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THERMALLY INDUCED RINGS FORMATION IN ALUMINOSILICATE STRUCTURES

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In the present study, we performed an investigation of phase transformation of zeolite Na-GIS in temperature interval from room temperature up to 1300°C. The collapse of S4R and S8R (secondary building units in zeolite Na-GIS) and the forming of pure sodium nepheline phase, consists of S6R, was examined. During the thermal transformation of Na-GIS zeolite symmetry of rings was changed and their deformation increases. The irregularity of rings causes the appearance of defect modes in the IR spectra of amorphous precursors. Investigated phases were characterized by XRPD, IR, NMR and DSC methods. A semiempirical method AM1 was used for calculation of vibrational spectrum of nepheline.

Keywords: *pure sodium nepheline, structural transitions, zeolite NaP*

Introduction

Ceramics based on alkaline or alkaline-earth framework aluminosilicates, are materials of great technological interest due to their thermal, electrical and other properties. The properties of ceramic materials depend on synthesis routes. The unit cell parameters are closely related with short range ordering of secondary building units. The mechanism of crystalline phase formation often depends on the transformation of rings as secondary building units. Different models and methods have been used to investigate the rings in aluminosilicates.

Formation of rings and their ordering in the framework aluminosilicate structures is not examined enough. Besides, theoretical studies based on Ab Initio and Monte Carlo simulations, forming and ordering of rings in framework aluminosilicate structures could be investigated by experimental techniques such as IR [1–3], Raman [4] and NMR [5, 6] spectroscopy. A disordering and breaking of rings, their reconnection and ordering could be studied during phase transitions of structurally known precursors.

Recently, Mozgawa and Handke [7–9] reported calculated vibrational spectra of aluminosilicate D4R and D6R structural units using Ab Initio methods. In these calculations, the model of isolated double four- and six-membered rings containing both AlO_4 and SiO_4 tetrahedra has been used. The obtained results were used for interpretation of zeolite spectra.

A disordering and breaking of rings, their reconnection and reordering could be examined during phase transitions of structurally known precursors. Generally, zeolites are suitable precursors for the synthesis of many types of aluminosilicate phases. The mechanism of transformation, transition temperatures, and structure of formed phases are very important for practical application of zeolites as precursors in the ceramic or ceramic composite materials [10–13]. The mechanism of thermally induced transformation strongly depends on extra framework cations and the type of used zeolite. The mechanism of transformation and the structure of obtained phases are mostly studied for zeolites Na-LTA and Na-FAU [13–19].

Besides, the influence of Si/Al ratio and secondary building units of zeolite structure are also important factors in the mechanism of thermally induced transformations [20–22]. The investigations of ring evolution by thermally induced transformation of zeolites offers several advantages due to the possibility of the framework vacant site creation (Si/Al ratio in the framework) or the selection secondary building unit, rings in the initial zeolite precursors. In the recently published paper [22] we showed that pure sodium nephelines, with Si/Al ratios between 1.0 and 1.5 were formed by the thermally induced transformation of Na-LTA, Na-FAU and Na-GIS zeolites. The

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nepheline framework consists of the single six-membered ring (S6R) tetrahedra building units [23] connected in a tridymite type topology. The TO_4 framework of parent Na-LTA zeolite consists of S6R secondary tetrahedra building units which are connected over common D4R units in a regular framework with two types of voids. The TO_4 framework of initial Na-FAU zeolite consist of S6R, S4R and D6R secondary building units connected in a regular framework topology that create two types of cages. The Na-GIS framework may have variable Si/Al ratio and contains only S4R building units.

In our previous paper [21] we studied rings evolution during rearrangement of six membered rings (from Na-LTA and Na-FAU to carnegieite and nepheline). In those cases, it was noticed that during thermal transformation of zeolites S6R were preserved. To the best of our knowledge, the corresponding investigations of Na-GIS were not reported.

Subject of our work was thermally induced evolution of rings in aluminosilicate structures. Due to the well-known structure and symmetry of rings in zeolites as well as in phases obtained by their thermal treatment these materials were used as a model system in our investigation. In this paper, breaking of S4R secondary building units in zeolite Na-GIS, forming of amorphous precursor, and crystallization of nepheline phase made from S6R is studied. In aim to investigate the influence of thermal treatment on deformation of rings in aluminosilicate structures, a comparison of experimentally obtained IR spectra and the calculated one (nepheline's) was done. Vibrational spectrum of nepheline (Si/Al=1.5) was calculated by semiempirical AM1 method, using the experimentally obtained XRD data corrected by Rietveld refinement.

