JOURNAL OF SOLID STATE CHEMISTRY **140,** 157–158 (1998)
ARTICLE NO. SC987967

LETTER TO THE EDITOR

Enhanced Negative Thermal Expansion in $Lu_2W_3O_{12}$

P. M. Forster, A. Yokochi, and A. W. Sleight

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, Orego 97331-4003

Communicated by J.M. Honis June 22, 1998; accepted June 28, 1998

Negative thermal expansion in the $Sc_2W_3O_{12}$ family has been pushed to much more pronounced values by substituting a large cation for Sc. X-ray diffraction measurements from 127 to 627°C give a linear thermal expansion coefficient of -6.8×10^{-6}/°C for $Lu_2W_3O_{12}$ compared to -2.2×10^{-6}/°C for $Sc_2W_3O_{12}$. Negative thermal expansion in this family is dependent on the rocking motions of polyhedra. However, polyhedra in this structure cannot rock without changing their shape. Larger cations expand the octahedra, reducing the oxygen–oxygen repulsions within the polyhedra. This facilitates the polyhedra shape changes necessary for the rocking motions required for negative thermal expansion. © 1998 Academic Press

Negative thermal expansion was recently discovered in a large family of molybdates and tungstates with the general formula $A_2M_3O_{12}$, where M is Mo^{6+} or W^{6+} (1, 2). The A cation can be nearly any trivalent cation capable of accepting octahedral coordination to oxygen. AO_6 octahedra and MO_4 tetrahedra share corners to form a network structure where every oxygen atom is bound to one A cation and one M cation. The negative thermal expansion is attributed to transverse thermal motion of oxygen in the A–O–M linkages. These motions of the oxygen atoms may be correlated by considering them to be based on rocking motions of the connected polyhedra. In this $Sc_2W_2O_{12}$-type structure, these rocking motions can only occur if the polyhedra undergo slight shape change during the rocking. Therefore, rigid polyhedra inhibit the rocking motion and inhibit negative thermal expansion. A major factor enhancing rigidity in polyhedra is anion–anion repulsion. As AO_6 octahedra or MO_4 tetrahedra become larger due to larger cation size, the oxygen–oxygen distances within the polyhedra increase and oxygen–oxygen repulsions are diminished. Thus, we expect larger cations to give enhanced negative thermal expansion in this structure. To test this hypothesis, we have measured the thermal expansion of $Lu_2W_3O_{12}$.

The largest A cations found in the $Sc_2W_3O_{12}$-type structure are rare earths from Lu to Ho (3). All of these $R_2W_3O_{12}$ phases are hygroscopic at room temperature. We choose to first study $Lu_2W_3O_{12}$ because it is the least hygroscopic of the $R_2W_3O_{12}$ series with the $Sc_2W_3O_{12}$ structure. Reactants used to synthesize $Lu_2W_3O_{12}$ were Lu_2O_3 (Rare Earth Products, 99.9%) and WO_3 (CERAC, 99.99%). Appropriate amounts of the reactants were intimately mixed by grinding using an agate mortar and pestle. This mixture was heated at 1100°C for 10 h, reground, and heated a second time for 10 h at 1100°C. The X-ray diffraction pattern of $Lu_2W_3O_{12}$ was readily indexed by analogy to $Sc_2W_3O_{12}$.

Powder X-ray diffraction data above room temperature were obtained using an Inel diffractometer. The X-rays from a copper tube were monochromated with a Ge crystal to give monochromatic $K\alpha_1$ radiation ($\lambda = 1.540598$ Å). The position-sensitive detector, fitted with a He beam path, collected data simultaneously over the range 0° to 90° 2θ. Data were obtained at 50°C intervals from 127 to 627°C. Cell edges were determined with GSAS software (4) using a LeBail fit.

The negative thermal expansion behavior of $Lu_2W_3O_{12}$ (Fig. 1) is much more pronounced than previously observed for the $Sc_2W_3O_{12}$ family. For $Sc_2W_3O_{12}$, $Sc_2Mo_3O_{12}$, and $Zr_2WP_2O_{12}$ with the $Sc_2W_3O_{12}$ structure, the b cell edge actually increases with increasing temperature, while the a and c cell edges are decreasing (1). However, in the case of $Lu_2W_3O_{12}$ all three cell edges contract with increasing temperature. The thermal expansion coefficients for the three cell edges based on the data in Fig. 1 are -9.9×10^{-6}/°C for a, -2.2×10^{-6}/°C for b, and -8.3×10^{-6}/°C for c. This gives an overall bulk linear thermal expansion of -6.8×10^{-6}/°C for $Lu_2W_3O_{12}$, compared to -2.2×10^{-6}/°C for $Sc_2W_3O_{12}$.

Based on the hypothesized correlation, now apparently confirmed, we might expect somewhat more pronounced negative thermal expansion on further increasing the size of the octahedral cation in the $Sc_2W_3O_{12}$ structure. Thus, $Ho_2W_3O_{12}$ is expected to have the strongest thermal

0022-4596/98 $25.00

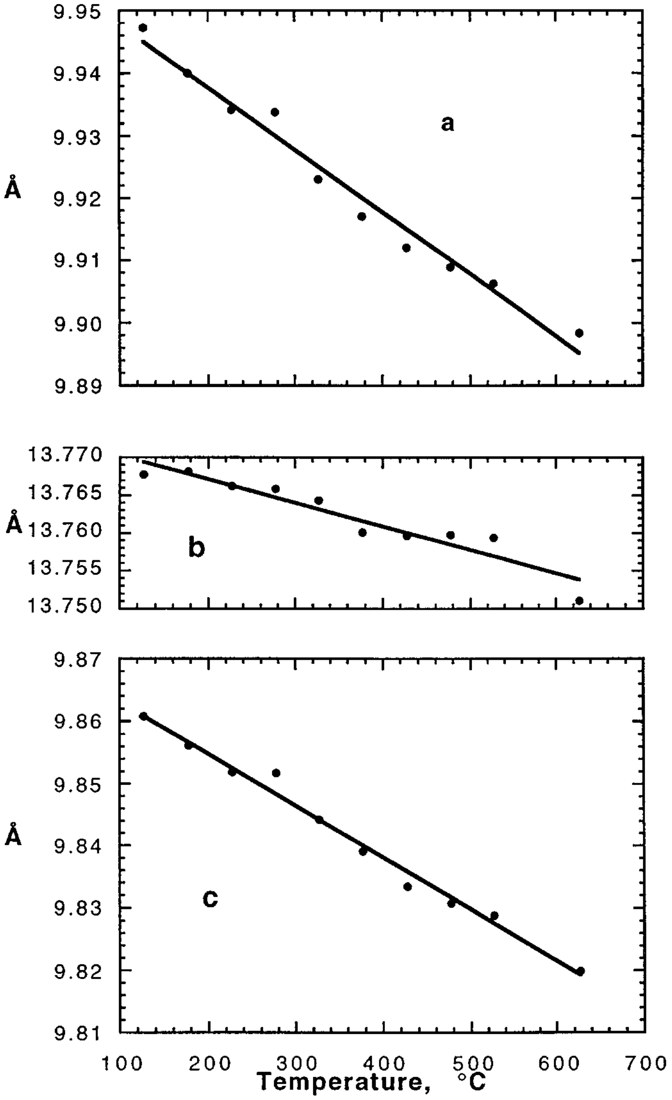

FIG. 1. Cell edges of $Lu_2W_3O_{12}$ as a function of temperature.

contraction because Ho^{3+} is the largest cation known to exist in this structure.

ACKNOWLEDGMENT

This work was supported by NSF Grant DMR-9308530.

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