

RECONSTRUCTIVE AND DISPLACIVE TRANSFORMATIONS OF TECTOSILICATES Non-stoichiometric carnegieite

*V. Dondur*¹, *S. Markovic*^{1*}, *R. Dimitrijevic*², *S. Macura*³ and
*D. Arandjelovic*¹

¹Faculty of Physical Chemistry, St. Trg 12, Belgrade, Yugoslavia

²Faculty of Mining and Geology, Department of Crystallography, Djusina 7, Belgrade, Yugoslavia

³Department of Biochemistry, Mayo Foundation, Rochester, Minnesota, USA

Abstract

By using the thermally induced phase transformation initial zeolites were converted into pure carnegieite, stuffed derivative of cristobalite. The polymorphs obtained from Na-LTA are stoichiometric (NaAlSiO_4), since those obtained from Na-FAU zeolite are non-stoichiometric ($\text{Na}_{1-x}\text{Al}_{1-x}\text{Si}_{1+x}\text{O}_4$). Stoichiometric carnegieite have cubic structure, while non-stoichiometric carnegieite crystallized in cubic and orthorhombic forms. ²⁹Si MAS NMR spectra show a very large but expecting difference between stoichiometric and non-stoichiometric carnegieite. The spectrum of stoichiometric carnegieite has only one peak Si(4Al), while the spectrum of non-stoichiometric carnegieite consist few superimposed peaks assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al). DTA study indicates the occurrence of displacive phase transition of all synthesized carnegieite. The transition temperature is depending on silicon aluminum order: $T_m=690^\circ\text{C}$ for stoichiometric, $T_m=565$ and 660°C for non-stoichiometric, low-temperature and high-temperature carnegieite, respectively.

Keywords: carnegieite, DTA, FAU zeolite, LTA zeolite

Introduction

A large part of modern materials science is concerned with understanding the reconstructive and displacive transformations in tectosilicates [1–3]. The stuffed silica polymorphs and zeolites are tectosilicates, made up of open three-dimensional framework of SiO_4 and AlO_4 tetrahedra with metals as interstitials charge balancing cations. Despite the importance of the system it appears that there has been no systematic investigation of the reconstructive transformations zeolite with different Si/Al into stuffed silica polymorphs.

Phases can be classified as stuffed silica derivatives if they comprise a silica framework topology with, alkali or alkaline earth, cations stuffed into the framework cavities [1]. Different framework distortions around the stuffing cations can lead to a

* Author for correspondence: E-mail: smilja@lotos.ffh.bg.ac.yu

variety of derivative structures with different ring/channel configuration. Generally, depending on the concentrations of substitutional M^+ and Al^{3+} stuffed derivative phases can have the composition $M_{1-x}Al_{1-x}Si_{1+x}O_4$ with $0 < x < 1$. Carnegieite, which is stuffed derivative of cristobalite, has $NaAlSiO_4$ composition obtained by partially replacing Si^{4+} ions with tetrahedrally coordinated Al^{3+} ions and by stuffing Na^+ ions into the cavities of the tetrahedral framework to maintain charge balance. Tetrahedra building units TO_4 ($T=Si, Al$) are arranged in a structure of single six rings (S6R) which are connected in a cristobalite type topology ‘...ABCABC...’.

The system of sodium LTA zeolite which contains equal number of silicon and aluminum tetrahedra in the structure possess only one type of Si–O–Al bridges and only 6-membered rings ($Al_3Si_3O_{18}$) can be recognized. Besides, in the system of Na-FAU zeolite with nonequal number Al and Si the existence of two types of Si–O–Al and Si–O–Si bridges is possible. In that case, the 6-membered rings with different number of Si and Al are presented.

Due to their open structure and the possibility of modifications, zeolites are potential precursors in the synthesis of new materials by thermal transformations. The earlier published results for the M-LTA precursors (M – alkaline or alkaline earth cation) [4–10] show that ordered LTA zeolite framework is an excellent medium for the investigation of phase relationship in the M_2O – Al_2O_3 – SiO_2 phase systems, particularly those of $MAIO_2$ – SiO_2 join.

Here we reported the formation of pure stoichiometric ($NaAlSiO_4$) stuffed derivative of cristobalite, carnegieite, obtained from Na-LTA and non-stoichiometric ($Na_{1-x}Al_{1-x}Si_{1+x}O_4$) obtained from Na-FAU zeolite. In addition the displacive phase transformations of synthesized carnegieites were also investigated. We present for the first time direct experimental evidence that displacive phase transformations of carnegieite depend on framework cation (Si, Al) disorder.