Experimental

The synthetic zeolite Na-GIS (Si/Al=1.50, produced in our laboratory) was used as starting material. Samples for further analysis were obtained by thermal treatment of zeolite Na-GIS in the temperature range from 500 up to 1300°C, in 20°C intervals. The samples were heated at constant temperature (1 to 4 h, ±2°C) using Carbolite CTF 15/75 electric furnace.

After the samples had been cooled, all XRD, IR and NMR measurements were performed at room temperature. The XRD patterns were obtained on Philips PW-1710 automatic diffractometer, using Cu tube operating at 40 kV and 35 mA. The IR measurements were performed at Perkin-Elmer 983 spectrophotometer using the KBr pellet technique, in the frequency interval 300–1400 cm^{-1}. The spectral resolution was 4 cm^{-1}. A semiempirical AM1 method was used for calculations of vibrational spectrum of nepheline structure containing S6R. The deconvolution of recorded IR spectra was done using PeakFit™ spectroscopy analysis software [24]. The Gaussian function was chosen for the fitting. First, the deconvolution procedure was carried out for the nepheline structure. The positions of bands in the deconvoluted spectra are the same as in calculated one. During the curve fitting process, the number and position of primary peaks were fixed, while the peak width and intensity were changed. The final values for obtained correlation factor r^2 are between 0.990 and 0.999.

MAS NMR spectra were obtained on a Bruker AMX300 spectrophotometer. ^{29}Si spectra were recorded at 59.61 MHz, using a WB-7BL (7 mm) probe and a MAS rate 3.0 KHz, with a single (7 μs, $\pi/2$) pulse acquisition. The ^{29}Si chemical shifts are reported relative to tetramethylsilane (TMS), using the previously calibrated signal from Na-LTA zeolite as a secondary reference. DSC experiments were performed on TA SDT 2960 instrument, between 25 and 1300°C under nitrogen flow, against an aluminum oxide reference. The heating rate was 20° min^{-1}.

Results and discussion

XRD analysis of phases obtained by thermal treatment of Na-GIS zeolite indicates three-phase transformations in the temperature range from 500 to 1300°C. Figure 1 presents XRD patterns of phases obtained during the heating of this system. At 580°C, first indications of partial collapse of Na-GIS structure are noticed in XRD patterns. Between 760 and 780°C the partially amorphous precursor is formed, and phase obtained at 780°C is completely amorphous, Fig. 1b. At 850°C, low-crystalline nepheline phase starts to grow, Fig. 1c. The pure nepheline structure with hexagonal symmetry was formed after the sample was heated for 4 h at 900°C, Fig. 1e. This phase is stabile up to 1250°C when glass transformation was observed, Fig. 1h. According to the obtained results, the following conversion scheme is recognized:

$$\text{Na-GIS}\rightarrow\text{amorphous}\rightarrow\text{nepheline}\rightarrow\text{glass}$$

The results of XRD measurements are confirmed by DSC method. The thermal behavior of Na-GIS zeolite during the heating is recorded in the temperature interval from room temperature up to 1300°C and is shown in Fig. 2. Endothermic peaks at 64, 129 and 289°C corresponds to water loss. Both TG and DSC plots indicate a three-stage desorption process, which could be attributed to the different locations of water molecules in the Na-GIS structure. Very wide region from 289 to about 900°C could be attributed to the existence of amorphous phase. Exothermic peak at 1117°C is due to the transformation of amorphous

