



Crystallization pathway of sol–gel derived zinc-doped mullite precursors



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ABSTRACT

Zinc doped mullite precursors were sol–gel prepared in order to study the Zn influence on crystallization pathways of the spinels first formed at about 920–970 °C. Precursors were calcined at 700 °C and thermally treated at 1000–1300 °C and thereafter characterized (DTA/TG, PXRD, Rietveld refinement). Thermal treatment of precursors at 1000 °C initiates segregation of ZnAl₂O₄ from first formed Zn-rich γ -alumina metastable solid solution. Remaining spinel reacts with amorphous silica yielding mullite; thereby further enriching γ -alumina on Zn.

Thermal treatment affects Zn-doped γ -alumina yielding crystallite size 11 ± 3 and 28 ± 4 nm at 1000 and 1300 °C, respectively. Parameter of inversion for ZnAl₂O₄, δ , increased from 0.05 to 0.20 upon heating from 1000 to 1300 °C.

SEM EDS analysis show the bodies sintered at 1600 °C reveal zinc deficiency due to Zn volatile nature. Electron microscopy (TEM, SEM) of sintered compacts exhibited microstructure with lower porosity having both elongated and equiaxial grains.

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1. Introduction

Mullite is a solid solution of Al₂O₃ and SiO₂ and may be represented by general formula Al₂^{VI}[Al_{2+2x}Si_{2-2x}]^{IV}O_{10-x}; x ranging between 0.18 and 0.88. The most frequent compositions of mullite are those with $x=0.25$ designated as 3/2 mullite (3Al₂O₃·2SiO₂) and $x=0.40$ designated as 2/1 mullite (2Al₂O₃·SiO₂), respectively. Unique combination of mullite properties such as: high melting point, good electrical resistance, good mechanical strength, low thermal expansion coefficient, high strength and high creep resistance at both low and high temperatures, low electric conductivity and low dielectric constant, as well as good chemical and thermal stability [1–5] display a wide range of mullite applications in structural, chemical, optical, and electrical industries.

Although mullite has been prepared using numerous different methods, during the last few years a sol–gel synthesized precursors have been widely employed for the processing of mullite. Sol–gel method provides a good option for the production of homogenous

materials as it allows uniform distribution of reactants before the gel formation takes place [6]. Additionally, a good stoichiometric control and production of ultrafine particles with narrow size distribution is achieved at comparatively low temperatures [7,8].

There is a general agreement the mixing scale in mullite sol–gel precursors actually controls the phase transformation sequence, the temperature of mullite formation as well as the properties of sintered bodies [9]. Gels obtained by a sol–gel procedure can be classified according to their homogeneity as: (i) monophasic gels, with molecular homogeneity and direct mullite crystallization from an amorphous phase at ~980 °C, and (ii) diphasic gels, inhomogeneous at molecular level, characterized by spinel phase crystallization at ~980 °C and mullite formation at about 1250 °C. Diphasic gels prepared with tetraethoxysilane (TEOS) and aluminium nitrate nonahydrate (ANN) in water environment are noncrystalline up to about 980 °C and mullite formation is preceded by the formation of a weak crystalline transition alumina with spinel structure, which later reacts with the amorphous silica forming mullite. The transition spinel phase has a poorly defined X-ray diffraction pattern with broad peaks very similar to those of γ -alumina. Such peak properties make the identification of spinel phase either as γ -alumina or as γ -alumina and silica solid solution (Al–Si spinel [10]) very difficult.

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γ - Al_2O_3 is traditionally considered to have a spinel structure. The spinels, usually denoted AB_2O_4 , have a cubic unit cell (space group $Fd\bar{3}m$) with 32 oxygen atoms situated in the Wyckoff 32e positions. The cations A and B are located in the 8a (tetrahedral) and 16d (octahedral) Wyckoff sites, respectively. There are also unoccupied tetrahedral (8b and 48f) and octahedral (16c) sites. The cation:anion ratio is 3:4 in the ideal spinel structure. To satisfy γ - Al_2O_3 stoichiometry, the Al atomic positions are not fully occupied. Vacancies are distributed over both the tetrahedral and octahedral sites 8a and 16d (spinel sites); however, the work of Zhou and Snyder [11] showed it is important to consider the location of Al atoms also in (lightly occupied) “non-spinel” positions. Recent work of Paglia et al. [12,13] offer strong evidence for the cation occupancy at “non-spinel” sites (vacant sites in the ideal spinel structure), namely the *c*-symmetry positions. The precise distribution of the Al atoms (and the vacancies) in γ - Al_2O_3 is controversial and seems to depend on the preparation conditions. Further complications arose as both cubic and its tetragonal distortion structures were found in equally prepared precursors, for example in the case of boehmite derived γ - Al_2O_3 [14]. In contrast, γ - Al_2O_3 derived from amorphous precursors (e.g., from a sol–gel synthesis) appear to preferentially adopt the cubic structure [11].

The Si incorporation into the intermediate γ - Al_2O_3 has been a point of controversy in many studies. Different mechanisms responsible for the thermal stabilization of the metastable alumina phases upon Si incorporation have been proposed in literature. The results obtained by Gerardin et al. [10] suggest the intermixing degree of alumina and silica in the amorphous state is responsible for the crystallization path and thereof, the possibility of Al–Si spinel formation, silica segregation and mullitization.