Experimental procedure

The sodium form of synthetic zeolite LTA (Si/Al=1), produced by Fluka Co. and FAU (Si/Al=1.23), produced by Union Carbide Co., were used as starting materials. The starting materials were air-heated in the Carbolite CTF 15/75 electric furnace in a programmed temperature regime, from room temperature up to 1400°C. In all experiments the heating rate was $10^\circ C \text{ min}^{-1}$.

The XRPD patterns were obtained on Philips PW-1710 automated diffractometer, using Cu tube operated at 40 kV and 35 mA. DTA experiments were performed on Stanton Redcroft STA 1000 instrument, between 30 and 1000°C under nitrogen flow, against an aluminum oxide reference. The heating rate was $20^\circ C \text{ min}^{-1}$. MAS NMR spectra were obtained on a Bruker AMX300 spectrometer at room temperature. ^{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. The IR measurements were performed on Perkin Elmer

983G spectrophotometer using the KBr pallet technique, in the frequency interval $300\text{--}1250\text{ cm}^{-1}$, since this part of the IR spectrum is sensitive to network topology. The deconvolution and fitting were done using PeakFit 4 computer program. The number of peaks for a given fit was selected as the number of obvious spectral features, such as clearly resolved peaks and shoulders. Gaussian line shapes were chosen for fitting. Peak widths (FWHM – full width at half maximum) and height (peak intensity) were varied to minimize residuals while peak positions were holding constant. Computer program PeakFit 4 was used for deconvolution of NMR spectra, too.

Results and discussion

Schmitz *et al.* [11] investigated the structural changes of Na-LTA zeolite, using DTA and high-temperature X-ray methods, and concluded that the DTA peak at 880°C was due to the collapse of framework, the peak at 920°C was due to the transformation of amorphous phase to carnegieite and peak at 980°C was due to transformation from carnegieite to nepheline. The phase-equilibrium diagram at high temperature shows formation of high-temperature carnegieite phase at 1254°C and melts at 1526°C . Therefore in this study the samples are heated up in the range $700\text{ to }1400^\circ\text{C}$. Before XRPD measurements were performed samples have been heated at different temperature/time conditions. XRPD patterns were taken after cooling to room temperature. XRPD patterns of phases obtained by polymorphous transformations in the system with 1:1 stoichiometric Si/Al ratio are expected. The pure low temperature carnegieite ($\text{lt}^{\text{cub}}\text{-Carn}_{\text{LTA}}$) obtained at 800°C , 4 h, and high-temperature polymorph ($\text{ht}^{\text{cub}}\text{-Carn}_{\text{LTA}}$) was synthesized after heating at 1400°C , 0.5 h. In the case of non-stoichiometric system with Si/Al ratio 1.23, four phase transformations were obtained in the same temperature range. Figure 1 presents XRPD patterns of phases obtained during temperature programmed heating of this system. According to the obtained results for polymorph transformations of stoichiometric (LTA)

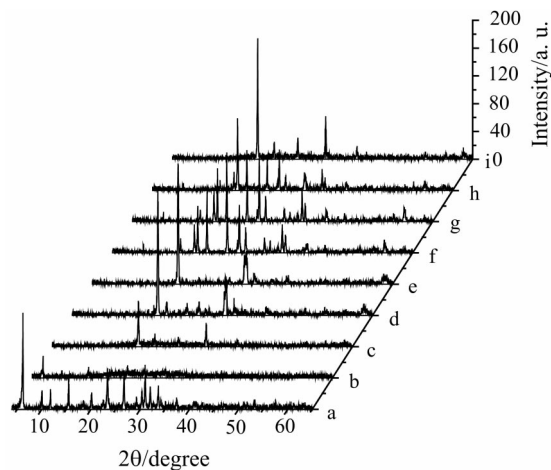
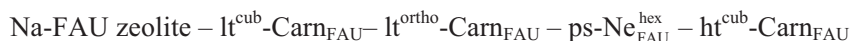