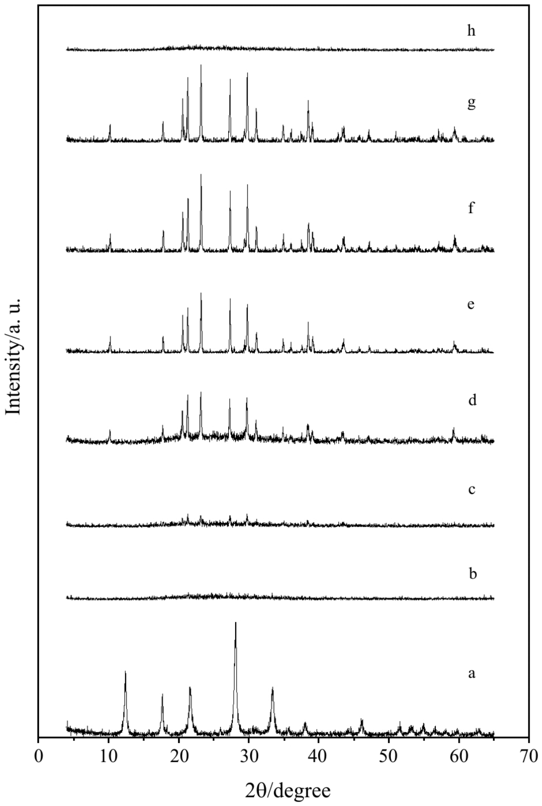

Fig. 1 XRD patterns of: a – zeolite Na-GIS at room temperature, b – amorphous phase obtained at 780°C, 1 h, c – amorphous phase with traces of nepheline at 850°C, 4 h, d – nepheline formed at 875°C, 3 h, e – nepheline formed at 900°C, 4 h, f – nepheline formed at 1000°C, 4 h, g – nepheline formed at 1100°C, 4 h and h – glass obtained at 1250°C, 4 h

precursor to nepheline structure. Phase transition from nepheline to glass induces endothermic peak at 1229°C. In Table 1 all examined samples, condition of their preparation and some structural characteristics are listed.

Figure 3 presents recorded infrared absorption spectra of zeolite Na-GIS and of the phases obtained during his thermal treatment. It can be noticed that IR spectra of synthesized samples are similar in general envelope. They posses three dominant groups of bands centered near 470, 710 and 1000 cm^{-1}, assigned to internal vibration of T–O–T bridge: rocking, bending and stretching, respectively. Other bands in spectra are assigned to external vibrations. Generally, the bands in the spectral range 500–650 cm^{-1} are due to framework ring vibrations, while bands below 400 cm^{-1} are due to the crystal lattice vibrations.

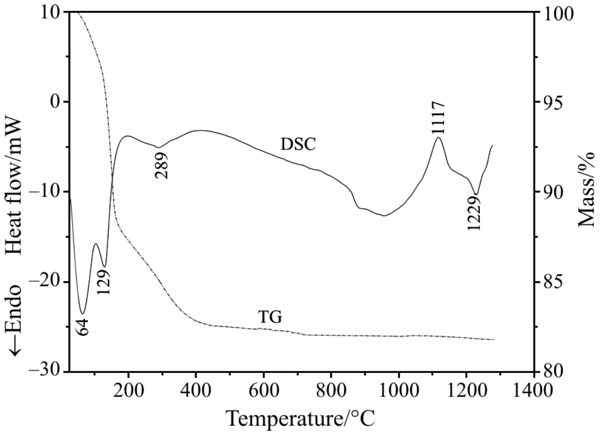

Fig. 2 DSC pattern of zeolite Na-GIS thermally treated from room temperature up to 1300°C. The heating rate was 20°C min^{-1}

In ordered aluminosilicate structures, the absorption peaks in IR spectra are usually well defined and sharp. It is worth noticing that in spectra of phases obtained during thermal treatment of zeolite Na-GIS all dominant groups of bands are composed of several overlapped bands. Because of that, the detailed interpretation of recorded spectra was difficult, especially in the case of rings vibration bands, which are of small intensity and very broad. Due to our interest in mechanism of rings evolution (indicated by rings vibration bands in IR spectra) we performed mathematical deconvolution of spectra into constituent bands (Fig. 4a–d), which enables the determination of main parameters of these bands [21]. Before deconvolution, approximate positions of the bands in nepheline IR spectrum were calculated by semi-empirical AM1 method, using by experimentally obtained XRD data corrected by Rietveld refinement. The calculation was done for two unit cells with 128 atoms (pseudo molecule). Calculated IR spectrum (possible wave numbers) of pure sodium nepheline is presented

