

# PREPARATION AND CHARACTERIZATION OF LIGHTWEIGHT MULLITE-SILICA RICH GLASS AGGREGATES

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*Phase compositions, microstructures and properties of four lightweight mullite-silica rich glass aggregates with high strength were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and FactSage6.2 software. It was found that the lightweight aggregates with higher  $Al_2O_3$  content had higher mullite content, porosity and larger mullite crystallites, but lower content and viscosity of melt at elevated temperature. Most of  $Fe_2O_3$  and  $TiO_2$  were incorporated in mullite and most of  $K_2O$  and  $Na_2O$  were in glass to reduce viscosity of melt at elevated temperature.*

## INTRODUCTION

In order to reduce the energy consumption and  $CO_2$  emission of industry furnace, more attention has been paid to lightweight refractory castables. The drawbacks of lightweight castables are low strength and thermal shock resistance [1]. Stainless steel fiber is added into lightweight castables to improve their strength, but it brings some problems because of low melting point of steel and the difference of expansion coefficient between stainless steel and refractory castables. The aggregates in the castables give strong effects on the properties of refractory castables. With increase of strength of aggregate, the strength of refractory castables increases. It is important for refractory castables to use high quality lightweight aggregates.

Lightweight chamotte aggregate is often used in lightweight refractory castables. Lightweight chamotte refractory has low thermal shock resistance because of existence of quartz or cristobalite and pores which is asymmetrically distributed in the microstructure [2]. The lightweight chamotte aggregate has the same problem.

In china, a great lot of coal gangues are produced every year. It brings serious environmental problems. They have been used in ceramics, refractories and cementing materials [3]. Ni and Liu used coal gangue to produce anorthite light refractories [4] and other lightweight refractories [5-8] or porous ceramics [9, 10]. The composition and impurity content of coal gangues

vary. Some of them contain more  $K_2O$  and  $Na_2O$  which are harmful to the refractoriness of the refractories. The harm will decrease if the  $K_2O$  and  $Na_2O$  with  $SiO_2$  to form a glass phase with high  $SiO_2$  content, namely  $SiO_2$  rich glass. In this material, the quartz and cristobalite will come into glass and a mullite- $SiO_2$  rich composite is formed. The refractories with  $SiO_2$  rich glass have higher thermal shock resistance because of lower thermal expansion coefficient of mullite and  $SiO_2$  rich glass and without quartz and cristobalite. At elevated temperature, the  $SiO_2$  rich glass is melted to form a  $SiO_2$  rich liquid which has high viscosity. It is beneficial to properties of refractories at elevated temperature. In this paper we reported the composition, properties and microstructure of mullite- $SiO_2$  rich glass lightweight aggregate made from coal gangues and bauxites with different  $Al_2O_3/SiO_2$  and impurity content. Their application in lightweight castable will be dealt with in next paper.

## EXPERIMENTAL

### Samples

Four lightweight aggregate samples made from gangues and bauxites with different  $Al_2O_3/SiO_2$  ratio and impurity content were chosen for investigation. Their chemical compositions were listed in Table 1. According to the  $Al_2O_3$  content, the samples have been divided into two kinds, which were named M50 and M70, respec-

tively. The  $\text{Al}_2\text{O}_3$  contents of sample A and B were 40~50%, while those of sample C and D were 60~70%. The samples were fired in a tunnel kiln at 1550°C and soaking time is of 8 hours.

### Characterization techniques

Phase analysis was conducted using X-ray diffractometry (XRD; Model Xpert TMP, Philips, Eindhoven, Netherlands) with a scanning speed of 2° per minute. The microstructure of these samples etched by HF acid was observed using a scanning electron microscopy (SEM; Model XL 30, Philips).

The content of the glass phase was measured by treatment of HF acid. The concentration of HF acid was 20 wt.% and particle size of the samples was less 80 meshes. The compositions of glass phase were calculated based on the compositions of samples and their crystalline phase. The viscosity of the glass phase was calculated using FactSage6.2 software.

The porosities of the samples were measured using Automatic True Density Analyzer (ACCUPYC1330). The pore size distribution of the samples was conducted using optical microscope (Axioskop40) and the corresponding image analysis software. The crushing strength was measured using the cubic sample with a side length of 7cm.

## RESULTS AND DISCUSSION

### Properties, phase compositions and microstructures

XRD patterns of samples were given in Figure 1. It can be seen that the main crystalline phase is mullite, with a few amount of corundum coexisting, and the corundum content of sample C and D is larger than A and B.

