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# Thermal Transformation of Various Potassium Aluminosilicate Precursors

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Dedicated to the memory of Professor Ljubo Golič

## Abstract

The isothermal amorphization of potassium exchanged zeolite A and recrystallization of the formed amorphous phase as well the crystallization of the X-ray amorphous K-aluminosilicates (prepared in two ways: (A) by ion-exchange of sodium ions from zeolitic Na-aluminosilicate gel with the alkaline cation K resulting in K-gel(A) and (B) by direct precipitation from the corresponding K-aluminate and K-silicate solutions resulting in K-gels(B)) at three different temperatures were investigated by powder X-ray diffraction method.

Phase analyses of the transformation/crystallization processes have shown that: pure crystalline tetragonal leucite crystallizes from K-gel (A) in the temperature range from 1423 to 1483 K whereas pure hexagonal kalsilite crystallizes from K-gel (B) and K-exchanged zeolite A in the temperature range between 1423 and 1483 K and 1258 and 1298 K, respectively.

**Keywords:** Temperature-induced transformation, zeolite KA, amorphous aluminosilicate, kalsilite, leucite

## 1. Introduction

The synthesis of leucite ( $\text{KAlSi}_2\text{O}_6$ ) and kalsilite ( $\text{KAlSiO}_4$ ) has attracted great attention in recent years because of its technological importance.<sup>1–7</sup> A number of properties of potassium aluminosilicates has been described<sup>4, 8</sup>. Leucite, because of its tone, color appeal and excellent biocompatibility found its usage in dental porcelain/glass materials<sup>9, 10</sup>. The thermal expansions of ceramic materials are generally lower than that of metals but leucite<sup>5</sup> and kalsilite<sup>3</sup> with high thermal expansion coefficients were prepared by appropriate procedures in order to achieve thermal compatibility when bonding to substructures and as reinforcing agent in all ceramic restorations.

Leucite has a melting point of 1693 °C<sup>11</sup> that makes the synthesis of pure leucite at relative low temperature difficult. Synthesis of leucite powders was done by coprecipitation<sup>12</sup>, salt bath<sup>13</sup>, sol-gel<sup>14</sup>, hydrothermal<sup>15</sup> and

solid state methods.<sup>5</sup> Kalsilite and its polymorphs such as kalliophilite, low- $\text{KAlSiO}_4\text{-O}_1$ ,  $\text{KAlSiO}_4\text{-ANA}$  and high  $\text{KAlSiO}_4\text{-O}_2$  were obtained by Dimitrijević and Dondur<sup>16</sup> after high-temperature thermal treatment in a temperature range 1073–2073 K using as starting material K-LTA zeolite. Kalsilite was also obtained by solid state reactions of kaolinite with  $\text{K}_2\text{CO}_3$  or KCl through intermediate phase of kaliophilite<sup>17</sup>. In all the mentioned procedures the authors tried to synthesize leucite or kalsilite of high purity. In order to achieve the necessary purity we chose as starting materials aluminosilicate gels that could be transformed by high temperature solid state transformation to the target product without by-products as impurities.

In this work we studied the synthesis of kalsilite and leucite using various K-aluminosilicate precursors in order to establish as to how the way of preparation of K-aluminosilicate influences the crystal structure, chemical composition and particulate properties of transformation products.

## 2. Experimental

### 2. 1. Materials

The following materials were used for the preparation of appropriate Me-aluminate, Me-chloride, Me-hydroxide and Me-silicate solutions (Me = NH<sub>4</sub>, Na, K):

- Aluminium wire, 99.999 wt. % Al (Sigma-Aldrich)
- Ammonium chloride, analytical grade NH<sub>4</sub>Cl (Kemika)
- Fumed silica, 99.8 wt. % amorphous SiO<sub>2</sub> (Sigma-Aldrich)
- Sodium aluminate, anhydrous technical grade NaAlO<sub>2</sub>; 41 wt. % Na<sub>2</sub>O, 54 wt. % Al<sub>2</sub>O<sub>3</sub> (Riedel-de-Haën)
- Sodium silicate, anhydrous technical grade Na<sub>2</sub>SiO<sub>3</sub>; 51 wt. % Na<sub>2</sub>O, 48 wt. % SiO<sub>2</sub> (Sigma-Aldrich)
- Potassium chloride, analytical grade KCl (Kemika)
- Potassium hydroxide, analytical grade KOH (Kemika)
- Demineralised water
- Zeolite 4A, prepared in our laboratory by a known procedure<sup>18</sup>.

