

# ACS Award Address for Chemistry of Materials

## Compounds That Contract on Heating<sup>†</sup>

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Received March 6, 1998

Various mechanisms to explain negative thermal expansion in oxides are presented. Our search for compounds having this unusual property has focused on the mechanism based on transverse thermal motion of oxygen in M–O–M linkages. Such a mechanism can give strong negative thermal expansion over broad temperature ranges. Examples of compounds where this mechanism operates to give negative thermal expansion are  $ZrW_2O_8$ , the  $Sc_2W_3O_{12}$  family,  $NbOPO_4$ ,  $AlPO_4$ -17, and faujasite  $SiO_2$ .

### Introduction

Usual explanations of thermal expansion start by considering the potential well of a diatomic molecule (Figure 1). As energy or temperature increases, vibrations increase. Due to the asymmetry of the potential well, excursions to longer interatomic distances are easier than to shorter interatomic distances. Thus, the average interatomic distance increases with increasing temperature. As bonds become stronger, the potential well becomes more symmetric and the vibrations therefore become more harmonic. For very strong bonds, there may be no detectable thermal expansion. The simplest way to achieve negative thermal expansion would be to reverse the potential well (Figure 1) so that with thermal excitation shorter distances become energetically favored over longer distances. There seems to be no example of such a situation for a diatomic molecule.

For larger molecules and for solids, the situation becomes more complicated. It has long been known that nonbonded interatomic distances may decrease with increasing temperature. In the case of  $CO_2$  at low temperatures, the O–O distance decreases with increasing temperature due to bending modes of the  $CO_2$  molecule. We will return later to this thermal striction mechanism as applied to solids.

### Symmetry-Related Negative Thermal Expansion

One route to negative thermal expansion is based on increasing symmetry of polyhedra with increasing temperature. The best examples of this mechanism are ferroelectric compounds such as  $PbTiO_3$ . At temperatures above 490 °C,  $PbTiO_3$  is cubic; its  $PbO_{12}$  and  $TiO_6$  polyhedra are perfectly regular. Below 490 °C the  $PbTiO_3$  structure is tetragonal, and both the  $PbO_{12}$  and  $TiO_6$  polyhedra become increasingly distorted as temperature decreases. In the temperature region where  $PbTiO_3$  becomes more distorted with decreasing temperature, it exhibits



Arthur W. Sleight was born in Ballston Spa, NY, in 1939. After graduation from Hamilton College in 1960, he began Ph.D. research in solid-state inorganic chemistry with Roland Ward at the University of Connecticut. Upon completion of this degree in 1963, Sleight was a postdoc for a year with Arne Magneli at the University of Stockholm. The next 25 years of Sleight's career were spent in the Central Research Department of the DuPont Company. Synthesis of new materials has been a major effort throughout his career. Materials of interest have included superconductors, transparent conductors, ionic conductors, ferroelectrics, ferroelastics, ferromagnets, phosphors, catalysts, and materials exhibiting semiconducting-to-metal transitions. He has authored or coauthored about 300 publications and 20 patents. It was during his DuPont days that Sleight first became interested in the thermal expansion of materials. Since 1989, Sleight has been the Milton Harris Professor of Materials Science in the Department of Chemistry at Oregon State University, where he also holds the title of Distinguished Professor.

negative thermal expansion (Figure 2 and Table 1). Both the *a* and *b* axes show positive thermal expansion, but the *c*-axis

<sup>†</sup> This paper is based largely on the address for the 1997 ACS Award for Chemistry of Materials presented as paper INOR 422 at the 213th National Meeting of the American Chemical Society, San Francisco, CA, April 15, 1997.

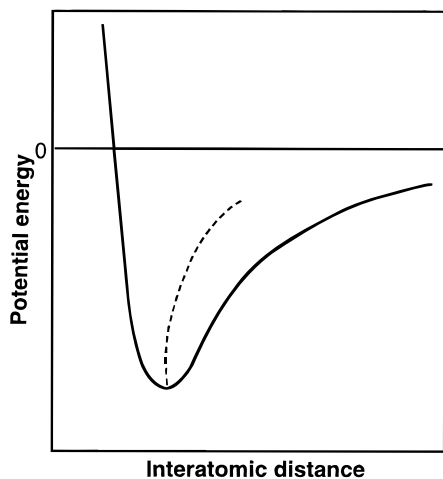


Figure 1. Potential energy vs interatomic distance for a diatomic molecule. The dotted line shows the average interatomic distance.

