

Synthesis and vibrational properties of aluminum-scandium tungstate solid-solution

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Abstract Homogeneous solid solutions $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ belonging to the orthorhombic structure were synthesized from stoichiometric mixtures of Al_2O_3 , Sc_2O_3 , and WO_3 using solid-state reaction method. The powder X-ray diffraction patterns confirmed the formation of single phase solid-solution and a monotonic variation of the cell parameters over the complete range of composition x . The vibrational properties of the mixed crystals were investigated using Raman spectroscopy. The Raman spectra consisted of lattice modes and internal modes of the tungstate tetrahedra. The end members exhibited large number of sharp Raman peaks while the mixed crystals of intermediate composition contained lesser number of broad peaks suggesting a positional disorder. Most of the prominent modes were found to exhibit the one-mode behaviour.

Keywords Negative thermal expansion · Phonons · X-ray diffraction · Mixed crystals

Introduction

There is considerable current interest in the negative thermal expansion (NTE) materials both from scientific and technological points of view. Isotropic network structures such as zirconium tungstate and vanadate, which exhibit NTE over a wide range of temperatures, have been investigated experimentally as well as theoretically to understand the mechanism of thermal expansion [1–4]. Low-frequency librational

modes and the bending modes of tungstate tetrahedral ion have been identified to contribute to NTE [5]. In addition to these cubic systems several compounds belonging to the family $A_2(\text{XO}_4)_3$, where $X:W$ and Mo , and A is the trivalent cation, have also been recently reported to exhibit NTE in the high temperature orthorhombic phase [6, 7]. On the other hand, the low-temperature monoclinic phase exhibits positive thermal expansion [7, 8]. The phase transition temperature appears to be correlated to the electronegativity of the cation in the molybdates [9]. However, some of the tungstates and molybdates with smaller cation such as those of aluminum exhibit positive thermal expansion even in the orthorhombic phase [10]. Existence of both positive and negative thermal expansion in isostructural systems opens the possibility of synthesizing homogeneous solid solution with an engineered coefficient of thermal expansion. For example, near zero thermal expansion ($\alpha < 2 \times 10^{-6} \text{ K}^{-1}$) has been reported in $\text{Al}_{1.7}\text{In}_{0.3}(\text{WO}_4)_3$ [11]. Although aluminum and indium tungstates exhibit the monoclinic-orthorhombic phase transitions at 267 and 523 K respectively, substitution of Al for In beyond some level fortunately suppressed the structural transition. These results suggest that solid solutions involving end members that do not exhibit structural transitions above ambient temperature could also be useful in obtaining zero thermal expansion.

Aluminum and scandium tungstates belong to the family of network structure $A_2(\text{WO}_4)_3$. The structure consists of WO_4 tetrahedra that are corner linked to AO_6 octahedra and vice-versa. Both Aluminum and Scandium tungstates crystallize in the orthorhombic $Pnca$ space group [10, 12]. From X-ray diffraction studies $\text{Al}_2(\text{WO}_4)_3$ has been found to show a positive thermal expansion [6, 10], whereas $\text{Sc}_2(\text{WO}_4)_3$ exhibits a negative thermal expansion [12, 13]. As the two end members are isostructural, it is worth examining the solid-solution of these two compounds for possible zero thermal

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expansion. The thermal expansion in materials arises due to anharmonic atomic vibrations [14]. All phonons contribute to the thermal expansion. The soft phonons are known to contribute to the negative thermal expansion whereas other phonons make a positive contribution [15]. Furthermore, phonons in the mixed crystals are influenced by the substitutional disorder [16, 17]. In view of this a study of phonon spectra of this mixed crystal system and identification of phonons of different symmetries is important. Here we report the synthesis of solid solution $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ over the complete range of composition x and Raman spectroscopic investigations of the vibrational properties of this solid-solution.