### 2. 2. Preparation of Me-chloride, Me-hydroxide, Me-aluminate and Me-silicate Solutions

0.5 M MeCl solutions (Me = NH<sub>4</sub>, K) were prepared by the dissolution of appropriate amounts of corresponding Me-chloride salts in appropriate volume of demineralised water. 1.810 and 3.277 M MeOH solutions were prepared by the dissolution of appropriate amounts of a corresponding Me-hydroxide (Me = Na, K) in an appropriate volume of demineralised water. Me-aluminate solutions having appropriate concentrations with respect to Me<sub>2</sub>O (= 0.904 mol dm<sup>-3</sup>) and Al<sub>2</sub>O<sub>3</sub> (= 0.724 mol dm<sup>-3</sup>) were prepared by the dissolution of Al wire in corresponding 1.81 M MeOH solutions (Me = Na, K) at 110 °C. Sodium aluminate solution ([Na<sub>2</sub>O] = 0.904 mol dm<sup>-3</sup>, [Al<sub>2</sub>O<sub>3</sub>] = 0.724 mol dm<sup>-3</sup>) was also prepared by the dissolution of an appropriate amount of sodium aluminate in demineralised water.

K-silicate solution having the appropriate concentration with respect to K<sub>2</sub>O (= 1.688 mol dm<sup>-3</sup>) and SiO<sub>2</sub> (= 1.639 mol dm<sup>-3</sup>) were prepared by the dissolution of fumed amorphous silica in corresponding 3.227 M KOH solutions at room temperature. Sodium silicate solution ([Na<sub>2</sub>O] = 1.668 mol dm<sup>-3</sup>, [Al<sub>2</sub>O<sub>3</sub>] = 1.639 mol dm<sup>-3</sup>) was also prepared by the dissolution of appropriate amount of sodium silicate in demineralised water.

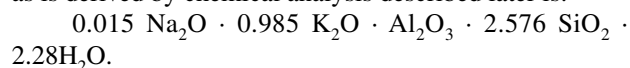
### 2. 3. Preparation of Me-aluminosilicate Hydrogels and Amorphous Me-aluminosilicate Precursors (gels)

Me-aluminosilicate hydrogel and the corresponding amorphous Me-aluminosilicate precursor (Me-gel) were prepared by two different procedures:

**Procedure A:** An aluminosilicate hydrogel having the molar oxide composition of 3.58Na<sub>2</sub>O · Al<sub>2</sub>O<sub>3</sub> · 2.264 SiO<sub>2</sub> · 153.47H<sub>2</sub>O was prepared by the addition of 250 ml of sodium silicate solution (prepared by the dissolution of Na<sub>2</sub>SiO<sub>3</sub> in demineralised water) into a plastic beaker containing 250 ml of stirred sodium aluminate solution (prepared by the dissolution of NaAlO<sub>2</sub> in demineralised water), at ambient temperature. The prepared hydrogel was additionally stirred for 5 min at room temperature before the phase separation. The precipitated solid phase (amorphous Na-aluminosilicate precursor; Na-gel (A)) was separated by centrifugation. After the centrifugation and removal of the liquid, the solid phase was redispersed in demineralised water and centrifuged repeatedly. The procedure was repeated until the pH was between 9 and 10. The washed Na-gel (A) was dried at 105 °C overnight and cooled down in a desiccator over dry silica gel.

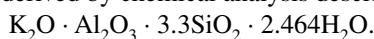
10 g of the Na-gel (A), prepared as described above, was placed into a plastic beaker containing 250 ml of 0.5 M NH<sub>4</sub>Cl solution. The suspension was stirred at 70 °C for 2 h and the solid phase (NH<sub>4</sub>-exchanged gel; NH<sub>4</sub>-gel) was separated by centrifugation. After centrifugation and removal of the liquid phase the solid phase (NH<sub>4</sub>-gel) was redispersed in demineralised water and centrifuged repeatedly. The procedure was repeated until the reaction on chloride ions in the liquid phase was negative. Then, the wet washed NH<sub>4</sub>-gel was dried in vacuum at 50 °C overnight and cooled down in a desiccator over dry silica gel. The obtained gel was placed in separate plastic beakers containing 250 ml of KCl solutions. Suspensions were stirred at 70 °C for 2 h and the solid phase (K-exchanged gel; K-gel (A)) was separated by centrifugation. The procedure of the solid-liquid separation and washing was the same as during the preparation of NH<sub>4</sub>-gel (see above). The washed K-gel (A) was dried at 105 °C overnight and cooled down in a desiccator over dry silica gel.

