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Very low thermal expansion in TaO₂F

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Abstract

X-ray diffraction data for TaO₂F from 20 to 400 K show a thermal expansion so low that we cannot be certain whether it is positive or negative. We estimate the absolute value of the thermal expansion coefficient to be less than $6 \times 10^{-7}/\text{K}$. This then is comparable to that of amorphous SiO₂ and is apparently unique behavior for a cubic material over such a large temperature range. © 2003 Elsevier Science (USA). All rights reserved.

1. Introduction

Although negative thermal expansion (NTE) was once considered very unusual, this property has now been found in many oxides where the oxygen coordination does not exceed two [1]. Apparently, it is the transverse thermal motion of oxygen atoms in $M-O-M$ linkages that pulls M atoms closer to one another giving rise to NTE. A simple way to describe [2] the likely correlations of the thermal motions of various oxygen atoms is to consider rocking motions of polyhedra as rigid unit modes (RUMs). This model is most easily illustrated with the cubic ReO₃ structure as shown in Fig. 1. Actually, ReO₃ itself shows a positive thermal expansion of $+23 \times 10^{-7}/\text{K}$ from 123 to 486 K [3]. However, this could be considered a low thermal expansion relative to typical metal oxides such as α -alumina, which has a thermal expansion coefficient of $+88 \times 10^{-7}/\text{K}$ [4]. The thermal expansion of WO₃, which has a distorted ReO₃ structure, is much greater than that of α -alumina [3]. Both NbO₂F and TaO₂F have the cubic ReO₃ structure [5], but their thermal expansion properties have apparently not been reported.

2. Experimental

The method of Frevel and Rinn [5] was used to prepare both NbO₂F and TaO₂F. The metal powders were dissolved in 48% HF in a Pt crucible at 353 K.

After evaporation to dryness, the white powders were heated at 723 K for 50 h and then at 573 K for 48 h.

Powder diffraction data were collected from 20 to 300 K at beamline X7A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The diluted samples were in 0.2 mm capillaries, and the wavelength used was 0.700418 Å. Powder diffraction data were also collected on an Inel diffractometer using CuK α 1 radiation. Data were collected from 200 to 400 K in a cryostat with a heater using the transmission mode and from 300 to 773 K in a furnace using the reflection mode.

3. Results

The cell edge for TaO₂F is plotted vs. temperature in Fig. 2. The three different data sets give small but significantly different absolute values for this cell edge due to the different systematic errors involved. Our interest is only in relative values, but the different slopes for the three data sets suggest that the systematic errors are somewhat temperature dependent. This is not surprising considering the different diffraction geometries for the three data sets. The Inel cryostat data (100–400 K) yield a thermal expansion coefficient of $-6(1) \times 10^{-7}/\text{K}$, while the Inel furnace data give a value of $+2.9(1) \times 10^{-7}/\text{K}$, and the NSLS data give a value of $+1(2) \times 10^{-7}/\text{K}$. The numbers in parentheses are standard deviations based on the fits to the data in Fig. 2. NSLS data for NbO₂F obtained (Fig. 2) showed a thermal expansion coefficient of $+104 \times 10^{-7}/\text{K}$ based

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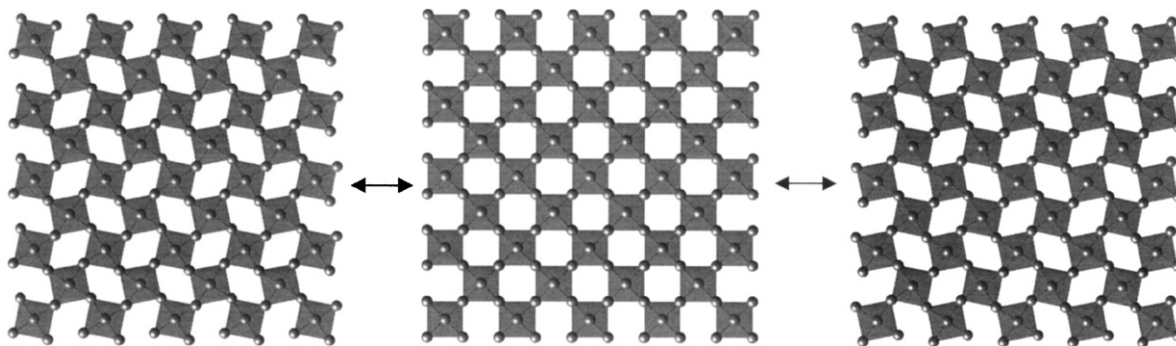


Fig. 1. Rocking of the ReO_3 structure indicating possible correlation of the transverse thermal motions of the oxygen atoms. The octahedra (squares) do not change volume on rocking, but the distance between the octahedra decreases as they rock away from the structure at the right.

