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Pronounced Negative Thermal Expansion from a Simple Structure: Cubic ScF_3

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Abstract: Scandium trifluoride maintains a cubic ReO_3 type structure down to at least 10 K, although the pressure at which its cubic to rhombohedral phase transition occurs drops from >0.5 GPa at ~300 K to 0.1−0.2 GPa at 50 K. At low temperatures it shows strong negative thermal expansion (NTE) (60−110 K, $\alpha_l \approx -14$ ppm K^{-1}). On heating, its coefficient of thermal expansion (CTE) smoothly increases, leading to a room temperature CTE that is similar to that of ZrW_2O_8 and positive thermal expansion above ~1100 K. While the cubic ReO_3 structure type is often used as a simple illustration of how negative thermal expansion can arise from the thermally induced rocking of rigid structural units, ScF_3 is the first material with this structure to provide a clear experimental illustration of this mechanism for NTE.

Since the report of negative thermal expansion (NTE) in ZrW_2O_8 between 0.3 and 1050 K ($\alpha_l = dl/l\ dT \approx -9$ ppm K^{-1} at low temperatures),[1] the number of materials known to display pronounced NTE over a wide temperature range has grown to include a variety of porous[2] and nonporous oxides,[3] cyanides,[4] and metal−organic frameworks.[5] In nearly all cases, their crystal structures are quite complex. As such, in introductory discussions of NTE in framework materials, the simpler cubic ReO_3 structure type is often used to illustrate how rigid unit vibrational modes (RUMs), and the associated transverse thermal motion of bridging atoms or moieties, can lead to volumetric contraction on heating.[6] However, thorough examination of the expansion characteristics and corresponding lattice dynamics of the archetypal material, ReO_3,[7] shows that it does not display NTE at room temperature, and at low temperatures most samples show modest NTE ($\alpha_l \approx -1$ ppm K^{-1}).[7a] The absence of NTE in ReO_3 at room temperature, which may be related to the delocalization of the rhenium's single d-electron, along with compelling arguments that this framework should be able to support strong NTE motivated us to search for other ReO_3-type materials that might display NTE.

Several metal trifluorides (MF_3, where M = Al, Ga, In, Sc, Ti, V, Cr, Mn, Fe, Co, Ir, Rh, Ru),[8] and some oxyfluorides (TaO_2F, NbO_2F, and $TiOF_2$), have ReO_3-type structures. With the exception of ScF_3 (and Jahn−Teller distorted MnF_3), all of these metal trifluorides adopt a rhombohedrally distorted structure at room temperature. This rhombohedral structure "unfolds" on heating (see insets in Figure 2), leading to strong positive thermal expansion[9] and, in some cases, a phase transition to the cubic ReO_3 structure at elevated temperatures.[8b,9,10] ScF_3 has previously been reported as either rhombohedral or cubic,[11] and tantalizingly, one paper[12] mentioned negative thermal expansion in passing while providing no data.

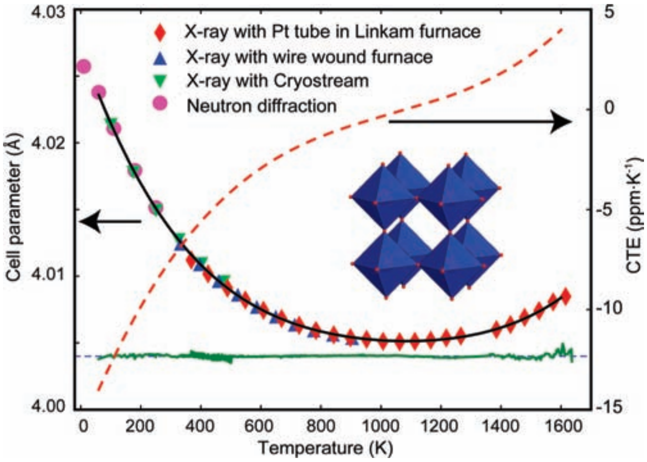

Figure 1. Selected experimentally determined lattice constants for cubic ScF_3 (solid symbols) along with a spline fit (black line) to nearly all the available values for ≥60 K (some at ~1350 K were excluded as outliers). The esds for the lattice constants are comparable to the symbol sizes. The difference between the experimentally determined lattice constants and the spline fit is shown as a green line. The lattice constants from different measurements were scaled to account for calibration discrepancies. The linear CTE, derived from the spline, is shown as a red dashed line. The cubic ReO_3 structure type is shown as an inset.

Here, we explore the temperature-dependent unit cell volume and phase behavior of ScF_3 using powder diffraction methods. Our data show that ScF_3 retains the cubic ReO_3 structure down to at least 10 K and that its coefficient of thermal expansion (CTE) is strongly negative at low temperatures but becomes increasingly less negative on heating, and eventually positive above ~1100 K.

Scandium trifluoride was used as supplied by American Elements. Its temperature-dependent behavior was initially examined by powder X-ray diffraction at the 1-BM-C beamline of the Advanced Photon Source, Argonne National Laboratory, using an Oxford Cryosystems Cryostream (100−500 K) and a wire-wound furnace[13] (333−1037 K) for temperature control. The measured temperature range was extended (>1600 K) using highly penetrating, high energy X-rays (~90 keV) available at beamline 11-ID-B of the Advanced Photon Source to probe the sample sealed in a platinum capillary within a Linkam furnace. Neutron powder diffraction, at the HB-2A beamline of the High Flux Isotope Reactor, Oak Ridge National Laboratory, was used to collect data down to ~10 K. Complementary high pressure data were collected within a diamond anvil cell (1-BM-C, ambient temperature) and within a gas pressure cell in a helium refrigerator (HB-2A, 10−280 K).

