CRYSTALLIZATION BEHAVIOR OF HYBRID PREMULLITE POWDERS SYNTHESIZED BY SOL-GEL METHOD

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Abstract: Hybrid premullite powders of stoichiometric composition (Al:Si = 3:1) were prepared by sol-gel process, making use of $Al(NO_3)_3 \cdot 9H_2O$ and $Si(OC_2H_5)_4$ (TEOS) as precursors. The quantity of water in the gelling system was systematically modified to influence the mechanism of hydrolysis and condensation reactions, either by adding water, or by previous drying of $Al(NO_3)_3 \cdot 9H_2O$. The crystallization behavior of premullite powders was investigated by combined differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) and X-ray diffraction (XRD). It was found that quantity of water present during the synthesis of the premullite powders significantly influences their subsequent crystallization behavior, and accordingly their structure. This is the result of the tendency of aluminum to form complex polymeric structures in aqueous solutions. Therefore it is possible to control the crystallization behavior of the premullite sol-gel powders through quantity of added water.

Key words: mullite, sol-gel, crystallization

1. INTRODUCTION

Mullite is a very important mineral in ceramics industry, as it is the main component in the final ceramic products sintered from the clay. Its low creep, low linear thermal expansion coefficient and good chemical stability at high temperatures make it an especially interesting high-temperature construction material. In order to achieve those properties, the ceramic must be of almost theoretical density and very pure and homogeneous [1]. Therefore sol-gel procedure is used to obtain very homogenous pre-mullite powders, which crystallize into mullite at relatively low temperatures of ~1000°C.

In sol-gel procedure TEOS ($Si(OC_2H_5)_4$) is hydrolyzed with the aid of acid or base catalysts and then condenses and gels to form an uninterrupted silicate network, as schematically shown in Figure 1 [2]. The duration of hydrolysis and condensation processes is decisive for good homogeneity of the premullite powders. Too short (< 2 days) or too long (> 30 days) aging process can lead to inhomogeneities [3], so the optimum aging time is taken to be 7 days.

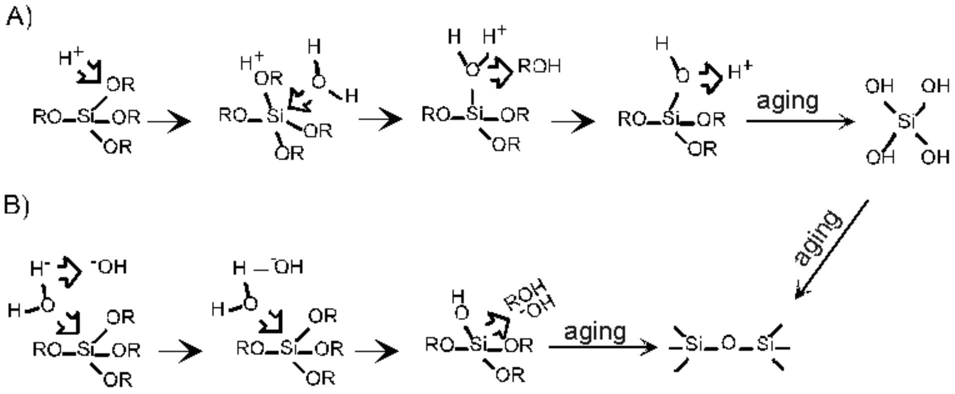

Figure 1 – Hydrolysis and condensation of TEOS with water in (A) acid and (B) base conditions

The premullite powders can be divided by their homogeneity and crystallization behavior into monophasic and diphasic systems [4]. The monophasic systems are homogeneous on the molecular level, so that mullite crystallizes straight from the amorphous powders at ~980°C. The diphasic systems, on the other hand, possess macroscopic homogeneity (1-100 nm), and mullite crystallizes at temperatures higher than 1200°C. Premullite powders that are a mixture of these two levels of homogeneity are called hybrid premullite powders. In the hybrid powders the monophasic part crystallizes at lower temperatures, thus creating seeds for subsequent crystallization of the diphasic part. This behavior is advantageous, since it allows an improved control of crystallization process, which results in more uniform crystal grains, and a final ceramic product that has a dense and homogeneous microstructure. Since the simple mechanical mixing of the powders is not sufficient for this purpose, the best approach is to synthesize premullite powders that are already hybrid. The aim of this work was to study the influence of the quantity of water added for the hydrolysis of TEOS on the structure and final crystallization behavior of premullite powders.

