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LETTER TO THE EDITOR

Negative Thermal Expansion in a Large Molybdate and Tungstate Family

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Negative thermal expansion has been discovered in a very large family of oxides represented by the formula $A_2M_3O_{12}$, where the A and M cations are coordinated by oxygen octahedrally and tetrahedrally, respectively. In the case of $Sc_2W_3O_{12}$, negative thermal expansion occurs over a temperature range of at least 10 to 1200 K. Ceramic bars of $Sc_2W_3O_{12}$ show a contraction with increasing temperature greater than that reported for any other material. Trends observed in this large $A_2M_3O_{12}$ family have provided insights on why many compounds showing negative thermal expansion cease to show this behavior below a certain temperature. Some members of this family show positive thermal expansion. Solid solutions have been made which show very low thermal expansion. © 1997 Academic Press

Negative thermal expansion is rare. When it occurs, it is usually limited to temperatures which do not include room temperature. Notable exceptions are ZrW_2O_8 and HfW_2O_8, which show negative thermal expansion over a very broad temperature range (1, 2). The negative thermal expansion in both the ZrW_2O_8 and the $A_2M_3O_{12}$ families is related to transverse thermal motion in Zr–O–W or A–O–M linkages. We have previously discussed how these thermal motions of oxygens are highly correlated with each other, so that properties of these materials can best be described in terms of librations and tilts of essentially rigid polyhedral building blocks. Negative thermal expansion by this mechanism can occur only in open framework structures.

The presence of an open framework is not in itself a sufficient condition for the observation of negative thermal expansion. In fact there is a strong tendency for framework lattices to undergo a volume-reducing displacive phase transition from their high symmetry structures as they are cooled. No strong bonds are broken or formed during such a framework collapse phase transition, and the process can often be pictured as again being related to coupled rotations of essentially rigid polyhedral building blocks. Such a transition occurs at about 370 K in ZrV_2O_7 (3), 120 K in $Sc_2Mo_3O_{12}$, and 530 K in the cristobalite form of SiO_2 (4). The immediate corollary of such a phase transition would seem at first to be an undesirable one in the quest for materials with low or negative thermal expansion: the existence of a volume-reducing phase transition on cooling implies that on heating there is a low energy expansive path way open to the material. Indeed many low symmetry framework structures show high thermal expansivity when initially heated. Once in their final, high symmetry form, however, the coefficient of thermal expansion of such phases is expected to be low or even negative.

Understanding, controlling, and eliminating this transition is a major goal in the development of new materials which show negative thermal expansion over a broad temperature range. Previously we have suggested that the connectivity in certain framework structures frustrates a phase transition to a lower symmetry, lower volume structure. That is, the framework topology itself can be used to prevent the undesirable phase transition (3). We have now identified another crucial factor related to the collapse of open framework structures: the effective charge of the oxygen atoms of the network.

The structure of the $A_2M_3O_{12}$ series of compounds is shown in Fig. 1 and contains a network of corner-sharing octahedral and tetrahedral sites. One of the major attractions of this family is the considerable chemical flexibility of the structure. When the tetrahedral M cation is Mo or W, the octahedral A cation site can be occupied by any one of 16 trivalent cations ranging in size from Al (radius of 0.675 Å) to Gd (radius of 1.075 Å) or solid solutions of these elements. With a view to eventual applications, nonisovalent A-site substitution is also possible, offering a route away from the often expensive rare earth ions. We have successfully prepared isostructural phases such as Zr_2P_2

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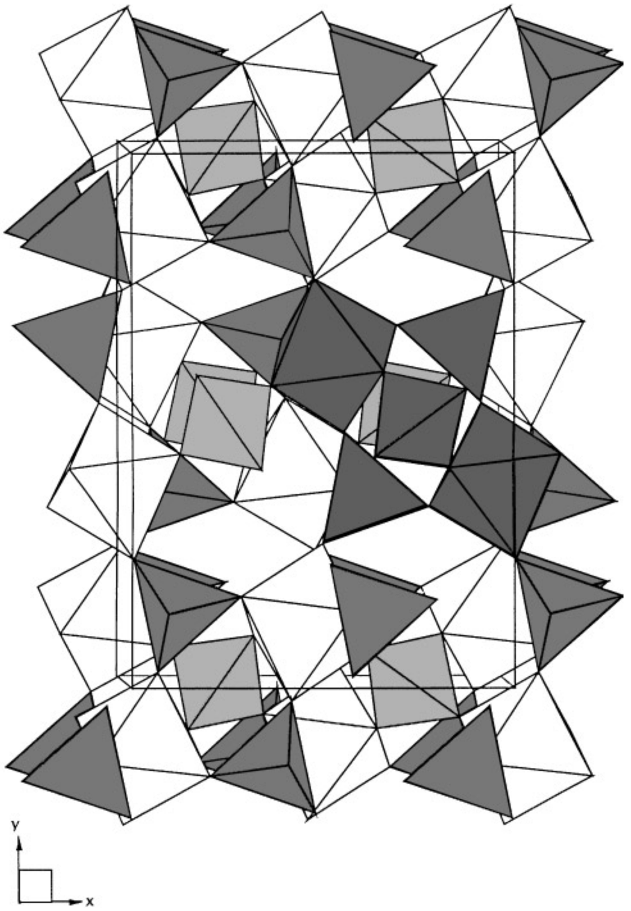

