ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 13, No. 3. 2007

Sol-gel Synthesis and Characterization of Kalsilite-type Alumosilicates

Irma BOGDANOVICIENĖ[1], **Audronė JANKEVICIUTĖ**[1], **Jiri PINKAS**[2], **Aldona BEGANSKIENĖ**[1], **Aivaras KAREIVA**[1*]

[1]*Department of General and Inorganic Chemistry, Vilnius University, LT-03225 Vilnius, Lithuania*
[2]*Department of Inorganic Chemistry, Masaryk Brno University, CZ-61137 Brno, Czeck Republic*

Received 12 July 2007; accepted 19 August 2007

In this paper, the sol-gel synthesis and characteristic properties of kalsilite-type alumosilicates ($KAlSiO_4$ and $K_{0.5}Na_{0.5}AlSiO_4$) are reported. The polycrystalline powders were characterized by thermal analysis (TG/DTA), powder X-ray diffraction analysis (XRD), IR spectroscopy and scanning electron microscopy (SEM). Single-phase kalsilite oxides have been obtained after annealing precursor gels for 5 h at 750 °C. It was demonstrated that crystallinity of the samples slightly depends on the duration of annealing. From the results obtained, it could be concluded that the $KAlSiO_4$ solids are composed of the volumetric plate-like grains grains with no regular size (from 5 μm to 30 μm). Larger crystallites for mixed potassium-sodium kalsilite have formed (from 10 μm to 80 μm) in comparison with potassium kalsilite samples.

Keywords: alumosilikates, kalsilite-type, $KAlSiO_4$, $K_{0.5}Na_{0.5}AlSiO_4$, sol-gel synthesis.

INTRODUCTION

Different materials are used as cements in restorative dentistry [1, 2]. Dental cements and resins are used intraorally to secure fixed orthodontic devices [3 – 6]. Besides, dental cements have a wide field of applications in clinical practice [7, 8]. Porcelain-fused-to-metal (PFM) is a widely used dental restoration in which several layers of porcelain are successively applied and fired in vacuum onto a metal framework which has been previously modelled and cast according to the anatomical conditions [9]. Porcelains for PFM restorations are very different in composition and structure from the traditional or tri-axial porcelains (that is, those made by the blending and the firing of clay, quartz and potassium feldspar). Actually, the bodies of dental porcelains are partially-crystallized feldspathic glasses (Na_2O-K_2O-Al_2O_3-SiO_2 system) that consists, at room temperature, of tetragonal leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$ or $KAlSi_2O_6$) embedded in a matrix of glass [9 – 11].

Alumosilicate glass-ceramics are manufactured for dental applications using a variety of methods [12 – 15]. The volume fraction, crystal size and morphology of the crystalline phases are dependent on the original glass composition, the stoichiometry of the crystal phases and crystallization heat treatment times and temperatures. Therefore, to produce uniform alumosilicate glass-ceramic microstructures consisting of fine grained single-phase crystals still is much desired. A more controlled crystallization regimen of the glass may therefore be a useful route to control the alumosilicate crystal size, volume fraction and morphology of these materials, which can influence the mechanical glass-ceramic properties. For similar purposes, the sol-gel synthesis method was very successfully used [16 – 20].

During the preparation of alumosilicate glass-ceramics the formation of multiphasic products (kalsilite, $KAlSiO_4$; leucite, $KAlSi_2O_6$; sanidine, $KAlSi_3O_8$) very ofthen occurs. Therefore, the main aim of the present study was for the first time to synthesize using aqueous sol-gel processing route and characterize kalsilite-type oxides having different nominal chemical composition: $KAlSiO_4$ and $K_{0.5}Na_{0.5}AlSiO_4$.

EXPERIMENTAL

For the synthesis of $KAlSiO_4$ and $K_{0.5}Na_{0.5}AlSiO_4$ compounds the analytical grade reagents (stoichiometric amounts of CH_3COOK, CH_3COONa, $Al(NO_3)_3 \cdot 9H_2O$ and $SiO_2 \cdot 0.3207\ H_2O$) were used. In the sol-gel process, 1.315 g of $SiO_2 \cdot 0.3207\ H_2O$ was mixed with 20 ml of H_2O and 70 ml concentrated acetic acid solution by stirring at 80 °C for 20 h. The turbid solution was obtained. In the next step, 3.75 g of $Al(NO_3)_3 \cdot 9H_2O$ dissolved in small amount of distilled water, was added with continuous stirring during 1 h at the same temperature. To this solution, 1.969 g of CH_3COOK dissolved in 25 ml of H_2O (synthesis of $KAlSiO_4$) or the mixture composed of 0.980 g of CH_3COOK and 1.360 g of CH_3COONa dissolved in 50 ml of H_2O (synthesis of $K_{0.5}Na_{0.5}AlSiO_4$) were added at the same temperature. After 1 h of stirring, 2 ml of 1,2-ethanediol as complexing agent was added to the above solutions, thus preventing crystallization of aluminium acetate during gelation. The obtained solutions were concentrated by slow evaporation (8 hours) at 80 °C in an open beaker. When nearly 90 % of the water has been evaporated under continuous stirring, turbidic gels were formed. After further drying in an oven at 100 °C for 24 h, fine-grained powders were obtained. To obtain kalsilite type ceramics, the gel samples were heated at 750 °C for 2 h – 5 h using heating rate of 5 °/min.

