

STRUCTURAL PROPERTIES AND CRYSTALLIZATION KINETICS OF LEUCITE AND KALSILITE FROM ALUMINOSILICATE AMORPHOUS PRECURSORS

*Iva Buljan¹, Cleo Kosanović¹, Boris Subotić¹, Nataša Novak Tušar², Alenka Ristić²,
Roman Gabrovšek² and Venčeslav Kaučič²*

¹ Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

² National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

E-mail: ibuljan@irb.hr

ABSTRACT

Kinetics of the isothermal crystallization of tetragonal modification of leucite and hexagonal modification of kalsilite from differently prepared precipitated amorphous aluminosilicate precursors were investigated at three different temperatures. Kinetic analyzes of the transformation processes have shown that the crystallization of leucite occurs in the same way as the crystallization of kalsilite and follows a pseudo-zero-rate kinetic equation. The apparent activation energies calculated by the Arrhenius equation were 373 KJ/mol for the crystallization of kalsilite and 403 KJ/mol for the crystallization of leucite, which is explained by the different microstructure of the prepared precursors.

Keywords: kinetics, crystallization, leucite, kalsilite, amorphous aluminosilicates

INTRODUCTION

In the last twenty years zeolite precursors and their cation-exchanged modifications were successfully used as precursors in the synthesis of aluminosilicate-based ceramic materials ¹⁻⁴. The first step of the thermal transformation of zeolites is the formation of an amorphous intermediate phase by the destruction of the zeolite structure ^{2, 5-6}. It is found that the thermal stability of the zeolite framework and the temperature of its transformation to the amorphous phase as well its recrystallization to a non-zeolitic crystal phase depend not only on the Si/Al ratio but also depend on the present alkali cation in the channel/voids of the zeolite framework and is increasing with the increasing ionic radius of the cation ². In our previous studies ⁷⁻⁹ it was presented that the process of the amorphization of zeolites (zeolite A -> amorphous aluminosilicate) does not influence the morphology and the size of the initial crystals (phenomena of pseudomorphism) but the amorphization of zeolite A as well the recrystallization to a ceramic material occur in each single particle that can be seen as "closed" micro-reactor with a stable shell ⁹. From our investigations by Fourier transform infrared spectroscopy, the gel that is used for the synthesis of zeolite has similar spectra to the spectra obtained for the amorphous phase obtained by the thermal treatment of zeolite ¹⁰. This and the fact that the thermally induced amorphous phase have the same chemical composition as the initial crystalline zeolite, gave the idea to use as starting material for the thermal transformation the amorphous aluminosilicate gel instead of the crystalline zeolite. Hence, the objectives of this study are:

- (1) To prove (or disapprove) the thesis that K-aluminosilicate based ceramics can be obtained by a thermal treatment of precipitated, X-ray amorphous potassium aluminosilicate
- (2) To observe (by appropriate microscopic techniques) the size and shape of the resulting crystalline phase(s)
- (3) To determine the mechanism of assumed crystallization processes in an isothermal mode.

EXPERIMENTAL

K-aluminosilicate hydrogels and the corresponding amorphous K-aluminosilicate precursors [K-gel(A), K-gel(B)] were prepared by two different procedures, as follows: Procedure (A): by the ion-exchange of sodium ions from Na-aluminosilicate gel with NH_4^+ and then with potassium cation resulting in K-gel(A) and Procedure (B): by the direct precipitation from K-aluminate and K-silicate solutions resulting in K-gel(B). The synthesis procedure is described in detail in ref [10].

In order to transform the dried gels, prepared by the described procedures (A and B) into ceramics, the gel samples were isothermally heated at three different temperatures T (= 1423 K, 1453 K, 1483 K) in a chamber furnace with controlled temperature (ELPH-2, Elektrosanitarij). At various times, after the beginning of heating at elevated temperatures, the samples were taken from the furnace and cooled down in order to stop the transformation process and prepare the sample for analysis.

