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METHOD OF A HIGH TEMPERATURE THERMAL INDUCED PHASE TRANSFORMATION OF ZEOLITE IN THE PROCESS OF OBTAINING THE DIFFERENT MATERIALS OF FELDSPAR TOPOLOGY

Ana Radosavljević-Mihajlović[1a], Srđan Matijašević[1b], Jelena Nikolić[1c]

[1]Institute for Technology of Nuclear and Other Raw Materials, Belgrade, Serbia

[1a] a.radosavljevic@itnms.ac.rs, https://orcid.org/0000-0003-1228-4058;
[1b] s.matijasevic@itnms.ac.rs, https://orcid.org/0000-0002-3897-8085;
[1c] j.nikolic@itnms.ac.rs, https://orcid.org/0000-0002-9624-8865

Abstract

The preparation of various aluminosilicate ceramic materials using synthetic zeolites as the precursors has been a topic of great interest during the last three decades. This method of synthesis is often called the thermal-induced transformation of zeolite (ZTIT) and has the certain advantages over the other conventional methods. This paper presents the comparative results of structural and microstructural tests the products of high-temperature thermal transformation of zeolite Pb, Mn - LTA topology. After thermal treatment at temperature between 700º - 1500º C, it is transformed into different feldspar structures. Mn-LTA zeolite at temperature of 1300 ºC is changed to the structure of Mn-anorthite with parameters (a=8.109(2) b= 12.824 (3) c=7.067 (4) β=115.89º(3). Pb-LTA zeolite transforms into the Pb-celsian structure at temperature of 1200 ºC (a=8.411(2) b= 13.047 (3) c=7.163 (4) β=115.35º(3). Structural and microstructural parameters were determined by the X-ray powder diffraction method on a polycrystalline sample, using the Fullprof program.

Keywords: *ZTIT, feldspar, Rietveld method*

1. INTRODUCTION

The preparation of various aluminosilicate ceramic materials using synthetic zeolites as the precursors has been a topic of a great interest during the last three decades. This method of synthesis is often called the thermal-induced transformation of zeolite (ZTIT) and has certain advantages over the other conventional methods. One of the basic physical and chemical properties of zeolites is that they possess an aluminosilicate network with a low density, compared to the analogous non-zeolitic materials. During heat treatment, zeolites change into a structure with a higher network density resulting in formation the new ceramic materials. All these properties indicate the possibility of using zeolite as a precursor for obtaining the ceramic products of exceptional quality. Classical methods of synthesis the phases in the system M - SiO_2 - Al_2O_3 (M = Li^+, Na^+, K^+, Rb^+, Cs^+ or Ba^{2+}, Ca^{2+}, Sr^{2+}) are crystallization by the "sol-gel" process [1, 2], hydrothermal synthesis [3], reaction in the solid state ("solid - solid" reaction) [4]. During the 80ʾs of the last century, a new way of synthesizing the aluminosilicate materials from zeolite precursors was promoted [5].

This paper represents a continuation of previous research and presents the comparative data in the process of forming the new materials using the ZTIT process. The ion-exchanged zeolites of the LTA topology with Pb and Mn cations were used.

2. EXPERIMENTAL

The starting materials for these studies were samples of synthetic zeolite LTA with Ca^{2+} as an extrafarmework cation. The procedure was as follows: 15 g of Ca-LTA zeolite were left in contact with 300 ml of solution of 0.17 M $MnSO_4 \cdot 4H_2O$ and 0.21 M $Pb(NO_3)_2$. The ion exchange lasted 72 h, with the constant stirring and temperature of 70°C. After every 24 h, a new amount of solution was added and content of the extrafarmework cations in the filter was checked. After three days of continuous exchange, samples were centrifuged and washed until the negative reactions to chloride ions, dried and ready for further characterization.

For characterization, the X-ray powder analysis on a polycrystalline sample was used (on an automatic powder diffractometer PW-1710, using a Cu tube at voltage of 40 kV and current of 30 *m*A). A program Fullprof was used to clarify the obtained data [6]. The diffraction data are collected in interval 4-130 °2θ with a step of 0.02° 2θ and retention time of 15.9 *s* at each step for the structure refinement using the Rietveld method [7]. Crystal morphology was studied using a scanning electron microscope equipped with a LINK AN 1000 EDS microanalyzer using a JEOL JSM-6460 LV, at voltage of 15 kV and current of 20 mA. The surface of an electron beam was measured at 1 mm^2 in a time interval of 250 s. The ZAF-4/FLS was the used software.