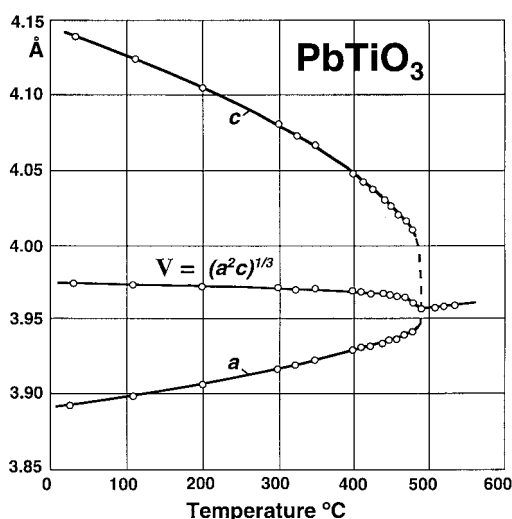


Figure 2. Cell edges and volume vs temperature for  $\text{PbTiO}_3$ .

Table 1. Thermal Expansion Coefficients

material	$\alpha^a \times 10^6$
polypropylene	90
copper	16.6
$\text{Al}_2\text{O}_3$	8.8
silicon	3
$\text{SiO}_2$ (amorphous)	0.5
$\text{SiO}_2$ (faujasite)	-4.2
$\text{LiAlSiO}_4$	-1
$\text{PbTiO}_3$	-3.5
$\text{Sc}_2\text{W}_3\text{O}_{12}$	-2.2
$\text{Lu}_2\text{W}_3\text{O}_{12}$	-6.8
$\text{ZrW}_2\text{O}_8$	-8.7
$\text{AlPO}_4$ -17	-11.7

<sup>a</sup>  $\Delta l/l$  per  $^\circ\text{C}$ .

thermal contraction is large enough to give a small volume contraction. A rationalization for this behavior is based on the decrease of anion-anion repulsion as polyhedra become more regular. A consequence of this decreased repulsion is smaller polyhedra.

There is an alternate complementary explanation for the negative thermal expansion of tetragonal  $\text{PbTiO}_3$ . This focuses on the symmetry of the oxygen environment instead of the cation environment. In the tetragonal form of  $\text{PbTiO}_3$ , the Ti-O bonds are alternately long and short extending in linear chains along the  $c$  axis. These long and short bonds may be regarded as

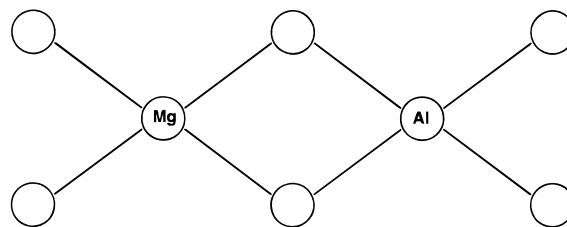


Figure 3. Schematic of a shared edge for a  $\text{MgO}_6$  octahedron and an  $\text{AlO}_4$  tetrahedron.

single and double bonds, respectively. Above  $490^\circ\text{C}$  in the cubic form of  $\text{PbTiO}_3$ , all Ti-O bonds are of equal length with a bond order of 1.5. It is well established from bond order vs bond distance relationships that a bond of 1.5 order is shorter than the average of the bonds with 1.0 and 2.0 order. Thus, as the unequal Ti-O bond lengths become equal, their average value decreases. From this approach, it follows naturally that the  $c$  axis in tetragonal  $\text{PbTiO}_3$  will be longer than the  $a$  and  $b$  axes and that it will decrease with increasing temperature. Positive thermal expansion always occurs for the  $a$  and  $b$  axes along which the Ti-O bonds are all of equal length in the tetragonal as well as the cubic form of  $\text{PbTiO}_3$ . In tetragonal  $\text{PbTiO}_3$ , there is a complimentary long-short alteration of Pb-O bond lengths along the  $c$  axis. It is this factor that accounts for the much more pronounced negative thermal expansion in tetragonal  $\text{PbTiO}_3$  relative to tetragonal  $\text{BaTiO}_3$ .

### Networks with Bond Thermal Expansion

Another way to approach negative thermal expansion is to consider the behavior of certain networks. Lake<sup>1</sup> has described cellular solids consisting of bilayer ribs. Depending on the relative thermal expansion of each layer, negative thermal expansion may be produced in two dimensions. There is apparently no known example of this mechanism at the atomic level. Molecular dynamics calculations of a polyacetylene network have predicted negative thermal expansion.<sup>2</sup> This is perhaps related to negative thermal expansion observed in certain elastomers.<sup>3</sup>

