Research Paper

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Mullite from High Temperature Chemical Reaction Method – Evaluation of Stoichiometric Al_2O_3/SiO_2 Ratio, Phase Composition and Microstructure

Engineering

KEYWORDS : Mullite, glass matrix, magnesia, cordierite, $MgAl_2O_4$ spinel

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ABSTRACT

Paper evaluates properties and microstructure of mullite prepared by high temperature solid state chemical reaction – of $Al_2(SO_4)_3$ and SiO_2 in molten Na_2SO_4 and also of $Al(OH)_3$ and SiO_2 with/without MgO. The Al_2O_3:SiO_2 molar ratio, phase composition and microstructure are discussed. The 3:2 mullite phase is formed by sintering Al(OH)3 and SiO2 at 1500 °C in presence of MgO addition. The higher content of MgO, the most advanced mullitization process. At 10wt% MgO, the highly elongated crystals of primary mullite and acicular crystals of secondary mullite are detected.

INTRODUCTION

Mullite is a solid solution compound with stoichiometry ranging from silica-rich $3Al_2O_3 \times 2SiO_2$ (3:2 mullite) to alumina-rich $2Al_2O_3 \times SiO_2$ [1]. Eutectic point of 3:2 mullite is about 1890°C.

Mullite is one of crystalline phases in siliceous fly ashes, in addition to quartz, the second largest next to glassy phase. Mullite structure is composed with chains of AlO_6 octahedra cross-linked by $(Si,Al)O_4$ tetrahedra. The same structural units are observed for glass in siliceous fly ash [2-3].

There are many methods for preparation of 3:2 mullite. Mostly, it is obtained by sintering of kaolin-alumina mixture [4-6]. An interesting method is synthesis by combustion [7,8]. Recent works are focused on sol-gel method [9-11].

In paper, the mullite is prepared by two methods: through reaction of $Al_2(SO_4)_3 \times 18H_2O$ and SiO_2 in molten Na_2SO_4 [12] and also of $Al(OH)_3$ and SiO_2 with/without MgO [13,14]. Aim of study is evaluation of Al_2O_3/SiO_2 molar ratio in synthesized samples, confirming possibility of obtaining of 3:2 mullite. Additionally, the morphology of mullite crystals is investigated.

2. EXPERIMENTAL

2.1 Mullite sample synthesis

2.1.1 Reaction of $Al_2(SO_4)_3$ and SiO_2 in molten Na_2SO_4

Mixture of $Al_2(SO_4)_3 18H_2O$, SiO_2 and Na_2SO_4 was heated at 1000°C for 3h. At 1000°C, the $Al_2(SO_4)_3$ is decomposed to Al_2O_3 and SO_3. Because Al_2O_3 and SiO_2 slightly dissolve in molten Na_2SO_4, they react with each other to form mullite from molten salt media. After water washing away the excess of salts, the powder was dried at 100°C. Sample was named as M1. Content of Al_2O_3 and SiO_2 in M1 sample is given in Table 1 and its XRD pattern – in Figure 1.

Table 1: Chemical composition of mullite samples

Sample	Al_2O_3		SiO_2	
	wt%	mol	wt%	mol
M1	49.48	0.485	28.79	0.479
M2	40.98	0.468	47.69	0.682
M3	75.01	0.736	24.07	0.401
M4	65.60	0.643	24.31	0.405

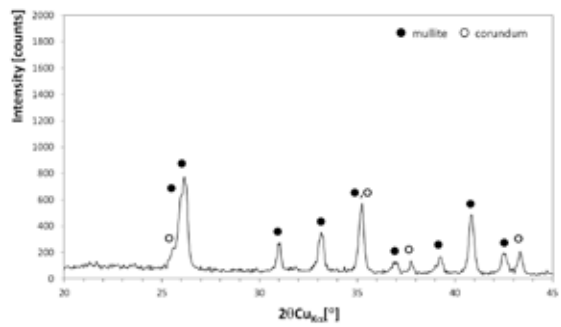


Figure 1: The XRD pattern of M1 sample

The XRD pattern of M1 sample (Figure 1) matched predominantly with patterns of mullite (JCPDS file 01-0613) and corundum (JCPDS 10-173). Mullite is shown by two main broadening and overlapping sharp peaks at 25.95 and 26.15°2θ, and corundum – by main peak at 25.60°2θ. Quantitative XRD analysis gives that M1 sample contains 91.9wt% mullite phase and 8.1wt% corundum. Authors [15] report that presence of corundum may be due to insufficient amount of Na_2SO_4 in mixture and consequently restricted diffusion of reactants in molten media, which is not favor formation of mullite crystals. Maybe corundum is crystallized before mullite formation [16]. The M1 sample is composed with 41.38wt% Al_2O_3 and 28.79wt% (Table 1). Taking the corundum content, the mullite phase in M1 sample consists about 33.28wt% Al_2O_3. Thus, the Al_2O_3/SiO_2 molar ratio in mullite phase is equal to 1:1. Thus, it may indicate that there is sillimanite phase in M1. According to authors [17], the sillimanite is transformed into mullite and silica at temperature range of 1300-1600°C, whereas results [18] suggest that this transformation is about 1130°C.

