid solution and cristobalite. A very little of amorphous phase exists between mullite crystals, and aluminum titanate solid solution is distributed dispersively and surrounded by mullite solid solution.

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## 1. Introduction

Mullite has been widely used as ceramic materials and refractories due to many of its outstanding properties such as high

temperature strength, thermal shock resistance, low thermal expansion, low thermal and electric conductivity, and exceptional chemical stability under harsh chemical environments [1–3]. The pure mullite phase, which is the only binary compound in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system, is a solid solution whose composition may be written as  $\text{Al}_2[\text{Al}_{2+x}\text{Si}_{2-2x}\text{O}_{10-x}]$  ( $0.18 \leq x \leq 0.88$ ) [3]. For crystal structure of mullite with different  $x$  values, 3:2 mullite ( $x = 0.25$ ) is

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a most stable phase [4].

The 3:2 mullite has a highly stable open structure [5,6] and it can accommodate a variety of transition metal ions into its structure as a solution, such as  $Ti^{4+}$ ,  $V^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Mn^{3+}$ , and  $Fe^{3+}$  [7–27]. The upper solubility limit is controlled by radii and oxidation states of the transition metal ions [7–9]: highest degrees of incorporation are observed for  $V^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  (approximately 11–13% wt. % as oxides) followed by  $Ti^{4+}$  [10–15]. Only very low amounts of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Co^{2+}$  ions can enter the mullite structure [14,21]. Several studies on the incorporation of metal-ion dopants in mullite have been given as follows. Murthy and Hummel [12] reported that solid solubility of  $TiO_2$  in mullite is 4 wt% at 1600 °C and solid solubility of  $Fe_2O_3$  in mullite 12 wt% at 1300 °C. Brownell [17] reported that with temperature rising, solid solubility of  $Fe_2O_3$  in mullite increases continuously; mullite can accommodate  $Fe_2O_3$  7.6 wt% at 1300 °C. Based on phase relationship of  $Fe_2O_3$ - $Al_2O_3$ - $SiO_2$  ternary diagram, Muan has worked out that  $Fe_2O_3$  10 wt% can incorporate into mullite under air condition. Schneider and Eberhard [18] have studied the effect of  $Fe_2O_3$  on thermal expansion of mullite by means of high-temperature Guinier X-ray diffraction method, giving the result that solid solubility of  $Fe_2O_3$  in mullite is 10.3 wt% at 900 °C. After studying natural mullite, Agrell and Smith [19] have found that the content of  $TiO_2$  in mullite is about 0.55–2.27 wt%. Baudin et al. [20] have pointed out that solid solubility of  $TiO_2$  in mullite is about  $2.9 \pm 0.2$  wt%.

In recent years, with continuous exploitation of high quality bauxite, the existing problems have been increasingly revealed: bauxite resource is wasted greatly and its use ratio is less than 30%, which leads to a result that a large of ore-crushing and ores ( $Fe_2O_3 \geq 5.0$  wt%) are left unused and are abandoned anywhere. The high-temperature industries, for instance, refractory industry require content of  $Fe_2O_3$  in the calcined bauxite is below 2.5 wt%, considering that  $Fe_2O_3$  will be transformed into  $Fe_3O_4$  or  $FeO$  and further reacts with  $Al_2O_3$  or  $SiO_2$  to generate some phases with low melting point such as  $2FeO \cdot 2Al_2O_3 \cdot 5SiO_2$  and  $2FeO \cdot SiO_2$  [28]. The formation of those phases with low melting point can have a bad impact on service life of the calcined bauxite at high temperatures and may even endanger staff's lives. Therefore, to realize recycle of the bauxite with mid-low grade ( $Fe_2O_3 \geq 5.0$  wt%),  $Fe_2O_3$  in the bauxite with mid-low grade must be transferred into these phases with high melting point such as mullite and aluminum titanium, avoiding isolated distribution of  $Fe_2O_3$  or its existence in the form of phases with low melting point. Based on analysis of the above literature, mullite can accommodate  $Fe_2O_3$  and its solid solubility in mullite reaches up to 7–13 wt%, which undoubtedly provides a feasible scheme for recycle of the bauxite with mid-low grade. For this reason, in this paper, controllable preparation of mullite was attained using the bauxite with mid-low grade as raw materials, by adjusting its mass ratio of  $(Fe_2O_3 + Al_2O_3)/SiO_2$  to about 2.57 based on theoretical design of  $Fe_2O_3$ - $Al_2O_3$  binary diagram and  $Al_2O_3$ - $SiO_2$ - $TiO_2$  ternary diagram. Phase characterization and synthetic mechanism of mullite from the bauxite with Fe-rich oxide content have been analyzed by XRD, SEM, EDS and TOPASS refinement software.