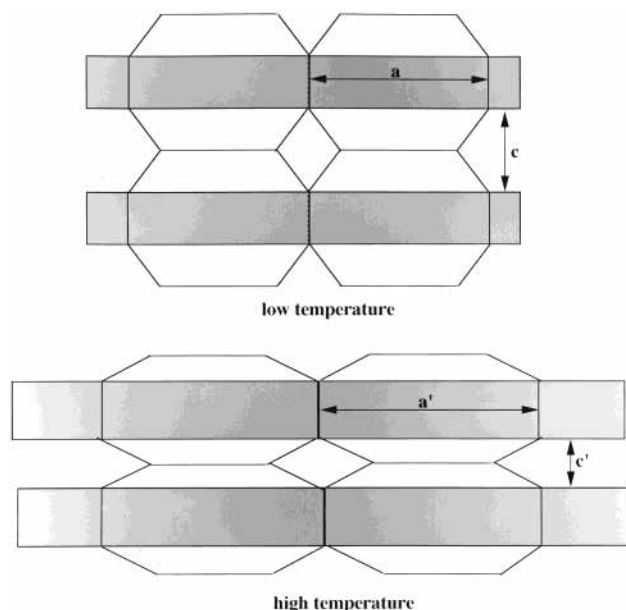
A class of oxides that exhibit negative thermal expansion in one or two dimensions only has structures that are best viewed as network structures. Three important members of this class have found application due to their very low volume thermal expansion: corderite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{12}$ ),  $\beta$ -eucryptite ( $\text{LiAlSiO}_4$ ), and NZP ( $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ). All three have hexagonal structures. For corderite and  $\beta$ -eucryptite, positive thermal expansion along  $a$  and  $b$  is coupled with negative thermal expansion along  $c$ . For NZP,  $c$ -axis positive thermal expansion is coupled with contraction along the  $a$  and  $b$  axes. The underlying mechanism is basically the same in all three of these compounds.<sup>4</sup> It is actually normal bond expansion that gives rise to the basic features of the thermal expansion properties of corderite,  $\beta$ -eucryptite, and NZP. In these compounds, the thermal expansion of the Al-O, Si-O, P-O, and Zr-O bonds is small enough to ignore. We can consider then just the effect on structure of thermal expansion of Mg-O, Li-O, and Na-O bonds. A key feature of these compounds is edge- or face-sharing polyhedra. This gives the possibility of polyhedron expansion in one or two directions only. Figure 3 shows a portion of the corderite structure. As Mg-O bonds lengthen

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**Figure 4.** Schematic of anisotropic thermal expansion in networks. The shaded areas represent layers in corderite and  $\beta$ -eucryptite but represent tubes in the case of NZP. As the layers or tubes undergo thermal expansion, they are pulled closer together in the other directions. The layer thickness and tube diameter do not change.

with increasing temperature, there is expansion only in the horizontal direction. Expansion in the vertical direction is inhibited by the cation–cation repulsion across the shared edge. This repulsion pulls the oxygen atoms at the edge into their contact position where they remain while Mg–O distances expand and contract. In corderite, the Mg–O–Al linkages form a layer which expands laterally while its thickness does not change significantly. Six-membered Si–O rings hold the Mg/Al/O layers together. The vertical contraction caused by horizontal expansion of layers is illustrated schematically in Figure 4. The wires holding the layers together are Si–O bonds, and the hinges are Si–O–Si and O–Si–O bond angles. Expansion in the  $ab$  plane directly causes contraction along  $c$ .

In both corderite and  $\beta$ -eucryptite, there are layers with polyhedra edge sharing only within the layers. In NZP, there is face sharing of ZrO<sub>6</sub> and NaO<sub>6</sub> octahedra along the  $c$  axis forming tubes. Cation–cation repulsion pulls the oxygen atoms of the shared faces to their contact distance, where they remain, while Na–O distances expand or contract with changing temperature. Thus, the tubes expand along the  $c$  axis as the Na–O distances expand with increasing temperature. The tubes do not increase their diameter but are pulled closer together by rotations of PO<sub>4</sub> tetrahedra linking the tubes together.

The mechanism just described gives excellent agreement with the observed thermal expansion behavior of corderite. In the case of  $\beta$ -eucryptite and some members of the NZP family, other factors must be considered for a complete explanation of their thermal expansion properties. Good Na<sup>+</sup> conductivity occurs in NZP, and good Li<sup>+</sup> conductivity occurs in  $\beta$ -eucryptite. The actual distribution of Na<sup>+</sup> and Li<sup>+</sup> in these lattices changes with changing temperature. Complete modeling of the thermal expansion of these compounds must include this changing distribution.

### Rocking Polyhedra

The most fruitful area for negative thermal expansion in oxides appears to be open framework structures where the framework oxygen is coordinated to just two metal atoms. If

the angle of the M–O–M linkage is 180°, transverse thermal motion of oxygen will pull the metal atoms closer together, provided that the M–O bonds are sufficiently strong that there is insignificant thermal expansion of these bonds. This is the same mechanism causing thermal striction of CO<sub>2</sub> at low temperatures. It is also a mechanism that has been invoked in oxides such as SiO<sub>2</sub>. However, it seemed that this mechanism operated only over limited temperature regions that did not include room temperature. We now know, however, that this mechanism can give very strong negative thermal expansion over broad temperature ranges that include room temperature.

One issue with thermal striction of the M–O–M linkage is whether the displacement of oxygen should be viewed as transverse motion or as a torus which increases its diameter with increasing temperature. There is not likely one answer to this question. The torus is probably more appropriate for Si–O–Si and P–O–P linkages with an angle close to the unfavorable 180° angle. However,  $\pi$  bonding stabilizes the 180° angle for linkages such as W–O–W with hexavalent W; then, the transverse motion modeled as a thermal ellipsoid becomes more likely. Many cases may represent a hybrid situation.

