Negative Thermal Expansion from 0.3 to 1050 Kelvin in ZrW₂O₈

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Negative thermal expansion was found for ZrW_2O_8 from 0.3 kelvin to its decomposition temperature of about 1050 kelvin. Both neutron and x-ray diffraction data were used to solve and refine the structure of this compound at various temperatures. Cubic symmetry persists for ZrW_2O_8 over its entire stability range. Thus, the negative thermal expansion behavior is isotropic. Essentially the same behavior was found for isostructural HfW_2O_8 . No other materials are known to exhibit such behavior over such a broad temperature range. These materials are finding applications as components in composites in order to reduce the composites' overall thermal expansion to near zero.

 \mathbf{N} egative thermal expansion is known in several oxide systems (1, 2). Usually, the contraction is small and anisotropic and occurs only over a small temperature range. We have studied negative thermal expansion in cubic phases of the type $ZrP_{2-x}V_xO_7$ (3, 4). Such materials can show negative thermal expansion at high temperatures, but this behavior does not persist below 100°C for any member of the series. The negative thermal expansion of these materials has been attributed to the transverse vibration of the central O in the O3P-O-PO3 or O₃V-O-VO₃ groups, coupled with frustration in finding a structural transition that would allow an ordered bending of P-O-P or V-O-V bond angles (3). By adjustment of x in $ZrP_{2-x}V_xO_7$, materials with near-zero thermal expansion can be obtained (3).

The synthesis of ZrW_2O_8 was described many years ago (5, 6). This compound was reported to be cubic, but the atomic structure was not determined. Thermal expansion data above room temperature suggested that negative thermal expansion ceased near room temperature (7). Our results (Fig. 1) show negative thermal expansion for ZrW_2O_8 from 0.3 to 1050 K. Agreement between dilatometry data and neutron diffraction data is very good in the region where both types of data were obtained. The neutron diffraction data also indicate that $\mathrm{Zr}\mathrm{W}_2\mathrm{O}_8$ is cubic over the entire temperature range. Both dilatometry data and neutron diffraction data suggest a phase transition near 430 K. It has been reported that HfW_2O_8 is isomorphous with ZrW_2O_8 (8), but no thermal expansion data were given. Our dilatometry data on HfW2O8 show negative thermal expansion behavior essentially identical to that of ZrW_2O_8 , including the phase transition at about 430 K.

We first solved the structure of ZrW_2O_8

using both x-ray and neutron powder diffraction data. Crystals were subsequently obtained, and the structure was confirmed from single-crystal x-ray diffraction data (9). The structure (Table 1 and Fig. 2) is similar to that of ZrP_2O_7 , which may be described as a NaCl-type structure with Zr^{4+} cations and $(P_2O_7)^{4-}$ anions. Much of the symmetry of the NaCl structure is destroyed by the oriented P2O7 groups, but the cubic symmetry is preserved in space group $Pa\bar{3}$. In the hightemperature ZrP_2O_7 structure, the P atoms and the central \tilde{O} of the P₂O₇ group lie on threefold axes. The site of the central O of the P2O7 groups is an inversion center. In the room-temperature ZrW₂O₈ structure, there are two crystallographically distinct WO4 tetrahedra. The W atoms and one O atom of each tetrahedron lie on the threefold axis. In the room-temperature ZrW_2O_8 structure, there is no inversion center and the space group becomes $P2_13$.

When ZrW_2O_8 is heated through its phase transition at about 430 K, changes in both the x-ray and the neutron diffraction patterns are readily apparent. Shifts in peak position are barely noticeable, but there are significant changes in peak intensities. For example, the (310) reflection, allowed in the acentric space group P213 but forbidden in the centric space group $Pa\overline{3}$, disappears. Analysis of data obtained above the transition reveals that this increase in symmetry is due to a disordering of the WO₄ tetrahedra (Fig. 3). This disorder can best be understood by consideration of the ZrW_2O_8 structure as a network of Zr and W atoms linked by two-coordinate O to give a framework of formula ZrW_2O_6 . The remaining two O atoms then complete the W tetrahedral coordination. At low temperature, each O is strongly bound to one W (distance, $d \sim 1.7$ Å), leading to an asymmetric arrangement of WO₄ groups (Fig. 3A). There is, however, a weak interaction between the "bridging" oxygen atom O3 and W1 (d = 2.39 Å) (10). Above the phase transition, however, the positions of both of these O atoms become disordered. The displacement of the bridging

Table 1. Structural data for ZrW₂O₈ at 293 K. These data are based on high-resolution neutron powder diffraction data collected at Brookhaven National Laboratory. Numbers in parentheses in the right column represent standard deviations from Rietveld refinement [GSAS software; A. C. Larson and R. B. Von Dreele, Los Alamos, 1994].

