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Microwave synthesis of Lithium aluminum silicate and its characterization

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Abstract:

Lithium aluminum silicate (LAS) was prepared using the sol-gel technique and starting from LiCl H_2O, $Al(NO_3)_3$ and Tetraethyl ortho silicate (TEOS). The final product $Li_2O : Al_2O_3 : 3SiO_2$. Acid catalysis was applied by using of HNO_3, H_3PO_4 or $HClO_4$ in addition to a catalyst free sample. Microwave heating was employed in both the hydrolysis, condensation and drying processes. The prepared samples were thermally analyzed by thermogravemetric analysis (TGA) and scanning electron microscope (SEM). TGA thermograms showed sharp decrease in weight

at 250°c that varied with the catalyst. SEM analysis also indicated variable shapes of the crystals with different catalysts.

Introduction:

Although the technology for microwave dielectric heating has been available for about 25 years [1], its exploitation for the synthesis of chemical compounds and materials was not fully recognized until recently. Chemists have been slow in developing the microwave technique because they had an incomplete appreciation of the mechanisms of dielectric heating at the microscopic level. Several research groups have reported successful application of the technique to synthesis problems in organic, organometallic, coordination and solid state chemistry [2-5]. Use of microwave dielectric heating techniques for processing and sintering ceramics has identified advantages. The reduced cracking and thermal stress associated with dielectric heating has its maximum effect in the center of the sample and can be useful in densifying ceramic samples. The process may be more economic because of the direct interaction between the microwaves and the sample. The rapid heating by microwave can lead to the absence of secondary crystallization or segregation of impurities which conduct to a strengthening of mechanical properties. The heat losses are less and the time of the synthesis is dramatically reduced. LAS represents the most common glass-ceramics family which after final processing may contain more than 95% by volume crystalline phases. The two crystalline phases of primary interest are the β-spodumene and β-

quartz solid solutions. They exhibit a low thermal expansion coefficient and high degree of thermal shock resistance [6] making them useful in the application of regenerator cores that salvage waste heat for improved fuel consumption[7], in addition to their use as an acid resistant enamels[8]. Porous β-eucryptite were characterized in modern applications as humidity sensors[9].

Experimental:

A mixed alkoxide-inorganic precursor composed of 1.51g of LiCl H_2O (Koch-light), 9.37g of $Al(NO_3)_3$ $9H_2O$ (Fisher) together, 10.91 ml of absolute ethanol (Merck) and 2.25 ml water was prepared and stirred in a 50 ml round bottom flask fitted with a reflux condenser inside the cavity of a domestic microwave oven (Hotpoint). The entire mixture was left for 5 minuets at the first power level of (220 w), then the mixture was cooled and 8.36 ml of TEOS (Aldrich) and 7.48 ml of formamide(Prolabo) were added and the whole sample was shacked for another 5 min till it reached homogeneity. The sample was then allowed to gel at ambient conditions. The obtained gel was aged for two weeks and then splitted into two parts, one was to be dried for 48 hour at 120°C while the other was to be dried in the microwave for another 5 minuets at the fifth power level (800 w) .The formed powders were set for TGA analysis performed on **NETZCH TG209** at a heating rate of 10 °C/min from ambient temperature to 1000°C in an inert N_2 gas atmosphere was passed at a flow rate 10 ml/min. While SEM were carried out by **Philips XL30** in which samples were sputtered with gold.

The experimental procedure was carried out according to the scheme in figure (1).

Results and Discussions:

Sol-gel method has the advantage of better homogeneity and lower temperature processing comparing with the conventional ceramic preparation methods[10].

A comparison based on the stress-free bodies obtained for LAS with 1:1:3 ratio is given in recent article[11]. In this article, the mixed oxides were compressed and then calcined at about 1400°C for at least one hour. In this study, it was planned to investigate the preparation via sol-gel where the precursors are to be hydrolyzed for one hour at 85°C, then dried at 120°C for 48 hours. As sol-gel provides a suitable possibility to generate multi-phase nano structured materials[12-13], microwave technique was chosen to reduce the processing time. Microwave energy has already been used for sintering ceramic materials and also for synthesis of solid state inorganic compounds[14].In this study, microwave was employed as a heating method to facilitate hydrolysis of precursors, formation of the gel through crosslinking, as well as drying of the formed gels as it provides a great deal of energy with good homogeneity in a short exposure time.