Another issue with the oxygen vibrations of the M–O–M linkages is how to account for the correlated motions of the various oxygen atoms of the network. In fact, there is a simple way to accommodate this correlation. Each MO<sub>x</sub> polyhedron can be considered as a rigid or semirigid polyhedron. Rocking of these linked polyhedra back and forth creates transverse thermal motion of the M–O–M linkages in a correlated manner. This is an approach that we had previously used to investigate the flexibility of various networks.<sup>5</sup> A flexible network is one where polyhedra can easily rotate back and forth with little or no change in shape. Not all frameworks based on corner-shared polyhedra are flexible.

Dove et al.<sup>6</sup> have taken a similar approach to describing features of framework structures. They define rigid unit modes (RUMs) that are rocking motions of polyhedra that do not change shape. Quasi-rigid unit modes (qRUMs) are rocking motions of polyhedra where small changes in polyhedral shape are required. A necessary condition for negative thermal expansion is the existence of RUMs or qRUMs.

A simple example of thermal rocking of polyhedra is illustrated in Figure 5 using the cubic ReO<sub>3</sub> structure. The structure is largest when the M–O–M angles are 180°. Rocking bends the M–O–M linkages, resulting in a volume decrease. No distance or angle within the MO<sub>6</sub> octahedron changes. Actually, ReO<sub>3</sub> itself does not show negative thermal expansion, possibly because the Re–O distance becomes larger as the Re–O–Re linkages bend away from 180°. This 180° bond angle is stabilized through  $\pi$  bonding.

For networks with oxygen in 2-fold coordination, there are constraints on possible formulas. For an oxide network based on corner-sharing octahedra only, the formula must be AO<sub>3</sub>. For an oxide network based on corner-sharing tetrahedra only, the formula must be MO<sub>2</sub>. For a network with only polyhedra corner sharing but with both tetrahedra and octahedra, there are several possibilities. Simple examples are AM<sub>2</sub>O<sub>7</sub>, A<sub>2</sub>M<sub>3</sub>O<sub>12</sub>, and AMO<sub>5</sub> where A and M are octahedral and tetrahedral cations, respectively. For the A<sub>2</sub>M<sub>3</sub>O<sub>12</sub> formula, each oxygen may be shared by one A and one M cation. For the AM<sub>2</sub>O<sub>7</sub> formula, there are both A–O–M and M–O–M linkages, whereas for the AMO<sub>5</sub> formula, there are both A–O–M and

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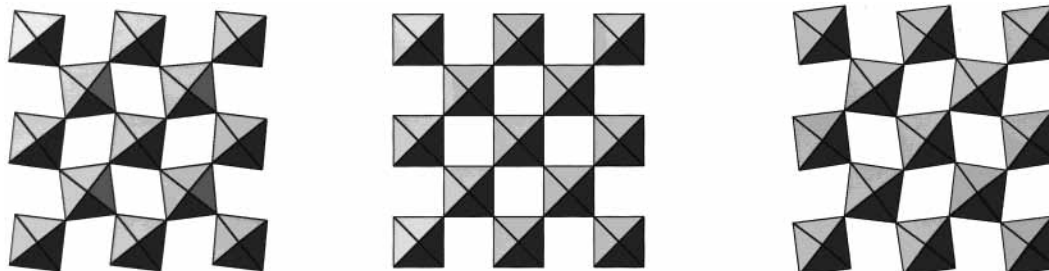


Figure 5. Octahedra tilting back and forth to give thermal contraction.

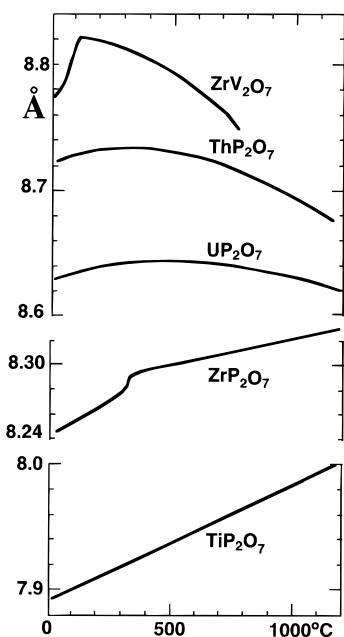


Figure 6. Thermal expansion for some cubic  $AM_2O_7$  compounds.

A—O—A linkages. All of these types can show negative thermal expansion behavior.

Figure 6 shows the thermal expansion of several members of the cubic  $AM_2O_7$  family.<sup>7</sup> Note that the tendency to exhibit negative thermal expansion behavior increases as the unit cell edge increases. This is a structure (Figure 7a) for which rocking motions of the linked tetrahedra and octahedra cannot occur without concurrent changes in polyhedral shapes. However, as polyhedra become larger, it is easier for them to change shape due to decreased anion—anion distances within polyhedra. Thus, the negative thermal expansion behavior in the cubic  $AM_2O_7$  series is dependent on the more facile rocking motions of larger polyhedra.

