



# Transformation of chemically fine tuned zeolite A precursor into dense lithium aluminosilicates – A comprehensive phase evolution and sintering study

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## ABSTRACT

Beyond their conventional revelation as catalysts, zeolites are being perceived as more challenging materials for modern applications. Thermal recrystallization of zeolite precursors is an efficient method for the preparation of dense aluminosilicate ceramics. However, factors viz., nature of the precursor and the way of firing it etc., influence the product quality. The present report is a systematic and detailed account of a phase transformation of Li modified zeolite A precursor using powder X-ray diffraction (PXRD), thermogravimetry (TG), differential thermal analysis (DTA), scanning electron micrographs (SEM), atomic absorption spectroscopy (AAS), energy dispersive X-ray (EDX) and density measurement techniques. It involves an amorphisation followed by a recrystallization into lithium aluminosilicate (LAS). A comprehensive correlation of PXRD, TG/DTA, SEM, EDX and density data explains the complexity of high temperature phase transition (25–1200 °C). A qualitative phase analysis revealed the mediation of formation of LAS ceramic,  $\beta$ -spodumene by few satellite transitions of  $\text{SiO}_2$ .

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## 1. Introduction

Many advanced materials fulfilling the property and reliability requirements for emerging applications demand innovative routes of materials syntheses. Ceramic research, in this regard has come up with many alternative precursors and processes. In this context, silicate based ceramic preparation using zeolite precursors is unique in many aspects [1–4]. The meta-stability and the microporosity of this class of highly ordered aluminosilicates were seen as versatile and potential precursors than just as conventional catalysts. Possibilities such as better control over chemical homogeneity, low temperature workability and cost effectiveness due to large availability for bulk production are few key attractions of this route. Though this route was reported [5] as earlier as 1971, it is still in a progressively developing stage [6–17]. As of now, there are various reports found on the preparation of electronic ceramics viz., cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), mullite ( $\text{Al}_6\text{SiO}_{18}$ ) and  $\beta$ -spodumene ( $\text{LiAlSi}_2\text{O}_6$ ) using this route [18,19]. Through the conventional routes, the lithium aluminosilicate (LAS),  $\beta$ -spodumene was already known to be a highly successful commercial ceramic, for instance, in electronic industries as substrate materials. Nevertheless, its preparation using zeolite as precursor (zeolite route) is a subsequent development [20,21]. In this

route, it is possible to fine tune the zeolite precursor for the desired stoichiometry by efficient means such as ion exchanges followed by firing at high temperatures into dense ceramic. It is observed that the precursor stoichiometry and firing approach have strong influences on the property of the final dense phase [21]. Moreover, the chemical homogeneity in the precursor influences the product quality. In the conventional routes, due to the physical mixtures of individual components, chemical homogeneity is possible only at particle level. In contrast, in the zeolite route, as ions are being exchanged it is highly assured at as lower as in atomic level. Contrasting the conventional precursors, the phase transformation course on firing the chemically altered zeolite precursors is distinct due to the enhanced chemical homogeneity. Reports suggest that the phase transformation is considerably complex with various intermediate phases depending upon the nature of the precursor [4,5,21,22]. The phase purity and many other properties such as density of the ceramic essentially decide a candidature in respective applications. A correlated and comprehensive information about the course of the phase evolution and sintering in tandem is though important for a better synthesis control, is however not available in the literature.

In this way, the present article reports a systematic and comprehensive study on the phase transformation of zeolite A precursor into lithium aluminosilicate (LAS) ceramic,  $\beta$ -spodumene. Several meta-stable phases formed during the phase transformation between room temperature (RT) and 1200 °C have been

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identified and qualitatively analyzed using the standard data files. The powder X-ray diffraction (PXRD) patterns recorded for samples fired at different temperatures revealed the thermodynamics of different intermediate phases. To understand the state of the material on its course of sintering, thermogravimetric (TG) and differential thermal analysis (DTA) data, scanning electron micrographs (SEM), atomic absorption spectroscopy (AAS), energy dispersive X-ray spectra (EDX) and apparent densities for samples heated at various temperatures were obtained and successfully correlated. A comprehensive analysis using these data in conjunction with that of the PXRD provided valuable clue on the onset and the co-existence of different high temperature (HT) phases and their transformations.