Table 1 List of examined samples and condition of their preparation

Sample	SBU* rings	Condition of sample treatment		Symmetry
		T/°C	*t*/h	
Na-GIS	S4R, S8R			Cubic
Amorphous phase	/	780	1	/
Amorphous and traces of nepheline structure	S6R*	850	4	/
Nepheline	S6R	900	4	Hexagonal
Glass	/	1250	4	/

*S6R in traces

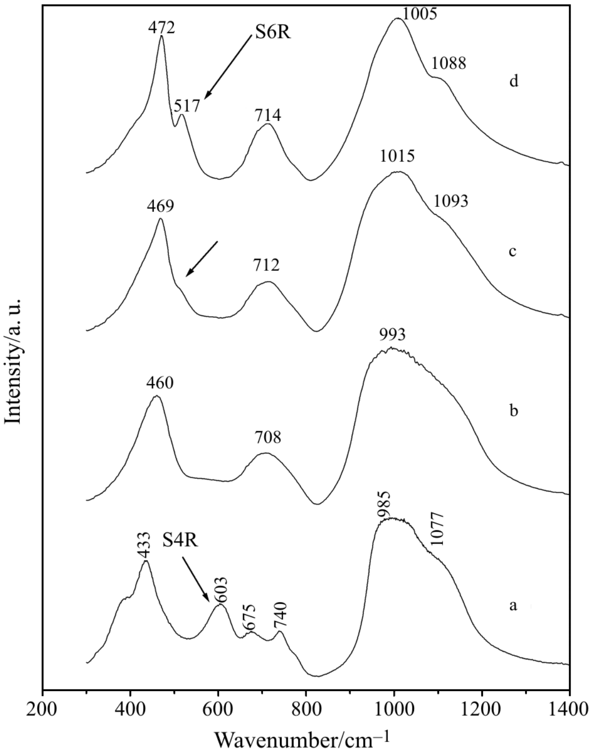

Fig. 3 IR spectra of: a – zeolite Na-GIS at room temperature, b – amorphous phase obtained at 780°C, 1 h, c – amorphous phase with traces of nepheline structure at 850°C, 4 h and d – nepheline phase obtained at 1100°C, 4 h

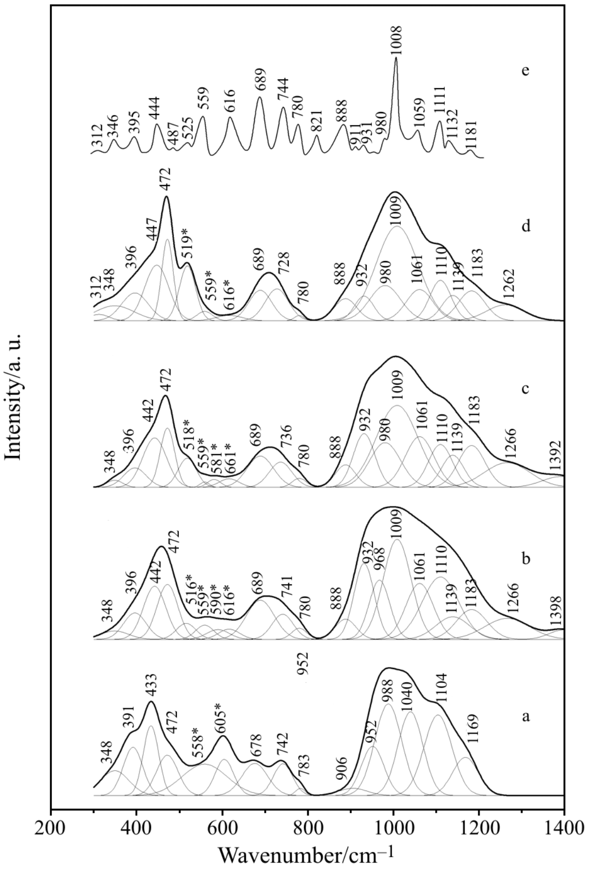

Fig. 4 Deconvoluted IR spectra of: a – zeolite Na-GIS at room temperature, b – amorphous phases obtained at 780°C, 1 h, c – amorphous phases with traces of nepheline structure at 850°C, 4 h, d – nepheline phases obtained at 1100°C, 4 h and e – calculated IR spectra of nepheline. An asterisk (*) denotes rings vibrations

in Fig. 4e. It can be observed that calculated bands positions and the deconvoluted one are very similar. The differences between these two spectra are probably caused by approximation on two unit cells used for the calculation, instead of framework (nepheline) structures. The bands assignments and the bands positions of the deconvoluted spectra are shown in Table 2. The positions of the internal vibration bands in these aluminosilicate structures are almost identical. Besides, the most significant difference is the appearance of a number of low intensity peaks in the range 500–650 cm^{-1}. It could be inferred that the bands in this region originate from the deformation of six membered rings.