Lattice constants, obtained by Rietveld analyses of these data, indicate that the CTE of ScF_3 is strongly and smoothly dependent on temperature (Figure 1). At room temperature, it has a similar

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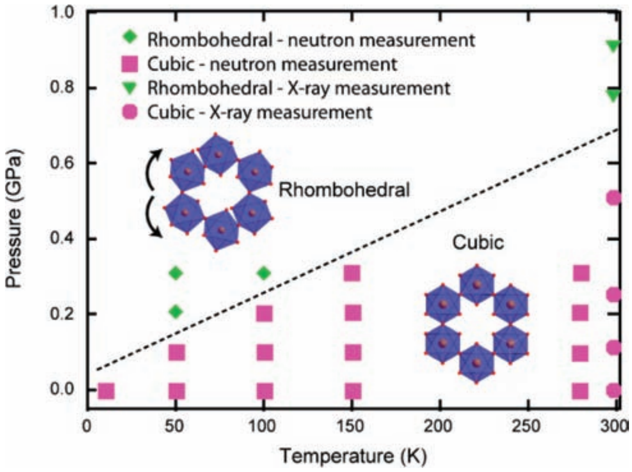

Figure 2. Pressure−temperature phase diagram for ScF_3. The dashed line is a guide to the eye. Two "layers" of octahedra in both the cubic and the rhombohedral ReO_3 structures (viewed along [111]) are shown. Upon pressurization, octahedral tilts "fold" the structure so that it is more compact and reduce the symmetry from cubic to rhombohedral.

CTE (~ -8 ppm K^{-1}) to that of cubic ZrW_2O_8 (~ -9 ppm K^{-1}) and shows even more pronounced NTE at lower temperatures, but its CTE approaches zero at ∼1100 K. Upon cooling (to 10 K), the sample remained cubic and displayed a CTE ($\alpha_l \approx -14$ ppm K^{-1}, 60−110 K) that is more negative than that of nearly all materials whose NTE arises from vibrational motion (excluding only those with much greater vibrational degrees of freedom, e.g. $Zn/Cd(CN)_2$)[4a,d] In materials where extremely large NTE effects are seen due to magnetostrictive effects,[14] or valence state changes,[15] the temperature range over which the NTE occurs is much smaller than that for ScF_3.

Most trifluorides with ReO_3 connectivity are unstable with respect to a static-correlated rotation ($a^-a^-a^-$ type in Glazer notation[16]) of the corner-sharing MF_6 octahedra that make up the framework structure. This rotation leads to rhombohedral symmetry ($R\bar{3}c$) and a smaller volume per formula unit. Dynamic tilts of this type are quite likely to be involved in ScF_3's NTE. Therefore, the pressure−temperature phase behavior of ScF_3 was investigated (Figure 2). At ambient temperature, ScF_3 transformed from cubic to rhombohedral symmetry between ∼0.5 and ∼0.8 GPa. This is consistent with previous high-pressure micro Raman studies[11b,17] reporting a transition at ∼0.7 GPa. However, at 50 K the transition was shifted to a much lower pressure: between 0.1 and 0.2 GPa. Our high pressure X-ray measurements suggest a bulk modulus for cubic ScF_3 of 57(3) GPa, somewhat lower than that (∼70 GPa) estimated in the prior Raman work.[11b,17]

The pronounced negative thermal expansion found here in ScF_3 at low temperatures is consistent with a rigid unit mode (RUM) model, perhaps involving the same R_5 mode that has been implicated in the cubic-to-rhombohedral phase transition seen in many metal trifluorides.[8b] This mechanism is supported by the large, strongly temperature dependent transverse component of the anisotropic displacement parameters for the bridging fluoride atoms (see Supporting Information). However, the factors underlying the pronounced, continuous variation in the CTE are less immediately obvious. It is unlikely that expansion of the individual Sc−F bond lengths alone would be sufficient to produce the observed change in CTE. Instead, we propose that an evolution of the rocking motion of essentially rigid ScF_6 units on heating gives rise to a more positive CTE. This may also incorporate a contribution to the CTE from static disorder as has been suggested for AlF_3 above its rhombohedral-to-cubic phase transition (the Al−F−Al links in AlF_3 are locally bent in the cubic phase).[9a,10c] A detailed understanding of the temperature dependence of the CTE will likely require a thorough examination of the local structure and lattice dynamics of ScF_3.

In summary, the thermal expansion characteristics of ScF_3 are striking: (1) prominent NTE at very low temperatures, which is more pronounced than that of most known NTE materials, (2) slowly and smoothly evolving toward positive thermal expansion above 1100 K, and (3) all from a very simple crystal structure. This behavior arises in part because, unlike most ReO_3-type materials, ScF_3 does not undergo a symmetry-lowering phase transition on cooling. This stability against distortion may arise because the bonding in ScF_3 is less covalent (more ionic) than that in many related MF_3 phases, and the cubic structure is electrostatically favored over the rhombohedral one as it maximizes the separation between ions of the same charge for a given M−F bond length.[18] The temperature dependence of its CTE presumably arises from a thermally induced evolution in the correlated rocking of ScF_6 octahedra on heating. Our findings experimentally validate the common use of the cubic ReO_3 structure type as an illustration of how RUMs can lead to negative thermal expansion. They also open up future avenues of exploration to both fully understand the remarkable properties of this material and prepare a family of controlled thermal expansion fluorides by the doping of ScF_3, some of which may have valuable applications.

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Supporting Information Available: Details of the X-ray and neutron experiments, lattice constants, anisotropic displacement parameters, and splittings on symmetry lowering. This material is available free of charge via the Internet at http://pubs.acs.org.

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