2.2 Reaction of $Al(OH)_3$ and SiO_2 with/without MgO addition

Mixture of $Al(OH)_3$ and SiO_2, was prepared without addition of MgO and sintered at 1500°C for 3h. Sample was called as M2. Content of Al_2O_3 and SiO_2 in M2 sample is given in Table 1 and its XRD pattern – in Figure 2. The XRD measurement gives that mixture of $Al(OH)_3$ and SiO_2 do not give completely mullitization process at 1500°C as it is presented in works [1,19]. The XRD pattern of M2 sample is very well matched to standard patterns of mullite, corundum and cristobalite (JCPDS 39-1425). Intensity of mullite lines at 25.95° and 26.15°2θ, expressed as counts per second, is respectively 453 and 776. As shown in Table 1, the M2 sample is composed with 57.51wt% Al_2O_3 and 42.48wt% SiO_2. Taking into account quantitative XRD analysis – 82.9wt% 3:2 mullite phase, 10.9wt% corundum and 6.2wt% cristobalite – it may be concluded that mullite phase in M2 is composed with about 59.69wt% Al_2O_3 and 23.21wt% SiO_2. Due to low sintering temperature, the M2 sample may also contain the 2:1 mullite phase, which is followed by 3:2 mullite formation [18].

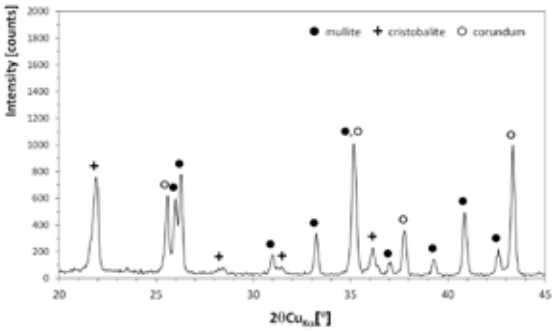


Figure 2: The XRD patterns of M2 sample

The MgO was introduced to mixture of $Al(OH)_3$ and SiO_2 in amount of 1 and 10wt%. The blends were sintered at 1500°C for 3h. Sample with 1wt% MgO was named as M3, and that with 10wt% MgO – as M4. Content of Al_2O_3 and SiO_2 in these samples is given in Table 1 and their XRD patterns – respectively in Figure 3 and 4.

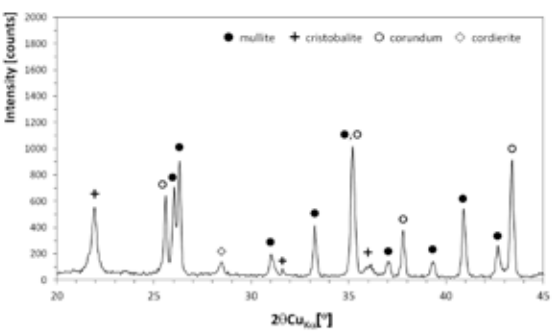


Figure 3: The XRD pattern of M3 sample

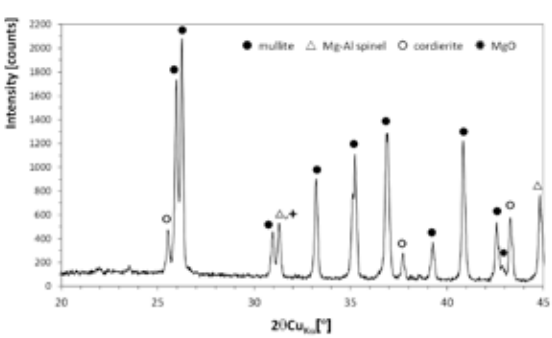
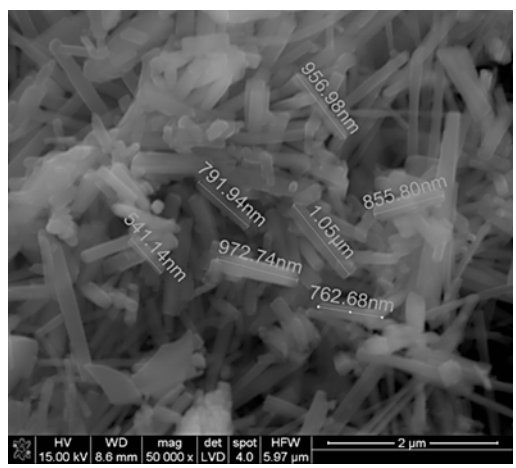


