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A Large Volume Contraction Accompanies the Low- to High-Temperature Phase Transition of Zeolite Sr-rho

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Upon heating, Sr-exchanged zeolite rho, $Sr_6Al_{12}Si_{36}O_{96}$, changes into a high-temperature form with a unit cell volume which is, surprisingly, about 7% smaller than the low-temperature modification. Both modifications crystallize in space group $I\bar{4}3m$. At 373 K in vacuum the unit cell constant a of Sr-rho is 14.5578(4) Å; at 473 K it is 14.2293(9) Å. Rietveld-type refinement of powder X-ray diffraction data shows that the two forms differ in the distribution of Sr atoms relative to the double eight-membered rings in the $(Si,Al)O_2$ framework of zeolite rho: in the high-temperature form the Sr atoms are concentrated in the centers of these rings and pull them together, while in the low-temperature form three-quarters of the Sr atoms are located in the plane of the single eight-membered ring (on the face of the double eight-membered rings) and thus prevent a collapse of these rings which, nevertheless, occurs in the high-temperature form. The transformation between the two forms is of the reconstructive type, as far as the Sr atom positions are concerned, but is fully reversible.

Zeolite rho is a microporous substance, consisting of an aluminosilicate framework with exchangeable cations. It crystallizes either in space group $Im\bar{3}m$ or in space group $I\bar{4}3m$. When it is centrosymmetric ($Im\bar{3}m$) the cell constant a is close to 15.0 Å. In its noncentrosymmetric lower symmetry form it has a remarkably flexible $(Si,Al)O_2$ framework with cell constants ranging from 14.9 Å down to 14.0 Å (*1–3*). In addition it has been observed that NH_4-exchanged zeolite rho, depending on the way in which it has been prepared, occurs in two forms, one with short cell constants of about 14.5 Å (*4*) and the other with a clearly longer cell constant of about 14.8 Å (*5*).

We prepared Sr-exchanged zeolite rho from NH_4-rho by repeated cation exchange in a strontium nitrate solution. The chemical composition of the sample after dehydration is approximately $Sr_6Al_{12}Si_{36}O_{96}$, but some of the Cs from the as-synthesized form of the original Na,Cs-rho was not removed during the various cation exchanges. All powder diffraction work was performed on a Siemens D500 diffractometer with Cu$K\alpha$ radiation with a secondary graphite monochromator equipped for some of the work

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TABLE I

DATA FOR Sr-rho-473/373 (= LT, a = 14.5578(4) Å) AND Sr-rho-473/473 (= HT, a = 14.2293(9) Å)

Atom	x	y	z	B	C	Wyckoff position	Site symmetry
Si/Al,LT	0.2688(2)	0.1197(2)	0.4208(3)	3.51(8)	48	48(h)	1
Si/Al,HT	0.2748(3)	0.1239(2)	0.4291(3)	4.1(1)	48	48(h)	1
O(1),LT	0.0309(4)	0.2096(4)	0.3893(5)	4.1(2)	48	48(h)	1
O(1),HT	0.0402(4)	0.2008(5)	0.3919(5)	3.8(2)	48	48(h)	1
O(2),LT	0.2136(5)	x	0.3938(7)	3.0(2)	24	24(g)	..m
O(2),HT	0.2268(6)	x	0.4033(14)	6.2(3)	24	24(g)	..m
O(3),LT	0.1338(5)	x	0.6151(6)	4.4(2)	24	24(g)	..m
O(3),HT	0.1242(5)	x	0.6140(6)	4.3(3)	24	24(g)	..m
Cs,LT	0	0	1/2	3.0	1.0(1)	6(b)	$\bar{4}2.m$
Cs,HT	0	0	1/2	3.0	1.1	6(b)	$\bar{4}2.m$
Sr(1),LT	1/2	1/2	0.049(8)	3.0	1.0(1)	12(e)	2.mm
Sr,HT	0.507(2)	0.467(2)	0.038(2)	5.8(2)	4.0(2)	48(h)	1
Sr(2),LT	0.0193(6)	x	0.3953(12)	3.0	3.4(1)	24(g)	..m
Sr(2)HT	Not present						

Note. Data are positional parameters in fractional coordinates (parameters without standard deviations were kept constant during refinement); temperature factors (Å^2); C, the number of atoms per unit cell; Wyckoff positions; site symmetry.

with a low-temperature Paar chamber, and for some of the work with a Kiehne high-temperature chamber.

After 12 hr at 373 K in vacuum the cell constant of Sr-rho was about 14.58 Å. Upon heating for several hours at 473 K the intensities of the diffractogram changed drastically and the unit cell constant dropped to about 14.23 Å. Quenching the sample rapidly to 90 K froze the high-temperature form without any pronounced change in cell constants. It took approximately a week at 293 K in vacuum to change the sample back to the low-temperature form with large cell constants. In vacuum, the transition temperature appears to be closer to 473 K than to 373 K. In any event the transformation between the two forms is reversible, even though it appears to take longer when one tries to reach the low-temperature. A differential scanning calorimetry run shows that at a temperature corresponding to the transition temperature there is a sharp exothermic peak.

