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Strong negative thermal expansion in the siliceous zeolites ITQ-1, ITQ-3 and SSZ-23

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Strong negative thermal expansion has been found for the pure SiO_2 zeolites ITQ-1 ($\alpha_v = -12.1 \times 10^{-6}$ K^{-1}), SSZ-23 ($\alpha_v = -10.3 \times 10^{-6}$ K^{-1}) and ITQ-3 ($\alpha_v = -11.4 \times 10^{-6}$ K^{-1}) from 50 to 500 °C and above.

Negative thermal expansion has recently enjoyed renewed interest with the discovery of ZrP_2O_7,[1] ZrW_2O_8,[2] $Sc_2(WO_4)_3$[3], $Lu_2(WO_4)_3$[4] and further developments on materials with the Nasicon structure.[5] However, it is within the field of microporous materials that the most contracting materials have been found. Zeolites and AlPOs are widely used in the chemical and petroleum industry as shape selective catalysts and molecular sieves.[6] Their properties are associated with their crystal structure, in which vertex linked SiO_4, AlO_4 and PO_4 tetrahedra form cages and encompass large channels and cavities through which small molecules may diffuse. Commercial catalytic applications thus depend critically on the structure and behaviour of these materials at high temperature. Computer simulations by Tschaufeser and Parker[7] and also by Gale[8] have suggested that many zeolites and AlPOs such as those with structure types (as defined by the International Zeolite Association) FAU, MAZ, RHO, OFF, MER, LTL, VFI (VPI-5), AFT (AlPO-52), ERI (AlPO-17), MWW (MCM-22) and IFR (SSZ-42) will show a negative coefficient of thermal expansion (CTE). Tschaufeser's calculations predict that the expansion will be very much affected by the Si and Al content: the more siliceous zeolites had much greater contraction or expansion. However, the relationship between expansivities and Si/Al ratios is not linear, an effect that is presumably due to the behaviour of extra-framework cations rather than simply the framework composition.

Recently Park *et al.*[9] recorded the coefficient of thermal expansion for MFI (ZSM-5), DOH (dodecasil 1H), DDR (decadodecasil 3R), MTN (dodecasil 3C) and AFI (AlPO-5). They found a volume expansion between 298 K and 345–534 K, followed by a contraction for each over a limited temperature range. Na-zeolite X has been found to contract by Couves *et al.*,[10] as has zeolite A by Colantuano,[11] but this is believed to be due to a partial structure collapse. Siliceous faujasite and AlPO-17 have both been identified by Attfield and Sleight[12,13] as contracting, AlPO-17 exceptionally so with a linear CTE of -11.7×10^{-6} K^{-1} (corresponding to $\alpha_v = -35.1 \times 10^{-6}$ K^{-1} over a temperature range of 18–300 K). This value is significantly more negative than previously reported for any material. We have chosen to carry out the present study over a temperature range which is both wider and encompassing catalytically useful temperatures. In addition, we have selected pure zeolitic SiO_2 polymorphs only, so that the results are not influenced by either extra-framework cations or water content. All three materials show a large negative α_v comparable to that of faujasite over this range, though none as large as that for AlPO-17.

The contraction is believed to be due to an increase in the amplitude of the anisotropic motion of the O atoms on increasing the temperature, resulting in an apparent shortening of the Si–O distances rather than any genuine change in Si–O–Si or O–Si–O bond angles. However, we have not undertaken qualitative structure refinements as a function of temperature so final conclusions must await the results of dedicated powder neutron diffraction measurements.

The samples were synthesised as described previously for ITQ-1,[14] ITQ-3[15] and SSZ-23.[16] They were calcined in dry, flowing O_2 at 550 °C for 8 h to remove the template and placed into a 0.5 mm quartz capillary within a few minutes. Thermogravimetric analysis was performed on each of the samples in order to ascertain whether water loss was responsible for any of the thermal contraction. This showed that no water was adsorbed on these hydrophobic materials.