Fig. 1 XRPD patterns of non-stoichiometric phases: a – 700°C , 1 h; b – 780°C , 1 h; c – 830°C , 2.5 h; d – 850°C , 4 h; e – 900°C , 1 h; f – 1000°C , 4 h; g – 1100°C , 1 h; h – 1300°C , 1 h and i – 1400°C , 0.5 h

and non-stoichiometric (FAU) system, in the temperature range from room temperature up to 1400°C, following conversion schemes are recognized:



where, ps-Ne_{LTA}^{hex} is pure sodium nepheline, lt^{cub}-Carn_{LTA} is low-temperature and ht^{cub}-Carn_{LTA} is high-temperature carnegieite of cubic symmetry, prepared from Na-LTA zeolite etc. Obviously the mechanism of thermally induced transformation of zeolite is very complex and it depends on Si/Al ratio. Some fine differences between same polymorphs obtained in the systems with different stoichiometry are observed [12]. The structures of lt^{cub}-Carn_{LTA} and lt^{cub}-Carn_{FAU} are different. Also, the differences between ht^{cub}-Carn_{LTA} and ht^{cub}-Carn_{FAU} were evident. One more characteristic of polymorph transformations in non-stoichiometric system is existence of lt^{ortho}-Carn_{FAU} phase, with orthorhombic structure.

IR spectra of synthesized carnegieite samples were similar in general envelope and consist mainly of many overlapped bands. The resulting spectra were treated according to the mathematical deconvolution method using the minimization of the number of the bands rule [13]. The deconvoluted and experimentally obtained spectra of stoichiometric (NaAlSiO₄) and non-stoichiometric (Na_{1-x}Al_{1-x}Si_{1+x}O₄) carnegieite phases are presented in Figs 2 and 3, respectively.

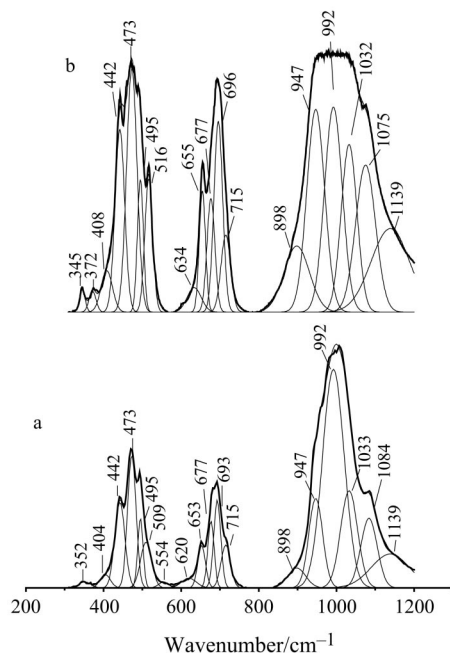


Fig. 2 Deconvoluted IR spectra of stoichiometric carnegieite phases: a – lt^{cub}-Carn_{LTA}, 800°C, 4 h and b – ht^{cub}-Carn_{LTA}, 1400°C, 0.5 h

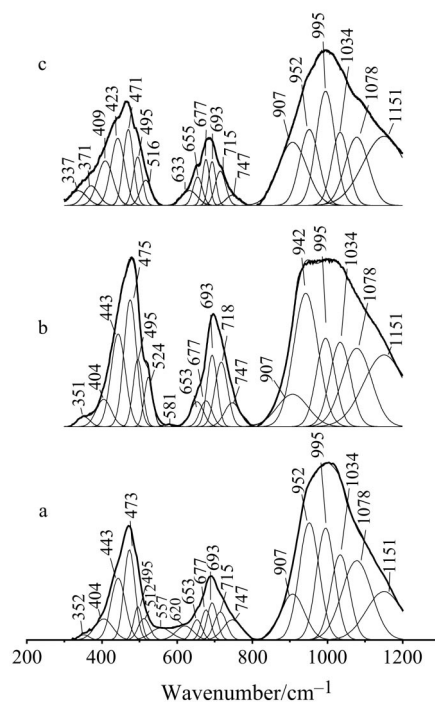


Fig. 3 Deconvoluted IR spectra of non-stoichiometric carnegieite phases:
 a – $\text{It}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, 830°C, 2.5 h; b – $\text{It}^{\text{ortho}}\text{-Carn}_{\text{FAU}}$, 900°C, 1 h and
 c – $\text{ht}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, 1400°C, 0.5 h