2. EXPERIMENTAL

Premullite powders were synthesized from TEOS and aluminum nitrate nonahidrate ($Al(NO_3)_3{\cdot}9H_2O$) as precursors, in an acid medium, with absolute ethanol as solvent. The of water was varied in two ways: aluminum nitrate was dried for 72 hours at 40°C, 60°C or 80°C, in order to remove some of its crystal water, and then dissolved in ethanol; conversely, extra water was added in molar ratios of 0, 1, 3, 6 and 25 to aluminum nitrate. After gelling and aging, the gel was dried for 72 hours in a laboratory oven at 110°C, and the resulting premullite powder ground in agate mortar and kept in dry atmosphere to prevent the degrading influence of ambient moisture. Crystallization behavior and consequently the structure of these premullite powders were investigated by combined differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) on a Netzsch thermoanalyzer STA 409. Samples were heated from room temperature to 1350°C at a heating rate of 10 $Kmin^{-1}$ in a synthetic air flow. The phase composition of the powders after isothermal annealing at given temperatures for 2 hours was investigated by X-ray diffraction spectroscopy (XRD) on Phillips PW 1010 instrument making use of CuKα radiation.

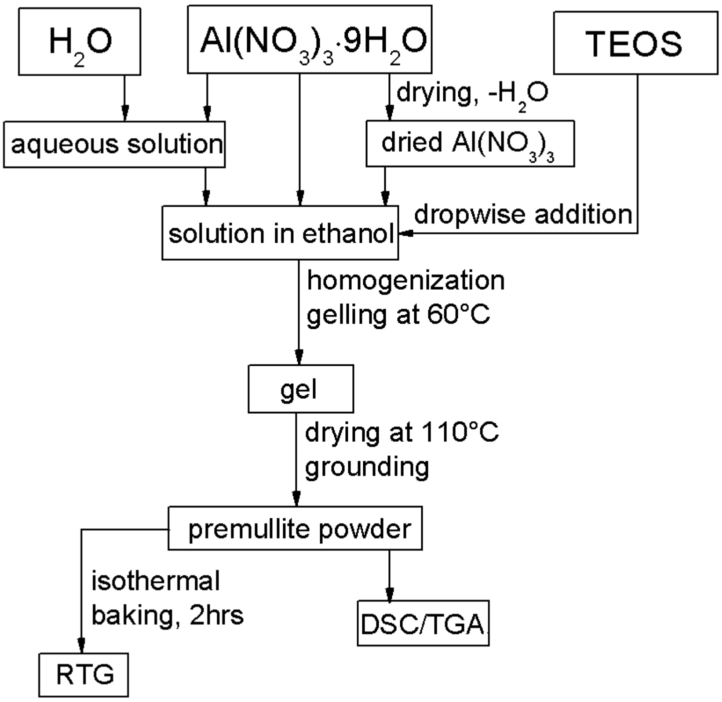

Figure 2 – Scheme of the synthesis and characterization of premullite powders

3. DISCUSSION OF RESULTS