Parameter	Value
Parameter Space group Cell dimension Number of reflections Number of parameters* wRp (%)† R_p (%) R_{F^2} (%) χ^2 ‡ x(Zr)§ u(Zr) x(W1) u(W1) u(W1) u(W1) u(W2) u(W2) u(W2) u(W2) u(W2) u(Q1) u(Q1) u(Q1) u(Q2) u(Q2)	Value P2,3 9.15993(5) Å 177 54 10.08 7.39 3.87 2.37 0.93 0.0003(4) 0.010(1) Å ² 0.3412(3) 0.012(1) Å ² 0.6008(3) 0.010(1) Å ² 0.6008(3) 0.010(1) Å ² 0.2071(3) 0.4378(4) 0.4470(3) 0.202(1) Å ² 0.7876(3) 0.5694(4) 0.5565(3) 0.020(1) Å ²
x(O3) u(O3) x(O4)	0.4916(5) 0.023(1) Å ² 0.2336(3)
u(O4)	0.037(1) Å ²

*The total number of parameters included zero point, peak shape parameters, and anisotropic thermal parameters. Only the isotropic equivalent of the anisotropic thermal parameters (*u*) are given here.

$$twR\rho = \left[\sum_{i} w_{i} [y_{i}(\text{obs}) - y_{i}(\text{calc})]^{2} / \sum_{i} w_{i} y_{i}^{2} (\text{obs})\right]^{1/2};$$

$$R\rho = \left[\sum_{i} [y_{i}(\text{obs}) - y_{i}(\text{calc})]^{2} / \sum_{i} y_{i}^{2} (\text{obs})\right]^{1/2}$$

where y_i (obs) and y_i (calc) are, respectively, the observed and calculated intensities at step *i*. $R_{\rm F^2}$ and $R_{\rm F}$ are conventional agreement factors.

$$t_{\chi^2} = (wRp/R_{exp})^2 = \sum_{i}^{\infty} w_i [y_i(obs) - y_i(calc)]^2 / (N - P)$$

where *N* is the numbers of observations and *P* is the number of parameters. §For atoms on the threefold axis (Zr, W1, W2, O3, and O4), only one coordinate is given because x = y = z.

O toward the two W atoms becomes random, and the "terminal" O atoms occupy disordered sites at either end of the tungstate groups. Thus the structure can be considered as containing two WO_4 tetrahedra, whose direction along the threefold axis is dynamically disordered. Alternatively, the structure can be considered as containing a disordered mixture of W_2O_7 and W_2O_9 groups, both of which could contain a local center of symmetry. Both explanations suggest the possibility of high O mobility in ZrW_2O_8 .

The ZrO_2 –WO₃ pseudo binary phase diagram (6) is unusual. No compounds containing only Zr^{4+} , W^{6+} , and O^{2-} have been found that are thermodynamically stable at room temperature and below. The

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temperature for ZrW_2O_8 . Open circles are dilatometer data; solid circles are neutron diffraction data.

compound ZrW_2O_8 is evidently only thermodynamically stable between 1380 and 1530 K (11). It must be rapidly cooled from high temperature to avoid decomposition into ZrO2 and WO3. Once formed, however, this compound has a high degree of kinetic stability at temperatures below about 1050 K. Thus, heating ZrW₂O₈ above 1050 K results in decomposition into ZrO_2 and WO₃, which react to reform ZrW_2O_8 if the temperature is increased to 1380 K. The ordering that occurs below 430 K lowers the free energy of this system; however, this is presumably not an equilibrium phase. If the system were to achieve equilibrium, ZrW₂O₈ would decompose into ZrO_2 and WO_3 . This decomposition reaction is frustrated by its high activation energy. The system is trapped in a high-energy state, and this phenomenon may be related to the unusual thermal expansion properties. Negative thermal expansion also occurs in AgI, but only in the metastable cubic form (12). Negative thermal expansion in cubic AgI is confined to a region no wider than 200°C, the thermal expansion at 100 K being positive.