Three different acids were used for catalyzing the preparation ($HClO_4$, HNO_3 and H_3PO_4) and a sample with no acid was also prepared as a reference for the measurements. The formed product was expected to be produced from the sol hydrolysis according to the following equations:

$$n\ Si(C_2H_5)_4 + 2n\ H_2O \rightarrow [\ Si\ O_x\ (OH)_y\ (C_2H_5)_z\ ]_n + 4n\ C_2H_5OH$$

Where $2x+y+z = 4$, i.e. spectrum of intermediate hydrolyzed species are generated. While Al species in aqueous solutions exist as $[Al(H_2O)_6]^{3+}$ which can be hydrolyzed as follows:

$$[Al(H_2O)_6]^{3+} + h\ H_2O \rightarrow [Al(OH)_h(H_2O)_{6-h}]^{(3-h)+} + h\ H_3O^+$$

Where (h) is the hydrolysis ratio. For Li species it may hydrolyzed as:

$$LiCl + H_2O \rightarrow LiOH + HCl$$

Condensation can start even before the complete hydrolysis, and may proceed between the various formed hydrolyzed species with different rates depending on the used catalyst.

TGA analysis were performed to investigate the effect of the catalyst type when microwave is used as a heating method[15].

Thermograms for samples dried at 120°C are shown in figure (2) where the weight loss starts as the temperature increase. As temperature reaches 250°C a sharp decrease in weight occurs where the catalyst free sample in curve(a) experiences a minimum loss of 74.1%.

The loss increases the oxidizing power of the acid increases. The loss of the H_3PO_4 catalyzed sample in curve (b) was 78.3% and that for the HNO_3 catalyzed sample in curve (c) was 80.1% while for the $HClO_4$ catalyzed sample in curve (d) is 85.9%. For H_3PO_4 catalyzed sample, another loss of 1.9% happens at a temperature of 450°C. The losses recorded below 250°C are due to the evaporation of the physically adsorbed water and alcohol. Losses at higher temperatures are due to the decomposition of the bounded organic components.

Different losses indicate different gel structure resulted from the different catalysts and mechanism. The samples dried in the used microwave oven

experience no weight loss up to 1000°C indicating that the microwave leads to a temperature above that of 450°C. Such high temperatures expel all the removable components..

Fig (3) shows the SEM of the samples prepared and dried using the microwaves. For the sample catalyzed by $HClO_4$ approximately spherical grains with a size range from 5-20 μm were obtained, while certain form of crystal structure was observed when examining the HNO_3 catalyzed sample. The H_3PO_4 catalyzed sample showed parallel lines which may be due to the differential stresses produced during the microwave drying. Partially sintered gains shown in the catalyst free sample may be due to he formation of a very fine powder which can be partially sintered during the microwave drying operation .