Influence of drying

Premullite powders prepared from previously dried $Al(NO_3)_3·9H_2O$ show a significant shift of exothermal peak characteristic for mullite crystallization to higher temperatures when compared to the sample prepared without drying (Fig 3). While samples fired at 600°C show the identical behavior regardless of the drying temperature (Fig. 3B), influence of the drying temperature is clearly visible for those kept at 110°C (Fig. 3A). Doubling of the peak as seen in samples synthesized from $Al(NO_3)_3·9H_2O$ dried at 40°C and 60°C could be caused by crystallization of mullite with two different compositions, but XRD could not confirm this supposition, and showed only rapid crystallization of mullite from the amorphous phase, characteristic of monophase powders. Further research of this phenomenon is in process. TGA results show that the weight loss decreases with the drying temperature (40°C – 58.31%, 60°C – 53.39°C; 80°C – 39.70°C) since there is less water firmly tied to aluminum ions which, along with products of nitrate decomposition, is the principal component of gasses liberated during the calcinations of premullite powders.

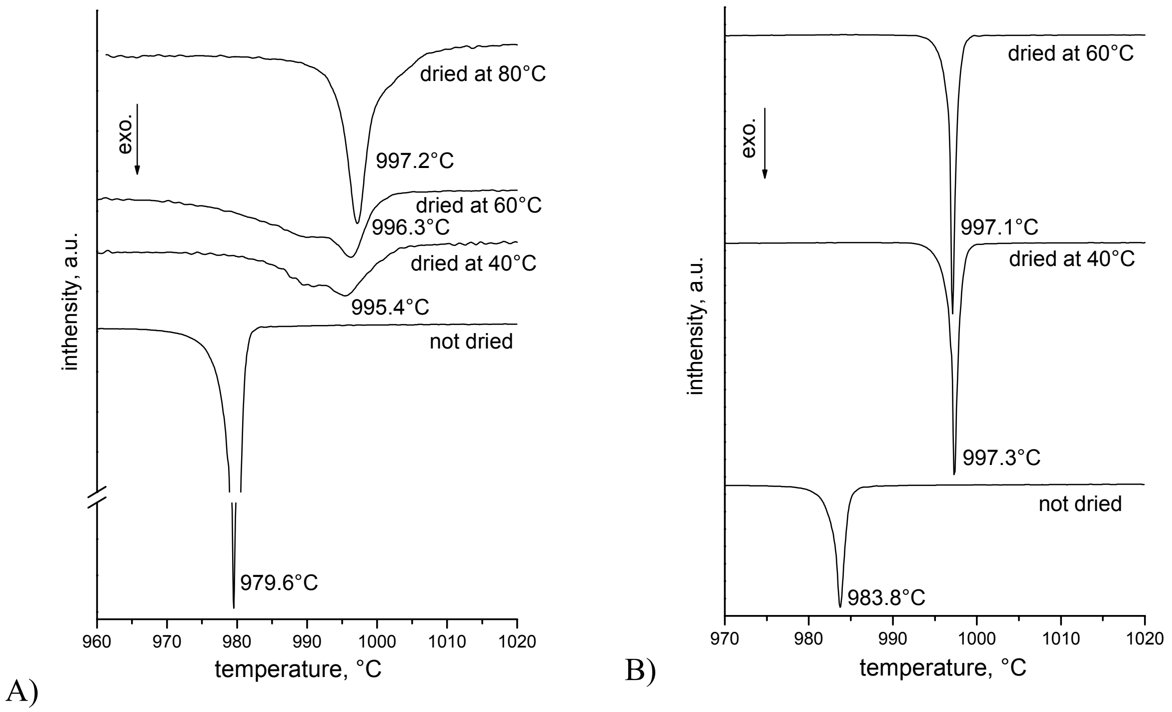

Figure 3 – DSC peaks of samples prepared with $Al(NO_3)_3 \cdot 9H_2O$ dried at given temperatures: A) samples dried at 110°C, B) samples annealed at 600°C/2hrs