Several members of the cubic  $AM_2O_7$  family have a network collapse phase transition with decreasing temperature (Figure 6). Below this transition, the thermal expansion is positive and more normal. The structures through these transitions have been studied in detail for  $ZrP_2O_7$  and  $ZrV_2O_7$ .<sup>8–11</sup> At room temperature, both of these compounds are cubic but with a  $3 \times 3 \times 3$  superstructure relative to their high-temperature structure. However, when this superstructure first appears on cooling from

high temperatures, it is incommensurate.<sup>11</sup> We will come back to these network collapse transitions, which also occur in other structures. One way to suppress this phase transition is through solid solutions such as the  $ZrP_2O_7$ — $ZrV_2O_7$  solid solution.<sup>12</sup>

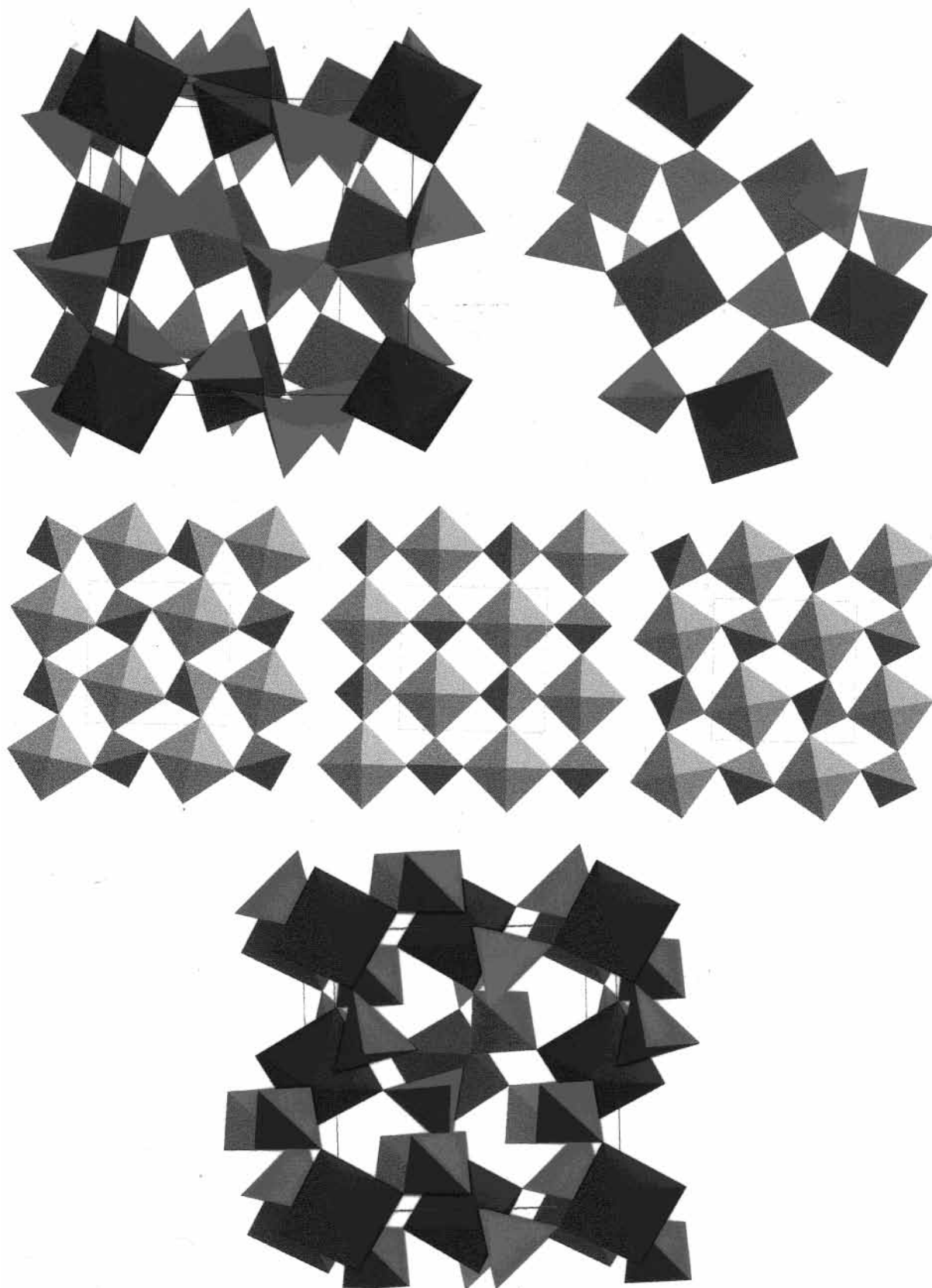
There are two different structures to consider for the  $A_2M_3O_{12}$  formula. One structure is the same as NZP ( $NaZr_2P_3O_{12}$ ) without Na. This is a hexagonal structure, and an example is  $NbZrP_3O_{12}$ . These phases can exhibit negative volume thermal expansion.<sup>13</sup> However, characteristics of the compounds reported with this structure are highly anisotropic thermal expansion and coefficients of thermal expansion which are strongly temperature dependent.