Experimental details

Syntheses of $\text{Al}_2(\text{WO}_4)_3$, $\text{Sc}_2(\text{WO}_4)_3$ and their solid solutions $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ were carried out from stoichiometric mixtures of Al_2O_3 , Sc_2O_3 , and WO_3 using solid-state reaction method. Appropriate quantities of the oxides were ground together thoroughly with an agate mortar and pestle and calcined in air at 1100°C for 24 h. The calcined powder was made into a pellet and sintered at 1200°C for 6 h. In order to minimize the loss of WO_3 from the synthesized compounds, sintering of the pellet was carried out in closed platinum crucibles along with a source of WO_3 in its immediate vicinity. In addition to the end members, the compositions $x = 0.4, 0.82, 1.2$, and 1.6 were synthesized. The powder X-ray diffraction patterns were recorded using a STOE diffractometer using Cu-K_α radiation. Raman spectra at the ambient were recorded in the back scattering geometry using the 488 nm line from an argon-ion laser. Scattered light was analyzed using a SPEX double monochromator and detected using a cooled photomultiplier tube operating in the photon counting mode [18]. Raman spectra were fitted to Lorentzian line-shapes for obtaining the mode frequencies.

Results and discussion

Aluminum and scandium tungstates are isostructural (orthorhombic space group $Pnca$) and their lattice parameters differ only by about 6%. Hence upon substitution of Al by Sc at the cation site one expects the solid-solution to remain homogeneous (single-phase) and the lattice parameters to vary monotonically between those of the two end members. In order to confirm this, powder X-ray diffraction measurements were done on all compositions. Figure 1 shows the diffraction patterns of the solid solutions. One can see that, as the composition x is increased, the diffraction peaks shift systematically to lower 2θ suggesting larger d -spacings for scandium rich compound. The diffraction patterns were analyzed

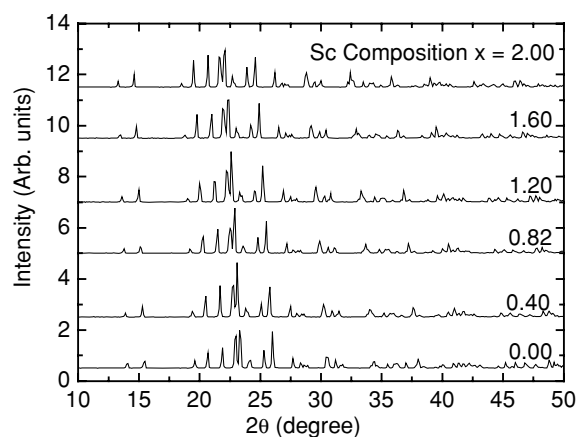


Fig. 1 Powder X-ray diffraction patterns of $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ solid-solution using Cu-K_α radiation

by fitting them to an orthorhombic unit cell. All the peaks could be indexed according to $Pnca$ space group. No peaks corresponding to individual oxides were found suggesting the formation of a single-phase material. The diffraction patterns of the end members, i.e., $\text{Al}_2(\text{WO}_4)_3$ and $\text{Sc}_2(\text{WO}_4)_3$ were consistent with the JCPDS data [19, 20] and the cell parameters agreed very well with the reported data [10, 12]. In the case of mixed crystals with intermediate composition the calculated cell parameters varied monotonically between those of Al- and Sc-tungstates as shown in Fig. 2. These results confirm the formation of a homogeneous substitutional solid-solution over the complete range of the composition.

The orthorhombic structure of $\text{Al}_2(\text{WO}_4)_3$ and $\text{Sc}_2(\text{WO}_4)_3$ consists of 4 formula units per unit cell and therefore the

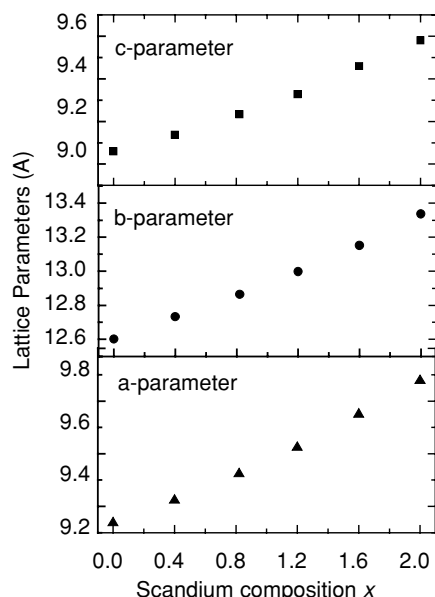


Fig. 2 Orthorhombic cell parameters as a function of scandium composition for the $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ solid solution