The thermal decomposition of the precursor gels was studied in air atmosphere by TG and DTA (thermogravimetric and differential thermal analyses, respectively) using a Setaram TG-DSC12 apparatus at a heating rate $10\ °C\ min^{-1}$. The X-ray powder (XRD)

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[*] Corresponding author. Tel.: + 370-5-2193110; fax.: +370-5-2330987.
E-mail address: *aivaras.kareiva@chf.vu.lt* (A. Kareiva)

analysis was performed with a Siemens D-500 diffractometer equipped with a conventional X-ray tube ($CuK\alpha_1$ radiation ($\lambda = 1.54060$ Å), power conditions (40 kV / 30 mA)). The germanium monochromated X-rays have been collected using linear PSD (opening angle: $2\theta = 6°$). The XRD patterns were measured in the range of 20° to 70° 2θ with the step size of 0.02° and 30 s counting per step at room temperature (25 °C). The IR spectra were recorded as KBr pellets on a Perkin-Elmer FTIR Spectrum BX II spectrometer. Scanning electron microscopy (SEM) was used to study the morphology of the samples obtained after the heat treatment. The SEM analysis was performed under vacuum in the specimen chamber of a scanning electron microscope CAM SCAN S4.

RESULTS AND DISCUSSION

The mechanism of the thermal decomposition in flowing air of the dried K-Al-Si-O and K-Na-Al-Si-O gels was studied by TG/DTA measurements. TG curves showed that in both of the cases the thermal decomposition proceeded in similar way (see Figs. 1 and 2).