Another family of compounds with the  $A_2M_3O_{12}$  formula ideally has a structure with orthorhombic symmetry (Figure 7b). This is a very large family where M can be Mo or W and A can be many trivalent cations ranging in size from  $Al^{3+}$  to the smaller rare-earth cations. The same structure also exists for  $A_2MP_2O_{12}$  phases where A is  $Zr^{4+}$  or  $Hf^{4+}$  and M is  $W^{6+}$  or  $Mo^{6+}$ . The thermal expansion in this family varies from positive to negative.<sup>14</sup> Thus, solid solutions can be prepared which show essentially zero thermal expansion. In view of the orthorhombic symmetry, members of this family must have anisotropic thermal expansion. However, for some members, the expansion is nearly isotropic. More typically, negative thermal expansion occurs along the *a* and *c* axes and positive thermal expansion along the *b* axis. As in the case of the cubic  $AM_2O_7$  family, coupled rocking of polyhedra cannot occur unless the polyhedra change shape while rocking.<sup>15</sup> Thus, we might again expect stronger negative thermal expansion with larger unit cells based on larger cation size. Studies of  $Lu_2W_3O_{12}$  confirm this expectations. The intrinsic linear thermal expansion for  $Sc_2W_3O_{12}$  is  $-2.2 \times 10^{-6} K^{-1}$ , while for  $Lu_2W_3O_{12}$ , which shows negative thermal expansion along all three axes, it is  $-6.8 \times 10^{-6} K^{-1}$ .<sup>16</sup> This is much more negative than for the NZP-related phases with the  $A_2M_3O_{12}$  formula.

Very little is yet known about compounds of the  $AMO_5$  or  $AOMO_4$  family. We have recently studied<sup>17</sup> the thermal expansion of tetragonal  $NbOPO_4$ . It has a phase transition at about 200 °C. Above that transition, negative thermal expansion is observed for the *a* and *b* axes coupled with positive thermal expansion for the *c* axis. Below the transition, all three axes show positive thermal expansion. The rocking motion related to the negative thermal expansion is illustrated in Figure 7c. Mirror planes present in the middle frame disappear on tilting

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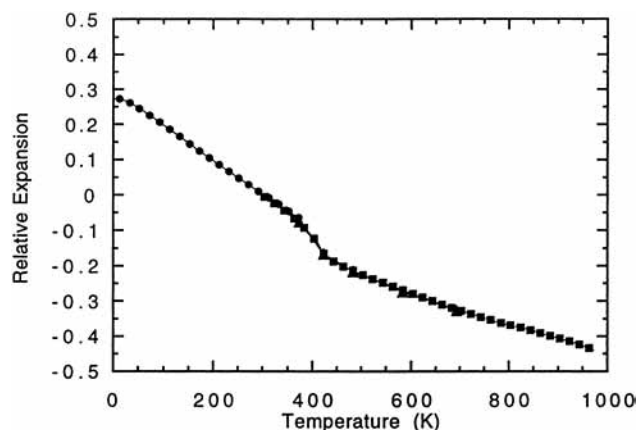
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**Figure 7.** (a, top left) The cubic  $AM_2O_7$  structure as corner-sharing  $AO_6$  octahedra (green) and  $MO_4$  tetrahedra (red). (b, top right) A fragment of the structure of the orthorhombic  $A_2M_3O_{12}$  family as  $AO_6$  octahedra (green) and  $MO_4$  tetrahedra (red). (c, middle) The tetragonal  $NbOPO_4$  structure looking down the  $c$  axis. Rocking of connected  $NbO_6$  octahedra and  $PO_4$  tetrahedra causes contraction along  $a$  and  $b$  but not along  $c$ . (d, bottom) The cubic  $ZrW_2O_8$  structure as  $ZrO_6$  octahedra (green) and  $WO_4$  tetrahedra (red).

just as in Figure 5. However, in this case, there are no  $180^\circ$  linkages when the mirror planes are present.

Calculations suggest that some  $MO_2$  networks based on corner-shared tetrahedra should have negative thermal expansion.



**Figure 8.** The expansion of cubic  $\text{ZrW}_2\text{O}_8$  vs temperature. Measurements from 3 separate experiments are combined.

sion, while others should have positive thermal expansion.<sup>18</sup> No explanation was offered for this different behavior. We have determined the thermal expansion of  $\text{SiO}_2$  with the faujasite structure.<sup>19</sup> It is indeed strongly negative over the entire range of measurement. Even stronger thermal expansion ( $\alpha_1 = -11.7 \times 10^{-6} \text{ K}^{-1}$ ) is found for  $\text{AlPO}_4$ -17, which has the hexagonal erionite structure.<sup>20</sup> This is apparently the strongest negative thermal expansion ever observed for any material.