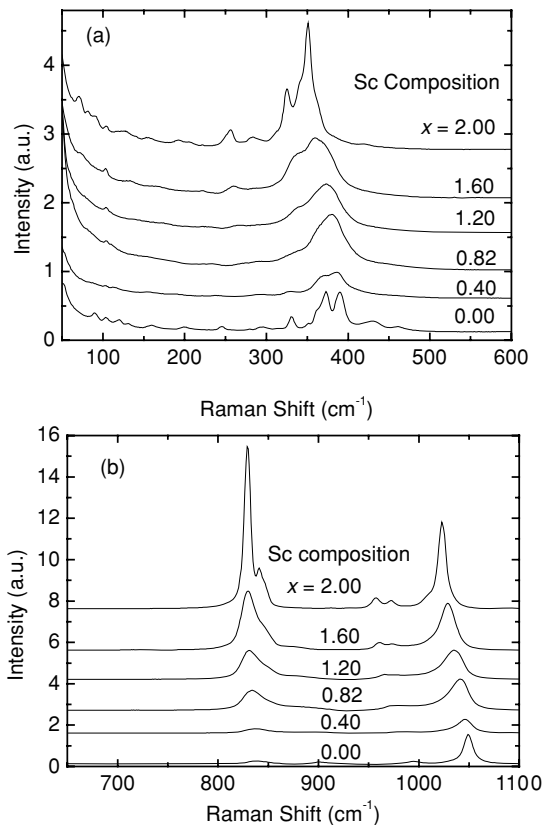


Fig. 3 Raman spectra of $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ solid solutions. (a) The lattice and bending mode region, (b) the stretching mode region of tungstate internal vibrations

system has 204 degrees of freedom. Out of these 3 degrees of freedom constitute the acoustic phonons and the remaining result in the optical phonons. The point group symmetry D_{2h} corresponding to this space group allows only nondegenerate phonons [7]. As the structure contains a point of inversion, the modes that are Raman active are not infrared active and vice-versa. Figure 3 shows the Raman spectra of the solid-solutions $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ including those of the end members. The vibrational modes in this system can be classified into two groups: first the internal modes of WO_4 tetrahedral ions and the second the external and lattice modes. From the knowledge of the frequencies of the internal modes of WO_4 tetrahedra in other tungstates [3, 7, 21] one can identify regions corresponding to different internal modes. The modes in the frequency range 950–1070 cm^{-1} , can be assigned to the symmetric stretching (ν_1) and those in 700–930 cm^{-1} to antisymmetric stretching (ν_3) modes. Similarly the modes in the frequency range 250–600 cm^{-1} can be assigned to the symmetric bending (ν_2) and the antisymmetric bending (ν_4) modes of WO_4 ion. Phonons below 250 cm^{-1} can be assigned to lattice, translational and librational modes of vibration. One can see from Fig. 3 that the pure compounds exhibit large number of sharp Raman peaks while the mixed crystals of intermediate composition contained lesser num-

ber of broad peaks. The broadening of the modes arises due to substitutional disorder in the cation sublattice [16]. The changes in the intensities of some of the modes arise due to the changes in the corresponding polarizabilities. It is also evident from Fig. 3 that some of the prominent peaks shift to lower frequencies as scandium composition is increased in the solid-solution. For example, the ν_1 mode shifts from 1049 to 1023 cm^{-1} and the main component of the ν_3 mode shifts from 839 to 829 cm^{-1} . It may be mentioned that several of the weak modes belonging to either $\text{Al}_2(\text{WO}_4)_3$ or $\text{Sc}_2(\text{WO}_4)_3$ could not be distinctly found in the mixed crystals. The frequencies of about ten modes, which could be followed over the complete range of the composition, are shown in Fig. 4. The phonons in mixed crystals are known to exhibit ‘one-mode’, ‘two-mode’ and ‘mixed-mode’ behaviors [17]. In the ‘one-mode’ behavior modes of one compound continuously evolve into those of the other as a function of composition. On the other hand, in the ‘two-mode’ behavior modes characteristic of both the end members are found in the spectra of the mixed crystals. Some of the mixed crystals are also found to exhibit a phonon behavior intermediate of the two