## 2. Experimental

The chemical fine tuning of the precursor zeolite was carried out using conventional hydrothermal solution based ion exchange procedure widely used for post-synthesis zeolite modifications as following. About 30 g of as-synthesized form (Na-form) of zeolite A (from Zeolyst Corporation, UK with Si/Al ratio = 1:1) powder was suspended in about 300 ml of 1 M  $\text{NH}_4\text{NO}_3$  solution and ion exchange was carried out under constant stirring conditions for about 6 h at  $\sim 95^\circ\text{C}$ . This was repeated for three times to get the  $\text{NH}_4$ -form of zeolite A. Later, the filtered powder was dried at  $110^\circ\text{C}$  for  $\sim 12$  h. Similar ion exchange process was repeated on the dry  $\text{NH}_4$ -form of zeolite A with 1 M  $\text{LiNO}_3$  solution for three times. The complete procedure for multiple ion exchange processes have been explained elsewhere in detail [21,22]. The final dry powder, i.e., Li-form of zeolite A, labeled as LASA3 was used for the further heat treatment and other characterisations. To consolidate the free dry powder, a binder solution of 1 wt.% polyvinyl alcohol (PVA) was prepared as discussed below. About 10 g of PVA [ $(-\text{CH}_2\text{CH}(\text{OH})-)_n$  of molecular weight  $\sim 1,00,000$  Da] was mixed with 90 ml of boiled distilled water and was kept on flame for 20–30 min with continuous stirring so as to get a clear solution (10% wt./wt.). It was further diluted to 10 times and used as binding agent. The dry LASA3 powder was added with the PVA binder and mixed in an agate mortar followed by drying under IR lamp for about 2 h. The powder was then consolidated into uniform sized pellets with a diameter of  $\sim 20$  mm and a thickness of  $\sim 5$  mm each. Each pellet was made using equally weighing ( $\sim 0.75$  g each) powder of LASA3 pressed in an isostatic hydraulic press at a pressure of 5000 psi. These pellets were subjected to heat treatment in an open coiled programmable (Nebourtherm) furnace at air atmosphere. The furnace could hold a set temperature with a sensitivity of  $\pm 0.5^\circ\text{C}$ . The samples were heated at a heating rate of  $4^\circ\text{C}/\text{min}$  as per the program shown in Fig. 1. To ensure error free analysis, multiple sampling was ensured by studying a set of at least three pellets for each temperature point simultaneously ( $T_2$  as seen in Fig. 1). Several temperature points ( $T_2$ ) were chosen between room temperature (RT) and  $1200^\circ\text{C}$  with an interval of  $100^\circ\text{C}$ , viz., 100, 200, 300, 400...  $1200^\circ\text{C}$ . Each set of pellets were held at  $525^\circ\text{C}$  ( $T_1$ ) for about 60 min ( $t_2 - t_1$  as seen in Fig 1) to burn off the binder (PVA). Subsequently they were raised to their intended final temperature point,  $T_2$  and soaked for 6 h ( $t_4 - t_3$ ). The fired pellets were later cooled naturally to RT and crushed into fine powder in an agate mortar. The structural details due to the phase transitions at different temperatures were observed using PXRD patterns recorded in a RIGAKU DMAX III VC instrument equipped with a graphite crystal monochromator and NaI scintillation counter. Nickel filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) was used. A powder of standard Si was used as an internal standard for a portion of few samples for lattice parameters calculations and for other samples it was used as external standard. The  $2\theta$  values

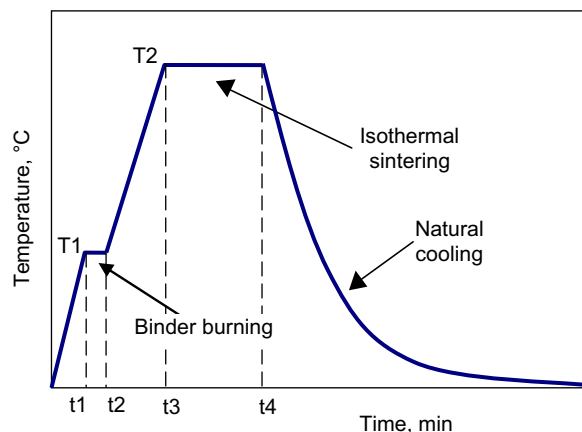


Fig. 1. Typical heating program for sintering of LASA3.

and interplanar 'd' spacings were corrected accordingly and refined using least square fitting. A qualitative phase analysis was carried out for the XRD patterns recorded at each temperature point ( $T_2$ ) to identify and estimate various intermediate phases. The reflections were indexed and compared with that of the different crystalline phases as available in the International Centre for Diffraction Data base (ICDD/JCPDS) [23].

Thermogravimetric analysis (TGA) was performed using about 35 mg of LASA3 powder using SETARAM TG DTA 92 instrument in air atmosphere at a heating rate of  $5^\circ\text{C}/\text{min}$ . The data was recorded for a range of temperature from  $\sim 25^\circ\text{C}$  (RT) to  $1000^\circ\text{C}$ . The derivative data (DTG) and differential thermal analysis (DTA) data were analyzed and plotted.

Scanning electron micrographs (SEM) were captured for the samples using LEO/Leica Cambridge, UK stereoscan 440 instrument. Energy dispersive X-ray spectra (EDX) were obtained using BRUKER EDS systems QUANTAX/200 attached with SD detector interfaced with the SEM instrument. EDX spectra were recorded for selected samples to understand the changes in the chemical composition of the materials due to heating. The elemental analysis was done using CHEMITO 201 atomic absorption spectrometer to understand the extent of ion exchanges.

The fired pellets after cooling (before crushing into powder for the XRD based phase evolution study), were weighed in a high precision single pan balance with accuracy up to  $10^{-4}$  g. The thickness and diameter of each pellet were measured (as an average of five different measurements at different places in the disc) by micrometer screw gauge. These data were used to calculate the apparent density. The comparison between the density before firing (green density) and of the sintered discs (sintered density) was considered as indices of the extent of sintering. The apparent densities of the samples were calculated as follows. Average thickness ( $t$ ) and the average diameter ( $d$ ) of the carefully lapped sintered discs of uniform thickness were measured and the volume ( $V$ ) was calculated considering the sample disc as a cylinder using the equation,

$$V = \pi r^2 t \quad (1)$$

where  $r$  is the radius of the disc ( $d/2 = r$ ). The weights of the discs ( $w$ ) were calculated on single pan balances to the precision up to  $10^{-4}$  g. The apparent densities of the samples were calculated using the relationship,

$$\text{Apparent density}(\rho_{\text{app}}) = \text{Volume}(V)/\text{Mass}(w) \quad (2)$$

The density changes at different temperature points during firing were plotted as function of temperature to understand the extent of sintering.

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