In the IR spectra of Na-GIS (Fig. 4a) the bands at 603 and 675 cm^{-1} are connected with vibrations of S4R and S8R, which are dominant SBU in that structure. In amorphous structure formed at 780°C (Fig. 4b) internal vibration bands still exists, but they are significantly broader then those in the spectra of highly crystalline alumosilicate phases. These bands are centered at 516, 559, 590 and 616 cm^{-1}. Further annealing at 850°C induces reorganization in connection of tetrahedra and the S6R start to form, Fig. 4c. This assumes is proved with relatively sharp band at 518 cm^{-1} and small, but no too broad, bands at 559, 581, 661 cm^{-1}. Besides, in XRD pattern of this sample (Fig. 1c) traces of nepheline structure are noticed. Increasing of temperature up to 1100°C leads to crystallization of pure sodium nepheline structure i.e. completely connection of TO_4 tetrahedra in form of single six-membered rings. This structure is stabile up to 1250°C. Figure 4d shows IR spectra of nepheline structure, where sharp band at 519 cm^{-1} confirms the existence of ordered S6R. This band is not sharp as in the cases of nepheline obtained from zeolite Na-LTA [21]. The main reason is different Si/Al ratio in these two zeolites. In zeolite Na-LTA Si/Al=1 and therefore the rings have hexagonal symmetry. However, Si/Al=1.5 in Na-GIS and S6R have oval symmetry. It is known that decrease of symmetry increases FWHM. In Table 2, positions of the vibrations are shown. It can be noticed by comparison of internal bands positions (which are very similar between zeolite GIS, amorphous intermediare and nepheline structure) that during thermal treatment of zeolite Na-GIS the structure of primary building units (TO_4 tetrahedra) is stable. However, the topology of

Table 2 The band positions in deconvoluted IR spectra of zeolite Na-GIS and phases obtained during their thermal treatment

Examined phases	Internal vibrations/cm^{-1}			External vibrations/cm^{-1}	
	rocking	bending	stretching	lattice	rings
Zeolite Na-GIS (room temperature)	433	678	906, 952	348	558
	472	742	988, 1040	391	605
		783	1104, 1169		
Amorphous phase (780°C, 1^{h})	442	689	888, 932	348	516
	472	741	968, 1009	396	559
		780	1061, 1110		590
			1139, 1183		616
			1266, 1398		
Amorphous phase and traces of nepheline structure (850°C, 4^{h})	442	689	888, 932	348	518
	472	736	980, 1009	396	559
		780	1061, 1110		581
			1139, 1183		661
			1266, 1392		
Nepheline (900°C, 4^{h})	447	689	888, 932	312	519
	472	728	980, 1009	348	559
		780	1061, 1110	396	616
			1139, 1183		
			1262		
Calculated nepheline spectrum (AM1 method)	444	689	888, 911	312	525
	487	744	931, 980	346	559
		780	1008, 1059	359	616
		821	1111, 1132		
			1181		

tetrahedras connection in secondary building units is different, from S4R (zeolite Na-GIS) via disordered structure (amorphous) to S6R (nepheline).

Due to number and shape of the bands in the spectral range 500–650 cm^{-1} it can be concluded that S4R and S8R, which exist in zeolite Na-GIS, are deformed and broken during thermal treatment. Followed, these rings are reconnected and reorganized in six-membered rings. With increasing of temperature symmetry of these S6R increases, too.