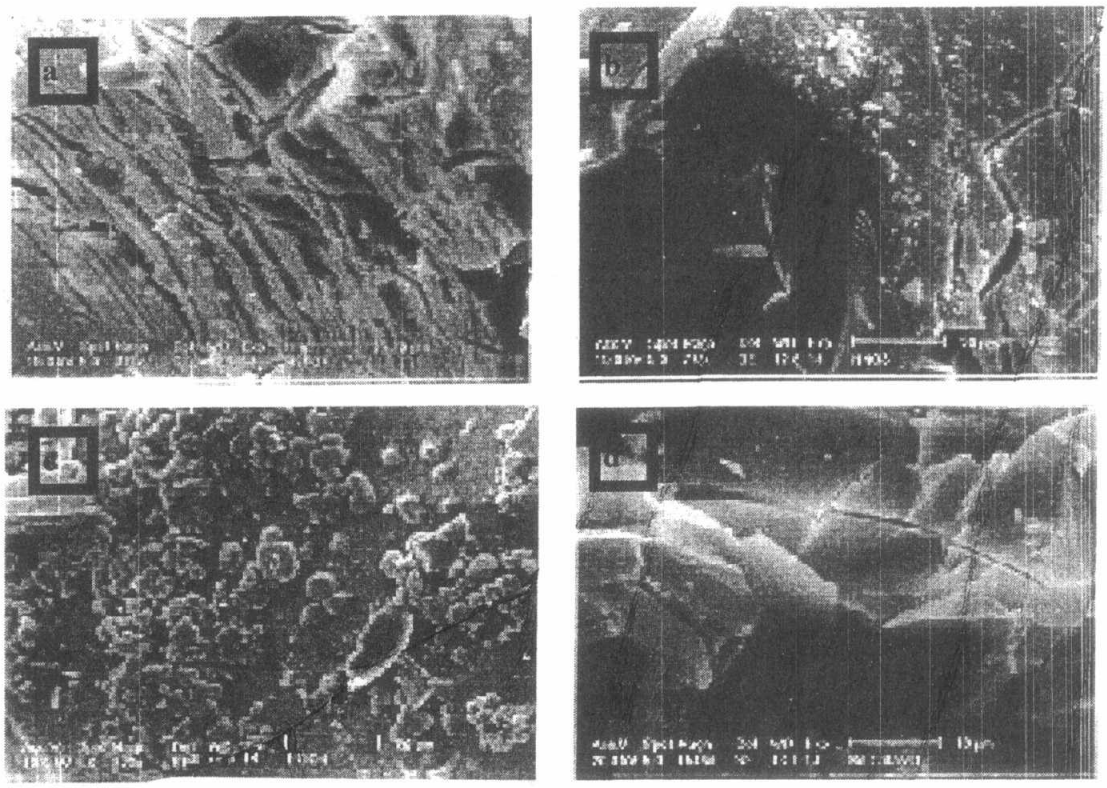
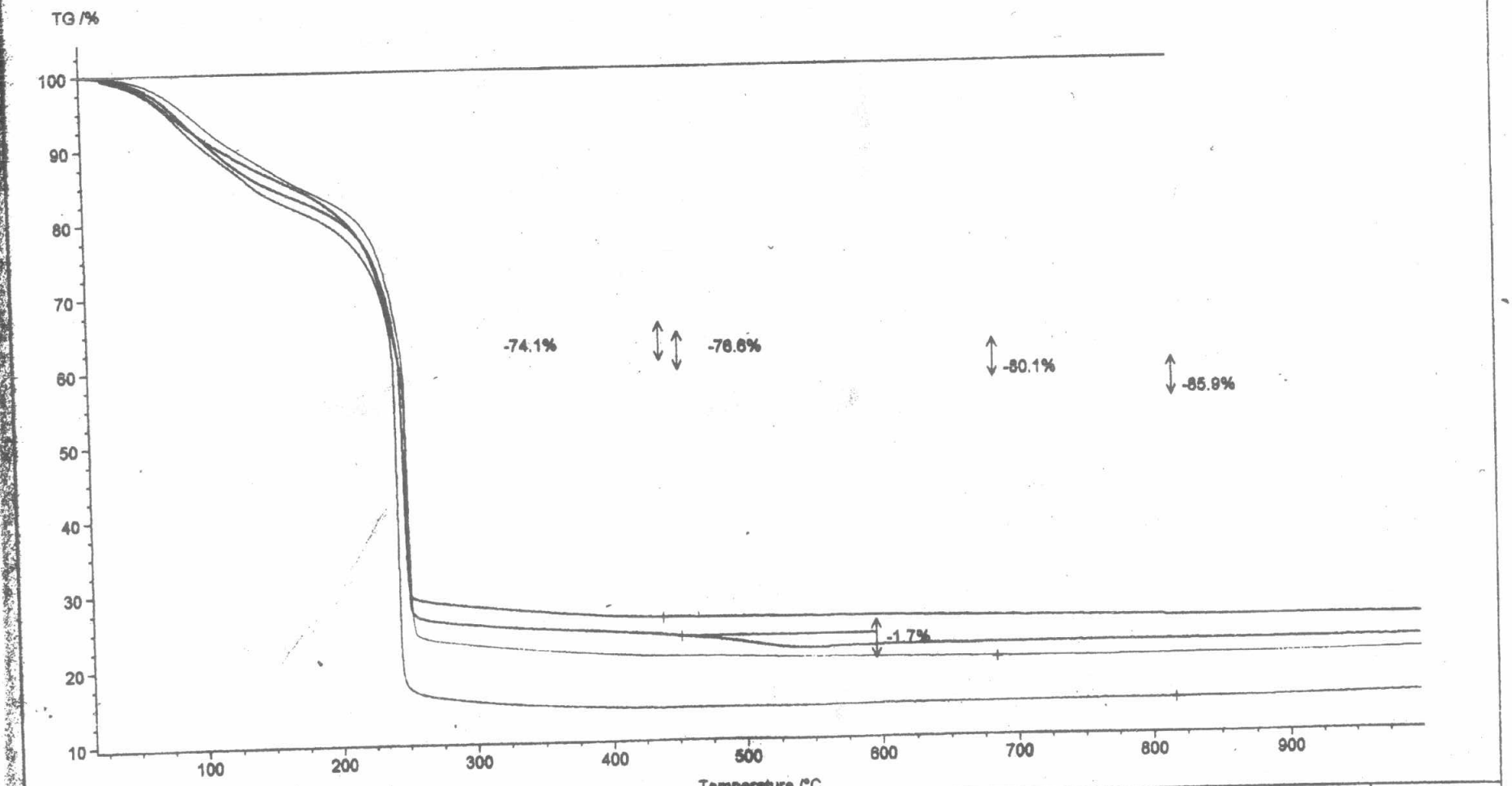