The starting gels and the obtained ceramic material were characterized using combined information from energy-dispersive X-ray spectroscopy (EDAX, LINK ISIS 300 system attached to the scanning-electron microscope JEOL JSM-5800), thermogravimetry (TG, SDT2960 thermal analysis system (TA Instruments Inc.)), X-ray powder diffraction (XRPD, PANalytical X'Pert Pro high resolution diffractometer), measuring of the specific surface area (BET method, TriStar 3000, Micromeritics), and light and polarization microscopy (LM and LP, A Leica light microscope, Model DMLS).

The weight fractions of the phases in the multi-phase systems were extracted from the X-ray diffraction data.

RESULTS AND DISCUSSION

The two gels although were prepared to have the same chemical composition differ among themselves in molar ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ [K-gel (A) ($0.96\text{K}_2\text{O}\cdot 0.08\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 2.65\text{SiO}_2\cdot 3.28\text{H}_2\text{O}$) and K-gel(B) ($1.01\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 3.31\text{SiO}_2\cdot 12.53\text{H}_2\text{O}$). The measurements of BET surface areas of the gels, ($53\text{ m}^2\text{g}^{-1}$ for Kgel(A) and $183\text{ m}^2\text{g}^{-1}$ for Kgel(B)) compared with the results of thermal analysis (TG) (higher content of water (12.533 moles in the Kgel(B) molar composition comparing to the 3.285 moles in the Kgel(A) molar composition) indicated “structural” differences between the gels and refer to a less dense Kgel (B) relative to the Kgel(A).

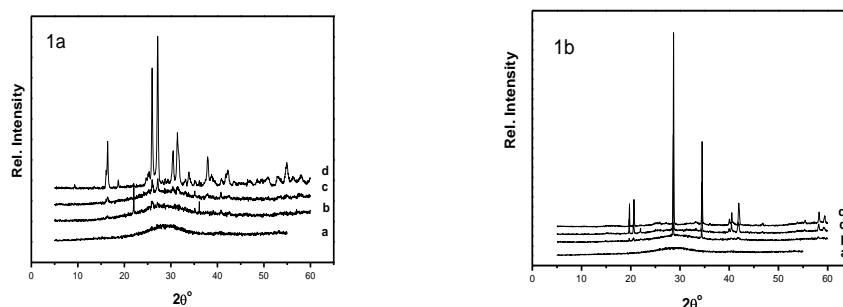


Figure 1a. X-ray diffraction patterns of the solid phases obtained by thermal treatment of K-gel(A) (a) at 1483 K for 0.5 h (b), 2 h (c), and 5h (d) and fig. 1b. X-ray diffraction patterns of the solid phases obtained by thermal treatment of K-gel (B) (a) at 1483 K for 0.5 h (b), 1 h (c), and 2h (d)

Fig.1a and 1b are showing that the thermal treatment of K-gel(A) results in gradual transformation of X-ray amorphous phase into leucite (1a) and K-gel(B) into kalsilite (1b). Fig. 2 and Fig. 3 show the changes in the mass fractions f_c of leucite and kalsilite formed during isothermal heating of the precursor at 1423, 1453 and 1483 K. Kinetic analysis of the

isothermal transformation process indicated that the rate of crystallization of leucite and kalsilite from the precipitated amorphous aluminosilicate can be expressed as

$$f_c = f_p^* [1 - \exp(-Kt)] \quad (1)$$

where f_c is the fraction of crystallized up to the time t . Although this kinetic equation implies the zero-order growth (formation of nuclei by homogeneous nucleation without their subsequent growth) the more detailed kinetic analysis showed that this kinetic equation can also be obtained in the case of limited growth, for example, when growth process is limited by the amount of aluminosilicate material in the vicinity of nuclei.