As mentioned before, in an ordered aluminosilicate structure the absorption peaks are usually well defined and sharp, and there are no sharp peaks in IR spectra of zeolite Na-GIS and phases obtained during thermal treatment. From this characteristic it could be concluded that the structure of examined samples are not ordered and that contain some degree of disorder of silicon and aluminum. These conclusions can be supported by NMR spectroscopy study. High-resolution MAS NMR spectroscopy has large contribution for understanding of Si/Al ordering in aluminosilicate structures [25, 26]. We use high-resolution ^{29}Si MAS NMR spectroscopy for examination of local structure in zeolites Na-LTA (Si/Al=1), Na-GIS (Si/Al=1.5) and obtained nepheline phase. The recorded ^{29}Si MAS NMR spectra are shown in Fig. 5. It is known from the literature, that in crystal structure of zeolite Na-LTA only one crystallographic site for *T* atoms exist,

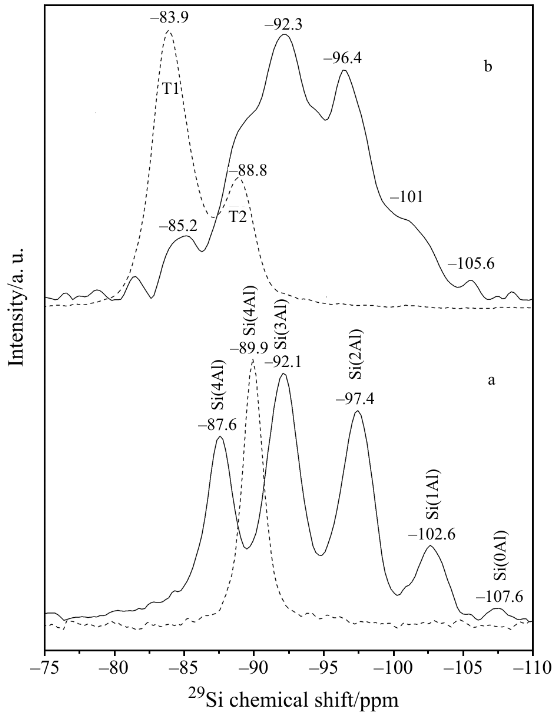

Fig. 5 ^{29}Si MAS NMR spectra of: a – zeolite Na-GIS (full line) and zeolite Na-LTA (dashed line) and b – nepheline phase obtained from zeolite Na-GIS at 1100°C, 4 h (full line) and nepheline phase obtained from zeolite Na-LTA at 1100°C, 1 h (dashed line)

while two different sites T1 and T2 exist in nepheline structure [27]. Figure 5a shows compared MAS NMR spectra of starting zeolite Na-LTA and Na-GIS. In spectrum of Na-LTA (Si/Al=1) (dashed line) there is one peak indicating Si(4Al) environments. The spectrum of Na-GIS (bold line) consists of five peaks at –87.6, –92.1, –97.4, –102.6 and –107.6 ppm, which are assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al), respectively. Besides, S4R have atom combinations 2Si2Al, 3Si1Al and 4Si. Figure 5b shows compared MAS NMR spectra of nepheline phases obtained from zeolite Na-LTA (dashed line) and zeolite Na-GIS (bold line). The ordering in terms of the number of Al next-nearest neighbors does not change during transformation Na-LTA zeolite into nepheline. In NMR spectra of nepheline obtained from Na-GIS, few overlapping peaks can be noticed, indicating Si/Al disorder. It should be noted that nepheline phase obtained from zeolite Na-GIS consists Si–O–Si and Si–O–Al bonds, and six-membered rings with atom combination 3Si–3Al, 4Si–2Al, 5Si–1Al and 6Si.

Conclusions

It is noticed that Na-GIS zeolite slowly collapses in the temperature region from 600 to 800°C. According to IR results it was assumed that Si–O–Si and Si–O–Al bonds, that form S4R and S8R secondary building units, are broken. At higher temperature, the bonds are reestablished and six-membered rings (S6R) are built. Only one exothermic peak in DSC plot indicates the rearrangement of formed S6R into nepheline structure. Because starting zeolite Na-GIS has Si/Al ratio 1.5 and disordered S4R (2Si2Al, 3Si1Al and 4Si) it is assumed that S6R in formed nepheline phase should have disordered structure, too. This assumption is confirmed by ^{29}Si MAS NMR spectroscopy. The results indicate that single six-membered rings with atom combinations 3Si3Al, 4Si2Al, 5Si1Al and 6Si exist. The deformation of rings at higher temperature causes the collapse of nepheline into glass and endothermic peak at 1229°C corresponds to glass forming.

Acknowledgements

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