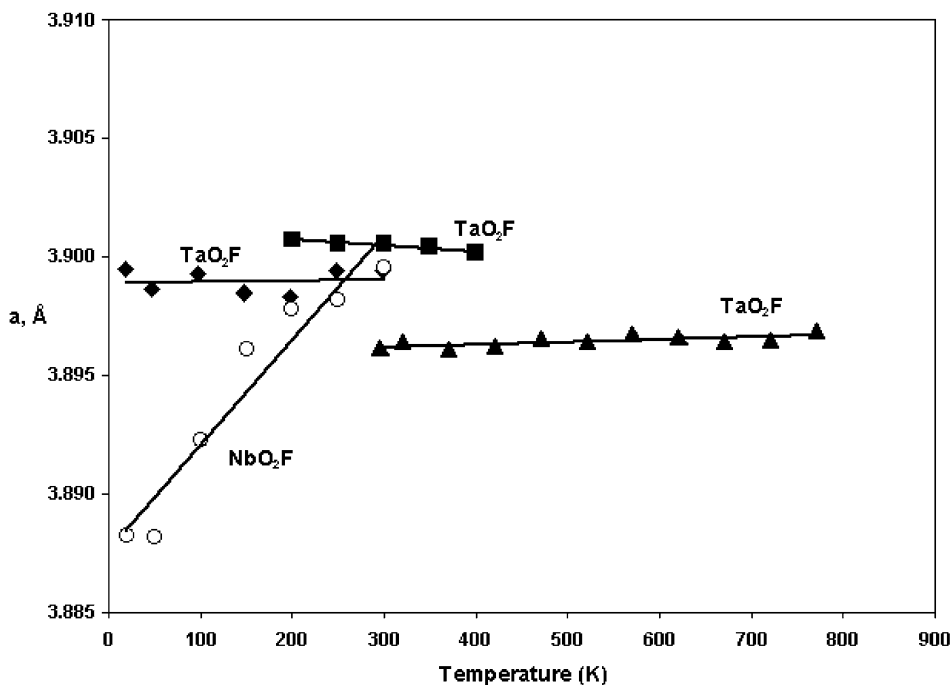


Fig. 2. Cubic cell edges of TaO_2F and NbO_2F vs. temperature.

on the fit of a straight line to the data. Actually, it appears that NbO_2F is headed toward low thermal expansion above room temperature.

Rietveld refinements with GSAS software were employed using the NLSLS data to obtain displacement factors for Ta and the O/F site. These factors indicate the average displacements of atoms from their ideal static positions. These are plotted vs. temperature in Fig. 3. There are no positional parameters for this structure, and the displacement factor for Ta is constrained by space group symmetry to be isotropic.

4. Discussion

The thermal expansion of TaO_2F is so low that we cannot be certain whether it is positive or negative. In any case, it is comparable to that of other materials

considered to have very low thermal expansion. For example, the thermal expansion of amorphous SiO_2 from 300 to 1200 K is $+5 \times 10^{-7}/\text{K}$ [4]. Crystalline oxides showing very low thermal expansion are nearly always anisotropic materials where different cell edges show significantly different thermal expansion, usually a mixture of positive and negative values. Cubic materials have an important advantage over anisotropic materials in applications because they are basically immune to the microcracking problems of ceramics based on anisotropic materials. The low thermal expansion of TaO_2F over an extended temperature range is apparently unique for a cubic material. However, its reported [5] decomposition at 773 K when heated in air will preclude some applications.

Very low thermal expansion over limited temperature ranges has been reported for some cubic relaxors of the type $\text{PbM}_{1/3}\text{Nb}_{2/3}\text{O}_3$ [6,7]. These reports were based on