## 2. Theoretical design

Both  $Fe_2O_3$  and  $Al_2O_3$  belong to sesquioxide and the difference between their metal ionic radius is not large. Therefore,  $Fe_2O_3$  and  $Al_2O_3$  can accommodate each other and form solid solutions such as  $Fe_2O_3(ss)$  and  $Al_2O_3(ss)$ . Solid solubility of  $Fe_2O_3$  in  $Al_2O_3$  is more than 10 wt% ranging from 1500 °C to 1600 °C, as shown in Fig. 1. Ignoring the influence of impurities such as  $MgO$ ,  $CaO$ ,  $Na_2O$  and  $K_2O$  on mullite, the system of mullite prepared from the bauxite with mid-low grade can be expressed as  $Al_2O_3$ - $SiO_2$ - $TiO_2$  ternary

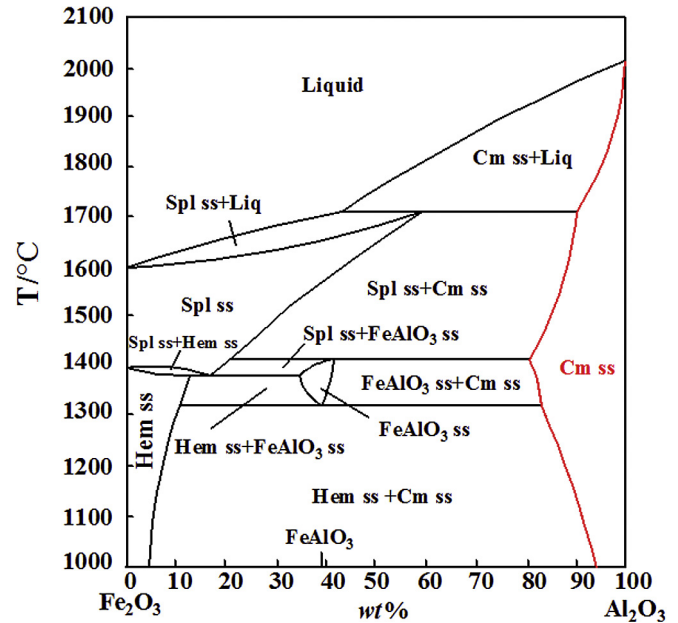


Fig. 1. Phase diagram of  $Fe_2O_3$ - $Al_2O_3$  binary system [29].

system. According to  $Al_2O_3$ - $SiO_2$ - $TiO_2$  ternary diagram (Fig. 2), to acquire above 90 wt% of mullite, composition points should be located within rich-mullite phase region, i.e.  $3Al_2O_3 \cdot 2SiO_2$ - $SiO_2$ - $Al_2O_3 \cdot TiO_2$  subsystem.

In consideration of a fact that production of the calcined bauxite cannot be sintered well and its organization structure have non-uniform characteristic due to mullitization of about 10% volume expansion ratio at high temperatures, therefore, after regulating chemical composition ( $Fe_2O_3 + Al_2O_3$ )/ $SiO_2$  ( $Fe_2O_3 \leq 10\%$ ) of the bauxite with mid-low grade to about 2.57 (mass ratio) and then co-grinding, mullite can be prepared by sintering method at 1600 °C under air condition. Equilibrium liquid point of materials located within  $3Al_2O_3 \cdot 2SiO_2$ - $SiO_2$ - $Al_2O_3 \cdot TiO_2$  subsystem is the point  $L_1$  at 1600 °C in air, and its equilibrium phases are  $3Al_2O_3 \cdot 2SiO_2$  and  $SiO_2$  or  $3Al_2O_3 \cdot 2SiO_2$  and  $Al_2O_3 \cdot TiO_2$ . Chemical composition of the bauxite with mid-low grade should be located within I region in

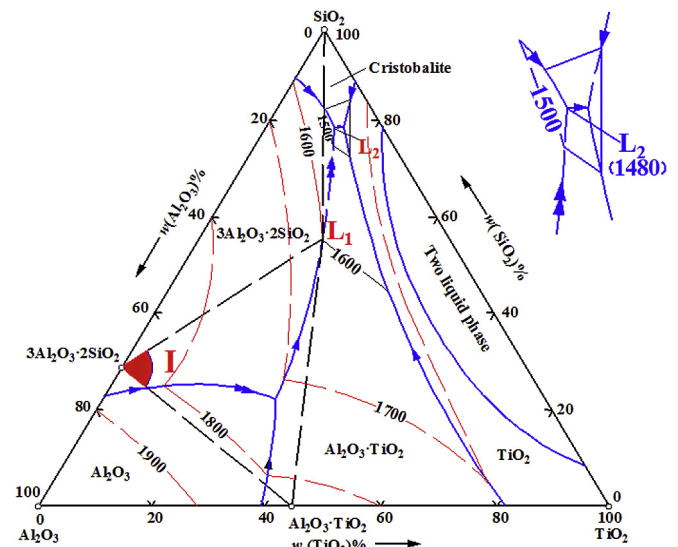


Fig. 2. Phase diagram of  $Al_2O_3$ - $SiO_2$ - $TiO_2$  ternary system [29].

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