The chemical composition of the obtained K-gel (A) as is derived by chemical analysis described later is:



**Procedure B:** The aluminosilicate hydrogel having the molar oxide composition 3.58K<sub>2</sub>O · Al<sub>2</sub>O<sub>3</sub> · 2.264SiO<sub>2</sub> · 153.47H<sub>2</sub>O was prepared by the addition of 250 ml of K-silicate solution (prepared by dissolution of fumed silica in KOH solution) into a plastic beaker containing 250 ml of stirred K-aluminate solution (prepared by the dissolution of Al wire in KOH solution) at ambient temperature. The prepared hydrogel was additionally stirred for 5 min before the phase separation. The precipitated solid phase (amorphous K-aluminosilicate precursor; K-gel (B)) was separated and washed in the same way as the phase separation and washing of the K-gel (A) obtained by Procedure A. The washed K-gel (B) was dried at 105 °C overnight, and cooled down in a desiccator over dry silica gel.

The chemical composition of the obtained K-gel (A) as is derived by chemical analysis described later is:



## 2. 4. Preparation of Potassium Exchanged Zeolite A

Zeolite A was prepared in our laboratory by a known procedure<sup>18</sup>, it was cation-exchanged in the same way as described above for the K-gel (A).

## 2. 5. Thermal Treatment of Gels

In order to transform zeolite KA, K-gel(A), K-gel(B) precursors into nonzeolitic ceramic materials, the samples were put in a chamber furnace with controlled temperature (ELPH –2, Elektrosanitarij) and preheated at transformation temperatures as follows:

1258, 1278 and 1298 K for zeolite KA,

1423, 1453 and 1483 K for K-gel (A)

1423, 1453 and 1483 K for K-gel (B).

At various times,  $t$ , after the beginning of heating at elevated temperature, samples were taken from the furnace and cooled down in a desiccator over silica gel in order to stop the transformation process and prepare the samples for analyses.

## 2. 6. Characterization/Analyses of the Samples

Potassium exchanged zeolite A, the gel K-gel(A) prepared by Procedure A, the gel K-gel(B) prepared by Procedure B as well as the crystalline products obtained by their thermal treatment (see 2.5.) were characterized/analyzed as follows:

Chemical composition of amorphous (gels) and crystalline samples (ceramics) was determined by EDAX technique using a LINK ISIS 300 system attached to the scanning-electron microscope JEOL JSM-5800.

X-ray powder diffraction patterns of all solid samples were taken on a Siemens D-5000 diffractometer using  $\text{CuK}\alpha$  radiation at room temperature. The XRPD data were collected in the  $2\theta$  range from 5 to 55° in steps of 0.04° with 1 s per step.

The weight fractions,  $f_{\text{KA}}$ , of zeolite KA,  $f_{\text{gel(A)}}$  of K-gel(A),  $f_{\text{gel(B)}}$  of K-gel(B),  $f_{\text{a}}$  of the amorphous aluminosilicate and  $f_{\text{CK}}$  of kalsilite and  $f_{\text{CL}}$  of leucite were calculated by three different methods; Hermans-Weidinger method<sup>19</sup>, the external standard method and the mixing method<sup>20</sup>, using the integral value of the broad amorphous peak ( $2\theta = 17 - 39^\circ$ ) and the corresponding sharp peaks of the crystalline phases. The first method was used for the determination of the weight fractions of the crystalline phases in two-phase systems and the other two methods were used in order to determine the weight fractions of different amorphous and crystalline phases in the multi-phase systems.

## 3. Results

Fig. 1 shows the X-ray diffraction patterns obtained by isothermal heating of potassium exchanged zeolite A (KA) at 1278 K for 0.083 (a), 0.5 (b), 2 (c) and 7 hours (d). X-ray diffraction pattern (a) shows all the characteristic peaks of K-exchanged zeolite A which begins to transform into an amorphous aluminosilicate at  $t_T > 0.083$  h (fig1.b).