Profile refinements of two of the resulting powder X-ray diffraction patterns were performed with the Rietveld refinement program LHPM 7 (*6*, *7*): one was the pattern of the sample heated to 473 K and also measured at 473 K, Sr-rho-473/473 (=HT), and the other was the pattern of the sample heated to 473 K, subsequently kept for a week at 293 K, and then measured at 373 K, Sr-rho-473/373 (=LT); the nomenclature follows Fischer *et al.* (*8*). Both refinements assumed space group $I\bar{4}3m$ for Sr-rho. In order to locate all possible cation sites we did grid search analyses (*9*). The agreement factors for the refinement of the Sr-rho-473/373 data are R_{wp} = 0.1084 and R_I = 0.0790 [for the definitions of the residuals, see Ref. (*7*)]; the cell constant a refined to 14.5578(4) Å. The evaluation of the Sr-rho-473/473 data yielded residuals of R_{wp} = 0.0929 and R_I = 0.0666 and a = 14.2293(9) Å. The final structural parameters for both refinements are listed in Table I.

In the low-temperature form, LT, the Sr

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN Sr-rho-473/373 (LT) AND Sr-rho-473/473 (HT)

		Framework			
	LT	HT		LT	HT
T–O(1)	1.62(1)	1.63(1)	O(2)–T–O(3)	110.2(5)	109.7(6)
T–O(3)	1.63(1)	1.63(1)	O(2)–T–O(1)	113.4(5)	115.1(7)
T–O(1)	1.64(1)	1.68(1)	O(2)–T–O(1)	109.8(4)	107.4(5)
T–O(2)	1.63(1)	1.66(1)	O(3)–T–O(1)	107.0(4)	104.5(4)
			O(3)–T–O(1)	107.9(4)	110.2(4)
T–O$_{mean}$	1.63	1.65	O(1)–T–O(1)	108.4(4)	110.0(4)
			2× T–O(1)–T	134.5(4)	126.7(5)
			T–O(2)–T	139.9(6)	132.8(9)
			T–O(3)–T	148.2(5)	144.3(5)
			T–O–T$_{mean}$	139.3	132.6

		Nonframework atoms		
	LT	HT	LT	HT
4× Cs–O(3)	3.22(1)	2.98(1)		1× Sr(1)–O(3) 2.52(3)
8× Cs–O(1)	3.48(1)	3.30(1)	2× Sr(1)–O(3) 2.92(4)	
				1× Sr(1)–O(3) 2.99(3)
				1× Sr(1)–O(3) 3.02(3)
				1× Sr(1)–O(1) 2.63(3)
			4× Sr(1)–O(1) 3.21(3)	1× Sr(1)–O(1) 2.93(3)
				1× Sr(1)–O(1) 3.29(3)
				1× Sr(1)–O(1) 3.23(3)
			2× Sr(2)–O(1) 2.78(1)	
			2× Sr(2)–O(3) 2.79(1)	

atoms are distributed over two different positions in the unit cell. More than three-quarters of them (3.4 of a total of 4.4 Sr atoms per unit cell) are located in position Sr(2) in the plane of one of the single eight-membered rings, two of which constitute a double eight-membered ring (Fig. 1). The aluminosilicate framework in turn can be described as composed of these double eight-membered rings. Sr(2) forms four bonds to the framework oxygen atoms (Table II). The remaining 1.0 Sr atom per unit cell in position Sr(1) is located close to the centers of the double eight-membered rings and adjacent to the Cs positions. The Sr(2) atoms within the plane of the single eight-membered ring allow only a limited distortion of these rings and of the framework as a whole. The ellipticity factor (ratio of the x-coordinates of O(2) to O(3)) for the LT form is 1.60. The pore opening of the double eight-membered ring measures 2.81 Å.

In the high-temperature form, HT, the distortion of the double eight-membered rings is much stronger (ellipticity factor = 1.83) and the pore size is reduced to 2.3 Å. The more pronounced distortion is possible because in the HT form all Sr atoms located in the refinement (4.0 Sr atoms per unit cell) are concentrated in position Sr(1) close to the center of the double eight-membered ring (Fig. 1). Each Sr(1) atom is coordinated to five framework oxygen atoms (Table II). The Sr(2) atoms within the face of the double eight-membered ring are not present in the HT form and cannot block the collapse of