The thermal expansion for  $\text{ReO}_3$  is small but positive.<sup>21</sup> The structure of  $\text{WO}_3$  is highly distorted relative to cubic  $\text{ReO}_3$ , and it shows only positive thermal expansion. Both  $\text{TaO}_2\text{F}$  and  $\text{NbO}_2\text{F}$  are known to have the cubic  $\text{ReO}_3$  structure. Our recent measurements<sup>22</sup> on these compounds indicate very low thermal expansion, lower than that of vitreous silica.

**Zirconium Tungstate.** A way to relieve the inhibition of rocking motions of polyhedra in the cubic  $\text{AM}_2\text{O}_7$  structure would be to break some of the bonds in this network. Breaking the M–O bond of the M–O–M linkage is conceptually possible, and this leads us to the cubic  $\text{ZrW}_2\text{O}_8$  structure (Figure 7d). The arrangement of  $\text{ZrO}_6$  octahedra is the same in both the  $\text{ZrW}_2\text{O}_8$  and  $\text{ZrV}_2\text{O}_7$  structures, but the  $\text{WO}_4$  groups in  $\text{ZrW}_2\text{O}_8$  are not linked to each other. The  $\text{ZrW}_2\text{O}_8$  structure is much more flexible than the  $\text{ZrV}_2\text{O}_7$  structure. The polyhedra can rock back and forth without any change in shape. Negative thermal expansion is observed<sup>23,24</sup> for  $\text{ZrW}_2\text{O}_8$  over its entire stability range (Figure 8), and this thermal contraction is especially strong from 10 to 425 K. Because  $\text{ZrW}_2\text{O}_3$  is cubic, its thermal expansion behavior is strictly isotropic. It has the strongest negative thermal expansion known for any isotropic material.

A change in slope of the thermal expansion curve for  $\text{ZrW}_2\text{O}_8$  occurs at about 425 K. Thermal expansion remains negative above this phase transition, but the magnitude is decreased. Structural studies<sup>23,24</sup> show that this is an order–disorder transition. Above the transition, there are various ways the structure can be described. All tetrahedra in the  $\text{ZrW}_2\text{O}_8$  structure are on 3-fold axes. They must point up or down. This pointing is ordered below the order–disorder transition. Above the transition, these tetrahedra may point randomly up or down.

Alternately, we may consider this disordered situation to be a dynamic mixture of  $\text{WO}_4$ ,  $\text{W}_2\text{O}_7$ , and  $\text{W}_2\text{O}_9$  groups. Still another view is to consider the structural formula to be  $\text{Zr}(\text{WO}_3)_2\text{O}_2$  where the network is  $\text{Zr}(\text{WO}_3)_2$  with two extra-framework oxygen atoms. One of these oxygen atoms is trapped between the two adjacent  $\text{WO}_3$  triangles, and the other extra-framework oxygen atom is mobile. In fact, analysis of ac impedance data suggests that above its order–disorder transition,  $\text{ZrW}_2\text{O}_8$  has oxygen ion conductivity similar to that, of  $\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ .<sup>24</sup> Hysteresis has been detected in this order–disorder transition.

Subjecting  $\text{ZrW}_2\text{O}_8$  to high pressure shows that its compressibility is not unusual.<sup>25</sup> However, at about 2 kbar it collapses into a denser structure. This denser structure has orthorhombic symmetry and is maintained on release of the pressure. This structure is cross braced with the addition of some more W–O bonds. This denser structure still possesses negative thermal expansion, but the magnitude is much less than that of the cubic form. This decrease is presumably a result of the cross bracing, which decreases the flexibility of the structure. On heating of orthorhombic  $\text{ZrW}_2\text{O}_8$  to 390 K at ambient pressure, it converts back to cubic  $\text{ZrW}_2\text{O}_8$ . The behavior of isostructural  $\text{HfW}_2\text{O}_8$  and  $\text{Zr}_{1-x}\text{Hf}_x\text{W}_x\text{O}_8$  solid solutions is essentially identical to that of  $\text{ZrW}_2\text{O}_8$  from the point of view of thermal expansion properties. However,  $\text{HfW}_2\text{O}_8$  requires higher pressures to convert it to the denser orthorhombic structure.