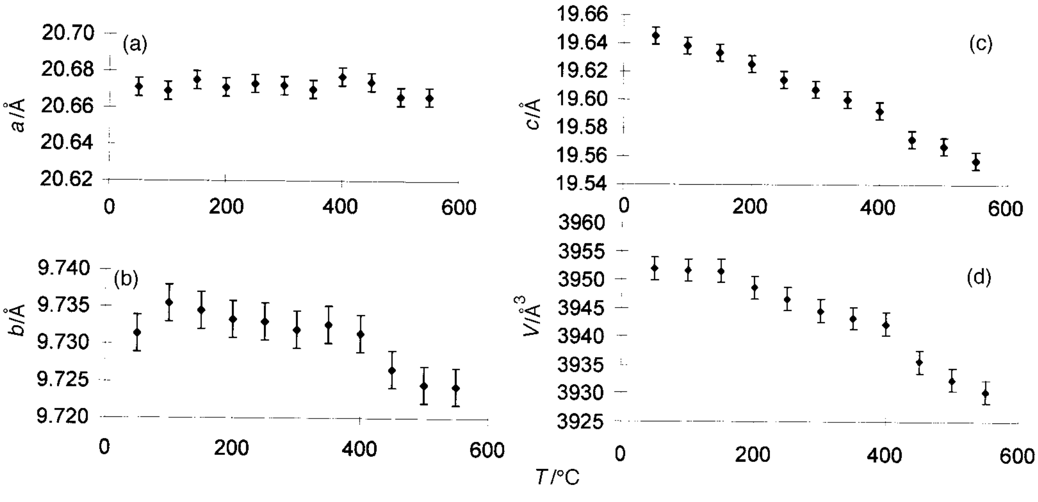

Fig. 1 Thermal evolution of lattice parameters for ITQ-3: (a) *a* axis, (b) *b* axis and (c) *c* axis. (d) Thermal evolution of volume for ITQ-3.

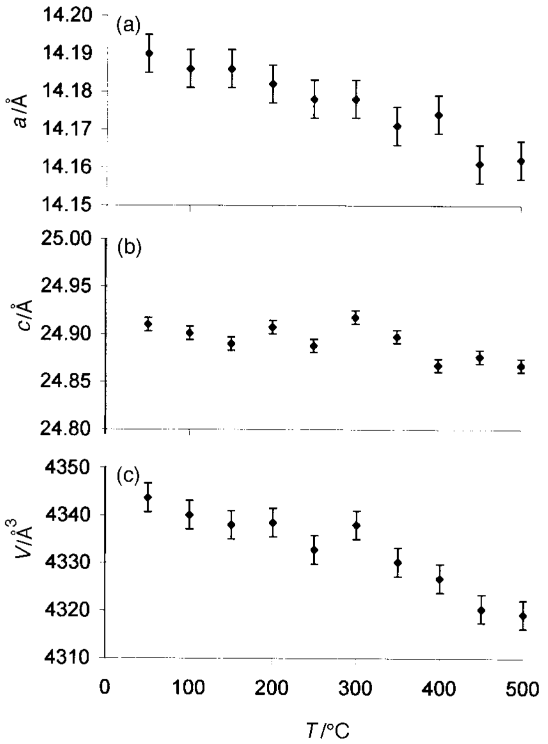

Fig. 2 Thermal evolution of lattice parameters for ITQ-1: (a) *a* axis and (b) *c* axis. (c) Thermal evolution of volume for ITQ-1.

Furthermore, the materials chosen for the study possess essentially no connectivity defects, so the observed thermal contraction cannot be caused by annealing of the defects. The absence of Si–OH groups is demonstrated by ^{29}Si MAS NMR of the calcined materials as shown by Camblor *et al.* for each material.[14–16]

X-Ray patterns were recorded at 50 °C intervals up to 500 °C for SSZ-23 and ITQ-1 and to 550 °C for ITQ-3 on a STOE Stadi-P transmission diffractometer using Cu-Kα_1 radiation at 1.54056 Å, over a 2θ range of 7.7–45.2°. The resultant histograms were processed using the GSAS program,[17] using literature values for atomic coordinates, and refining scale factor, lattice parameters, zero point, background and peak shapes only.

The values of α found are detailed in Table 1. Note that the negative thermal expansion found for MFI, AFI, DOH, MTN and DDR does not occur over the full temperature range studied, and that faujasite and AlPO-17 have been studied under cryogenic conditions. In order to compare the materials directly it would be necessary to study them over the same temperature range. For example, our experiments on AlPO-17 over the range 50–500 °C showed a small contraction of *a* and a large expansion of *c* leading to an overall volume expansion.

The aim of this work was to measure the variation of lattice parameters by X-ray diffraction. This technique is precise enough to show trends in the evolution of lattice parameters. However, structure determination from powder neutron diffraction data would be required to study the mechanism more closely. For example, the current data show highly anisotropic contraction, especially for ITQ-3 and SSZ-23, which at first does not correlate significantly with structural features such as the chains of cages arranged along *b* in ITQ-

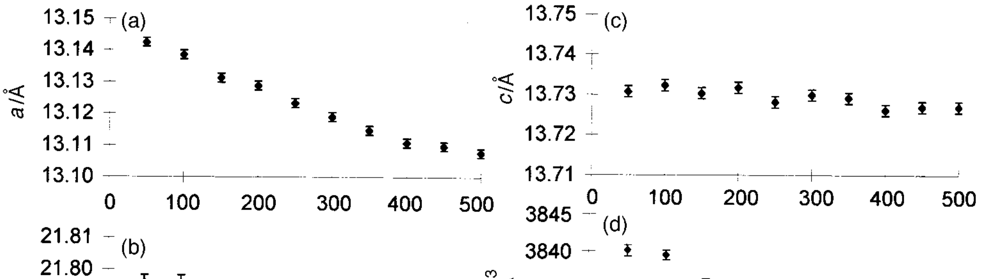

Fig. 3 Thermal evolution of lattice parameters for SSZ-23: (a) *a* axis, (b) *b* axis and (c) *c* axis. (d) Thermal evolution of volume for SSZ-23.

