



Kinetic study of crystallisation of sol–gel derived calcia–alumina binary compounds



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ABSTRACT

In-situ High Temperature X-ray Diffraction (HTXRD) and Differential Scanning Calorimetric (DSC) studies were performed on a sol–gel derived binary compound of a calcia–alumina (C12A7) system consisting of calcium oxide (CaO) and aluminium oxide (Al₂O₃) in a ratio of 12:7 for in situ investigation into the phase transformations under progressively increasing thermal activation from room-temperature to 1200 °C. The crystallisation of amorphous samples formulated at room-temperature on magnesium oxide (MgO) single crystal (100) substrates was found to be complete on heat treatment at 1100 °C for 3 h. This observation was further supported by independent Fourier Transform Infrared (FTIR) and Raman Spectroscopies. Values of 348 kJ/mol and 375 kJ/mol were estimated from Kissinger plots for activation energies of crystallisation of CaO and Al₂O₃ constituents, respectively.

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1. Introduction

Transparent oxides are extensively used in a wide range of applications in electronic and optoelectronic systems including fully transparent high performance transistors, ultraviolet (UV) light emitting diodes (LED) [1], invisible circuits [2], flat-panel displays, solar cells [3] and energy conservation (smart windows) devices [4]. One promising transparent oxide that can be used as an insulating, semiconducting or metallic layer is the zeolite-like metal oxide compound 12CaO·7Al₂O₃ (C12A7). This novel oxide exhibits physically interesting properties by exploiting its high-density intrinsic defect nanostructure [5].

The crystal growth of C12A7 is similar to that of zeolite crystals, where the oxygen ions work as templates to grow the framework. Unlike zeolite crystals, these oxygen ions remain inside the crystal as free ions trapped inside nano-sized cages. In each unit cell the framework is composed of 116 atoms in the form of 12 Ca–O–Al cages, capable of taking up two O²⁻ ions into its structure. The cages have an entrance of 0.1 nm in diameter, which controls the elemental substitution within the cages. Only a limited number of ions meet the criteria to be substituted for the oxygen ions, inducing a wide range of exceptional characteristics into this oxide material [6–8]. C12A7 single nanoparticles have been synthesized

through different routes including solid-state reaction at high temperature [9] and self-propagating combustion at low temperature [10]. We have recently reported the synthesis of C12A7 thin films on magnesium oxide (MgO) single crystal (100) substrates using room temperature sol–gel technique [11]. The partial crystallisation of the C12A7 thin film was observed at 800 °C and the crystallisation was completed on heat treatment at 1100 °C for 3 h. UV–visible optical spectra showed two absorption peaks at 5.3 eV and 6.1 eV. The peak at 5.3 eV is believed to be associated with an O²⁻ – Cage Conduction Band type transition whereas the Framework Valence Band to Framework Conduction Band transition was found to be responsible for the peak at 6.1 eV [12]. This sol–gel route produces crystalline C12A7 nanoparticles loaded with O²⁻/OH⁻ ions through hydrolysis and condensation process of precursor materials. The mono-dispersed, stable solution formed undergoes a series of chemical reactions and phase transformations during hydrolysis, condensation and thermal treatment. In this present investigation, an attempt has been made to study the effect of the heating rate on crystallisation behaviour and the activation energy of structural relaxation and crystallisation has been determined. The peak temperature of crystallisation is known to depend strongly upon the heating rate [13].

This paper reports the results of in situ X-ray diffraction studies on the C12A7 samples as they were vacuum annealed at different rates by progressively increasing the temperature from 25 °C to 1200 °C. Differential scanning calorimetric (DSC) studies were performed to investigate the crystallisation behaviour. Further evidence for crystallisation of sol–gel synthesised C12A7 materials

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was obtained from FTIR and Raman spectroscopies. A range of chemical reactions and phase transformations was identified through these structural and analytical characterisations to be associated with sol–gel synthesis of C12A7, building on our previous work in this field of study [11].