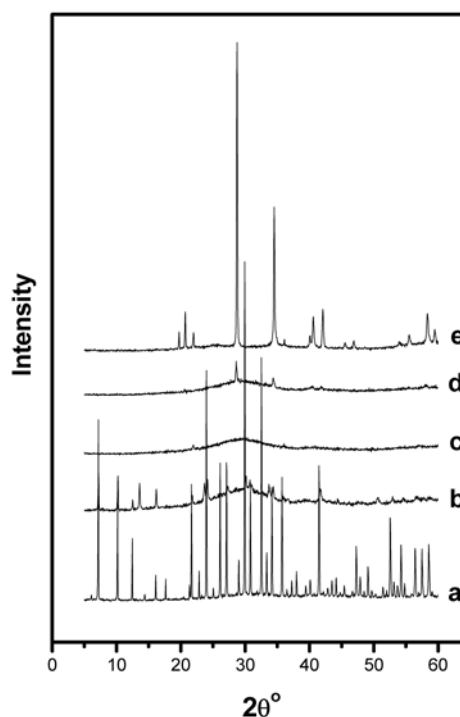
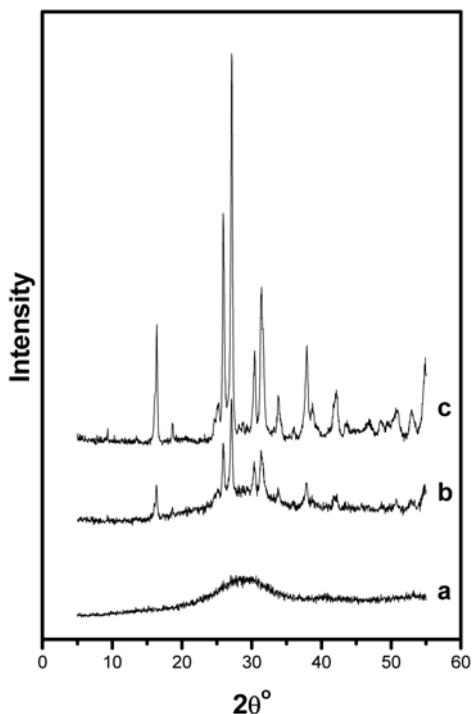


Fig. 1. X-ray diffraction patterns of solid phases obtained by thermal treatment of zeolite KA (a) at 1278 K for 0.083 (a), 0.5 (b), 2 (c) and 7 hours (d).

While the KA is transforming to an amorphous aluminosilicate phase, the amorphous aluminosilicate phase starts to transform to kalsilite (fig1.c, d) until the solid phase is completely transformed into kalsilite (fig. 1e). Progress of X-ray diffraction patterns obtained by heating K-exchanged zeolite A at 1258 K and 1298 K exhibits the same general feature as the one presented in fig.1. The process of the transformation of K-exchanged zeolite A takes place in the sequence characteristic of the most temperature induced transformations of zeolites: zeolite (K-exchanged zeolite A) → amorphous aluminosilicate → non-zeolitic crystalline aluminosilicate (kalsilite)<sup>21–26</sup>. From our previous investigations it is found that at lower temperatures (see table 1. and ref.7, 24) first crystallizes kaliophilite and then is transformed to more stable phase of kalsilite.