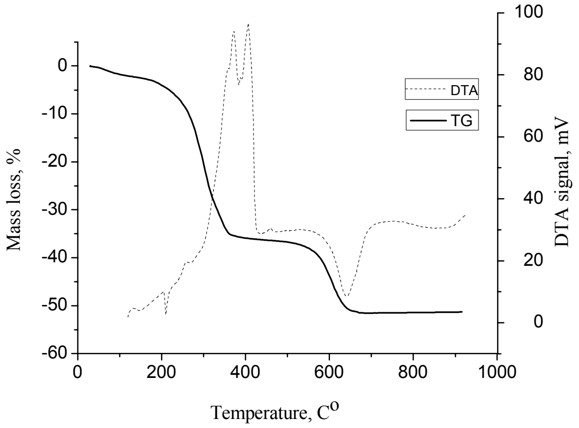

Fig. 1. TG/DTA curves recorded for the K-Al-Si-O gel

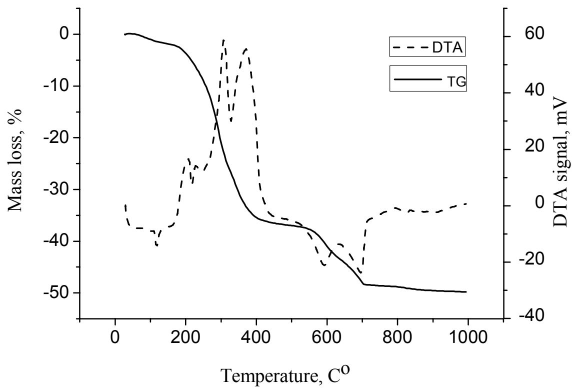

Fig. 2. TG/DTA curves recorded for the K-Na-Al-Si-O gel

The initial weight loss (~4 %) due to the loss of moisture and/or crystallization water is seen on the TG curves by heating the gel samples up to 200 °C. Both TG curves showed two main weight losses in the temperature ranges of 200 °C – 385 °C (~31 % – 32 %) and 385 °C – 700 °C (~13 % – 16 %). The thermal decomposition behaviour is associated with endothermic and exothermic effects in the DTA curves. Again, the DTA curves obtained for the two gel samples were almost identical. The first decomposition step assignable to removal of adsorbed and chemisorbed water is indicated by broad endothermic peaks on the DTA curve. Exothermic peaks from 200 °C to 450 °C in the DTA curves are due to the decomposition of aluminium constituent part [21, 22]. The final weight loss observed on the TG curves is also accompanied by strong endothermic peaks. These peaks probably correspond to the decomposition of the potassium and sodium acetates and formation of kalsilite phase. Thus, thermal characterization of the gel samples yields information about mechanisms of thermal decomposition of precursor, i.e. temperatures (or temperature intervals) of most important changes in weight. The optimum conditions for solid-state reaction could be also determined. According to the thermogravimetric analysis data the final annealing temperature for the preparation of lanthanide-codoped YAG could vary from 700 °C to 750 °C.

X-ray diffraction pattern of the ceramic sample prepared by annealing K-Al-Si-O precursor gel for 2 h at 750 °C is shown in Fig. 3.

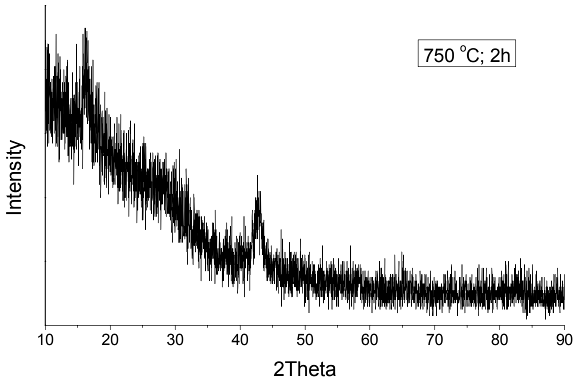

Fig. 3. XRD pattern of K-Al-Si-O precursor gel annealed at 750°C for 2 h

XRD pattern presented in Fig. 3 shows only broad peaks due to the amorphous character of the powders. Two broad peaks located at around $2\theta \approx 16° - 17°$ and $43° - 44°$ in the XRD pattern originate from the sample holder.

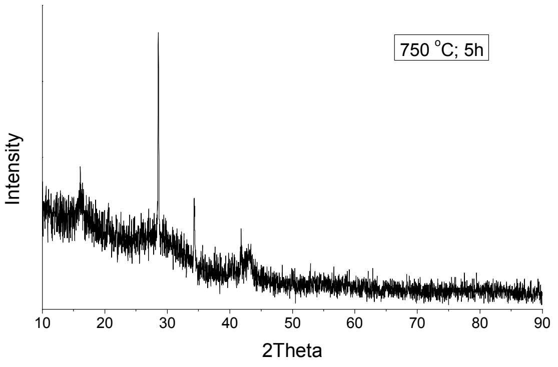

Fig. 4. XRD pattern of K-Al-Si-O precursor gel annealed at 750 °C for 5 h

However, after intermediate grinding and longer heat treatment the situation has changed drastically. Fig. 4

shows XRD pattern of the same samples synthesized at the same temperature for 5 h.

It can be observed that three peaks at $2\theta \approx 28.5°$, 34.8° and 42.4° appear in the XRD pattern after longer heat treatment of the sample. These peaks, could be attributed the kalsilite ($KAlSiO_4$) phase [14, 15]. No even traces of leucite, $KAlSi_2O_6$ or sanidine, $KAlSi_3O_8$ was formed during heat treatment of gels.

X-ray diffraction pattern of the ceramic sample prepared by annealing K-Na-Al-Si-O precursor gel for 2 h at 750 °C is shown in Fig. 5.

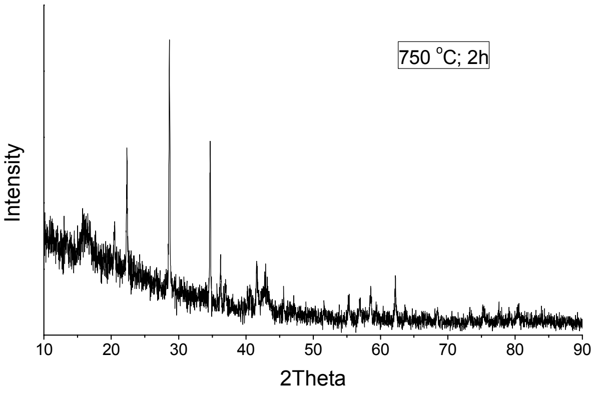

Fig. 5. XRD pattern of K-Na-Al-Si-O precursor gel annealed at 750 °C for 2 h

As seen from Fig. 5, in case of K-Na-Al-Si-O precursor, the sintering at 750 °C already for 2 h gave well-crystalline phase. All observed diffraction lines belong to the $K_{0.5}Na_{0.5}AlSiO_4$ phase.