2. Experimental

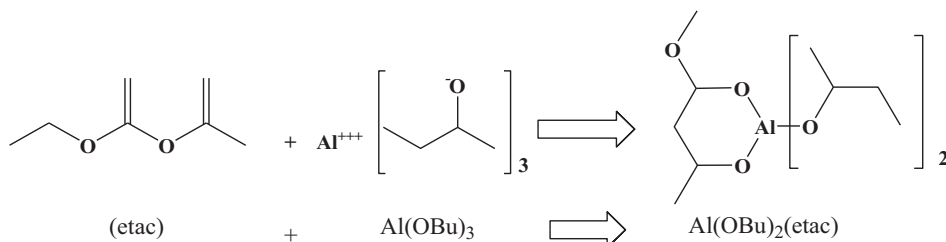
The method consists of the preparation of binary compound of a calcia-alumina (C12A7) from appropriate chemicals and spectroscopic studies for phase changes.

2.1. Materials

Aluminium sec-butoxide ($\text{Al}[\text{OCH}(\text{CH}_3)_2\text{C}_2\text{H}_5]_3$) known as $\text{Al}(\text{OBU})_3$ with purity of 99.99%, ethyl acetoacetate ($\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$) known as Etac with purity of $\geq 90.0\%$, calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) with purity of $\geq 90.0\%$, hydrochloric acid 1M (HCl) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) with purity of $\geq 98.0\%$, all chemicals were purchased from Sigma Aldrich Chemicals Ltd., UK.

2.2. Sol–gel synthesis of C12A7

C12A7 sol was synthesized through hydrolysis of two separate solutions. Aluminium oxide hydroxide (AIOOH) sol was prepared using aluminium sec-butoxide $\text{Al}(\text{OBU})_3$ as the precursor. In order to avoid precipitation this precursor was modified using ethyl acetoacetate (Etac), forming $\text{Al}(\text{OBU})_3$ that is hydrolytically unstable and its hydrolysis leads to immediate precipitation. However, the modification of $\text{Al}(\text{OBU})_3$ using ethyl acetoacetate (Etac) mediates the hydrolysis of Al^{3+} ions, through substitution of monodentate butoxy ligands of $\text{Al}(\text{OBU})_3$ with Etac groups. Etac groups will be bonded to Al atoms in an enolic form [14].



$\text{Al}(\text{OBU})_3$ was mixed with Etac with a molar ratio of $\text{Al}(\text{OBU})_2$: Etac = 1:1. The mixture was magnetically stirred for 30 min followed by 1 h of ultrasonic mixing in an Ultrawave U50 Bath for 1 h in order to achieve the formation of a stable transparent C12A7 solution. An $\text{Al}(\text{OBU})_2$ (Etac) complexes was formed through this stage. This new precursor was diluted with ethanol ($\text{Al}(\text{OBU})_2$: ethanol = 1:4) prior to hydrolysis. In the final step, distilled water was diluted with ethanol followed by pH regulation using hydrogen chloride (HCl) acid and ($\text{Al}(\text{OBU})_2$: H_2O : HCl = 1:3:0.15). Diluted distilled water was then added to the $\text{Al}(\text{OBU})_2$ (Etac) solution initiating the hydrolysis process. The hydrolysis was performed under vigorous stirring using an ultrasonic bath at 1000 Hz, followed by gentle stirring (~ 400 rpm) at room temperature for 24 h using a RCT basic safety control IKAMA magnetic stirrer. During hydrolysis of the modified $\text{Al}(\text{OBU})_2$ (Etac) compound, Etac groups will be separated from the compound in both enolic and ketonic forms. Following the separation of butoxy ligands, AlO bonding will be exposed to OH bonding of water, resulting in the formation of boehmite ($(\gamma\text{-AlO}(\text{OH}))$). The reaction at this water content may be derived as:



The acid concentration used in the synthesis of AIOOH particles was chosen at molar ratio of $\text{Al}(\text{OBU})_3$: HCl = 1:0.15, thereby reducing the pH of the solution from 10.4 to 8 [15,16], well below the isoelectric point of boehmite particles. Such acid regulation will reduce the chance of agglomeration due to Columbic interactions between particles [17,18]. The final product was AIOOH molecules dissolved in ethanol. A second solution was prepared using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in ethanol. Additional water was added to the solution ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$: H_2O = 3:4) to initiate partial hydrolysis. Addition of water expels some salt ions to form HNO_3 , decreasing the pH of the solution to 4 [6]. The dispersion of calcium nitrate in the solvent was facilitated using an ultrasonic bath (1000 Hz) followed by 24 h of magnetic stirring (400 r.p.m). The solution formed required no further acid addition since HNO_3 was formed within the solution.