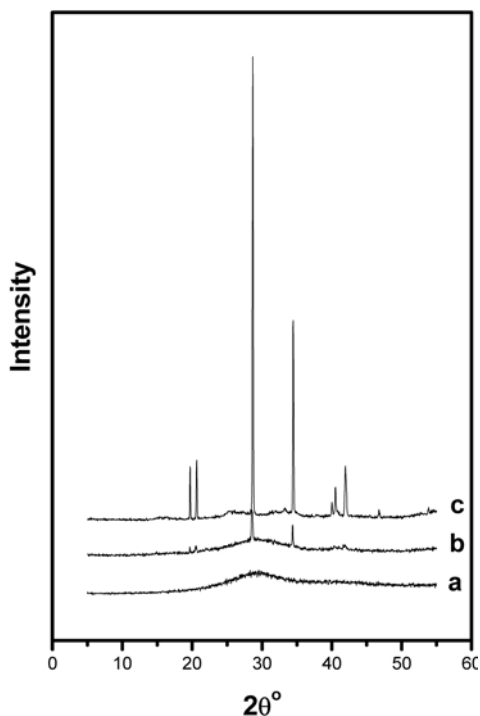


**Fig. 2.** X-ray diffraction (XRD) patterns of samples obtained after thermally induced transformations of the amorphous K-aluminosilicate precursor obtained by Procedure A [K-gel(A)] (a) at 1453 K for 1.5 (b) and 6.833 h (c).

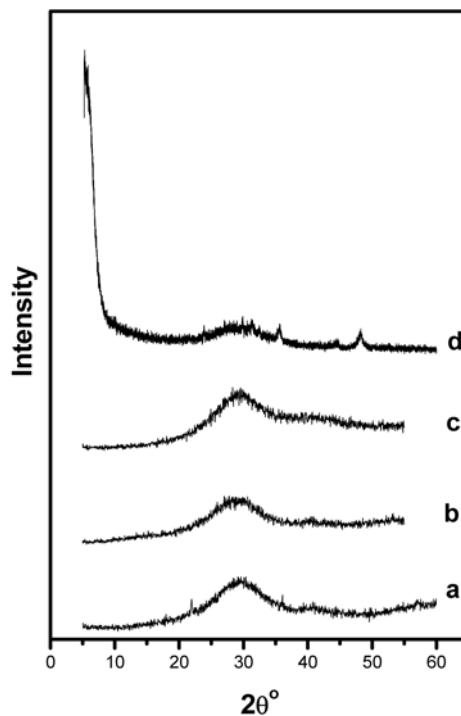
Fig. 2 shows X-ray diffraction patterns of the precursor K-gel(A) (a) and of products obtained by the isothermal heating of precursor at 1423 K for  $t = 1.5$  h (b), and  $t = 6.833$  h (c). It is evident that the intensity of the broad “maximum” of the amorphous gradually decreases and the sharp maxima of the formed crystalline phase (leucite) gradually increase with the increasing time of heating, and that the crystallization process is completed after  $t = 6.833$  h (fig. 2c). The progress of X-ray diffraction patterns of products obtained by the heating of K-gel (A) at 1453 K and 1483 K exhibits the same general feature as previously presented in Fig.2.

Fig. 3 shows X-ray diffraction patterns of the precursor K-gel(B) (a) and of products obtained by the isothermal heating of the precursor at 1483 K for  $t = 0.5$  h (b), and  $t = 3$  h (c). The crystallization process is completed sooner than in the case when using zeolite KA or K-gel (A) as a starting material at the same temperature. The progress of X-ray diffraction patterns of products obtained by the heating of K-gel(B) at 1423 K and 1453 K exhibits the same general feature as already presented in fig.3.

Two-stage ion-exchange process of the original (host) sodium ions from the X-ray amorphous Na-aluminosilicate [Na-gel(A)] with other alkaline ions ( $\text{Me}^+ = \text{NH}_4^+, \text{K}^+$ ) does not considerably change either the chemical composition of the aluminosilicate part of gel or the



**Fig. 3.** X-ray diffraction (XRD) patterns of samples obtained after thermally-induced transformations of amorphous Me-aluminosilicate precursors obtained by Procedure B [Me-gels(B)] (a) at 1483 K for 0.5 (b) and 3 h (c).



**Fig.4.** X-ray diffraction (XRD) patterns of amorphous starting materials: Amorphous intermediate phase of thermally induced K-exchanged zeolite A (a), product obtained by ball milling of the K-exchanged zeolite A (b), K-gel(A) (c), K-gel (B) (d).

gel “framework” structure as well as the surface and micro-structural (presence of structural subunits or even more complex zeolite-like structures) properties. Hence it is concluded that hydrated exchangeable  $\text{Na}^+$  ions in the gel “framework structure” of the Na-gel(A) are simply replaced by the  $\text{Me}^+$  ions from solution, thus forming Me-gels(A), without any chemical interactions.