The interpretation of vibrational spectra of tectosilicates is complicated. The assignment applied here is that generally accepted for framework silicates [14] and SiO_2 polymorphs [15, 16] combined with those applied for the zeolites [17]. The three characteristic group frequencies 400–500, 650–750 and 900–1050 cm^{-1} , can be assigned to internal vibrations. They are due respectively to rocking, bending and stretching vibrations of T–O–T bridge. All other bands in silica polymorphs spectra should be considered in terms of the T–O–T approach as external vibration. Generally, bands found in the spectral range 500–650 cm^{-1} are assigned to framework ring vibrations, while bands below 400 cm^{-1} are due to crystal lattice vibrations. The positions of the bands assigned to bending and asymmetric stretching vibrations of almost all studied phases are not shifted more than 10 cm^{-1} . This fact can be explained by approximately identical mean T–O distance and T–O–T angles in those phases. In the spectra of non-stoichiometric ($\text{Na}_{1-x}\text{Al}_{1-x}\text{Si}_{1+x}\text{O}_4$) phases a new band at 747 cm^{-1} appears. This can be explained as a result increased number of Si–O–Si bridges instead of Si–O–Al bridges in $\text{It}^{\text{cub}}\text{-Carn}_{\text{LTA}}$ phase.

The deconvoluted spectrum of $\text{ht}^{\text{cub}}\text{-Carn}_{\text{LTA}}$ shows that in the region of rocking and bending vibration very sharp strong bands exist (Fig. 2b). In the case of non-stoichiometric ($\text{Na}_{1-x}\text{Al}_{1-x}\text{Si}_{1+x}\text{O}_4$) phases; $\text{It}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, $\text{It}^{\text{ortho}}\text{-Carn}_{\text{FAU}}$ and $\text{ht}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, the number of well-resolved bands is not too high, Fig. 3. The bands exhibit

significantly higher width at half maximum than bands of stoichiometric phases ($ht^{\text{cub}}\text{-Carn}_{\text{LTA}}$ or $lt^{\text{cub}}\text{-Carn}_{\text{LTA}}$). A progressive loss of resolution with increasing Si content suggests a concomitant increase in disorder in the carnegieite samples. These changes result from different distribution of the bond lengths and angles as well as from disorder of Si and Al owing to the increased number of Si–O–Si bridges.

Some differences between low-temperature carnegieite ($lt^{\text{cub}}\text{-Carn}_{\text{LTA}}$, $lt^{\text{cub}}\text{-Carn}_{\text{FAU}}$ and $lt^{\text{ortho}}\text{-Carn}_{\text{FAU}}$) and high-temperature carnegieite ($ht^{\text{cub}}\text{-Carn}_{\text{LTA}}$ and $ht^{\text{cub}}\text{-Carn}_{\text{FAU}}$) have been observed in the range of external vibrations. The appearance of a medium (509, 516, 512 and 524 cm^{-1}) and low intensity broad bands in the region 550–650 cm^{-1} is due to 6-membered rings. The highly ordered $ht^{\text{cub}}\text{-Carn}_{\text{LTA}}$ has sharp band at 516 cm^{-1} , while the same band in the spectrum $ht^{\text{cub}}\text{-Carn}_{\text{FAU}}$ carnegieite is less intensive and broad. It indicates that 6-membered rings are disordered, owing to the existence of Si–O–Si bridges in non-stoichiometric $ht^{\text{cub}}\text{-Carn}_{\text{FAU}}$.

In an ordered structure the absorption peaks are usually well defined and sharp. There are not sharp peaks in the phases formed from FAU zeolites, and all the bands are quite broad. From this characteristic, it could be concluded that the structure of the phases are not ordered and contain varying degrees of disorder of aluminum and silicon. These conclusions can be supported by the data obtained by NMR study. The use magic-angle sample-spinnig (MAS) Si-29 high resolution NMR spectra provide information about local structure and order in stoichiometric and non-stoichiometric polymorphs produced by thermally induced transformation of zeolites.