3. RESULTS AND DISCUSSION

The process of thermally induced phase transformation takes place in four stages [8, 9]. The first stage represents the process of dehydration and ion exchange of the extrafarmework cation of the starting zeolite. Process of amorphization of the dehydrated sample is the second phase and occurring in the different temperature. Then follows the crystallization of a new aluminosilicate phase (diphylloalumosilicate), which is stable for a short period of time. The last is the process of phase transformation of the zeolitic topological structure into the feldspar topological structure. The four phases in the thermally induced phase transformation of the modified LTA-topology zeolite sample, based on the scanning electron microscope results, are presented in Figure 1.

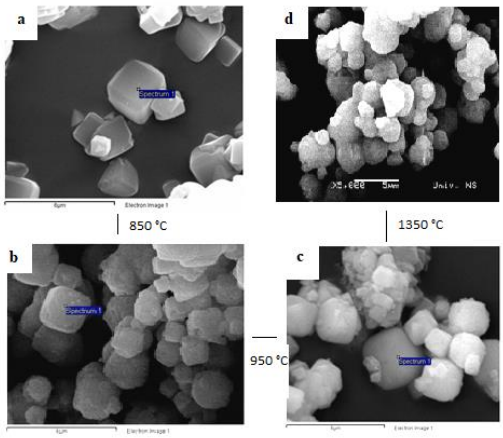

Figure 1. *Four stages of thermally induced phase transformation of Pb-LTA zeolite based on the SEM analysis; (a) initial Ca-LTA; (b) Ca-LTA annealed at 850°C/1 h; (c) hexacelsian; (d) recrystallization of hexacelsian into celsian at temperature of 1350°C/1h*

Structural reorganizations of (Si, Al) O_4 tetrahedra occur at temperatures higher than 800ºC. Based on the literature data [9,10], it was observed that the extrafarmework cations play a significant role in the coordination of tetrahedral rings during the structural thermal transformation. The Si–O–Al bridges, D4R SIJ, were found to be broken in such a way as to leave a cation with the six members preserved around the extraframework cation [10-12]. During formation the stable phase of feldspar, this symmetrical configuration around the extrafarmework cation is retained, Figure 2.

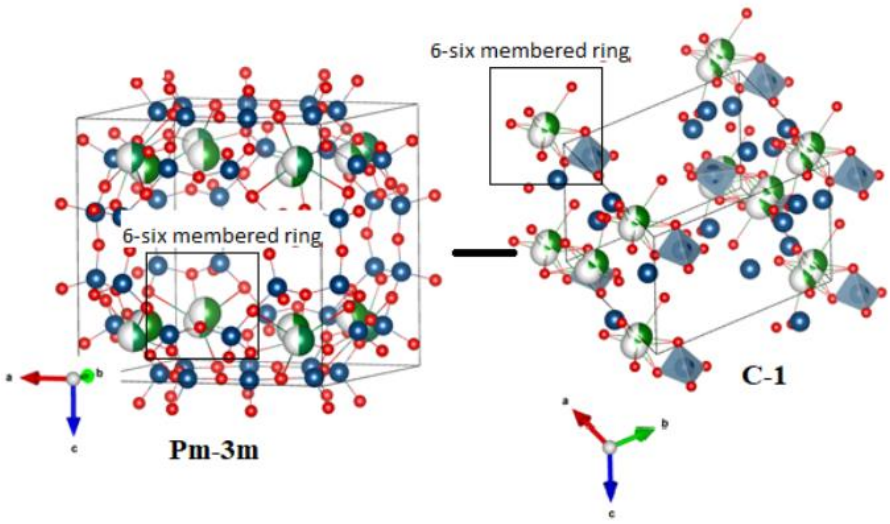

Figure 2. *The symmetrical configuration around the extrafarmework cation in the structure of thermal treated Mn-LTA zeolite (in temperature range from a room temperature to 800º C, [11])*

The thermal conversion in the finale stage includes the polymorphous transformations into to the more stable structure. After an annealing temperature of 800ºC, the zeolite precursor of Mn-LTA topology directly recrystallized to anorthite, which is stable up to temperatures of 1300ºC. The Pb-LTA zeolite topology was transformed into Pb celsian with an increase in temperature over 900ºC. The stability of obtained structures in the process of prolonged heating depends on the temperature/time, as well as the internal arrangement. The Mn-feldspar phase is stable over a small temperature range of 900-1100ºC. Increasing temperature to 1300º C leads to the formation of a phase of mineral diopside. The Pb-feldspar phase is stable in temperature range of 900-1300ºC. At temperatures above 1300ºC, the Pb crystal-glasses are formed.