FIG. 1. Structure of $A_2M_3O_{12}$ compounds shown as MO_4 tetrahedra and AO_6 octahedra sharing corners. Two octahedra linked by three tetrahedra are highlighted.

MoO_{12}, $Zr_2P_2WO_{12}$, $Hf_2P_2MoO_{12}$, and $Hf_2P_2MoO_{12}$, where a 4+ cation is introduced of the A site, and charge balance is maintained by the introduction of P of two of the three W positions (5). Table 1 gives the thermal expansion results for several compounds of the $A_2M_3O_{12}$ family. Through solid solutions within this family, one can obtain essentially any value of thermal expansion from positive, to zero, to strongly negative. Many other properties of interest for applications of negative thermal expansion materials (refractive index, dielectric constant, etc.) can also be systematically varied. Such applications include circuit boards, optical substrates, and dental restorations.

Analysis of neutron diffraction data from $Sc_2W_3O_{12}$ using rigid bodies allows us to extract librations vs temperature (6). These librations are anharmonic and lead to coupled tiltings of polyhedra. The average bridging Sc–O–W angle therefore decreases and the average Sc–W distance decreases. The lattice topology is such that with increasing temperature these tilts cause a and c to decrease while b increases (Fig. 2).

TABLE 1
Thermal Expansion[a] of Selected $A_2W_3O_{12}$ Compounds

Compound	$\alpha(d)$	$\alpha(X)$
$Sc_2W_3O_{12}$	− 11	− 2.2
$Sc_2Mo_3O_{12}$	− 5	− 1.1
$Al_2W_3O_{12}$	− 3	+ 2.2
$Al_2Mo_3O_{12}$		
$In_2W_3O_{12}$	+ 10	
$Al_{1.5}In_{0.5}W_3O_{12}$	+ 1.0	
$Al_{1.6}In_{0.4}W_3O_{12}$	+ 1.5	+ 1.6
$Al_{1.7}In_{0.3}W_3O_{12}$	+ 0.2	
$Al_{1.8}In_{0.2}W_3O_{12}$	− 1	
$YAlW_3O_{12}$	− 5	
$ScAlW_3O_{12}$	− 1	
$ScGaW_3O_{12}$	− 5	
$ScInW_3O_{12}$	− 1	
$ScHoW_3O_{12}$	− 7	
$ScYbMo_3O_{12}$	− 5	
$ErInW_3O_{12}$	+ 10	
$Al_{1.68}Sc_{0.02}In_{0.3}W_3O_{12}$	0	
$Zr_2WP_2O_{12}$	− 6	− 3
$Zr_2MoP_2O_{12}$	− 6	
$Hf_2WP_2O_{12}$	− 5	
$Hf_2MoP_2O_{12}$	− 4	

[a] α is $\Delta l/l$ per degree. Values have been multiplied by 10^6. $\alpha(d)$ is determined from dilatometer data, and $\alpha(X)$ is determined from diffraction data.

Thermal expansion of these phases has been determined either by dilatometry, which measures the change in length of a ceramic bar, or by diffraction using X-rays or neutrons. These two methods always gave the same thermal expansion values in our past studies of negative thermal expansion materials which had cubic crystal structures (1–3). Ceramic bars of strongly anisotropic materials can show negative thermal expansion even when the unit cell thermal expansion is slightly positive. This can be considered an extrinsic effect due to microstructure changes occurring as a function of temperature (7). The structure of the $A_2M_3O_{12}$ family of materials is anisotropic; thus, not surprisingly, we frequently found (Table 1) that a dilatometer measurement of a particular material showed smaller or more negative thermal expansion than expected based on the thermal expansion of the unit cell. For $Sc_2W_3O_{12}$ (Fig. 2), thermal contraction along the a and c axes is coupled with thermal expansion along the b axis. Such behavior is typical for this family, but for some members we have seen nearly isotropic thermal expansion. For example, $Al_{1.6}In_{0.4}W_3O_{12}$ shows nearly isotropic behavior with a very low thermal expansion, α less than $2 \times 10^{-6}/°$, as measured by both diffraction and dilatometry. A ceramic bar of $Sc_2W_3O_{12}$ shows stronger negative thermal expansion than that shown by ZrW_2O_8 even though the intrinsic negative thermal expansion of $Sc_2W_3O_{12}$ is much lower. Thus, an extrinsic effect

