Investigation of Aluminosilicate Crystallization Behavior in SiO_2-Al_2O_3 System

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1. Introduction

Mullite with the chemical formula of $[Al_{4+2x}Si_{2-2x}]O_{10-x}$, where x refers to the concentration of the oxygen vacancy, is the most stable intermediate phase in the alumina-silica system at atmospheric pressure. Silica-rich $3Al_2O_3.2SiO_2$ (3:2 mullite) is more stable than the alumina-rich $2Al_2O_3.SiO_2$ (2:1 mullite) crystallized in x=0.4. Amongst various methods, the sol-gel method due to its repeatability is very significant. The aim of the present research was to evaluate how the starting ratio between Al_2O_3/ SiO_2, and temperature of heat treatment could affect the properties of final composition. The purpose is to synthesize mullite using the sol-gel method with a stoichiometric and non-stoichiometric ratio (mullite-alumina and mullite-silica), and sequentially phase and microstructural characterization of the synthesized samples.

2. Experimental

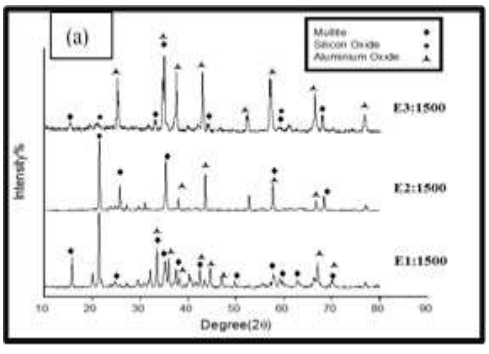
Aluminum nitrate nonahydrate $Al(NO_3)_3.9H_2O$ (Merc No.7784-27-2) and Tetraethyl orthosilicate $(C_2\ H_5\ O)_4\ Si$ (Merk No.78-10-4) were used as alumina and silica precursors, respectively. Different precursors with three ratios between Al_2O_3 and SiO_2 i.e. 3:2, 2:1, and 3:4were prepared. TEOS hydrolysis was accomplished at 75 °C and in specific volumetric ratios of H_2O/TEOS = 1.6. Aluminum nitrate nonahydrate was dissolved (H2O/ANN = 25.3) by magnetic stirring at ambient temperature. The resulting solution was added slowly to the solution obtained from TEOS hydrolysis. Increasing the pH with mixture of water/nitric acid converts the sols into gels. Obtained gels were aged at room temperatures for 10 days. The aged gels were dried in oven at 70 °C and 110 °C for 20 and 4 hours, respectively. The two-step heat treatment of dry gels was performed for 3 hours at 600 °C, and then repeated for another 3 hours individually at 900, 1100, 1250, 1350 and 1500 °C. The rate of thermal heat treatment was 5°/min. Table 1 shows different alumino-silicate ratios at heat treatment temperatures with A-E samples, and samples X1-X3 are alumino-silicate samples with different ratios. XRD analysis (PW1730 X-ray diffraction with Cu Kα radiation) was used to determine formed phases. For thermal analysis, DTA / TGA test (STA PT1600 LINSEIS) was used.

Table 1. Alumino-silicate specimen specification

Sample code	ratio	(°C) temperature
E1-1500	3:2	1500
E2-1500	3:4	1500
E3-1500	2:1	1500

3. Results and Discussion

XRD patterns of samples mentioned in Table 1 are presented in Figure 3. According to the Figure 3. (a), in A1-900, A2-900, A3-900 samples at 900 °C, the composition of cristoballite was observed at 2θ angle of 22º. At this temperature, in all three samples, cristoballite, aluminum oxide, and mullite peaks were observed. In contrast, in the A2-900 specimen, with 3:4 ratios, the magnesium and aluminum oxide peaks, appeared slightly. In the three samples, the peaks of mullite and aluminum oxide at 2ɵ angle of 34° were appeared, which overlap with each other. Only in A1-900 (3:2 ratio) and A3-900 (2:1 ratio) specimens a hundred mullite peak at 2θ angle of 18º was observed. Generally, in TGA results curves (Figure 4), weight loss in B1-1100, B2-1100 and B3-1100 samples were 60%, 80%, and 65%, respectively, which are mainly caused by water, solvent, and ethoxy or nitrate groups, removal. Higher weight loss of B2, in comparison to other samples, could be attributed to the higher amounts of ethoxy and nitrate groups as a result of 3:4 ratio between aluminum nitrate nonahydrate and TEOS, respectively. An endothermic DTA peak around 200 °C which was seen in all 3 samples could be related to the removal of structural water and decomposition of nitrate groups (effect of bohemite).



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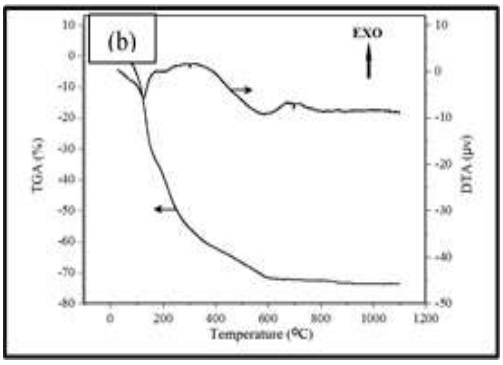

Fig. 1. (a) XRD and (b) DTA-TG results of prepared samples

4. Conclusion

This study investigated the effect of different Al_2O_3/SiO_2 ratios and heat treatment temperatures on the mullite crystallization using aluminum nitrate nonahydrate and tetraethylorthosilicate. Generally, in the results of XRD test, in all samples, a strong peak of cristobalite was observed. At 900 °C, little nucleus of mullite in two aluminosilicate samples with 3:2 and 2:1 ratios were formed, which can be ignored. By increasing temperature up to 1500 °C, crystallization of aluminum oxide increased and further temperature increases had a greater effect on the mullite crystallization in 3:4 ratio sample. Generally, in samples with higher alumina content, more mullite compositions have been crystallized. The obtained data from DTA/TGA curves indicate that the maximum changes in both curves are related to temperature below 650 °C, which caused by the exhaust of water, moisture, organic, and nitrate groups at two temperatures of 125 °C and 300 °C and formation of γ-alumina or alumina-spinel compounds at 575 °C.