High-resolution MAS NMR has contributed largely to understanding of Si, Al ordering of tectosilicates [18, 19]. The 1:1 Si/Al ratio requires that complete short-range order correspond to strict alternation of Si and Al in the framework, which would give ^{29}Si MAS NMR peaks only for Si(4Al) type environments. It is already known from crystallographic data [1] that there is only one crystallographic site for silicon atoms in carnegieite structure. The spectrum of stoichiometric carnegieite is classical example of system where only Si–O–Al, or Si(4Al) exist. ^{29}Si MAS NMR spectra of carnegieite phases are presented in Fig. 4. Only one peak centered at -83.3 and -82.9 ppm exists in the spectra of $lt^{\text{cub}}\text{-Carn}_{\text{LTA}}$ and $ht^{\text{cub}}\text{-Carn}_{\text{LTA}}$, respectively. The ordering in terms of the number of Al next-nearest neighbors does not change during transformation Na-LTA zeolite into carnegieite_{LTA}. The chemical shift of $ht^{\text{cub}}\text{-Carn}_{\text{LTA}}$, at -82.9 ppm, agrees well with the chemical shift for carnegieite cited in literature, at -82.2 ppm. The results of curve fitting of ^{29}Si MAS NMR spectra of carnegieite_{FAU} are also presented in Fig. 4. At the bottom, the spectrum of Na-FAU is given for comparison. In the spectra of carnegieite_{FAU} few broad overlapped peaks have been observed. The deconvolution with five Gaussian peaks suggests that the carnegieite_{FAU} samples ^{29}Si spectra are examples of combination of five contributions namely Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al). The number of Al next-nearest neighbors not change during transformation Na-FAU zeolite into carnegieite_{FAU}. However, the populations of the Si sites in Na-FAU and carnegieite_{FAU} are not equal. The different chemical shifts and the different populations Si(nAl) suggest not equal Si/Al order in orthorhombic and cubic carnegieite_{FAU} polymorphs. The narrowing of NMR peaks of carnegieite_{FAU} annealed at 900°C suggests that during trans-

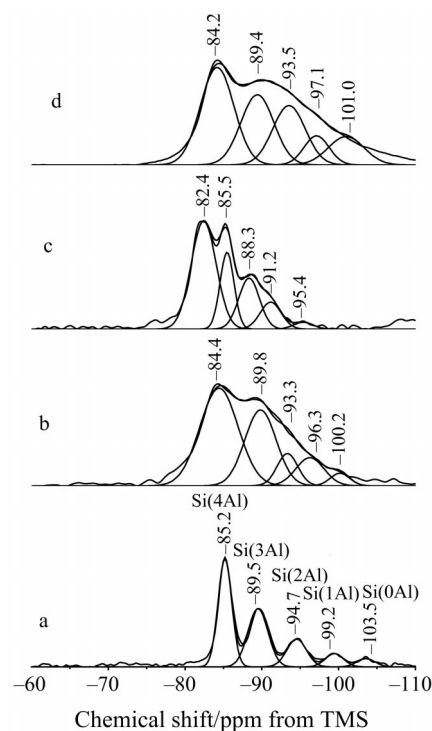


Fig. 4 Deconvoluted ^{29}Si MAS NMR spectra of non-stoichiometric carnegieite phases: a – Na-FAU zeolite; b – $\text{It}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, 830°C, 2.5h; c – $\text{It}^{\text{ortho}}\text{-Carn}_{\text{FAU}}$, 900°C, 1 h and d – $\text{ht}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, 1400°C, 0.5 h

formation $\text{It}^{\text{cub}}\text{-Carn}_{\text{FAU}}$ into $\text{It}^{\text{ortho}}\text{-Carn}_{\text{FAU}}$ some Si–Al ordering occurs. The high-temperature carnegieite_{FAU} spectrum, like low-temperature carnegieite_{FAU} spectrum, is combination of five peaks, centered at the same positions as cubic polymorph. The relative intensity of the peaks of Si(4Al) and Si(3Al) increase as result of further Si, Al ordering.

All the silica polymorphs have displacive α – β transformation [1]. The high-temperature, β -phase and low-temperature, α -phase have the same framework structures but differ by deformations of their framework. Displacive transformations involve only slight rearrangements of the atom positions, without breaking any bonds. Displacive transformations are fast and unquenchable (*i.e.*, the high temperature polymorph cannot be ‘frozen’ in no matter how rapid the cooling is). The stuffed derivatives of cristobalite synthesized by thermally induced transformation of zeolites also show the reversible displacive α – β transformation. DTA patterns of carnegieite phases are shown in Fig. 5. In all cases the displacive transformations are reversible after three heating–cooling cycles. The stoichiometric carnegieite (NaAlSiO_4), $\text{It}^{\text{cub}}\text{-Carn}_{\text{LTA}}$ and $\text{ht}^{\text{cub}}\text{-Carn}_{\text{LTA}}$ have phase transition at 690°C. The DTA peak of $\text{ht}^{\text{cub}}\text{-Carn}_{\text{LTA}}$ has higher intensity due to better ordering of the sample annealed at 1400°C, 0.5h. However, the non-stoichiometric ($\text{Na}_{1-x}\text{Al}_{1-x}\text{Si}_{1+x}\text{O}_4$) polymorphs, $\text{It}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, $\text{It}^{\text{ortho}}\text{-Carn}_{\text{FAU}}$ and $\text{ht}^{\text{cub}}\text{-Carn}_{\text{FAU}}$, have