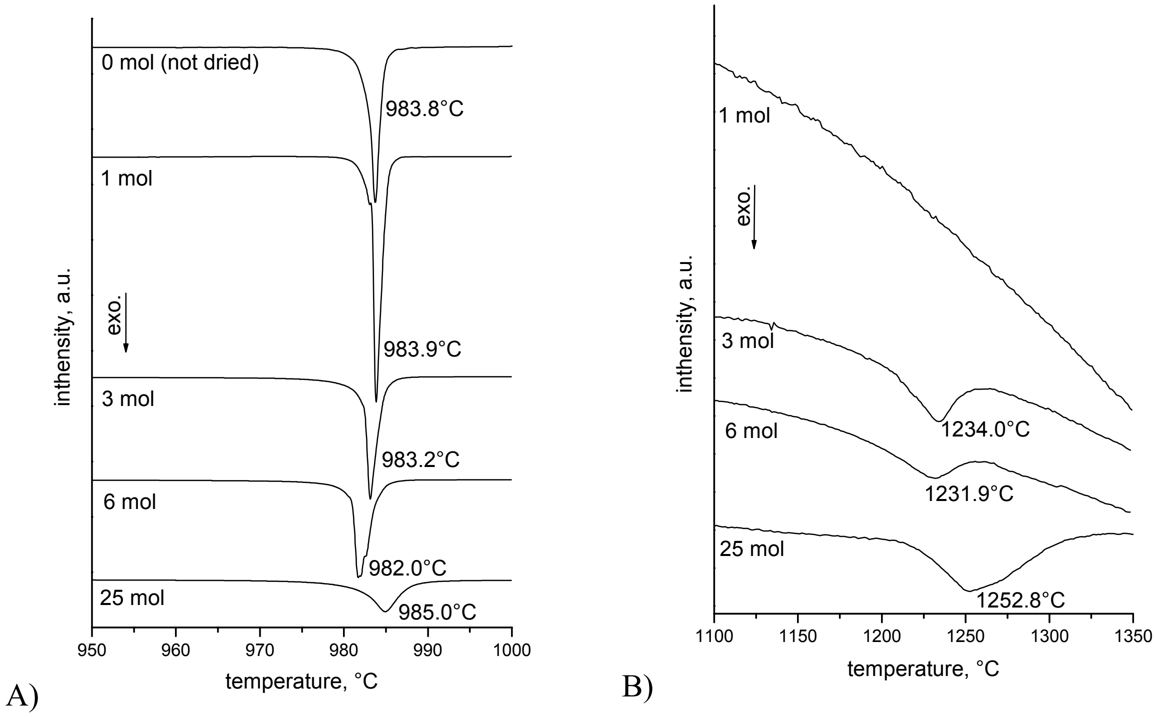

Figure 4 – DSC peaks of samples prepared with given amount of water added per 1 mole of $Al(NO_3)_3 \cdot 9H_2O$ and annealed at 600°C/2hrs: A) the first exothermal peak at ~980°C, B) the second exothermal peak at >1200°C

Influence of addition of water

Figure 4. shows exothermal peaks of samples prepared by adding water to $Al(NO_3)_3{\cdot}9H_2O$. Samples without added water and with 1:1 molar ratio of water to Al have only one peak at ~980°C, and XRD confirms that only mullite crystallizes at that temperature. DSC curves of other premullite powders synthesized by adding water to $Al(NO_3)_3{\cdot}9H_2O$ also show a second exothermal peak at 1230-1250°C, characteristic for crystallization of mullite from diphasic compositions [5,6]. X-ray spectra (Fig. 5) confirm that because of the lower homogeneity of the powders crystallization proceeds in two steps. First to crystallize at ~980°C is Al-Si spinel with varying content of SiO_2 (from 6% to 23%), which then reacts with the remaining amorphous SiO_2 to form mullite at temperatures above 1200°C.