The pore characterization, crushing strength and the phase content were given in Table 2. The sample C and D have higher porosity and content of crystalline phase than those of sample A and B, but lower d50, crushing strength and glass content than those of sample A and B. However, the crushing strength of the four samples is higher than that of the lightweight chamotte aggregates available. As shown in Table 1, sample A and B have lower  $\text{Al}_2\text{O}_3$  content and higher impurity content, especially higher  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  content. The sintering

of sample A and B is easier than that of sample C and D, resulting in decreasing porosity and increasing pore size and strength.

The microstructures of samples etched by HF acid were shown in Figure 2. The shape of mullite crystallines in sample A, B and C, D are different. The mullite in sample A and B are needle crystal, but the mullite in sample C and D are column crystal, and the size of mullite crystal in sample C and D are larger than those in sample A and B. The sample C and D are made from bauxites which consist of kaolin and diaspore. Kaolin is decomposed into mullite and vitreous  $\text{SiO}_2$  at elevated temperature. Mullite crystallites grow by reaction between  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  which come from decomposition of diaspore during sintering. The mullite crystallites in sample A and B can not grow because there is no  $\text{Al}_2\text{O}_3$  to react with  $\text{SiO}_2$ . From Figure 1, it is evident that mullite content in sample C and D are larger than that in sample A and B.

Table 2. Property and phase composition.

	A	B	C	D
Porosity (%)	54.4	48.4	65.2	57.2
Pores size (d50, $\mu\text{m}$ )	60.97	35.54	30.07	28.76
Crushing strength (MPa)	20.9	19.1	7.6	10.5
Content of the glass (%)	51.86	39.97	24.16	13.44
Content of the crystalline phase (%)	48.14	60.03	75.84	86.56

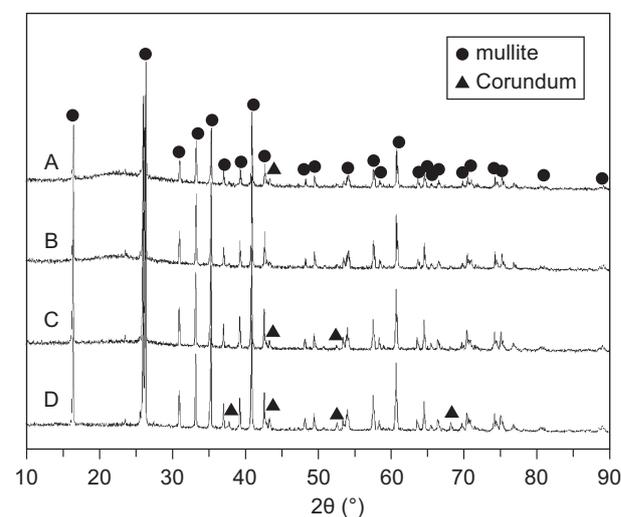


Figure 1. XRD patterns of samples.

Table 1. Chemical composition of lightweight mullite-silica rich glass aggregates (wt%).

		$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{TiO}_2$	Impurity total
M50	A	51.42	41.31	0.95	1.00	0.51	1.96	1.11	1.27	6.80
	B	46.03	47.74	0.96	1.08	0.55	1.18	0.47	1.51	5.75
M70	C	33.81	60.12	1.09	0.31	0.34	1.08	0.67	2.36	5.85
	D	26.69	67.44	1.15	0.29	0.33	0.76	0.48	2.71	5.72