Figure 4: The XRD pattern of M4 sample

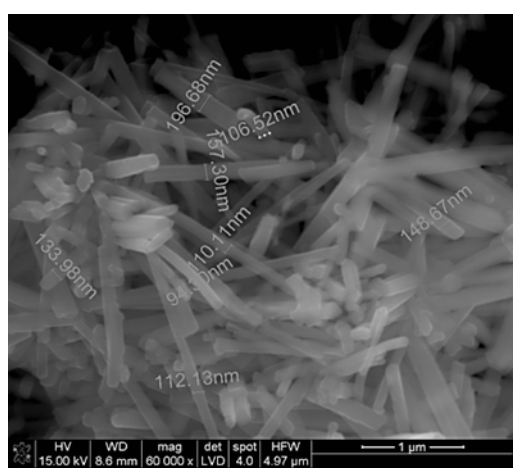
As shown in Figures 3 and 4, in M3 and M4 samples not only mullite phase, corundum and cristobalite are present, but also $Mg_2Al_4Si_5O_{18}$ (cordierite) and $MgAl_2O_4$ spinel are detected. Of course, the mullite is major phase in both samples. On XRD pattern of M3, the intensity of mullite peak at 26.15°2θ is 924 (Figure 3) and is by about 19% higher than for M2. Simultaneously, the intensity of diffraction lines of corundum (25.64°2θ) and cristobalite (21.92°2θ) is respectively 908 and 1454, and is respectively by about 9% lower and by 2-times higher than for M2. According to $MgO\text{-}Al_2O_3\text{-}SiO_2$ system, the liquid phase represents more silica and less alumina than 3:2 mullite, resulting in the appearance of corundum during cooling. Amount of SiO_2 is decreased as a result of its reaction with MgO to form glassy phase and/or cordierite [20]. Increase in intensity of SiO_2 peak on XRD pattern of M3 may be caused by inaccurate mixing of raw materials, so not all amount of SiO_2 may react with MgO. On XRD pattern of M4 sample (Figure 4) the mullite peaks are very strong and of the highest intensity, resulting from the most complete mullitization process [21]. Intensity of mullite peak at 26.15°2θ is 2080 and is 2-times higher than for M3 and 2.2-times higher than for M2. Amount of corundum is decreased in comparison to M3 sample, probably because cordierite is decomposed to mullite and magnesia-rich liquid phase [17]. The SiO_2 lines are not observed in M4 sample. Quantitative XRD analysis shows that the M4 sample contains 85.8wt% mullite phase, 9.8wt% $MgAl_2O_4$ spinel, 3.4wt% cordierite and 1.0wt% MgO. As shown in Table 1, the M3 sample contains 75.01wt% Al_2O_3 and 24.07wt% SiO_2, giving mullite phase of molar composition between 3:2 and 2:1. In M4 sample, the content of Al_2O_3 is 75.01wt% and that of SiO_2 – 24.31wt%. It gives the Al_2O_3/SiO_2 molar ratio equal to 1.59, which shows that M4 sample contains 3:2 mullite phase.

2.3 Mullite sample microstructure

Microstructure observations are performed using FEI's Nova200 Nano SEM equipped with energy dispersive spectrometer (EDS). Micrographs of M1 are shown in Figures 5-7, whereas those of M4 – in Figures 8-10.



a)



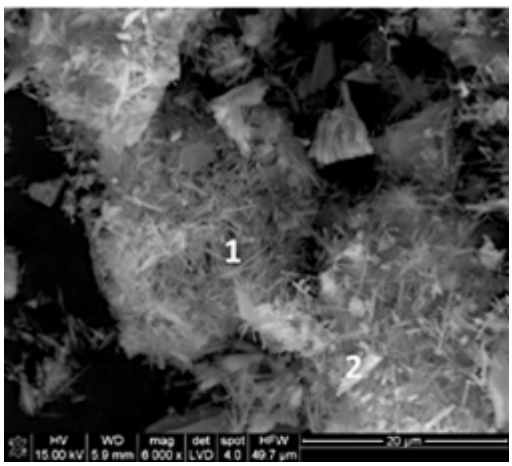
b)