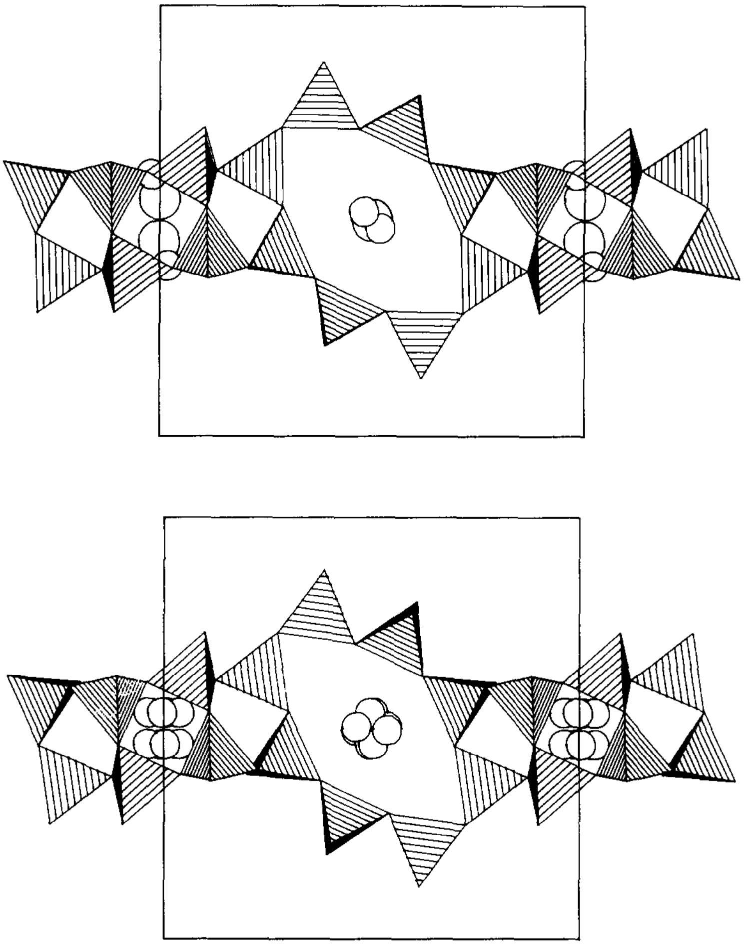

FIG. 1. Polyhedral representation of the eight-membered rings in the crystal structure of Sr-rho-473/373 (LT, top) and of Sr-rho-473/473 (HT, bottom) using STRUPLO [Fischer, Ref. (*13*)]; the view is parallel to [100], and the outline indicates one unit cell. In the center an eight-membered ring is seen from above, and to the left and right double eight-membered rings are seen from the side. In LT, position Sr(1) is shown by large circles, and position Sr(2) by small circles; in HT there is only one Sr position, indicated by small circles. The different Sr positions influence the degree of distortion of the eight-membered rings and consequently the cell constants of Sr-rho.

the framework. The relationship between the LT and the HT forms of Sr-rho is, therefore, in principle the same as that between the two forms of NH_4-rho with short and long cell constants (*4*, *5*); however, in the case of NH_4-rho it is not a high–low relationship. The stronger distortion of the framework of the HT form is also reflected in the smaller T–O–T angles subtended at the oxygen atoms between the coordination tetrahedra: the average drops from 139° to 133°. In neither refinement could we locate all the Sr atoms which should be present in Sr-rho. Either some of the Sr atoms are distributed with low occupancy over sites which we could not identify or our assumptions about the chemical composition are incomplete. The total of the occupancies of the two Sr positions in the LT form is within less than two combined e.s.d.'s identical to the occupancy of the Sr position in the HT form.

Changes in cation positions as a function of temperature have been observed in Ca-exchanged zeolite X (*10*), but there they are connected with a chemical change: during the process the zeolite was dehydrated. However, in the case of Sr-rho we are dealing strictly with a dehydrated zeolite. No chemical change was involved in a study of dehydrated Sr-exchanged zeolite Y (*11*). In that case with increasing temperature a Boltzmann-like distribution was observed, no phase transition was reported, and the changes in cell constants were well below those in Sr-rho (less than 0.1% over a 300° range). For Sr-rho we observe with an increase in temperature across the transition point not a more equal distribution of cations, but instead a concentration in one crystallographic site.

The transition observed here for Sr-rho is, as far as the framework is concerned, a displacive transformation. As far as the Sr positions are concerned, it is a reconstructive transformation [in both cases we are following Buerger's nomenclature, Ref. (*12*)], because Sr–O bonds are broken and formed anew. As a consequence the location and coordination of the Sr atoms change across the phase transition.

The most surprising aspect is that in this case a high-temperature form has a clearly smaller cell volume than the corresponding low-temperature form of the same compound and that this change in volume is so pronounced, while the space group of the compound does not change. Again this underscores the exceptional flexibility of the framework of zeolite rho (*2*). We do not know of a similar observation on other substances.

Computer programs used for this work were mainly LHPM 7 Rietveld (*6*, *7*), STRUPLO (*13*), and SADIAN86 (*14*). We thank R. D. Shannon for the preparation of the NH_4-rho sample, H. Kiehne for the construction of the HT powder chamber, and D. Kassner for improvement of the computer programs and their adaptation to our local Vax-cluster and for discussions.

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