The sol–gel process starts with a homogenous solution of AIOOH and $\text{Ca}(\text{NO}_3)_2$ in ethanol solvent with the concentrations meeting the nominal composition of C12A7 compound. The AIOOH and $\text{Ca}(\text{NO}_3)_2$ solutions were mixed allowing the formation of a homogenous C12A7 amorphous solution. C12A7 nanoparticles were prepared by dispensing a thin layer of sol in a petri dish followed by a 72 h drying process at room temperature. During drying, evaporation of ethanol progressively facilitates the formation of an amorphous phase from the solution. Continued drying of the sol and evaporation of the solvent promotes the inorganic precursors and organic additives into the desired structure. The powders were then subjected to a heat treatment at ambient atmosphere with the annealing temperature set to 1100 °C for the duration of 3 h. Thermal treatment of the dried gel at 1100 °C will lock in the nano-caged structure of C12A7 and develops covalent bonds of Ca–O–Al to form the framework. The crystalline C12A7 formed along with amorphous C12A7 dried gels were used for various characterizations.

2.3. Characterisation

High Temperature X-ray Diffraction (HTXRD) was performed at variable temperature using a D5000 X-ray diffractometer equipped with an Anton Paar HTK-16 vacuum furnace using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). An Anton Parr TCU 2000 temperature control unit provided direct temperature control. The detector was a Panalytical X'Celerator solid-state detector, which scans continuously. Samples were placed on a pre-stressed platinum strip. Experiments were performed from room temperature up to 1200 °C with a heating rate of 10 °C/min, in the 5°–65° 2 θ domain. The dried C12A7 gel was placed in a small crucible and fitted inside the STA1500 (Thorn Scientific, UK) differential scanning calorimeter (DSC) and exposed to heat treatment at various rates over a programmed temperature range from 25 °C to 1200 °C.

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, UK) in conjunction with an MTEC Photoacoustic Spectrum (PAS) cell. Spectra were obtained in

the mid infrared region (4000–400 cm^{-1}) at 4 cm^{-1} resolution and averaging of 256 scans on two different samples; one with amorphous C12A7 dried gel and the other with crystallized C12A7 powder.

Raman Spectroscopy was carried out using a Nicolet Almega XR dispersive Raman spectrophotometer (Thermo Fisher Scientific, Madison Wisconsin, USA), equipped with 532 nm and 785 nm lasers on two different samples; one with amorphous C12A7 dried gel and the other with crystallized C12A7 powder. All the spectra were collected in the range of 400–4000 cm^{-1} using a 10X objective and over an average of 256 scans, with 1 s exposure time at low resolution.

3. Results and discussions

3.1. HTXRD and DSC

Fig. 1 shows a sequence of data collected from the HTXRD performed on amorphous C12A7 dried gel in the temperature range of 25–1200 °C. The phase transformations at different stages of thermal treatment are depicted in Fig. 2 as DSC patterns at three different heating rates of 5 °C/min, 10 °C/min and 20 °C/min from room temperature to 1200 °C. During the sol–gel process, two distinct compounds, calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and aluminium oxide hydroxide (AIOOH) have been formed at room temperature. $\text{Ca}(\text{NO}_3)_2$ is a metallic salt and exists as a cubic crystalline phase in primitive cubic space group P213 at room temperature. This structure is depicted in Fig. 1 with the diffraction pattern at 100 °C fitting the one for $\text{Ca}(\text{NO}_3)_2$ collected from International Centre for Diffraction Database. This pattern remains strictly identical to the one for $\text{Ca}(\text{NO}_3)_2$ up to 500 °C. As observed in the DSC pattern, the tetrahydrate molecule attached to $\text{Ca}(\text{NO}_3)_2$

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