Figure 5: SEM. Mullite whiskers in M1 sample. 50 000x (a) and 60 000x (b)

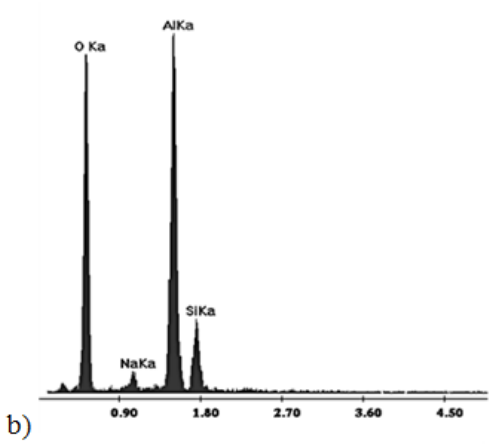
The M1 sample showed a needle-like mullite crystals of 0.5-1.0 µm in length (Figure 5a) and 100-200 nm in diameter (Figure 5b). Formation of mullite whiskers is favoured by existence of molten salt media, in which growth of mullite crystals follows

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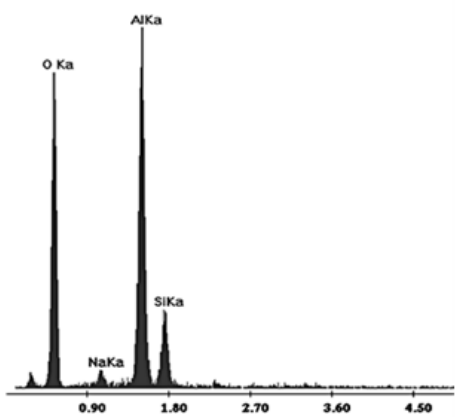
their crystallizing. Mullite whiskers clusters enriched in Al_2O_3 (Figure 6) and small plate-like mullite crystals (Figure 7) are also found.



a)



b)



c)

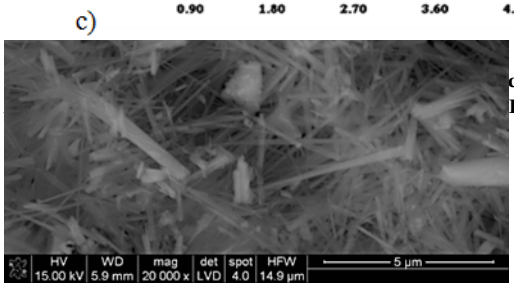
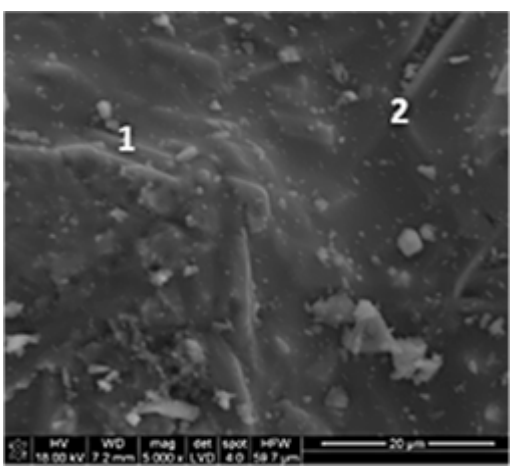


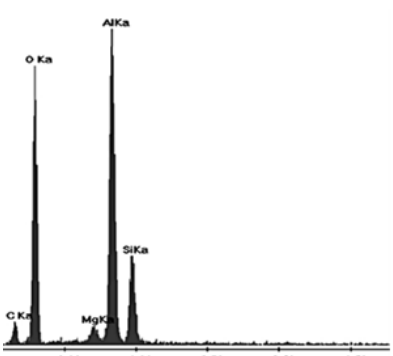
Figure 7: SEM. Plate-like mullite crystals in M1 sample.