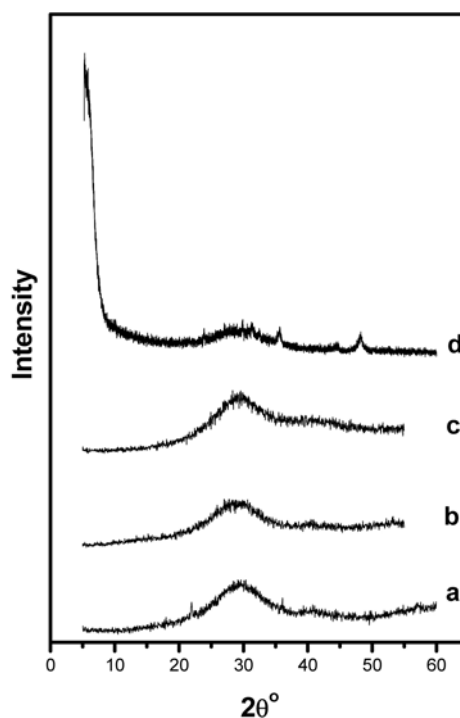
The differences (fig.4.) in the “framework structure” among the amorphous aluminosilicate materials i.e. K-gel(A), K-gel(B), the intermediate amorphous phase obtained by the heating of K-exchanged zeolite A in a comparison with the amorphous aluminosilicate material obtained by ball milling of K-exchanged zeolite A (see fig.4 in<sup>7</sup>) (indicated by shifting of the “peak” position of the broad “maxima” in X-ray diffraction patterns) are probably caused by differences in their “short order structure units”.

Although the crystallization of kalsilite/kaliophilite was expected during the heating of both K-gel (A) and K-gel(B)<sup>7,27</sup>, only kalsilite ( $\text{KAlSiO}_4$ , 11-0579)<sup>28</sup> was crystallized during the heating of K-gel(B) (see Table 1); the heating of K-gel(A) resulted in the crystallization of leucite ( $\text{KAlSi}_2\text{O}_6$ , 01-071-1147). From our previous study<sup>26</sup> it is known that the isothermal heating of K-exchanged zeolite A at the temperature of the exothermic peak in its DSC curve (1235 K) resulted in the formation of a mixture of 80% of kalsilite and 20% of kaliophilite since the calcination at the same temperature of the X-ray amorphous aluminosilicate, obtained by ball milling of K-exchanged zeolite A, resulted in the formation of kalsilite.

**Table 1.** Phase transformations of the samples obtained by Procedure A [K-gel(A)] and Procedure B [K-gel(B)], K-exchanged zeolite A and K-gel obtained by ball milling after thermal treatment at the appropriate temperature.

	Temperature of heating, K	Transformed phase
K-exchanged zeolite A	1235 [7]	80% kalsilite + 20% kaliophilite
	1258	100% kalsilite
	1278	100% kalsilite
	1298	100% kalsilite
K-gel(A)	1423	100% leucite
	1453	100% leucite
	1483	100% leucite
K-gel(B)	1423	100% kalsilite
	1453	100% kalsilite
	1483	100% kalsilite
K-gel obtained by ball milling	1235[7]	100% kalsilite

It is obvious that the “gel structure” consists of different primary and secondary structure units that influence the formation of a certain crystallization product. For this reason, our further investigation will be the AFM (Atomic Force Microscopy) study of the various gel precursors.



**Fig. 5.** A. FT-IR spectra of amorphous starting materials: Amorphous intermediate phase of thermally induced K-exchanged zeolite A (a), product obtained by ball milling of the K-exchanged zeolite A (b), K-gel(A) (c), K-gel (B) (d). B. FT-IR spectra of products obtained by the calcination of amorphous materials described in A.

### 3. Conclusions

High purity kalsilite and leucite may be prepared at the temperature of about 1273 K by using gels, prepared as above by procedures A and B, as starting materials. Although kalsilite may also be prepared from amorphous ball milled samples of K-exchanged zeolite A, the obtained product contains impurities caused by the use of milling balls made of tungsten carbide.

### 4. Acknowledgements

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### 5. References

1. S. Hashimoto, A. Yamaguchi, K. Fukuda, S. Zhang, *Mat. Res. Bull.* **2005**, 40, 1557–1583.
2. M. J. Cattell, T. C. Chadwick, J. C. Knowles, R. L. Clarke, D. Y. D. Samarawickrama, *Dent. Mat.* **2006**, 22, 925–933.
3. T. Ota, T. Takebayashi, M. Takahashi, Y. Hikichi, H. Suzuki, *J. Mat. Sci.* **1996**, 31, 1431–1433.