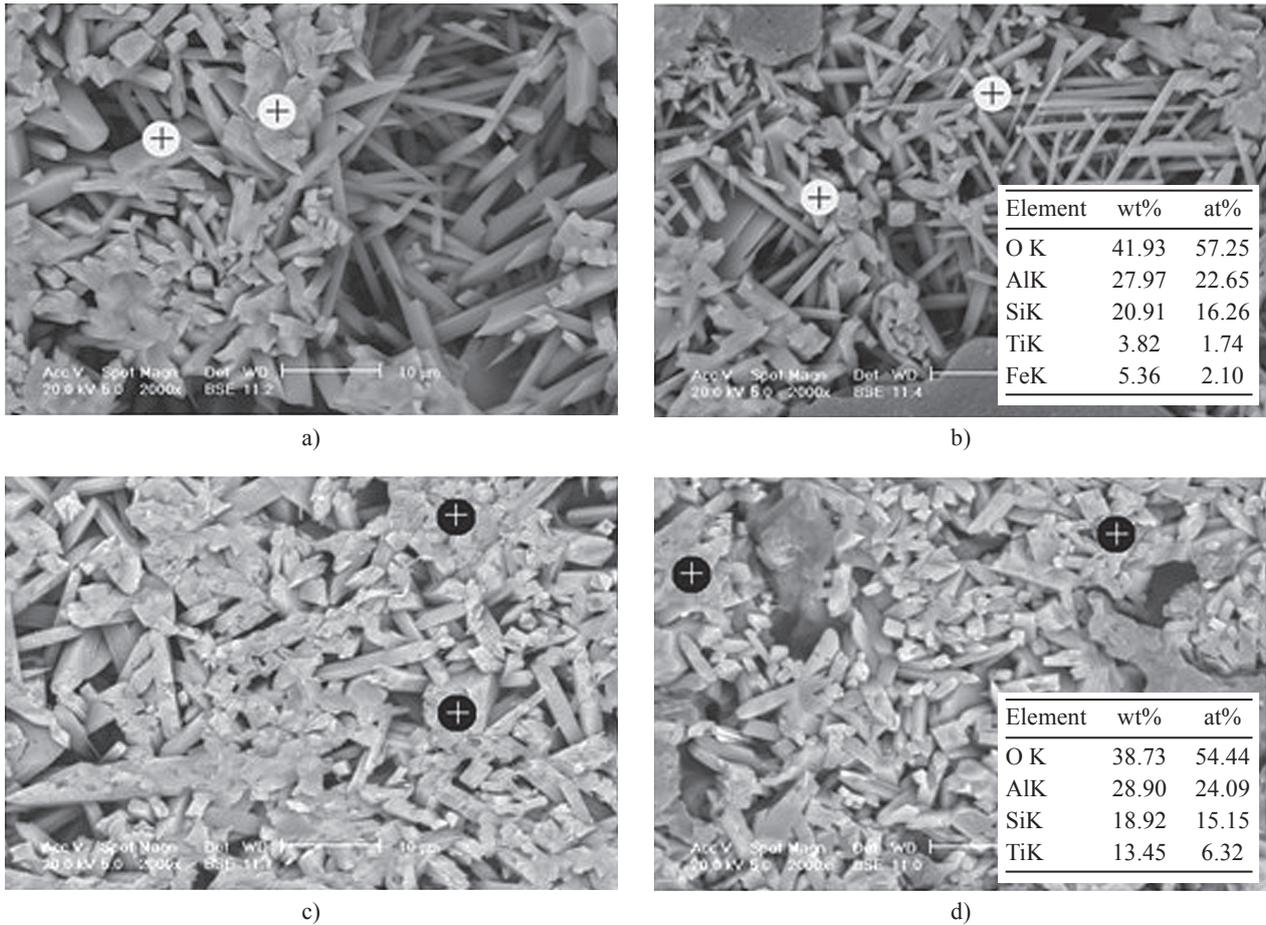


Figure 2. SEM micrographs and EDS analysis of HF-etched samples (+ : Mullite).

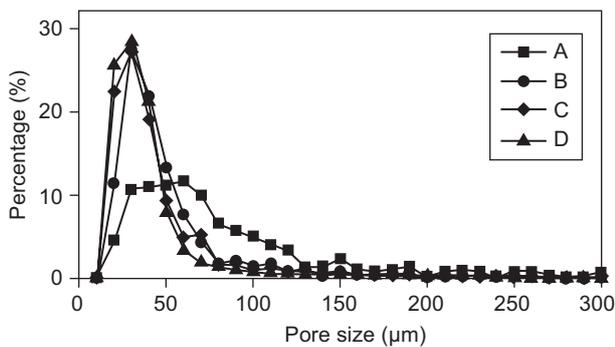


Figure 3. Variation of the pore size distribution of the samples.

The pore size distributions of the samples were demonstrated in Figure 3. It can be observed that the curves of pore size distributions of sample B, C and D are similar, although there are differences between their d50. The shape of pore size distribution curve of sample A is quite different from that of sample B, C and D. Sample A has higher content of impurities and liquid content. Liquid improves sintering and pore growth to form a broad curve of pore size distribution.

