Strong negative thermal expansion in siliceous faujasite

Martin P. Attfield and Arthur W. Sleight*†

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, OR 97331-4003, USA

Strong isotropic negative thermal expansion ($\alpha = -4.2 \times 10^{-6}$ K^{-1}) found for siliceous faujasite over a temperature range of 25 to 573 K is attributed to transverse vibrations of the bridging oxygen atoms, a model supported by structural refinements of X-ray diffraction data as a function of temperature.

Negative thermal expansion is not a common phenomenon in solid materials. When it does arise, it is usually of small magnitude and displayed over a limited temperature range. Such thermal expansion is most usually found in anisotropic materials, for example, $LiAlSiO_4$,[1] $NbZrP_3O_{12}$[1] and $Sc_2W_3O_{12}$,[2] where the intrinsic linear thermal expansion is not more negative than -2.2×10^{-6} K^{-1}. Ceramic bodies made from such materials can show greater negative thermal expansion owing to microcracking effects which tend to become larger at lower temperatures. For instance a ceramic body of $Sc_2W_3O_{12}$, depending on how it is processed, can give a thermal expansion of up to -11×10^{-6} K^{-1}. Problems with microcracking in such ceramic bodies can be avoided if the material shows isotropic negative thermal expansion as is the case for the cubic material ZrW_2O_8 which exhibits strong isotropic negative thermal expansion (-8.7×10^{-6} K^{-1}) over a broad temperature range.[3,4]

An apparent requirement for an oxide material to have strong intrinsic negative thermal expansion is that it has an open framework structure with two-coordinate oxygen atoms. Several classes of such framework structures exist, including those of the family of SiO_2 structures and their derivatives. Various forms of the more condensed polymorphs of SiO_2 are known to exhibit negative thermal expansion over limited temperature ranges which do not include room temperature. Amorphous SiO_2 shows this behaviour below room temperature, and certain crystalline forms (quartz, cristobalite and tridymite) show weak negative thermal expansion above 1000 °C.[5] Zeolites are a group of open framework structures that derive from the SiO_2 family of structures in which some aluminium replaces the silicon atoms in the framework structure. The presence of aluminium atoms in the framework causes complications when considering thermal expansion properties. The charge of the aluminium in the framework is balanced by extraframework cations which influence the thermal expansion in several ways. In particular, bonds between framework oxygen atoms and alkali or alkaline earth cations exhibit large positive thermal expansion so these cations will provide a positive contribution to the expansion of the zeolite as the temperature increases. The position of the extraframework cations is also known to vary with temperature, as has been shown for Ca-mordenite,[6] again affecting the thermal expansion properties of the zeolite. The presence of the extraframework cations also increases the amount of water taken up by the zeolite. This water is often difficult to fully remove and can influence the thermal expansion properties of the system. These difficulties appear to play a large factor in the experimental data for the thermal expansion of Na-zeolite X, (the only data reported for the faujasite family that the authors are aware of) which has a net negative thermal expansion between 25 and 200 K and appears to expand above 200 K.[8,9]

In this work, we chose to study the thermal expansion of a purely siliceous zeolite, thus avoiding the complications associated with the extraframework cations and greatly reducing the water content of the zeolite. Here, we report the thermal expansion properties of siliceous faujasite from 25 to 573 K, it being strongly negative (-4.2×10^{-6} K^{-1}) over the entire range.