The crystallinity increases with increasing duration of annealing at the same temperature (see Fig. 6), however, no progressive changes in the phase development could be observed.

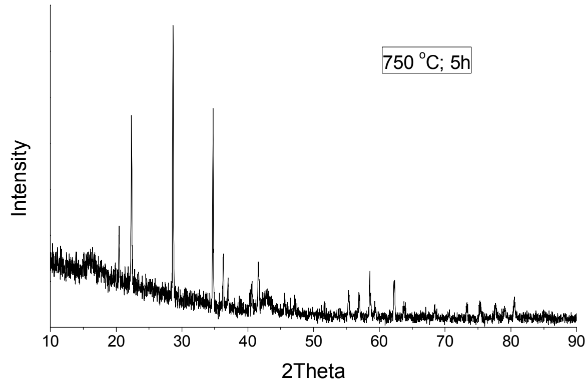

Fig. 6. XRD pattern of K-Na-Al-Si-O precursor gel annealed at 750 °C for 5 h

It is well known, that definite substances can be identified by their IR spectra, interpreted like fingerprints. To facilitate the interpretation of the XRD results the biceramic samples were also analyzed by IR spectroscopy. Fig. 7 shows IR spectrum for the calcined for 5 h at 750 °C single-phase $KAlSiO_4$ sample.

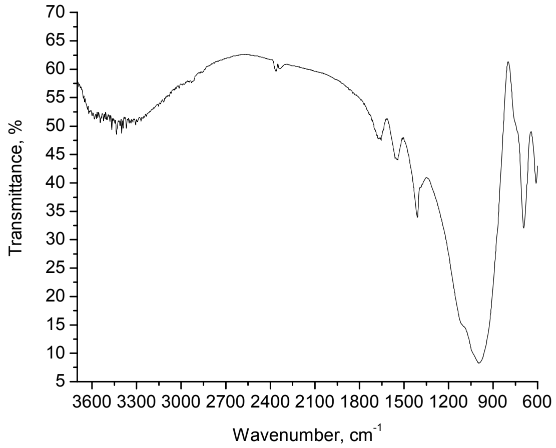

Fig. 7. IR spectrum of $KAlSiO_4$ sample

The absorptions from the main Si-O vibrations could be easily identified in the IR spectrum of $KAlSiO_4$ (1300, 1165, 1080, 788, 615 cm^{-1}) [23]. Moreover, broad bands between 3700 cm^{-1} – 3000 cm^{-1} and 1700 cm^{-1} – 1600 cm^{-1} can be assigned to the adsorbed water (or water of crystallization) and O-H vibrations [24].

Fig. 8 shows IR spectrum of the $K_{0.5}Na_{0.5}AlSiO_4$ sample synthesized at the same conditions.

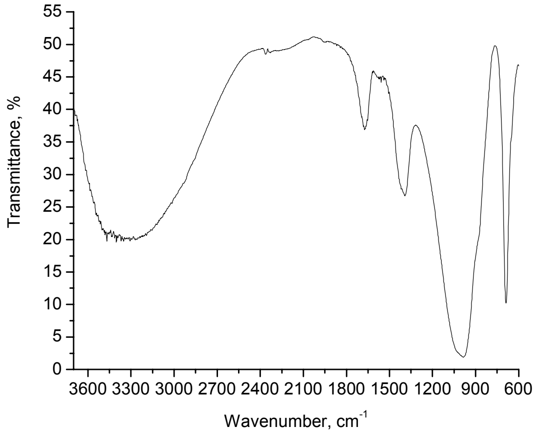

Fig. 8. IR spectrum of $KNaAlSiO_4$ sample

As seen from Fig. 8, the similar bands as in the case of IR spectrum of $KAlSiO_4$ sample could be easily determined.

Scanning electron microscopy was used for the characterization of surface microstructure of synthesized samples. SEM images of the ceramic samples prepared by annealing K-Al-Si-O precursor gel for 2 h and 5 h at 750 °C are shown in Figs. 9 and 10, respectively.

Fig. 9 shows the surface features of the powder calcined for 2 h at 750 °C. Evidently, the surface of the ceramic sample is mostly composed of amorphous particles. It can be seen from Fig. 10, however, that a progressive change in morphology is evident with increased calcination time. The kalsilite solids are composed of the volumetric plate-like grains grains with no regular size (from 5 μm to 30 μm).