### Composition and viscosity of glass phase

In mullite-SiO<sub>2</sub> rich glass composite, the glass phase is an important constitute. Its composition and properties play an important role to the characteristics of lightweight aggregates and the castables with these lightweight aggregates. The chemical compositions of the crystalline and glass phase in the lightweight aggregate were listed in Table 3 and Table 4, respectively. It clearly appears that the crystals are the mullite and Al<sub>2</sub>O<sub>3</sub> content of mullite crystals in sample C and D is slightly higher than that of A and B. The content of SiO<sub>2</sub> in the glass phase is significantly high.

The distributions of impurities (K<sub>2</sub>O, Na<sub>2</sub>O, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) in crystalline phase and glass phase of the samples were illustrated in Figure 4. The significant differences are shown. For sample A and B, most of the Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in impurity are in glass phase. However, for sample C and D, most of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are in mullite crystalline, because sample C and D have more mullite content and mullite can accommodate a large amount of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> [11]. In all the four samples, more CaO and MgO are in crystalline phase.

Some of new substances may form. For example,  $\text{CaSiO}_3$  is found in a mullite- $\text{SiO}_2$  rich glass composite [12]. Most of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  in four samples are in glass phase.

Viscosity of liquids of four samples as a function of temperature was shown in Figure 5. Viscosities decrease notably with the increase of temperature. It is worth noting that the viscosities are significantly high even at  $1600^\circ\text{C}$ , and the smallest viscosity of the samples is  $1309.18 \text{ Nsm}^{-2}$ . It would be beneficial to the properties of the materials at elevated temperatures.

The liquid in sample A and B have higher viscosity than liquid in sample C and D, because the formers have higher  $\text{SiO}_2$  content and lower content of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ , though the content of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  in sample A and B are larger than that in sample C and D. In liquid phase  $\text{SiO}_2$  forms  $-\text{Si}-\text{O}-\text{Si}-$  chains to increase viscosity of liquid, and alkali oxides break  $-\text{Si}-\text{O}-\text{Si}-$  chains to decrease viscosity of liquid.  $\text{SiO}_2$  content of liquid in sample B is higher than that in sample A and content of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  of liquid in sample B are lower than those in sample A, but the viscosity of liquid in sample B is slightly lower than that in sample A. The reason is

not clear. Perhaps, it is related to different  $\text{Al}_2\text{O}_3$  content in sample A and B. The effect of  $\text{Al}_2\text{O}_3$  on the viscosity of liquid is complex. In a case  $\text{Al}_2\text{O}_3$  increases viscosity of liquid and in other case  $\text{Al}_2\text{O}_3$  decreases viscosity of liquid.

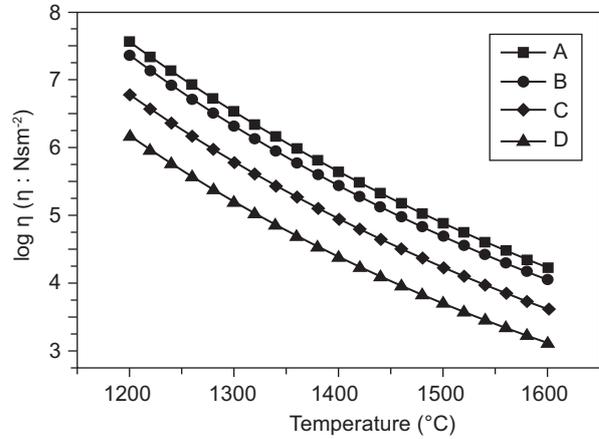


Figure 5. Viscosity of liquids of four samples as a function of temperature.