The sample of dealuminated Y (DAY) was kindly supplied by Amoco Chemical Company and was prepared as described previously.[9,10] The Al content was 120 ppm by ICP analysis. DAY was heated to 550° for 8 h in air to produce what has been referred to[9,10] as 'zero defect' DAY or ZDDAY. This treatment removes the defects caused by dealumination as determined by ^{29}Si MAS NMR; only one type of ^{29}Si is observed in ZDDAY. The sample was dehydrated for 12 h at 330 °C under a vacuum of *ca.* 10^{-5} Torr and transferred to an argon-filled glovebox where it was loaded, and sealed, into 0.5 mm and 0.3 mm diameter Lindemann glass capillary tubes. Before dehydration, the water content can be indicated as $SiO_2{\cdot}xH_2O$ with $x = 0.08$. After dehydration, water was undetected indicating that x was <0.005. Synchrotron X-ray powder diffraction data were collected on the sample at beamline X7A, National Synchrotron Light Source, Brookhaven National Laboratory. The diffractometer set up included the use of a Si(111) monochromator and a krypton filled position sensitive detector (p.s.d.). All data were collected at a wavelength of 1.099 32(6) Å. The temperature of the sample for each data collection was controlled using an Air Products Displex, and data were collected at seven temperatures between 25.16 and 297.5 K, inclusive. X-Ray data on the sample from 303 to 573 K were collected on an INEL XRG 3000 diffractometer using Cu-Kα_1 radiation monochromated by a Ge(111) crystal and adjustable vertical slits. The detector used was an INEL CPS 90 p.s.d. filled with an ethane–argon mixture. The sample was held within a capillary furnace fitted with resistive heating elements.

The synchrotron X-ray data sets were refined using the Rietveld method.[11] The refinement at each temperature was performed using the same procedure. The first four peaks were excluded from each refinement owing to their highly asymmetric peak shape. All backgrounds were fitted by linear interpolation using the same number of points in each case. The starting model for the siliceous faujasite was taken from that described by Hriljac *et al.*[10] The last cycle of least-squares refinement included the histogram scale factor, zero point, lattice parameter, five peak shape parameters, and the coordinates and isotropic temperature factors of each atom. The X-ray data sets collected on the laboratory diffractometer were fitted using the Le Bail method only.[12] Again, the background was fitted by linear interpolation and the last cycle of least-squares refinement included the zero point, lattice parameter, and five peak shape parameters. All refinements were carried out using the GSAS suite of programs.[13]

The negative thermal expansion properties of siliceous faujasite are shown in Fig. 1. An approximately linear decrease in cell dimension is seen over the entire temperature range 25.16–572.0 K. The overall coefficient of thermal expansion {defined as $(l_{T2} - l_{T1})/[l_{T1}(T_2 - T_1)]$} calculated for the whole temperature range is -4.2×10^{-6} K^{-1}. This value is in good

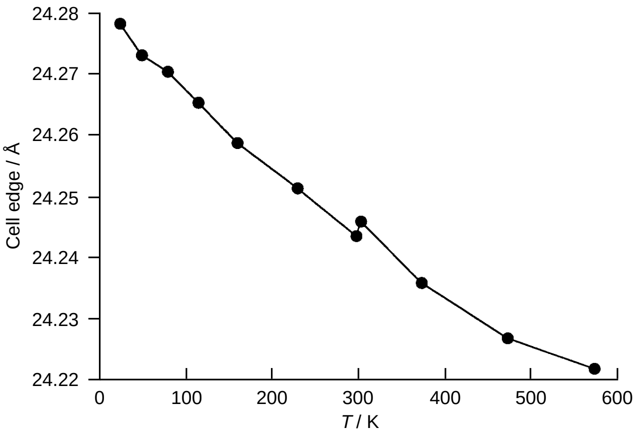

Fig. 1 Cubic cell edge as a function of temperature for siliceous faujasite

agreement with that calculated for siliceous faujasite by Couves *et al.* (-4.1×10^{-6} K^{-1}), but is significantly more negative than the values obtained from their computational and experimental studies on Na-zeolite X (-3.0×10^{-6} K^{-1} and -0.7×10^{-6} K^{-1}, respectively).[7,8]

The results from the Rietveld refinements at the seven temperatures between 25 and 298 K enable us to gain some insight into the structural changes giving rise to the negative thermal expansioin of siliceous faujasite. As in other negative thermal expansion materials,[2–4] the overall changes in bond distances and angles are small relative to their e.s.d.s. A cell dimension change of that observed between 25.16 and 297.5 K (24.2782–24.2442 Å), when placed on the same scale as a typical Si–O bond represents a change of only 1.600–1.598 Å, where a typical Rietveld e.s.d. on a bond length is only 0.002 Å.