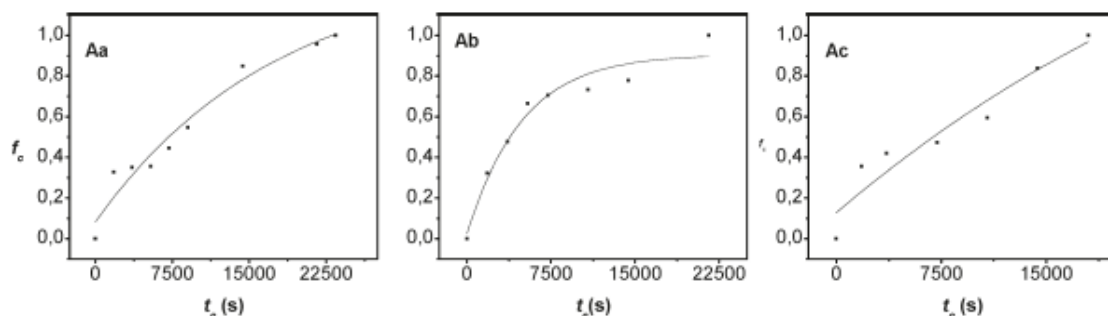


Figure 2. Changes in the measured mass fractions, f_c of leucite and the calculated mass fractions f_c , using the corresponding numerical values of K (asymptotic rate coefficient) and m (slope) listed in Table 1. during isothermal heating of the precipitated amorphous precursor K-gel(A) at 1423 (a), 1453 (b), and 1483 K (c).

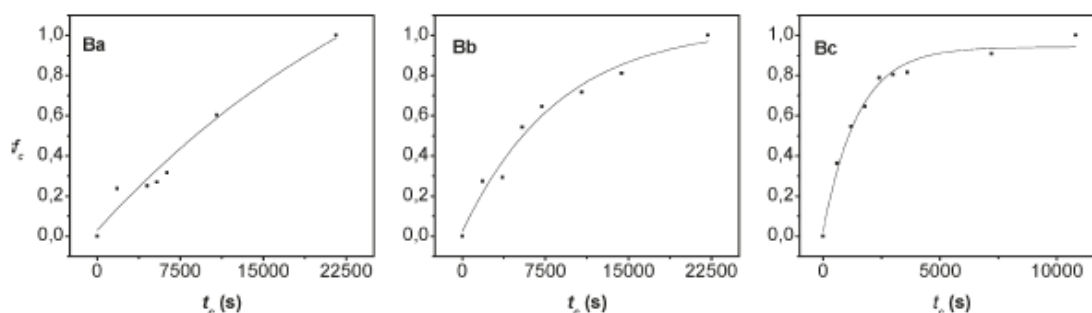


Figure 3. Changes in the measured mass fractions, f_c of kalsilite and the calculated mass fractions f_c , using the corresponding numerical values of K (asymptotic rate coefficient) and m (slope) listed in Table 1. during isothermal heating of the precipitated amorphous precursor K-gel(B) at 1423 (a), 1453 (b), and 1483 K (c).

Table 1. Numerical Values of the Constants K and m that Correspond to the Crystallization of Leucite and Kalsilite from the K-gel(A) and K-gel(B)

material	T(K)	$K[s^{-1}]$	m
leucite	1423	5.341×10^{-4}	0.85~1
leucite	1453	1.037×10^{-3}	0.85~1
leucite	1483	4.955×10^{-3}	0.73~1
kalsilite	1423	8.400×10^{-5}	1.01~1
kalsilite	1453	1.978×10^{-4}	0.98~1
kalsilite	1483	6.962×10^{-4}	1.03~1

The asymptotic rate coefficients K are strongly temperature - dependent, as shown in Fig. 4., which plots the usual Arrhenius plot of $\ln K$ versus $1/T$. The apparent activation energy (E_a , fig.4) is calculated from the Arrhenius plot (i.e., from the slope of $\ln K$ vs $1/T$ straight line) for both materials. The difference in activation energy (E_a for leucite and kalsilite crystallization was 403 and 373 kJ/mol, respectively) could be ascribed to the different primary and secondary units formed in the gel, as shown by different techniques, and also to the different way of the compounding as the crystal is being formed.