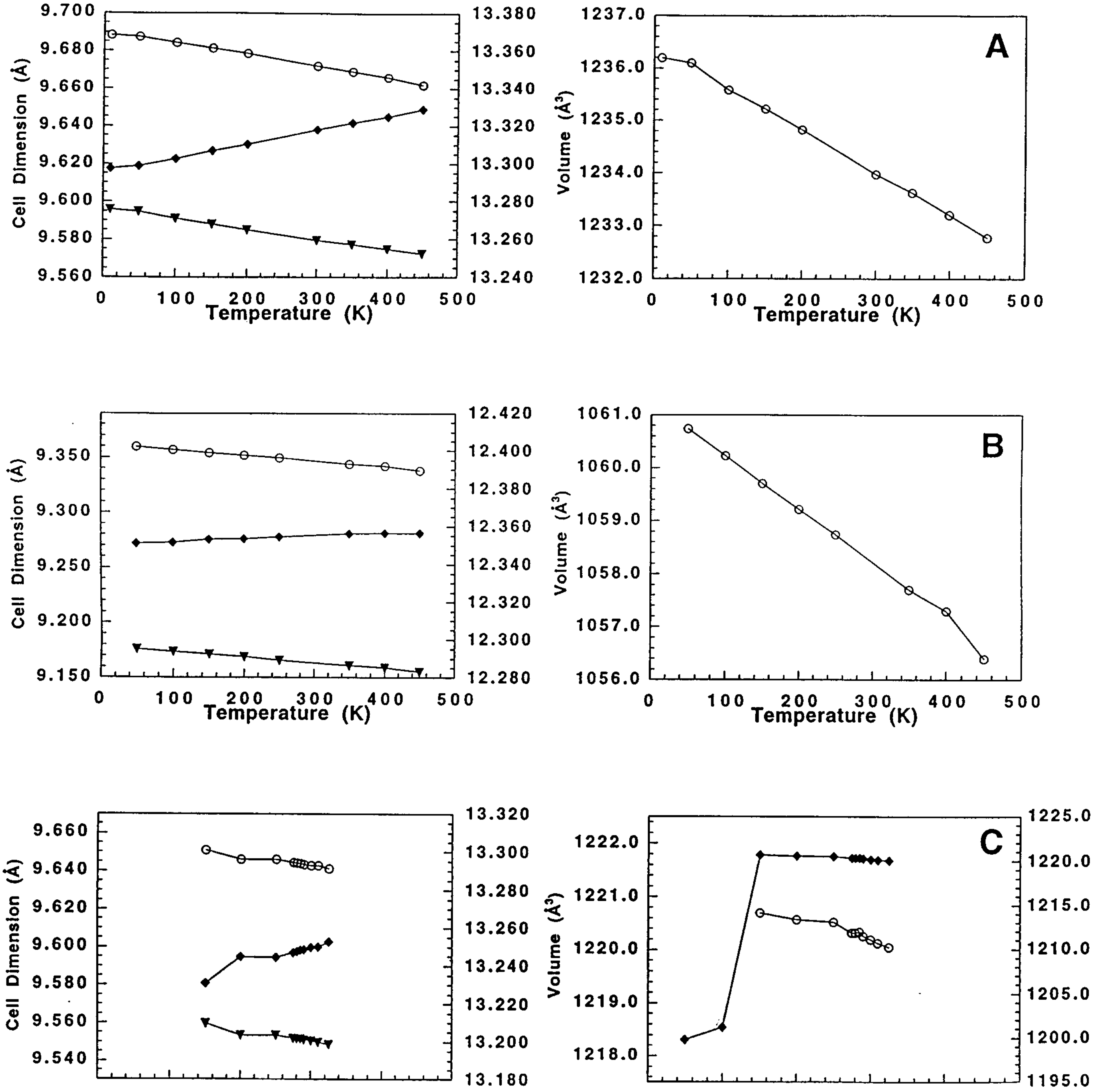

FIG. 2. Unit cell dimensional changes as a function of temperature for (A) $Sc_2W_3O_{12}$, (B) $Zr_2WP_2O_{12}$, and (C) $Sc_2Mo_3O_{12}$. For cell edges, open circles are *a*; closed diamonds are *b*, and closed triangles are *c*. In the volume plot for $Sc_2Mo_3O_{12}$, the open circles are for the scale on the left, and the closed diamonds are for the scale on the right.

has very significantly magnified the intrinsic negative thermal expansion behavior of $Sc_2W_3O_{12}$. Dilatometer results for $Sc_2W_3O_{12}$ show (6) that the negative thermal expansion behavior continues to 1200 K, the upper temperature limit of our equipment. This behavior may well continue up to the melting point of $Sc_2W_3O_{12}$, ~1925 K.