The observed O–Si–O and Si–O–Si angles varied from 107 to 113° and 137 to 149°, respectively, with no detectable change with temperature in either case. There was an apparent decrease in the average Si–O bond distance of 1.614 to 1.610 Å from 25 to 298 K. However, after correcting for the thermal motion of oxygen,[14] there was no detectable change in the Si–O bond length over this temperature range. The fact that the bond angles and corrected bond distances within the SiO_4 tetrahedra remain essentially constant over the temperature range studied allows the latter to be considered as rigid tetrahedra.

The results from the structure refinements lead us to believe that the negative thermal expansion of this material is related to the transverse vibrations to the two-coordinate bridging oxygen atoms, a mode of lattice vibration that is of low enough energy to be readily excited at low temperatures. These vibrations lead to coupled rotations of the essentially rigid tetrahedra making up the structure of the zeolite. The lack of any systematic changes in atomic coordinates and bond angles over the temperature range studied implies that the transverse vibrations of the bridging oxygen atoms are essentially harmonic in nature and the bending of the Si–O–Si bonds is dynamic rather than static in nature. As the temperature of the material is increased, the magnitude of the transverse vibrations of the bridging oxygen atoms, as well as the resulting coupled rotations of the tetrahedra, increases, which manifests itself in the structure refinement results as a decrease in the average Si–O distance. With the decrease in the Si–O bond length accompanying the increase in temperature, a decrease in the average Si–Si nonbonding distance occurs, resulting in the negative thermal expansion observed. Again we emphasise that the apparent reduction of the Si–O bond length results from the increased thermal motion and not from actual changes in the magnitude of the Si–O vector. The explanation of the mechanism of negative thermal expansion for siliceous faujasite is the same as that suggested for other materials such as ZrW_2O_8[3,4] and the usual forms of SiO_2.[15]

The strong negative thermal expansion found in siliceous faujasite indicates that other zeolites and ALPOs might exhibit similar behaviour, as has been suggested qualitatively by computational methods.[7,8] However, the latter also predicts that some such framework materials exhibit positive thermal expansion. The reasons for the difference in behaviour for similar materials remain unclear and merit further investigation.

We thank G. J. Ray, Amoco Chemical Company, for provision of the dealuminated zeolite-Y sample. This work was supported through NSF grant No. DMR-9308530. Some data were collected at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-76CH00016.

Notes and References

† E-mail: Sleighta@chem.orst.edu

1 A. W. Sleight, *Endeavour*, 1995, **19**, 64.
2 J. S. O. Evans, T. A. Mary and A. W. Sleight, *J. Solid State Chem.*, 1997, **133**, 580.
3 J. S. O. Evans, T. A. Mary, T. Vogt, M. A. S. Subramanian and A. W. Sleight, *Chem. Mater.*, 1996, **8**, 2809.
4 J. S. O. Evans, T. A. Mary, A. W. Sleight and T. Vogt, *Science*, 1996, **272**, 90.
5 D. Taylor, *Br. Ceram. Trans. J.*, 1984, **83**, 129.
6 W. J. Mortier, *J. Phys. Chem.*, 1977, **81**, 1334.
7 J. W. Couves, R. H. Jones, S. C. Parker, P. Tschaufeser and C. R. A. Catlow, *J. Phys.: Condens. Matter*, 1993, **5**, L329.
8 P. Tschaufeser and S. C. Parker, *J. Phys. Chem.*, 1995, **99**, 10 600.
9 G. J. Ray, A. G. Nerheim and J. A. Donohue, *Zeolites*, 1988, **8**, 458.
10 J. A. Hriljac, M. M. Eddy, A. K. Cheetham, J. A. Donohue and G. J. Ray, *J. Solid State Chem.*, 1993, **106**, 66.
11 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
12 A. C. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447.
13 A. C. Larson and R. B. Von Dreele, GSAS, Tech. Rept. LA-UR-86-748, Los Alamos National Laboratory, NM, 1987.
14 D. W. J. Cruickshank, *Acta Crystallogr.*, 1956, **9**, 757.
15 T. H. K. Barron, J. G. Collins and G. K. White, *Adv. Phys.*, 1980, **29**, 609.

Received in Bloomington, IN, USA, 2nd October 1997; 7/07141H