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High-pressure behavior of HEU-type zeolites: X-ray diffraction study of clinoptilolite-Na

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ABSTRACT

Clinoptilolite-Na, $Na_{2.55}Ca_{1.67}K_{0.37}(H_2O)_{21.5}[Al_{6.21}Si_{29.79}O_{72}]$, with the space group $C2/m$, $a = 17.6229(4)$, $b = 17.9957(3)$, $c = 7.39625(15)$ Å, $\beta = 116.353(3)^\circ$, $V = 2101.85(7)$ Å^3, and $Z = 1$ has been studied by single-crystal X-ray diffraction method in normal conditions as well as under compression in penetrating (water-containing) and non-penetrating (paraffin) media. When compressing in water medium, clinoptilolite is subjected to the additional hydration at the starting stage unlike the structurally similar heulandite with persistent increasing the content of H_2O over the wide pressure range. This occurs owing to the additional population of partially vacant positions. With further increasing the pressure, H_2O molecules are redistributed in the extraframework subsystem saving the total number. Both literature and our data on compression of zeolites of the isomorphous heulandite-clinoptilolite series in non-penetrating media evidence that the compressibility along the coordinate directions noticeably differs from sample to sample including differences in the direction of the largest compression. This is evidently associated with variations in the zeolite composition.

1. Introduction

HEU-type zeolites include two mineral species – heulandite and clinoptilolite – and form the so-called “heulandite group” of natural zeolites [1]. Heulandite and clinoptilolite cannot be distinguished from one another solely on the basis of XRD because the unit-cell parameters are sensitive to changes in water content and extra-framework cation composition [2]. Chemical composition of HEU-type zeolites ranges in wide limits that in turn results in very dissimilar thermal properties among the members of this mineral group. Chemical composition, as well as its combination with thermal behavior of zeolites were used as the base for the systematization and attribution of the species to heulandite or clinoptilolite.

So, Mason and Sand [3] proposed the definition on the base of their extraframework composition. The chemical composition (both extraframework and framework) was used by Hawkings [4]. Other authors [5–10] proposed a combination of compositional and thermal stability parameters in order to define the two zeolites. However, the Zeolite Subcommittee of the Commision on New Minerals and Mineral Names of the International Mineralogical Association (IMA) [11] and also Bish and Boak [12], emphasized that the distinction between heulandite and clinoptilolite must be based on structural and compositional trends and not on thermal behavior which is a derivative property of crystal structure and composition and therefore not acceptable basis for definition of mineral species. For this reason a relevant framework/extraframework compositional diagram is presented in Refs. [12], revealing either a “heulandite trend” or a “clinoptilolite trend” for species exhibiting the crystal structure of zeolites belonging to the heulandite group.

Currently, according to the committee recommendations [11] heulandite is defined as the zeolite mineral series having the distinctive framework topology of heulandite and the ratio Si/Al < 4, while clinoptilolite is defined as the series with the same framework topology and Si/Al ≥ 4.

The influence of the composition on thermal behavior of the heulandite-clinoptilolite minerals was studied in detail [5–7,13–20] while the high-pressure behavior of zeolites is less

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Table 1
Lattice parameters and volumes of clinoptilolite at high pressure.

P, GPa	*a*, Å	*b*, Å	*c*, Å	β, °	V, Å^3
0.0001	17.6229(4)	17.9957(3)	7.39625(15)	116.353(3)	2101.85(7)
Compression in water:ethanol 1:1					
0.75	17.5263(8)	17.915(8)	7.3594(3)	116.483(6)	2068.3(9)
1.59	17.3911(10)	17.819(9)	7.3148(4)	116.706(7)	2025.0(10)
2.23	17.2894(9)	17.759(9)	7.2767(4)	116.798(7)	1994.3(10)
2.90	17.1989(9)	17.695(8)	7.2475(3)	116.779(6)	1969.1(9)
3.43	17.1508(10)	17.565(9)	7.2302(4)	116.808(7)	1944.0(10)
4.06	17.0961(12)	17.469(11)	7.2051(5)	116.796(8)	1920.7(12)
4.73	17.0609(14)	17.331(11)	7.1886(5)	116.803(9)	1897.2(12)
0.0001*	17.6357(11)	17.965(11)	7.3981(4)	116.366(8)	2100.1(13)
Compression in paraffin					
0.49	17.5128(9)	17.932(9)	7.3607(4)	116.529(7)	2068.2(10)
1.15	17.3480(8)	17.804(9)	7.3142(3)	116.716(6)	2017.9(10)
1.73	17.2220(8)	17.751(9)	7.2750(4)	116.793(6)	1985.3(10)
2.53	17.0171(15)	17.663(16)	7.2146(7)	116.667(12)	1937.8(18)
3.23	16.9723(19)	17.56(2)	7.1948(9)	116.679(15)	1916(2)
3.92	16.900(3)	17.48(3)	7.1648(12)	116.73(2)	1891(3)
4.62	16.895(3)	17.31(3)	7.1605(15)	116.77(2)	1870(3)

* Data collected under decompression.

well understood. Heulandite was among the first those structurally studied at high pressures [21]. The structural evolution of heulandite of the different composition was currently studied upon compressing in non-penetrating (paraffin) and water-containing media [22]. Structural changes of clinoptilolite at high pressure was not studied.

In general, structural evolution features of zeolites depend on both the cation and pressure-transmissing medium compositions [23]. Zeolite structures are characterized by “open” system of interconnected channels and cavities, responsible for their reversible dehydration [1]. Additional H_2O molecules can enter the channels on compression in water-containing medium; this process is reversible also [24].