Many members of the $A_2M_3O_{12}$ family show a phase transition from orthorhombic to monoclinic symmetry with decreasing temperature. No strong bonds are formed or broken during this transition; the framework connectivity remains unchanged. There is, however, an abrupt volume decrease on going to the monoclinic structure which itself shows strong positive expansion (Fig. 2). A likely cause of this network collapse is oxygen–oxygen attraction. While it is initially counterintuitive to think of oxygen–oxygen attractive interactions in the solid state as being important, oxygen–oxygen dispersive attractions are in fact no more exotic than the van der Waals attractions familiar in molecular chemistry. A feel for this attraction can be obtained from the observation that the simple molecular oxide OsO_4 becomes a solid at 40°C. Oxygen–oxygen attractive forces drive this phase transition. Similarly molecular Re_2O_7 does not melt until 330°C and boils at 360°C. Such oxygen–oxygen attractive forces must be balanced against repulsive forces arising from the fact that oxygen is expected to have some negative charge in a metal oxide compound. The effective charge on oxygen will, however, be directly related to the electronegativity of the cations present.[1] The temperature of the framework collapse phase transition in the $A_2Mo_3O_{12}$ series is plotted against the electronegativity of the A^{3+} cation in Fig. 3. As the electronegativity of the A cation increases, the effective negative charge on oxygen decreases. Thus, the oxygen–oxygen repulsion decreases, and oxygen–oxygen attractive forces cause the network collapse transition to occur at higher temperatures. The electronegativity of W^{6+} is less than that of Mo^{6+}, and the phase transition for an $A_2W_3O_{12}$ compound with a given A cation is always at a lower temperature than that of the corresponding $A_2Mo_3O_{12}$ compound. Again as cation electronegativity increases, the effective charge on oxygen decreases and the volume collapse phase transition moves to a lower temperature. In the case of $Sc_2W_3O_{12}$, the relatively high electropositive character of both Sc and W apparently prevents a phase transition in the temperature range examined. Thus, negative thermal expansion can exist over a very broad temperature range.

It is now apparent that just the right balance in ionic vs covalent bonding should be achieved for an open framework structure to show negative thermal expansion over a broad temperature range. The metal–oxygen bond must be sufficiently covalent that this bond length does not itself show significant lengthening with increasing temperature. However, some ionic nature in the metal–oxygen bonding is crucial for oxygen–oxygen repulsion which can inhibit framework collapse. Another trend in the $A_2M_3O_{12}$ family illustrates an additional requirement for useful negative thermal expansion materials. As the size of the A cation increases, the openings in the network become large enough to admit water. In the case of the $A_3Mo_3O_{12}$ and $A_2W_3O_{12}$ series, for A cations larger than Lu this water attacks and hydrates the compound, destroying the framework structure which is essential for negative thermal expansion.

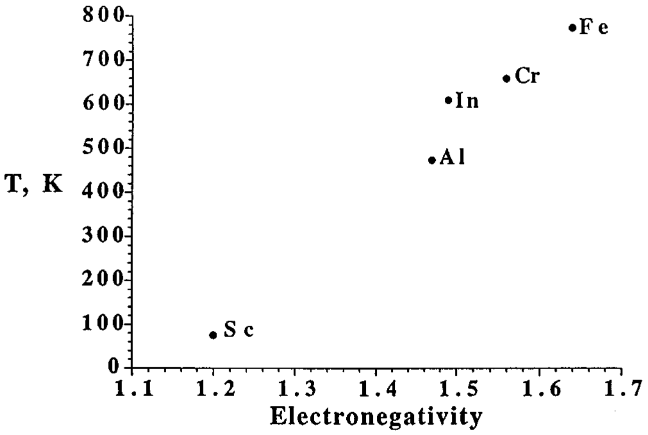

FIG. 3. Structure collapse temperature plotted against electronegativity of A^{3+}.

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[1] For a discussion of partial charges calculated from electronegativity values, see R. T. Sanderson, "Chemical Bonds and Bond Energy," 2nd ed., pp. 77–104, Academic Press, New York, 1976. For example, the partial charge of oxygen in CaO is calculated to be -0.60 in CaO but only -0.36 in BeO due to the higher electronegativity of Be relative to Ca. The electronegativity values used in this paper are from A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.* **5,** 264 (1968). The correlation between electronegativity and the temperature of the phase transition in the $A_2Mo_3O_{12}$ series had been noted by A. W. Sleight and L. H. Brixner, *J. Solid State Chem.* **7,** 172 (1973), but no explanation of this correlation was offered at that time.