20 000x

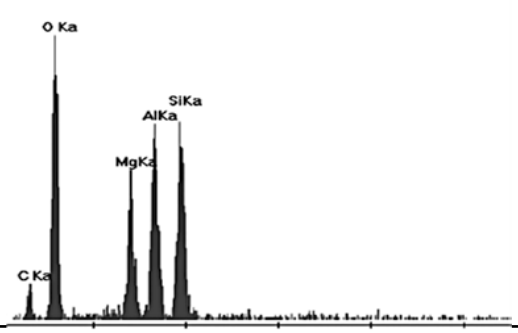
The M4 sample exhibits more dense microstructure (Figure 8a). Needle-like mullite crystals are greater and grow considerably in all directions and are embedded in liquid phase. The EDS analysis in Point 1 (Figure 8b) shows the Al_2O_3/SiO_2 ratio of about 3.5, which is much higher than that in 3:2 mullite. The high content of alumina may be due to excessive growth of mullite nuclei through aluminosilicate glassy phase and entrapment of alumina in 3:2 mullite crystals. The EDS analysis in Point 2 (Figure 8c) confirms the presence of $MgAl_2O_4$ crystals in M4 sample. High content of Mg atomic may suggest that the $MgAl_2O_4$ spinel phase is placed far away from Al_2O_3 layer [22]. Figure 9 shows agglomeration of mullite whiskers probably on surface of $MgAl_2O_4$ crystal. Length of mullite whiskers in M4 sample is 0.5-1.5 µm (Figure 10a) and their diameter –150-230 nm (Figure 10b).



a)



b)



ched in

Point 2

c)

Figure 8: SEM/EDS. Mullite whiskers embedded in aluminosilicate glass in M4 sample. 5 000x. EDS – Point 1 (b) and Point 2 (c)

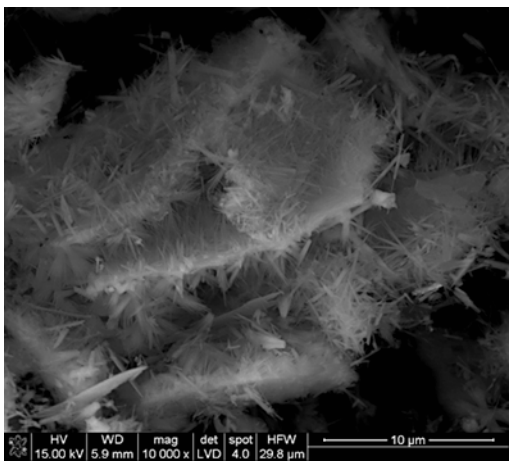
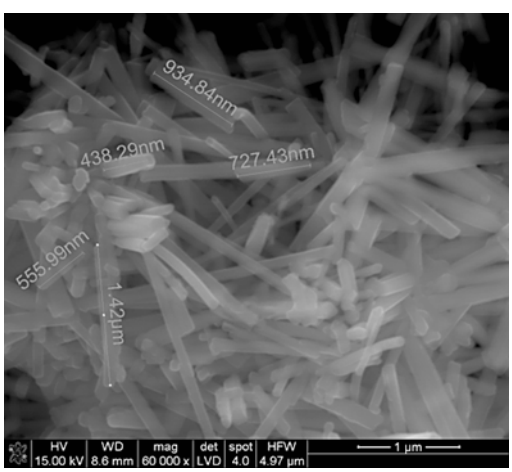
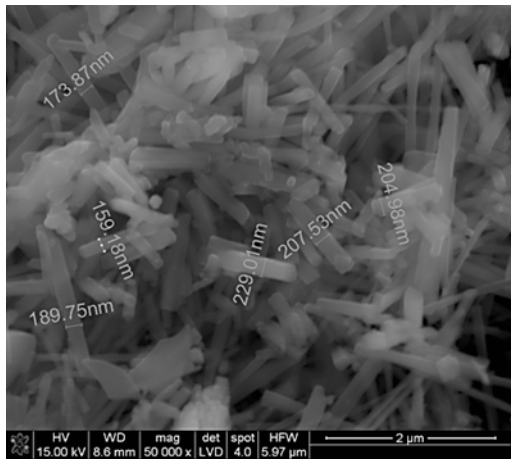


Figure 9. SEM. Mullite whiskers on surface of $MgAl_2O_4$ crystal in M4 sample. 10 000x



a)



b)

Figure 10: SEM. Mullite whiskers in M4 sample. 60 000x (a) and 50 000x (b)

3. CONCLUSIONS

Mullite phase synthesized at 1000°C using mixture of $Al_2(SO_4)_3$ and SiO_2 in molten Na_2SO_4 has molar composition 1:1. Microstructure exhibits very fine needle-like crystals, which somewhere form clusters.

Mullite phase synthesized from mixture of $Al(OH)_3$ and SiO_2 at 1500°C has molar composition between 3:2 and 2:1. Addition of 10wt% MgO improves mullitization process at 1500°C, giving 3:2 mullite phase. Mullite whiskers are more elongated and embedded in aluminosilicate glass.

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