The influence of the composition of microporous compounds on their high-pressure behavior can be clearly seen from the investigations of zeolites with natrolite topology [25–28]. Ordered natrolite exhibits two sequential pressure-induced hydrations leading first to paranatrolite-like phase [25] and then to a superhydrated natrolite [26] above 0.8 and 1.5 GPa, respectively.

Table 2
Parameters of data collection and structure refinement for clinoptilolite compressed in penetrating medium.

Pressure (GPa)	0.0001	0.75	1.59	2.23	2.90	3.43	4.06	4.73	0.0001*
a (Å)	17.6229(4)	17.5263(8)	17.3911(10)	17.2894(9)	17.1989(9)	17.1508(10)	17.0961(12)	17.0609(14)	17.6357(11)
b (Å)	17.9957(3)	17.915(8)	17.819(9)	17.759(9)	17.695(8)	17.565(9)	17.469(11)	17.331(11)	17.965(11)
c (Å)	7.39625(15)	7.3594(3)	7.3148(4)	7.2767(4)	7.2475(3)	7.2302(4)	7.2051(5)	7.1886(5)	7.3981(4)
β (°)	116.353(3)	116.483(6)	116.706(7)	116.798(7)	116.779(6)	116.808(7)	116.796(8)	116.803(9)	116.366(8)
V (Å^3)	2101.85(7)	2068.3(9)	2025.0(10)	1994.3(10)	1969.1(9)	1944.0(10)	1920.7(12)	1897.2(12)	2100.1(13)
Space group	*C*2/*m*								
d (g/cm^3)	2.118	2.197	2.247	2.283	2.312	2.341	2.371	2.404	2.138
Scan width (°/frame)	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Exposure (s/frame)	60	60	60	60	60	60	60	60	60
2θ range (°)	6.86–68.54	3.46–63.26	3.48–63.52	3.50–63.74	3.52–63.44	5.32–63.64	5.34–63.10	5.36–63.04	5.16–62.78
μ (MoKα) (mm^{-1})	0.787	0.805	0.822	0.835	0.846	0.857	0.867	0.879	0.790
Number of I_{hkl} measured	27950	6971	6803	6735	6664	6584	6453	6296	7108
Number of unique F^2_{hkl}	4370	1156	1122	1104	1088	1046	1028	1018	1027
R_{int}	0.0493	0.0809	0.0760	0.0745	0.0773	0.0763	0.0877	0.1054	0.0689
Reflections with $I > 2\sigma(I)$	3620	957	919	887	861	833	644	575	714
Number of variables	198	176	186	186	184	180	175	188	173
*R*1, *wR*2 for observed reflections [$I > 2\sigma(I)$]	0.0439, 0.1061	0.0578, 0.1325	0.0577, 0.1297	0.0580, 0.1301	0.0586, 0.1445	0.0616, 0.1491	0.0542, 0.1316	0.0624, 0.1399	0.0422, 0.0934
*R*1, *wR*2 for all data	0.0574, 0.1141	0.0729, 0.1417	0.0727, 0.1375	0.0738, 0.1372	0.0765, 0.1543	0.0802, 0.1585	0.0953, 0.1429	0.1154, 0.1552	0.0692, 0.0971
GooF	1.045	1.086	1.259	1.254	1.225	1.195	0.994	1.032	1.108
Residual electron density (*e*/Å^3)	0.986, −1.021	0.536, −0.435	0.636, −0.555	0.655, −0.494	0.870, −0.550	0.835, −0.440	0.549, −0.386	0.430, −0.389	0.343, −0.316

*Data collected under decompression.

Table 3
Parameters of data collection and structure refinement for clinoptilolite compressed in paraffin.

Pressure (GPa)	0.49	1.15	1.73	2.53
a (Å)	17.5128(9)	17.3480(8)	17.2220(8)	17.0171(15)
b (Å)	17.932(9)	17.804(9)	17.751(9)	17.663(16)
c (Å)	7.3607(4)	7.3142(3)	7.2750(4)	7.2146(7)
β (°)	116.529(7)	116.716(6)	116.793(6)	116.667(12)
V (Å^3)	2068.2(10)	2017.9(10)	1985.3(10)	1937.8(18)
Space group	*C*2/*m*			
d (g/cm^3)	2.171	2.225	2.261	2.328
Scan width (°/frame)	0.5	0.5	0.5	0.5
Exposure (s/frame)	60	60	60	60
2θ range (°)	5.20–63.68	5.26–63.38	5.30–62.78	5.36–64.46
μ (MoKα) (mm^{-1})	0.802	0.822	0.835	0.857
Number of I_{hkl} measured	6942	6587	6715	6426
Number of unique F^2_{hkl}	1009	989	974	944
R_{int}	0.0774	0.0812	0.0793	0.1260
Reflections with $I > 2\sigma(I)$	689	676	792	558
Number of variables	178	168	163	186
*R*1, *wR*2 for observed reflections [$I > 2\sigma(I)$]	0.0444, 0.1084	0.0499, 0.1146	0.0616, 0.1530	0.0946, 0.2211
*R*1, *wR*2 for all data	0.0722, 0.1157	0.791, 0.1220	0.0775, 0.1629	0.1505, 0.2358
GooF	0.940	0.965	1.115	1.440
Residual electron density (*e*/Å^3)	0.339, −0.320	0.427, −0.414	0.442, −0.382	0.639, −0.547