Figure (3) SEM of the prepared samples

a-H_3PO_4 b-HNO_3 c-$HClO_4$ d-no-catalyst

MTC Explosives



#	FILE	IDENTITY	SAMPLE	MASS/mg	DATE	SEGMENT	RANGE	CORR
1	HCLO4-MI	bon_g10.tgb	HClO4microwave	13.866	15.01.1998	1/ 1	20 °C/10.0/1000 °C	00t
2	NO_MIC	bon_g10.tgb	Ni-cata microwave	20.219	17.01.1998	1/ 1	20 °C/10.0/1000 °C	00t
3	H3PO4_MI	bon_g10.tgb	H3PO4-microwave	11.260	17.01.1998	1/ 1	20 °C/10.0/1000 °C	00t
4	HNO3-MIC	bon_g10.tgb	HNO3 microwave	20.843	15.01.1998	1/ 1	20 °C/10.0/1000 °C	00t

Figure (2) Termogram TGA of the samples dried at 120°c

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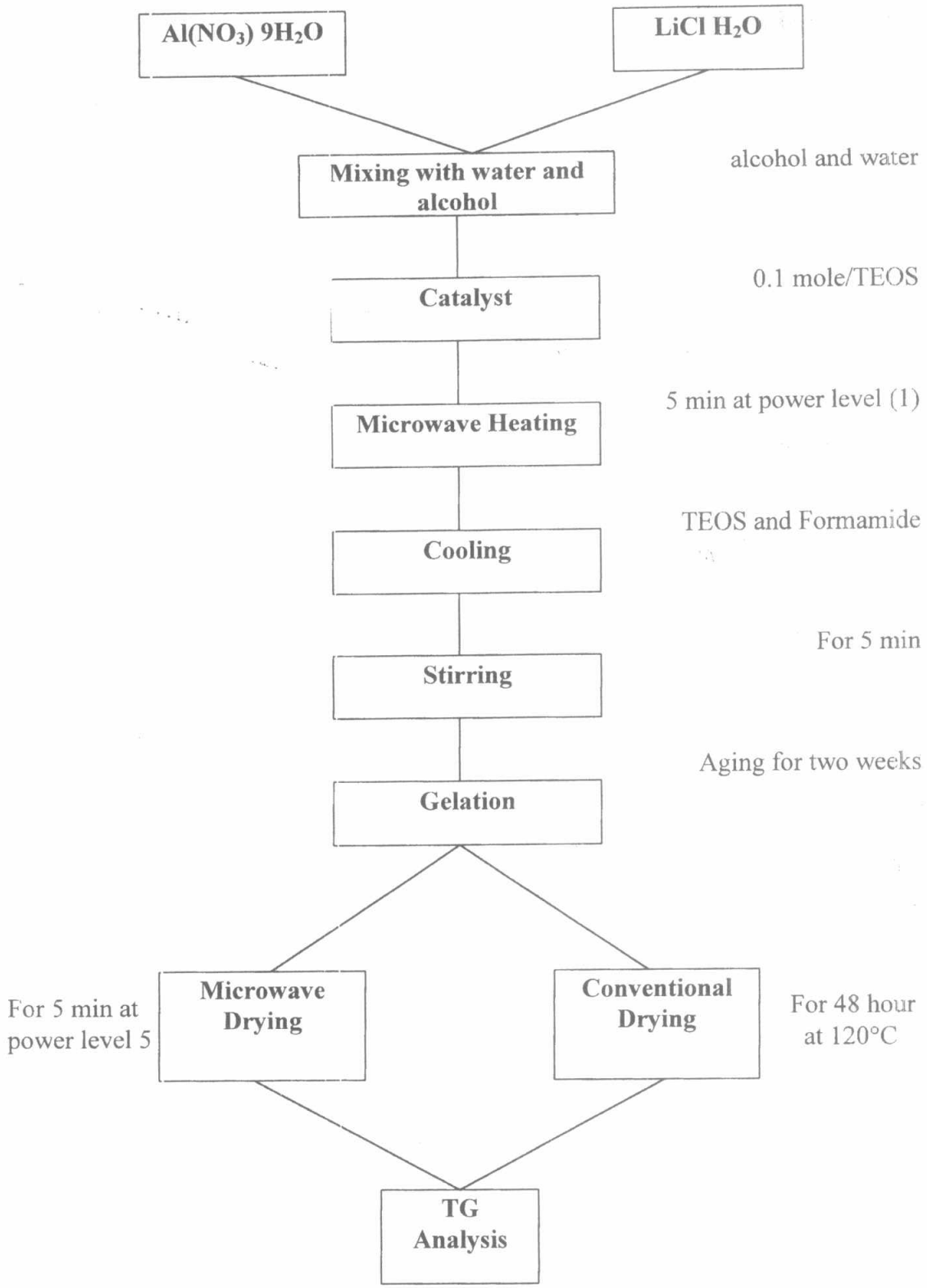

Figure (1) Scheme of preparation of LAS samples

Conclusion:

Dry LAS samples can be prepared within 5 minuets using a domestic microwave oven. Similar samples need about 48 hours at 120°C to remove all physically adsorbed and chemically bounded groups. Microwave heating reduces the processing time considerably and produces a crystalline structure even at this very small exposure time.

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