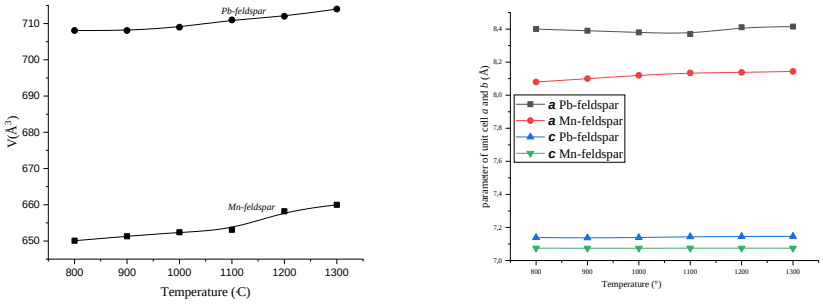

Figure 3. *The value of parameter the unit cell (a, b, c, V) of Mn, Pb – feldspar during the thermal treatment in temperature range 800-1300°C*

The parameters of unit cell (Mn, Pb - feldspar) in correlation with temperature, during the thermal treatment are presented in Figure 3. Based on the literature data, after thermal treatment, the parameters of unit cell in the system of $MnAl_2Si_2O_8$ –$PbAl_2Si_2O_8$ are decreased and correlated with the ion exchange of Mn, Pb/Ca. The results are in accordance with the literature data [13]. Figure 3 shows the structures of Mn-feldspar and Pb feldspar at temperature of 1000°C.

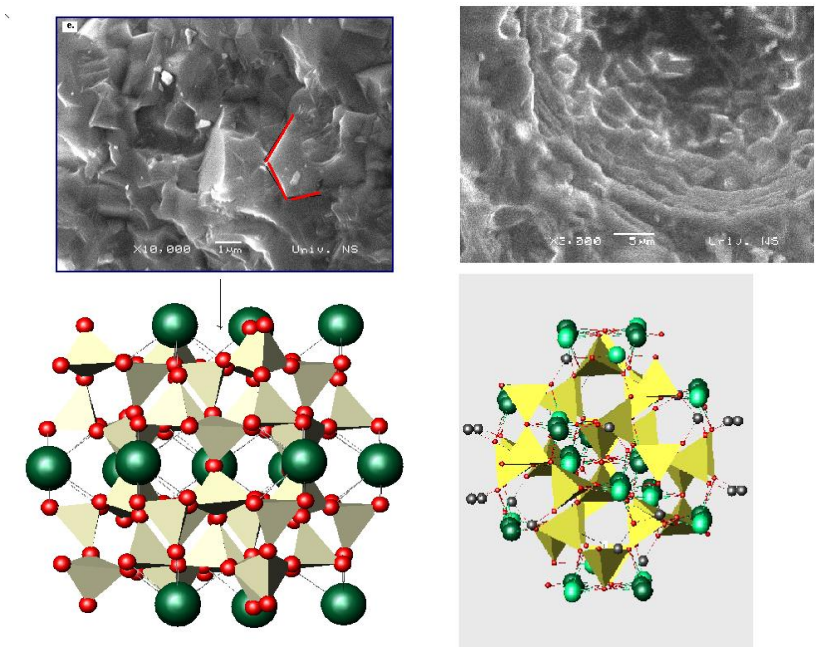

Figure 4. *Structure of Mn-feldspar and Pb-feldspar (T=1000ºC) [11, 12]*

The structures of Mn-feldspar and Pb feldspar, obtained at temperature of 1000ºC, are shown in Figure 4.

4. CONCLUSION

During the process of thermally induced phase transformation the ion-exchanged zeolite precursors, a stable tetrahedral network with a statistical distribution of Si4+/Al3+ is formed. Deviations, present in the structural parameters, are most likely the result of impact the extrafarmework cation in the aluminosilicate network. The aluminosilicate network of the ion-exchanged LTA zeolites becomes unstable with increasing temperature, and amorphization begins at temperatures between 600 and 750°C. At temperatures over 900ºC, the structures become stable and transition into the feldspathic topologies. The formed structures are thermally stable and can be used in further processes, obtaining the Pb-glass or similar materials. Materials obtained in this way have found a wide application due to their exceptional thermal and dielectric properties.

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