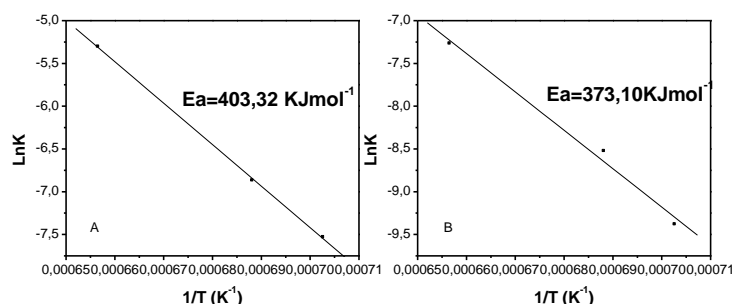


Figure 4. Arrhenius plot of isothermal crystallization of leucite (A) and kalsilite (B) from K-gel(A) and K-gel(B).

The images obtained by light and polarimetric microscopy of the final products are presented in Fig.5. The size of the fully crystalline particles (see X-ray diffraction patterns of the final products in figs. 1a and 1b) does not extent 10 nm. That confirms the assumption the crystalline leucite and kalsilite is possible to obtaine using amorphous aluminosilicate gels.

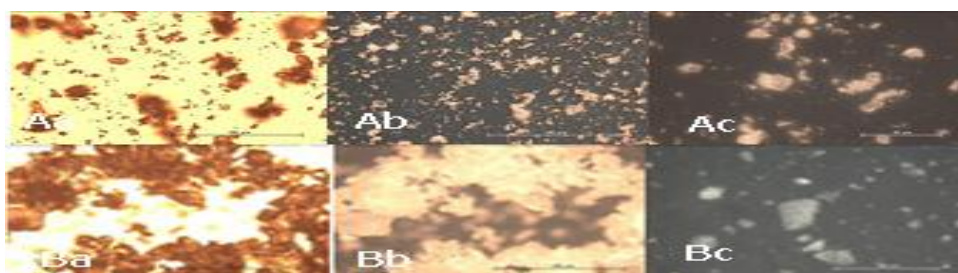


Figure 5. Leucite pictures (A) and Kalsilite pictures (B) obtained by light (a), polarizing microscope (b) and polarizing microscope with the sample in cedar oil (c).

CONCLUSION

Thermal transformations of the amorphous aluminosilicate precursors enable the formation of pure ceramic materials. The synthesis route is simple and relatively cheaper than the conventional procedures. Further transformation after thermal treatment of gels that have the same or almost the same chemical composition, yields to different ceramic materials which is explained by the structural particularities of the formed gels. That also explains the difference in E_a between the two samples.

REFERENCES

- [1] M. A. Subramanian, D. R. Corbin, U. Chowdhry, *Advances in Ceramics*, 1989, **26**, 239-247.
- [2] C. Kosanović, B. Subotić and I. Šmit, *Thermochimica Acta*, 1998, **317**, 25-37.
- [3] P. Norby and H. Fjellvag, *Zeolites*, 1992, **12**, 898-908.
- [4] G. Dell'Agli, C. Ferone, M. C. Mascolo, M. Pansini, *Solid State Ionics*, 2000, **127**, 309-317.
- [5] B. Hoghooghi, J. McKittrick, C. Butler, P. Desch, *J. Cryst. Solids*, 1994, **170**, 303-.
- [6] L. Stoch, I. Waclawska, *High temperature materials and Processes*, (ed. A. Rosen) Vol.13, No.3, 181-201.
- [7] C. Kosanović, B. Subotić, *Microporous Materials*, 1997, **12**, 261-266.
- [8] C. Kosanović, B. Subotić, V. Kaučić and M. Škrebilin, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3447-3451.
- [9] C. Kosanović and B. Subotić, *Microporous and Mesoporous Materials*, 2003, **66**, 311-319.
- [10] C. Kosanović, I. Buljan, S. Bosnar, B. Subotić, N. Novak Tušar, A. Ristić, R. Gabrovšek, V. Kaučić, *Acta Chimica Slovenica*, 2008, **55**, 960-965.