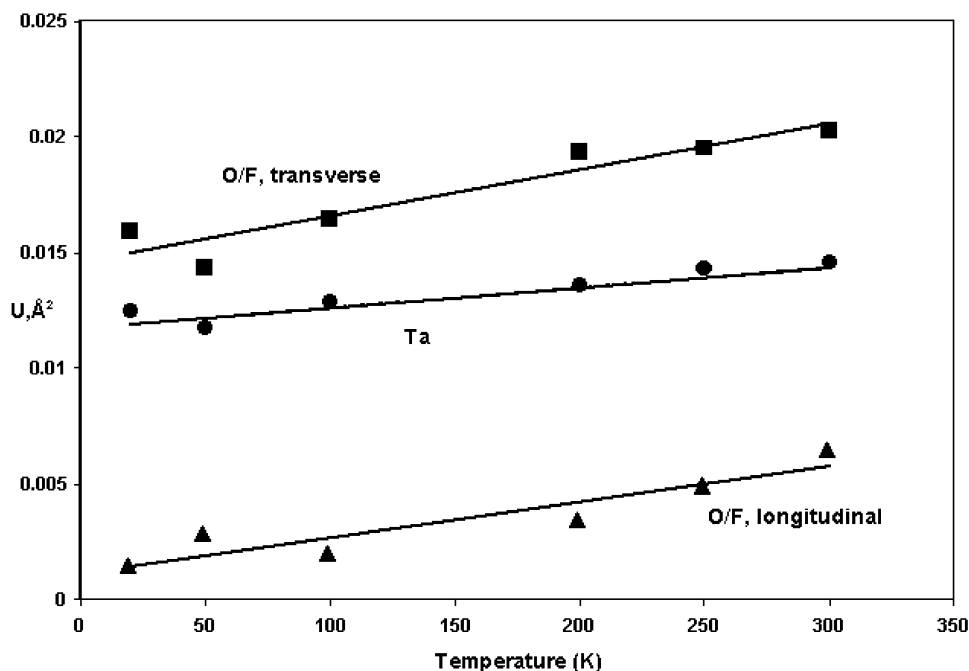


Fig. 3. Displacement factors for Ta and the O/F site vs. temperature.

dilatometer data obtained from 298 to 773 K. Over most of this temperature range, these materials all showed rather normal thermal expansion coefficients of 70 to $110 \times 10^{-7}/\text{K}$. The very low thermal expansion was reported only in the region from 298 to about 400 K. This is a region where dilatometer data are frequently unreliable when the starting temperature is 298 K. There are ways of overcoming this artifact [8]. Another report on the thermal expansion of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (two of the compounds studied in Ref. [6] from 120 to 500 K shows that the lowest thermal expansion coefficient over this range is about $20 \times 10^{-7}/\text{K}$ [9].

The displacement factors for Ta and the O/F site increase with increasing temperature, as would be expected for thermal displacement parameters (Fig. 3). However, only the anion displacement factor along the Ta–(O,F)–Ta linkage tends toward very low values at low temperature. Thus, only this parameter can be assumed to be a true thermal displacement factor. The higher values of the Ta and the transverse anion displacement factors that persist to very low temperatures indicate that these displacements are dominated by static displacements that remain at very low temperatures. A very recent paper [10] on NbO_2F has found one-dimensional order of O and F. Associated with this are significant static displacements of Nb from its ideal site. An analogous situation in TaO_2F is likely the cause of the high displacement factor we find for Ta. Our finding of a high transverse anion displacement factor persisting to low temperatures indicates that tilting of the octahedra is largely not dynamic. Instead this tilting

is mostly static with no long-range order in three dimensions. The fact that this tilting is more static than dynamic indicates the rocking motions depicted in Fig. 1 are not strong enough to give NTE. It is possible that the π bonding between Ta and the anion resists this type of rocking motion.

Understanding the thermal expansion of TaO_2F and NbO_2F is impeded by our lack of understanding of these structures. The long-range average structures are very simple. In the case on NbO_2F , one-dimensional order of O and F has been established [10]. This order may be different in TaO_2F , and this order may be dependent on prior history of the samples for both NbO_2F and TaO_2F . There are well-known differences in the bonding on Nb and Ta in oxides, and this may be responsible for the differences we observed in their thermal expansion properties. For example, Nb is much more prone than Ta to adopt an off center position within an octahedron.

If we accept the RUM model for NTE behavior, the lack of NTE behavior for TaO_2F can be understood based on the observed transverse displacement factor for the anion. The large static component means the Ta–(O,F)–Ta bond angles are bent away from 180° . NTE behavior would be optimized if this angle were oscillating around 180° , which will not occur if there is a static bending too far from 180° . The difference between TaO_2F and NbO_2F then might be that cation–anion–cation angles closer to 180° on average in TaO_2F than in NbO_2F .

The RUM model for NTE clearly does not apply in all cases. Some structures without RUMs, such as the $\text{Y}_2\text{W}_3\text{O}_{12}$ and ZrV_2O_7 structures, show strong NTE behavior [1], and some structures with RUMs, such as a

zeolite-type structure known as CIT-5, do not show any NTE behavior [11]. Nonetheless, the transverse thermal motion of O in ReO_3 may be a factor in its rather low thermal expansion, and the transverse thermal motion of O and F in TaO_2F may be responsible for its very low thermal expansion.

Acknowledgments

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