According to the  $\text{ZrO}_2$ – $\text{WO}_3$  phase diagram,<sup>26</sup> there is only one ternary compound in this system,  $\text{ZrW}_2\text{O}_8$ . This compound is thermodynamically stable only between 1380 and 1530 K. Thus, final synthesis conditions normally involve heating in that temperature range. However, using certain precursors, cubic  $\text{ZrW}_2\text{O}_8$  can be prepared at about 600 °C.<sup>27</sup> This low-temperature synthesis route has enabled the synthesis of  $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$  solid solutions up to  $x = 1.5$ .<sup>27</sup> The structure of  $\text{ZrMo}_2\text{O}_8$  is very different from that of  $\text{ZrW}_2\text{O}_8$ , and attempts to prepare  $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$  solid solutions at high temperature have failed. One effect of substituting Mo for W in  $\text{ZrW}_2\text{O}_8$  is to lower the order–disorder transition temperature.<sup>27</sup> Samples with  $x$  of 0.7 or greater have the disordered structure at room temperature. High yields of cubic  $\text{ZrW}_2\text{O}_8$  have also been obtained by a combustion synthesis.<sup>28</sup> In this synthesis, urea is added to a nitrate solution containing Zr and W. Placing this mixture in a furnace preheated to 500 °C initiates an exothermic reaction. In this way,  $\text{ZrW}_2\text{O}_8$  can be produced in a few minutes.

**Maximum Volume Networks.** If the angle of a M–O–M linkage is not 180°, it is no longer obvious that transverse oxygen thermal motion will lead to M–M contraction. It could as well lead to M–M expansion. There is, however, a condition where we might expect M–M thermal contraction regardless of the angle of the M–O–M linkage. In the ionic limit, we should expect the lowest energy configuration of a network to be its most open form.<sup>29</sup> This maximizes cation–cation distances without affecting cation–anion bonding distances. It will increase the angles of the M–O–M linkages to their maximum values consistent with the connectivity of the network. In such a network at its maximum volume, bending the the

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M—O—M linkages to smaller angles will generally be easier than bending to larger angles.<sup>5</sup> Thus, transverse thermal motions of this oxygen will lead to thermal contraction of the network. This leads us to a possible explanation of the theoretical predictions for thermal expansion of some zeolites. Our studies of zeolite network flexibility<sup>5</sup> indicate a symmetric potential well for sodalite instead of the asymmetric well found for all other cubic zeolites investigated. There is, therefore, no driving force for negative thermal expansion in the sodalite framework. This was the only cubic framework for which positive thermal expansion was predicted.<sup>18</sup> There is thus a suggestion that the asymmetric well is a requirement for negative thermal expansion in zeolites.

Just as for the diatomic molecule situation shown in Figure 1, the transverse motion of oxygen in the M—O—M linkage may be described by either a harmonic or an anharmonic well. If, for example, the linkage angle is constrained by symmetry to be 180°, the well is strictly harmonic. Thermal contraction can occur regardless of whether this well is harmonic or anharmonic. If the well is harmonic or very close to harmonic, the average position of the oxygen will not change as temperature changes. However, for an anharmonic well, the average position will change. These two different situations might be described as two different mechanisms. In only one mechanism would there be static tilting of the polyhedra with changing temperature. Basically, however, this is one mechanism, the difference being whether the potential well is harmonic or anharmonic.

For some network structures, negative expansion occurs only at high temperature. As temperature decreases, there is a framework collapse transition. Once the framework has collapsed, it exhibits normal positive thermal expansion. Examples of this are several crystallite forms of SiO<sub>2</sub> and several members of the cubic AM<sub>2</sub>O<sub>7</sub> family. A big factor here is the unfavorable 180° for M—O—M linkages where M is Si, P, or V. Oxygen displacements bending this angle at high temperature are disordered. Below the network collapse transition, these displacements become partially or completely ordered. The situation for the A<sub>2</sub>M<sub>3</sub>O<sub>12</sub> family is different. There are no 180°

linkage angles even for the highest symmetry form of the network. Still, many of the orthorhombic A<sub>2</sub>M<sub>3</sub>O<sub>12</sub> compounds have a network collapse phase transition. Below the transition, they have monoclinic structures which exhibit only normal positive thermal expansion. This is a violation of the maximum volume principle, which suggests that the structures are not sufficiently ionic for it to apply. This conclusion is supported by correlations between network ionicity and the temperature of the phase transition.<sup>14</sup> As the effective charges on anions and cations decrease, anion—anion and cation—cation repulsion decreases. These repulsions can then be overcome by a van der Waals attraction which drives the collapse. Thus, in some networks, it is important to adjust the ionicity to avoid the network collapse transition.

## Outlook

Undoubtedly, the list of compounds that contract on heating will continue to grow, and some of these compounds will likely find application. We have qualitative ideas that successfully guide our search for such compounds. Definitive correlation of theory with experiment is difficult. It is easy to determine the thermal expansion or contraction of a material with great precision, but the same level of precision cannot be obtained for the expansion and contraction of individual interatomic distances. It thus frequently happens that when a compound expands or contracts, we cannot attribute this behavior with absolute certainty to any particular bond distance or bond angle. Our approach is then to compare computer modeling with observed expansion or contraction. Accurate structure analyses as a function of temperature are nonetheless important because significant structural changes are sometimes readily detected.<sup>15</sup>

**Acknowledgment.** Our studies on compounds that contract on heating have been supported by the National Science Foundation. The undergraduate students, graduate students, postdocs, and other collaborators in these studies are indicated in the references.

IC980253H