Gani and McPherson [15], studying the structure of Al_2O_3 – SiO_2 sub-micron powders, observed the restrained transformation of the metastable γ - Al_2O_3 to the stable α - Al_2O_3 . The authors suggest the incorporation of Si atoms at Al sites of the initial γ - Al_2O_3 structure may increase the activation energy of the γ - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_3 transformation process. This was based on the high energy required to break the Si–O bonds in the distorted face centred cubic packing of oxygen ions of γ - Al_2O_3 phase. The formation of the metastable γ -(Al,Si) $_2\text{O}_3$ phase can only be expected during the non-equilibrium processing where the decomposition is kinetically hindered. On the base of density functional theory Nahif et al. [16] suggested the Si-induced changes in stability of this metastable solid solution may be based on the changes in electronic structure. Namely, as the Si content is increased, stiff silicon–oxygen bonds are formed giving rise to the observed γ -phase stabilization. On the contrary, the same authors [17] also observed the presence of SiO_2 at the grain boundaries. SiO_2 residing at the grain boundaries may impede the mass transport and hence the crystalline growth, which appears to be the cause of the reported stabilization.

The incorporation of nano-sized second-phase ceramic particles into a ceramic matrix may lead to significant improvements in the material properties. Different transition metal oxides have been shown to possess favourable mineralizing effect on the formation of mullite ceramics prepared from the sol–gel precursors. Mazza et al. [18] found fine dispersed Me-aluminate (Me = Cu, Ni, Co) reacted with pre-formed γ - Al_2O_3 nanoparticles and promoted the formation of mullite without being incorporated in the mullite structure. Among the most interesting materials for the purpose, zinc aluminate ZnAl_2O_4 (gahnite), is widely known as a ceramic and catalytic material [19–21]. Gahnite crystallizes in the spinel structure type belonging to $Fd\bar{3}m$ space group, and offers many advantages adding up to the final ceramic properties such as high thermal and chemical stability, hydrophobic behavior, high mechanical resistance and low sintering temperature [22].

The goal of the present investigation is to study the effect of in situ formed ZnAl_2O_4 (gahnite) on the crystallization pathway

of diphasic gels with 3/2 mullite composition in which 0, 3, 6 and 9 at.% of Zn^{2+} was substituted on account of Al^{3+} . Crystallization pathway of two compositionally different spinel phases (γ - Al_2O_3 or Zn doped γ - Al_2O_3 and gahnite), as well as mullite, were studied by differential thermal analysis. Detailed structural characterization have been performed by powder X-ray diffraction (PXRD) in order to correlate Zn content and thermal treatment temperature to phase composition of ceramics in the temperature range 1000–1300 °C. Rietveld structure refinement enabled determination of the lattice parameters, the quantity of crystalline phases, the crystallite size of spinel solid solutions, as well as the inversion parameter of ZnAl_2O_4 lattice. Having in mind the behavior of gels at lower temperatures highly correlates with properties at higher temperature, study of the system in the temperature range 1000–1300 °C is of fundamental importance.

2. Experimental

2.1. Gel preparations

Gels were prepared using sol–gel technique. Tetraethoxysilane (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$, 98% Merck), aluminium nitrate nonahydrate (AlNN, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5% Kemika), zinc nitrate hexahydrate (ZnNH , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98% Acros) and ethyl alcohol (EtOH, $\text{C}_2\text{H}_6\text{O}$, 96% Kemika) were used. Diphasic gel with 3:2 mullite nominal composition ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as well as gels where 3, 6 and 9 atomic% of Zn^{2+} was introduced on account of Al^{3+} (Zn-doped 3:2 mullite) (denoted as ZM0, ZM3, ZM6 and ZM9, respectively) were prepared by dissolving AlNN and ZnNH in water while TEOS in EtOH separately. Overall molar ratio of reactants was $\text{TEOS}:\text{AlNN}:\text{ZnNH}:\text{EtOH}:\text{H}_2\text{O} = 1:3-3y/100:3y/100:10:30$ ($y = 0, 3, 6, 9$) (nitrate:solvents = $\text{TEOS}:\text{solvents} = 1:10$). Thereafter the TEOS solution was added dropwise to the nitrates solution under vigorous stirring. Homogeneous mixture was further stirred under reflux at 60 °C for 8 days. Prepared gels were dried at 120 °C for 72 h, calcined at 700 °C for 2 h, then crushed and ground to fine powder, sized to <63 μm and stored in a desiccator.

2.2. Methods

Differential thermal analysis (DTA) was performed on Netzsch STA 409 Simultaneous Thermal Analyzer. Approximately 50 mg of powder was placed in Pt pans and heated at the rate of 10 °C min^{-1} with synthetic air purge gas flow of 30 mL min^{-1} and N_2 protective gas flow of 150 mL min^{-1} ; α - Al_2O_3 was used as a reference.

Calcined powders were heat-treated to temperatures 1000 to 1300 °C and 1600 °C for 2 h in a laboratory furnace in static air and then subjected to XRD analysis.

The XRD analysis was performed on Shimadzu XRD6000 diffractometer with $\text{CuK}\alpha$ radiation. Crystal structure refinement and size-strain analysis were performed by the Rietveld method with the X'Pert HighScore Plus program [23,24], using a pseudo-Voigt profile function and the polynomial background model. Isotropic vibration modes were assumed for all atoms. For the purpose of size-strain analysis, LaB_6 standard was used for instrumental diffraction line broadening. XRD patterns were scanned from 10 to 120° 2θ with step of 0.02° 2θ , and fixed counting time of 4.5 s per step. For the purpose of unit cell parameters of spinels (γ - Al_2O_3 and gahnite) 10 wt% of silicon (99.999%, Aldrich, Germany) was added as internal standard. Whole-powder-pattern decomposition method was used for data evaluation.

Sintering of prepared raw bodies was performed by heat-treatment at 1600 °C for 2 h. Polished and thermally etched surfaces (1550 °C, 45 min) of sintered material was analyzed by scanning electron microscopy (SEM) JEOL model 7000F equipped by

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