We begin our explanation of the unique properties of ZrW_2O_8 and HfW_2O_8 by eliminating certain possibilities. In both ZrO_2 and HfO_2 , there is an abrupt negative volume expansion at a tetragonal-to-monoclinic phase transition. This transition is associated with a



Fig. 2. Section of the ZrW₂O₈ structure (thermal ellipsoids are used for atoms).

change in the coordination number of Zr and Hf from 8 to 7 with decreasing temperature. No such coordination change occurs in ZrW_2O_8 . The shortest Zr–O distance beyond the 2.1 Å octahedral coordination sphere (Table 2) is 3.66 Å at both 0.3 and 700 K. We also eliminate from consideration any changes with temperature of the Zr-O or W-O bond distances. Structure refinements conducted at 12 temperatures from 0.3 to 700 K show no decreases in these distances with increasing temperature. Furthermore, because of differences in Zr-O and Hf-O bonding in isostructural ZrO_2 and HfO_2 , the temperature of the tetragonal-to-monoclinic phase transition in these two compounds differs by about 400°C. By contrast, in ZrW_2O_8 as compared to HfW_2O_8 , there is no detectable difference in their phase transition temperature or in their thermal expansion properties. Significant changes in W-O bonding occur at the 430 K phase transition (Fig. 3), but the negative coefficient of thermal expansion remains similar above and below this transition. We thus conclude that subtleties of

W–O, Zr–O, or Hf–O bonding are unlikely to be the cause of the negative thermal expansion.

We are thus left with Zr–O–W linkages as the source of the negative thermal expansion. A systematic change in the angles of this linkage could have been the source, but this is not supported by our structural refinements. It is, however, well documented that the potential for M-O-M transverse vibrations (corresponding in a static picture to bond bending) is significantly lower than for longitudinal vibrations (which correspond to changes in the M-O bond lengths). A transverse vibration of a bridging O in a framework in which M-O bond distances remain largely unchanged will cause a contraction of the M-M distance and a negative coefficient of thermal expansion. Because of the asymmetry of a typical M-O potential, however, longitudinal vibrations tend to lead to an overall increase in M-M distances. As discussed above, the network arrangement of ZrW2O8 leads to a highly flexible structure that can readily accommodate the changes in M-O-M





Fig. 3. (A) The two crystallographically distinct WO_4 tetrahedra of low-temperature ZrW_2O_8 in space group $P2_13_.$ (B) The WO_4 "tetrahedra" of high-temperature ZrW_2O_8 in space group Pa3. The O4 position is only 50% occupied, and the large ellipsoid of W is due to disorder along the threefold axis.

Table 2. Selected bond distances and angles from the refinement at 293 K. Numbers in parentheses represent standard deviations.

			1000000 0.0000 0000 0.000
Bond	Distance (Å)	Bond angle	Size (deg)
Zr1-01	2.042(4)	01-Zr1-01	91.44(21)
Zr1–02	2.108(4)	01-Zr1-02	89.57(13)
		01-Zr1-02	87.58(12)
		02–Zr1–02	91.44(22)
W1-01	1.798(3)	01-W1-01	116.1(1)
W1-04	1.709(7)	01–W1–O4	101.6(2)
W2-02	1.782(3)	02-W2-02	109.7(2)
W2-03	1.733(8)	02-W2-03	109.3(2)
W1-O3	2.386(9)	Zr-01-W1	154.29(22)
		Zr02W2	171.81(26)

bond angles due to transverse vibrations. This flexibility is shown by lattice energy calculations on model compounds in which the thermal contraction is modeled as being caused by a coupled three-dimensional rotation of the rigid polyhedra that make up the lattice network (13). Over a volume range corresponding to that observed up to the phase transition, essentially no change in the overall lattice energy is observed; any increases in the nonbonded anion-anion and cation-cation repulsions due to the contraction are offset by an increase in the W1–O3 attraction.