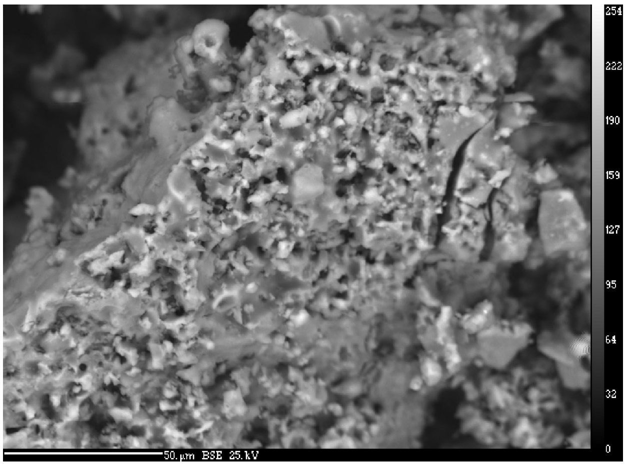

Fig. 9. SEM micrograph of K-Al-Si-O precursor gel annealed at 750 °C for 2 h

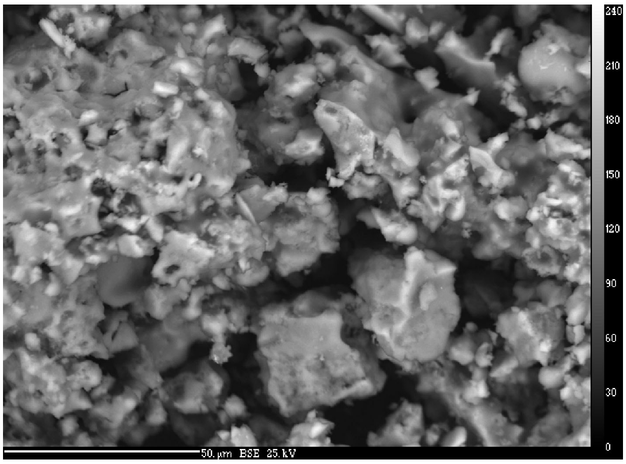

Fig. 10. SEM micrograph of K-Al-Si-O precursor gel annealed at 750 °C for 5 h

SEM images of the ceramic samples prepared by annealing K-Na-Al-Si-O precursor gel for 2 h and 5 h at 750 °C are shown in Figs. 11 and 12, respectively.

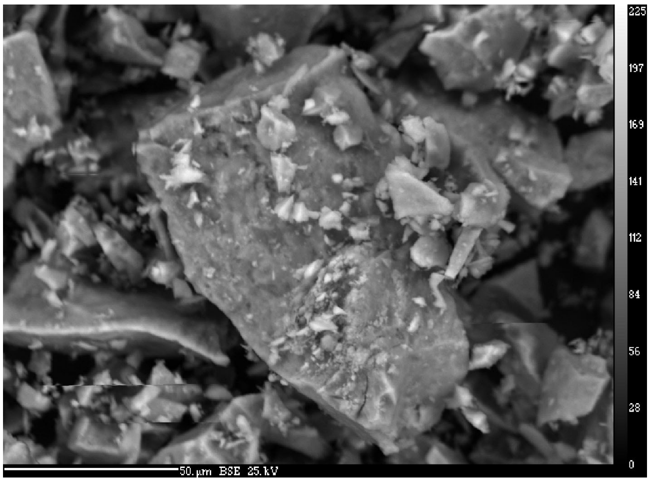

Fig. 11. SEM micrograph of K-Na-Al-Si-O precursor gel annealed at 750 °C for 2 h

As seen, both $KNaAlSiO_4$ samples synthesized at 750 °C show well-resolved crystalline morphology. Moreover, mixed potassium-sodium kalsilite crystallites are much larger (from 10 µm to 80 µm) in comparison with potassium kalsilite samples.

Fig. 12. SEM micrograph of K-Na-Al-Si-O precursor gel annealed at 750 °C for 5 h

CONCLUSIONS

For the first time kalsilite ceramics having different nominal chemical composition $KAlSiO_4$ and $KNaAlSiO_4$ have been synthesized using aqueous sol-gel method at 750 °C. Interestingly, our attempts to prepare $KAlSiO_4$ and $KNaAlSiO_4$ phases using this synthetic approach resulted in both cases to the formation of monophasic kalsilite. The obtained ceramic samples were characterized by XRD analysis, IR spectroscopy and SEM methods. It was demonstrated that crystallinity of the samples slightly depends on the duration of annealing. From the results obtained, it could be concluded that the $KAlSiO_4$ solids are composed of the volumetric plate-like grains grains with no regular size (from 5 µm to 30 µm). Larger crystallites for mixed potassium-sodium kalsilite have formed (from 10 µm to 80 µm) in comparison with potassium kalsilite samples.

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