4. M. J. Cattell, T. C. Chadwick, J. C. Knowles, R. L. Clarke, Dent. Mat. **2005**, 21, 811–822.
5. T. Ota, M. Takahashi, I. Yamai, J. Am. Ceram. Soc., **1993**, 76(9), 2379–81.
6. Y. Zhang, J. Wu, P. Rao, M. Lv, Mat. Lett. **2006**, 60 2819–2823.
7. C. Kosanović, B. Subotić, I. Šmit, A. Čížmek, M. Stubičar, A. Tonejc, J. Mat. Sci. **1997**, 32, 73–78.
8. I. Szabo, B. Nagy, G. Völksch, W. Höland, J. Non-Cryst. Solids **2000**, 272, 191–199.
9. S. Ban, K. Matuo, N. Muzutani, H. Iwase, J. Hasegawa, Dent. Mat. J. **1998**, 17, 264–274.
10. K. Hirao, N. Soga, M. Kunugi, J. Phys. Chem., **1976**, 80, no.14, 1612–1616.
11. E. M. Levin, C.R. Robbins, H. F. Mcmurdie, Phase Diagrams for Chemists, The American Ceramic Society, 1964, p.156, Fig. 407.
12. T. S. Sheu, W. J. O'Brien, S. T. Rasmussen, J. Mater. Sci. **1994**, 29 125–128.
13. S. Oishi, T. Miyata, T. Suzuki, J. Mater. Sci. Lett. **2003**, 22, 927–929.
14. C. Liu, R. Komarneni, R. Roy, J. Am. Ceram. Soc. **1994**, 77 (12), 3105–3112.
15. M. Novotna, V. Satava, P. Kostka, Glass Technol. **2004**, 45, 105–107.
16. R. Dimitrijević, V. Dondur, J. Solid state chem, **1995**, 115 (1), 214–224.
17. L. Heller-Kallai, I. Lapidés, J. Of thermal analysis & Calorimetry **2003**, 71 (3), 689–698.
18. R. W. Thompson, K. C. Franklin, Verified syntheses of zeolitic materials, (ed. H. Robson) 2<sup>nd</sup> Rev. Ed. **2001**. p. 179.
19. P. H. Hermans, A. Weidinger, Makromol. Chem. **1961**, 44/46, 24.
20. L. S. Zevin, L. L. Zavyalova, Kolichestvenniy Rentgenographicheskiy Prazovij Analiz, Nedra, Moscow, **1974**, 37.
21. M. A. Subramanian, D.R. Corbin, U. Chowdhry, Bull. Mat. Sci. **1993**, 16, 665–678.
22. H. Mimura, T. Kanno, Sci. Rep. RITU. **1980**, 29A ,102–111.
23. B. Hoghooghi, J. McKittrick, C. Butler, P. Desch, J. Non-Cryst. Solids **1994**, 170, 303–307.
24. C. Kosanović, B. Subotić, I. Šmit, Thermochem. Acta **1998**, 317, 25–37.
25. G. Dell'Agli, C. Ferone, M.C. Mascolo, M. Pansini, Solid State Ionics **2000**, 127, 309–317.
26. C. Kosanović, A. Čížmek, B. Subotić, I. Šmit, M. Stubičar, A. Tonejc, Zeolites **1995**, 15, 51–57.
27. C. Kosanović, B. Subotić, V. Kaučič, M. Škrebliin, Phys. Chem. Chem. Phys. **2000**, 2, 3447–3451.
28. JCPDS-International Centre for Diffraction Data, Swarthmore, PA, USA, 2003.

## Povzetek

Izotermna amorfizacija kalijevega izmenjalnega zeolita A, rekristalizacija nastale amorfne faze in kristalizacija K-alumosilikatov so bile študirane pri treh različnih temperaturah z metodo rentgenske praškovne analize. Kalijeve alumosilikati so bili pripravljene na dva načina: z ionsko izmenjaov iz natrijevih alumosilikatnih gelov in z neposrednim obarjanjem iz ustreznih raztopin K-aluminatov in K-silikatov.