Table 1 Reported coefficients of thermal expansion for zeolites[a]

Sample	α_a	α_b	α_c	α_v	Range (T/K)	Reference
ITQ-1 (ITO)	−4.23	−4.23	−3.21	−12.1	323–773	This work
ITQ-3 (ITE)	−0.29	−2.06	−10.1	−11.4	323–823	This work
SSZ-23 (STT)	−6.09	−3.21	−0.73	−10.3	323–773	This work
MFI	−5.5	−6.9	−2.8	−15.1	393–975	8
AFI	−5.1	−5.1	−3.7	−14.5	424–774	8
DOH	−0.6	−0.6	−3.1	−3.1	573–996	8
MTN	−1.7	−1.7	−1.7	−5.0	463–1002	8
DDR	−2.8	−2.8	−3.1	−8.7	492–1185	8
Faujasite (FAU)	−4.2[b]	−4.2[b]	−4.2[b]	−12.6[b]	25–573	11
AlPO-17 (ERI)	−15.3[c]	−15.3[c]	−4.52[c]	−35.1[b]	18–300	12

[a] All α values are $\times 10^{-6}$ K^{-1}. [b] These values are calculated from the values quoted for linear α values which are equal to $\alpha_v/3$. [c] Values for AlPO-17 are calculated from the values given in Å K^{-1}.

3, the layers in the *ab* plane in ITQ-1 or with the puckered layers parallel to (101) in SSZ-23. Interestingly MCM-22, analogous to ITQ-1 has been predicted to contract by Gale.[8] However, the predicted CTEs of $\alpha_a = -2 \times 10^{-6}$ K^{-1} and $\alpha_c = -9 \times 10^{-6}$ K^{-1} do not correlate with our results.

It is important also that studies incorporate high temperature as well as low, since the variation of the lattice parameters *versus* temperature does not appear to be linear. From the data currently available, it is possible that the trends found at low temperature are much more dramatic.

The overall conclusion is that negative thermal expansion in microporous structures appears to be much more widespread than previously thought. Of the nine samples we have studied recently, seven have shown negative axial thermal expansion and most of these have also shown a volume contraction. Further detailed structure analysis will be carried out in order to pinpoint specific structural and compositional features which may be responsible for this unusual behaviour.

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Notes and references

1 V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree and W. W. Warren, *Chem. Mater.*, 1995, **7**, 412.
2 J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian and A. W. Sleight, *Chem. Mater.*, 1996, **8**, 2809.
3 J. S. O. Evans, T. A. Mary and A. W. Sleight, *J. Solid State Chem.*, 1998, **137**, 148.
4 P. M. Forster, A. Yokochi and A. W. Sleight, *J. Solid State Chem.*, 1998, **140**, 157.
5 D. A. Woodcock, P. Lightfoot and C. Ritter, *Chem. Commun.*, 1998, 107.
6 J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1673.
7 P. Tschaufeser and S. C. Parker, *J. Phys. Chem.*, 1995, **99**, 10609.
8 J. D. Gale, *J. Phys. Chem. B*, 1998, **102**, 5423.
9 S. H. Park, R. W. Große Kunstleve, H. Graetsch and H. Gies, *Stud. Surf. Sci. Catal.*, 1997, **105**, 1989.
10 J. W. Couves, R. H. Jones, S. C. Parker, P. Tschaufeser and C. R. A. Catlow, *J. Phys.: Condens. Matter*, 1993, **5**, L329.
11 A. Colantuano, S. Dal Vecchio, G. Mascolo and M. Pansini, *Thermochim. Acta*, 1997, **29**, 659.
12 M. P. Attfield and A. W. Sleight, *Chem. Commun.*, 1998, 601.
13 M. P. Attfield and A. W. Sleight, *Chem. Mater.*, 1998, **10**, 2013.
14 M. A. Camblor, A. Corma, M.-J. Díaz Cabañas and C. Baerlocher, *J. Phys. Chem. B*, 1998, **102**, 44.
15 M. A. Camblor, A. Corma, P. Lightfoot, L. A. Villaescusa and P. A. Wright, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2659.
16 M. A. Camblor, M.-J. Díaz Cabañas, J. Perez-Pariente, S. J. Teat, W. Clegg, I. J. Shannon, P. Lightfoot, P. A. Wright and R. E. Morris, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2122.
17 A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987.

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