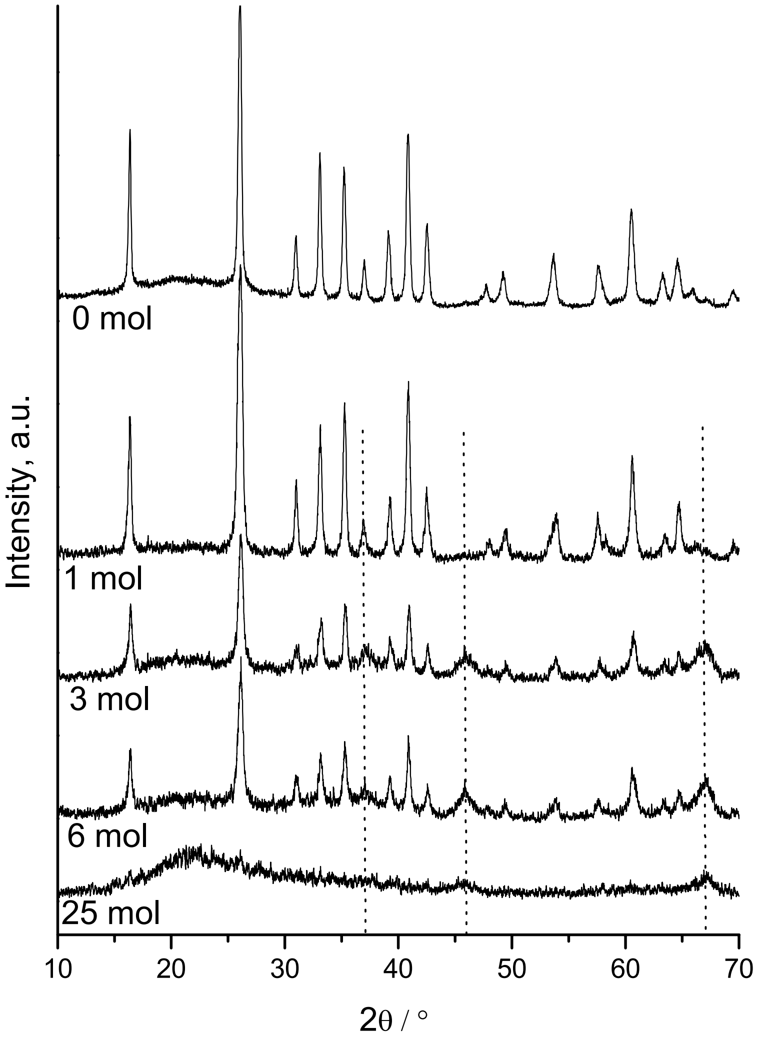

Figure 5 – X-ray spectra of powders prepared by adding the listed quantity of water per mole of aluminum, after isothermal annealing at 1000°C for 2 hours. All maxima belong to mullite, except those marked by dashed lines, which are characteristic for Al-Si spinel.

For the samples with water to Al ratio 3:1 and 6:1, mullite is present simultaneously with the spinel, and it can be concluded that these powders show the desired hybrid behavior. Thus, depending on the quantity of water added to the system the structure changes from pure monophasic powders (without added water, and with 1:1 ratio of water to Al) across hybrid compositons (mixed mono- and diphasic powders, ratios 3:1 and 6:1) to completely diphasic powders (ratio H_2O:Al = 25:1). This change in the structure of premullite powders is caused by the tendency of aluminum to polymerize in aqueous medium. Thus domains rich in aluminum are formed, which decrease the homogeneity of premullite powders and preferably crystallize into Al-Si spinel.

Comparably to the samples prepared from dried $Al(NO_3)_3 \cdot 9H_2O$, the mass losses increase with the increasing water content, since water binds to aluminum more strongly than alcohol does, and thus is harder to remove even by annealing at 600°C.

4. CONCLUSIONS

The quantity of water present during the synthesis of premullite powders was found to influence their structure and subsequent crystallization behavior, and thus enables their control. It was determined that the structure of the powders varied from monophasic (no extra water added and H_2O:Al = 1:1) to diphasic (H_2O:Al = 25:1) system, through several hybrid systems (H_2O:Al = 1, 3 and 6:1). The influence of water on the level of homogeneity of the premullite powders is explained by the tendency of aluminum to form complex polymeric structures in aqueous solutions.

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