Sol-gel Synthesis and Characterization of Kalsilite-type Alumosilicates

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In this paper, the sol-gel synthesis and characteristic properties of kalsilite-type alumosilicates (KAISiO₄ and K₀.₅Na₀.₅AlSiO₄) 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 KAISiO₄ solids are composed of the volumetric plate-like 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, KAISiO₄, K₀.₅Na₀.₅AlSiO₄, 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 compositions the analytical grade reagents (stoichiometric amounts of CH₃COOK, CH₃COONa, Al(NO₃)₃·9H₂O and SiO₂·0.3207 H₂O) were used. In the sol-gel process, the mixture composed of 0.980 g SiO₂·0.3207 H₂O was mixed with 20 ml of H₂O 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(NO₃)₃·9H₂O 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 CH₃COOK dissolved in 25 ml of H₂O (synthesis of KAISiO₄) or the mixture composed of 0.980 g of CH₃COOK and 1.360 g of CH₃COONa dissolved in 50 ml of H₂O (synthesis of K₀.₅Na₀.₅AlSiO₄) 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 °C/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)
analysis was performed with a Siemens D-500 diffractometer equipped with a conventional X-ray tube \( \text{CuK}_{\alpha_1} \) radiation \( (\lambda = 1.54060 \text{ Å}) \), power conditions \( (40 \text{ kV} / 30 \text{ mA}) \). The XRD patterns were measured in the range of 20° to 70° 2\( \theta \) with the step size of 0.02° and 30 s counting per step at room temperature \( (25 \text{ °C}) \). 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](image1)

![Fig. 2. TG/DTA curves recorded for the K-Na-Al-Si-O gel](image2)

The initial weight loss \( (\sim 4 \%) \) 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](image3)

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](image4)

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 $2\theta \approx 28.5^\circ$, $34.8^\circ$ and $42.4^\circ$ 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$_2$O$_6$ or sanidine, KAlSi$_3$O$_8$ 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 $^\circ$C is shown in Fig. 5.

As seen from Fig. 5, in case of K-Na-Al-Si-O precursor, the sintering at 750 $^\circ$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. 5. XRD pattern of K-Na-Al-Si-O precursor gel annealed at 750 $^\circ$C for 2 h

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Fig. 6. XRD pattern of K-Na-Al-Si-O precursor gel annealed at 750 $^\circ$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 $^\circ$C single-phase 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. 7. IR spectrum of KAlSiO$_4$ sample

As seen from Fig. 7, the similar bands as in the case of IR spectrum of KAlSiO$_4$ sample could be easily determined.

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 $^\circ$C are shown in Figs. 9 and 10, respectively.

Fig. 9 shows the surface features of the powder calcined for 2 h at 750 $^\circ$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 $\mu$m to 30 $\mu$m).
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 KNaAlSiO₄ 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.

CONCLUSIONS

For the first time kalsilite ceramics having different nominal chemical composition KAlSiO₄ and KNaAlSiO₄ have been synthesized using aqueous sol-gel method at 750 °C. Interestingly, our attempts to prepare KAlSiO₄ and KNaAlSiO₄ 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 KAlSiO₄ solids are composed of the volumetric plate-like 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.

REFERENCES