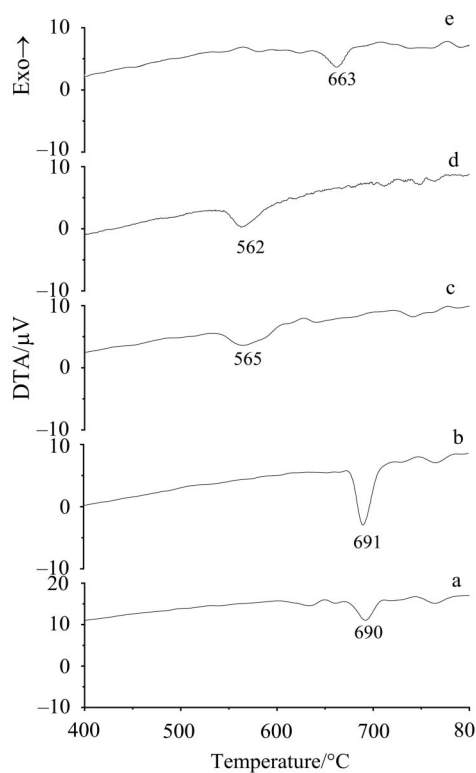


Fig. 5 DTA patterns of carnegieite phases: a – It^{cub} -Carn_{LTA}, 800°C, 4 h; b – ht^{cub} -Carn_{LTA}, 1400°C, 0.5 h; c – It^{cub} -Carn_{FAU}, 830°C, 2.5 h; d – It^{ortho} -Carn_{FAU}, 900°C, 1 h and e – ht^{cub} -Carn_{FAU}, 1400°C, 0.5 h. The heating rate was 20°C min⁻¹

DTA peaks at different temperature; at 565, 562 and 663°C, respectively. Disordered It^{cub} -Carn_{FAU} has low intensity wide peak while high polymorph ht^{cub} -Carn_{FAU} has distinct peak at higher temperature. This suggests that temperature α - β transition increase as increase order in carnegieite phases.

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References

- 1 D. C. Palmer, *Reviews in Mineralogy*, 29 (1995) 83.
- 2 M. T. Dove, *Am. Miner.*, 82 (1997) 213.
- 3 D. de Ligny, P. Richet, E. F. Westrum Jr. and J. Roux, *Phys. Chem. Miner.*, 29 (2002) 267.
- 4 V. Dondur and R. Dimitrijevic, *J. Solid State Chem.*, 63 (1986) 46.
- 5 R. Dimitrijevic and V. Dondur, *J. Solid State Chem.*, 115 (1995) 214.

- 6 V. Dondur, S. Markovic, R. Dimitrijevic and M. Mitrovic, *Mat. Sci. Forum*, 352 (2000) 105.
- 7 C. Kosanovic, B. Subotic, I. Smit, A. Cizmek, M. Stubicar and A. Tonejc, *J. Mat. Sci.*, 32 (1997) 73.
- 8 J. M. Newsam, *J. Phys. Chem.*, 92 (1988) 445.
- 9 P. Norby, *Zeolites*, 10 (1990) 193.
- 10 B. Badger and F. A. Hummel, *J. Am. Ceram. Soc.*, 68 (1985) C-46.
- 11 W. Schmitz, H. Siegel and R. Schollner, *Cryst. Res. Technol.*, 16 (1981) 385.
- 12 R. Dimitrijevic, V. Dondur, P. Vulic, S. Markovic and S. Macura (in press).
- 13 M. Rokita, M. Handke and W. Mozgawa, *J. Mol. Struct.*, 511–512 (1999) 277.
- 14 A. Dyer, in *An Introduction to Zeolite Molecular Sieves*, Wiley, Chichester 1988.
- 15 M. Handke and W. Mozgawa, *J. Mol. Struct.*, 348 (1995) 341.
- 16 M. Handke and W. Mozgawa, *Vib. Spectroscopy*, 5 (1993) 75.
- 17 E. M. Flanigan, H. Khatami and H. A. Szymanski, *Adv. Chem. Series*, 101 (1971) 201.
- 18 G. Engelhardt and D. Michel, in *High-Resolution Solid-State NMR of Silicates and Zeolite*, Wiley, Chichester 1987.
- 19 J. F. Stebbins, in *Mineral Physics and Crystallography, A Handbook of Physical Constants*, American Geophysical Union 1995, p. 303.