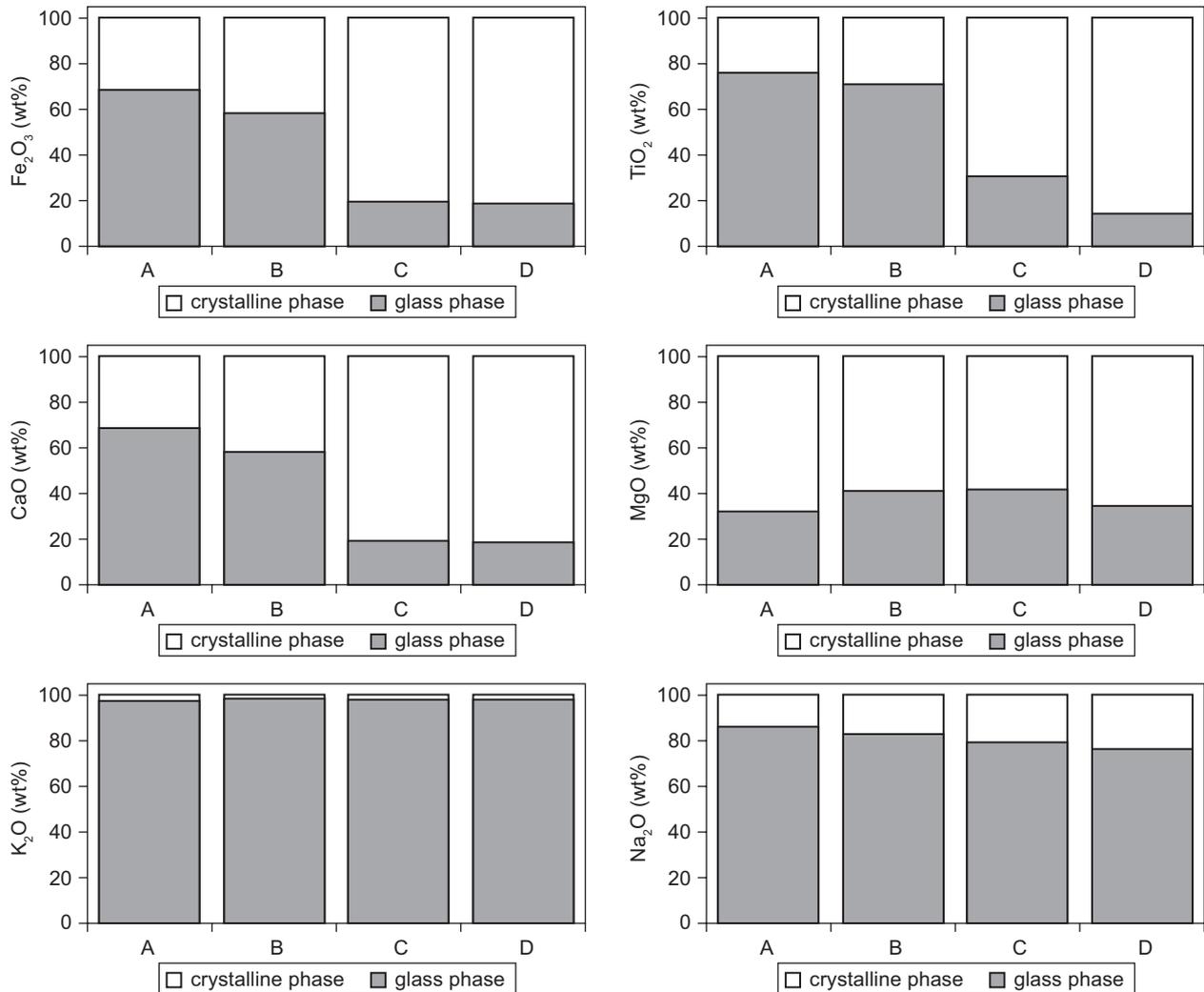


Figure 4. Variation of the impurity distributions of the samples.

Table 3. Chemical composition of the crystalline phase of samples (wt%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>
A	23.38	72.06	0.62	1.78	0.72	0.09	0.32	0.63
B	24.15	72.29	0.67	1.35	0.54	0.03	0.13	0.73
C	21.66	73.63	1.16	0.21	0.26	0.02	0.18	2.16
D	21.21	74.40	1.08	0.17	0.25	0.01	0.13	2.68

Table 4. Chemical composition of the glass phase of samples (wt%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>
A	77.87	12.83	1.26	0.28	0.32	3.71	1.85	1.87
B	79.71	10.98	1.41	0.68	0.57	2.94	0.99	2.71
C	71.00	17.48	0.86	0.62	0.58	4.34	2.18	2.95
D	62.41	22.77	1.61	1.07	0.85	5.61	2.75	2.92

### CONCLUSIONS

The phase compositions, microstructures and properties of mullite-SiO<sub>2</sub> rich glass lightweight aggregates depend on their chemical composition. The higher Al<sub>2</sub>O<sub>3</sub> content results in more mullite content and larger size of mullite crystallites, higher porosity and lower crushing strength, but lower SiO<sub>2</sub> content and higher alkali oxides content in liquid to reduce viscosity of liquid.

The content of impurities, especially alkali improves sintering, to decrease porosity and increase crushing strength. At the same time, higher alkali oxide content of sample A and B does not result in increasing alkali oxide content in glass of sample A and B, but increasing SiO<sub>2</sub> content of the liquid increases its viscosity.

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