This result suggests the possibility of low-energy phonon modes in the lattice corresponding to these coupled rotations. Such modes will, by definition, exhibit negative Gruneisen parameters, γ_i (14), and their population will lead to a negative contribution to the overall coefficient of thermal expansion (15-17). Similar arguments have been applied to rationalize the thermal contraction over narrow temperature ranges in other materials (12). The large temperature range of negative thermal expansion in this material suggests that the framework structure of this material is such that the overall effective Gruneisen parameter, γ_{eff} (14) (which will include contributions from all active modes, both the low-energy transverse modes that tend to contract the lattice and the higher energy longitudinal modes that tend to expand the lattice), remains negative at all temperatures.

The anisotropic thermal vibrations present in ZrW_2O_8 and HfW_2O_8 , which cause negative thermal expansion, are presumably present in many other materials, but they are overwhelmed by the more familiar forces that cause positive thermal expansion. Negative thermal expansion cannot be expected in a material unless the distances between bonded atoms increase very little with increasing temperature. Such small changes with temperature occur only in oxides of cations with relatively high formal charge and low coordination number (18), which lead to a highly covalent bond. The vibration of O will only produce a significant contribution to negative thermal expansion when it has a coordination number of 2. The metaloxygen network must also be close to chargeneutral. Charged networks contain interstitial ions, and the ionic bonds between these interstitial ions and the network will have significant positive thermal expansion (18). A prerequisite for negative thermal expansion is thus a highly covalent, charge-neutral network with O in twofold coordination.

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- 11. Synthesis of ZrW_2O_8 requires several days of heating at about 1500 K (5–7). Even then, the reaction between ZrO_2 and WO_3 is not complete. Synthesis of ZrW_2O_8 is further complicated by the fact that volatilization of WO_3 is pronounced at such high temperatures. We have discovered precursor approaches that allow synthesis of single-phase ZrW_2O_8 with heating times shorter than 2 hours. One such approach yields ZrW_2O_8 at temperatures as low as 850 K, where ZrW_2O_8 is actually metastable. Small crystals suitable for x-ray diffraction studies were isolated from a sample that had been heated at 1475 K for 4 hours.
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- 14. The Gruneisen parameter γ_i is defined as γ_i = dlnν_i/ dlnV, where ν is the frequency of the *i*th normal mode and V is the volume. Population of modes with a negative γ_i will give rise to a decrease in the overall volume. The overall Gruneisen parameter

$$\gamma_{\text{eff}} = \sum_{j} \gamma_{j} \exp(-h\nu_{j}/kT) / \sum_{j} \exp(-h\nu_{j}/kT)$$

represents a weighted average over all the populated normal modes, both those with negative (contracting) and those with positive (expanding) contributions to the overall volume.

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- Supported by the Oregon Metals Initiative, Teledyne Wah Chang Albany, NSF, and the U.S. Department of Energy.

29 November 1995; accepted 19 January 1996

Homogeneous NMR Spectra in Inhomogeneous Fields

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Researchers interested in high-resolution nuclear magnetic resonance (NMR) spectroscopy have long sought higher magnetic fields to enhance resolution and simplify spectra. Magnets with substantially larger fields than those available in the best commercial spectrometers are available, but the inhomogeneity is unacceptable for high-resolution spectra. A detection method (termed HOMOGENIZED) is presented that removes inhomogeneity while retaining chemical shift differences and *J* couplings. With existing inhomogeneous magnets, this method could nearly double the largest resonance frequency available for high-resolution NMR. The HOMOGENIZED sequence is based on observations of intermolecular zero-quantum coherences between a solute molecule and solvent molecules that are micrometers away; as long as the field is homogeneous over this short distance, sharp resonances are recovered without echoes. Experimental demonstrations and a detailed density matrix theory to explain the effect are presented.

For decades, spectroscopists studying highresolution NMR have sought ever higher magnetic fields, largely because the spectral width (dominated by chemical shifts) is linearly proportional to the field strength and the intrinsic (homogeneous) linewidth depends only weakly on field strength. Hence, higher fields imply better resolution, as long as inhomogeneous broadening

SCIENCE • VOL. 272 • 5 APRIL 1996

from magnetic field nonuniformity can be neglected. Extremely good homogeneity (on the order of 1 part in 10^9) is needed and has traditionally been achieved by sample spinning and by adjusting a large number of shim coils (additional coils used to homogenize the field). As a result, commercial high-resolution spectrometers today operate at fields up to ~18 T (750-MHz proton resonance frequency), higher by about a factor of 25 than in the pioneering NMR experiments half a century ago.

Magnets with substantially higher fields

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