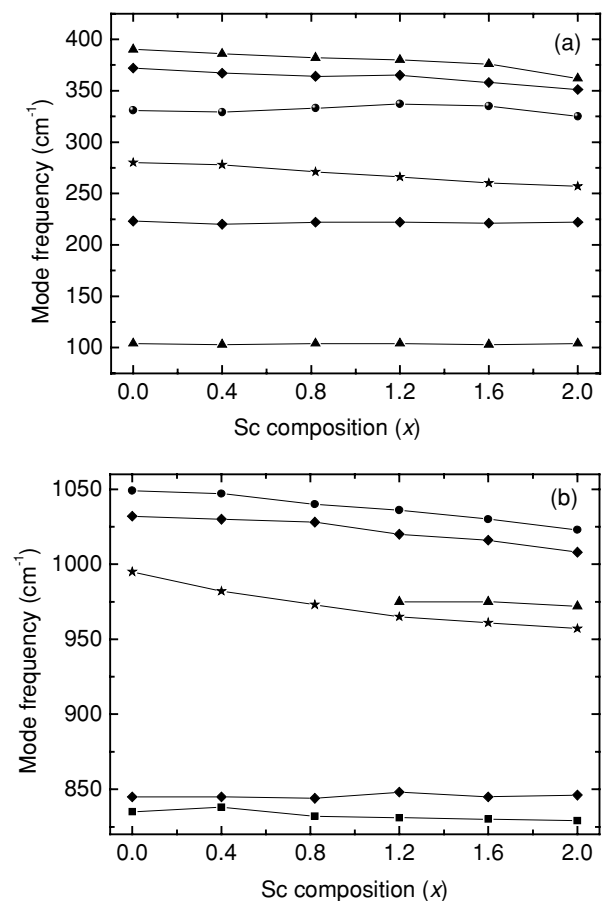


Fig. 4 Compositional dependence of the phonon frequencies in the $\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ solid solution. (a) The lattice and bending mode region, (b) the stretching mode region of tungstate internal vibrations

behaviors. This is known as the ‘mixed-mode behavior. The smooth monotonic variation of the phonon frequencies as a function of composition in the present case suggests that this mixed crystal system exhibits a ‘one-mode’ behavior.

In the network structure such as those of $\text{Zr}(\text{WO}_4)_2$ [3] or $\text{In}_2(\text{WO}_4)_3$ [7], a number of low frequency modes have been identified as the rigid unit modes. These modes correspond to the rigid translational and rotation of polyhedra network and have been argued to be responsible for NTE in these materials. The lowest modes in $\text{Zr}(\text{WO}_4)_2$ and $\text{In}_2(\text{WO}_4)_3$ are found at 41 and 96 cm^{-1} respectively. These and other low frequency phonon modes are found to exhibit negative Gruneisen parameter (γ). The phonons with negative γ contribute to negative thermal expansion while other phonons with positive γ contribute to positive thermal expansion. Thus the phonons responsible for NTE can be identified from high pressure Raman experiment. The present system also exhibits several phonons at low frequencies, e.g., $\text{Sc}_2(\text{WO}_4)_3$ has modes at 70, 81 and 86 cm^{-1} while $\text{Al}_2(\text{WO}_4)_3$ shows modes at 90, 104 and 120 cm^{-1} . The mixed crystal system is expected to have frequencies intermediate of the end members as this solid solution show one mode behaviour. A high pressure study of these phonons is expected to yield further information about their role in thermal expansion properties of this system.

As seen in the Fig. 2, the lattice parameters in the mixed crystals change monotonically between those of the end members. It may be pointed out that *a*- and *c*-lattice parameters have been found to show negative thermal expansion for both end members while *b*-lattice parameter exhibits positive thermal expansion [10, 12]. In view of this, the solid solution is also expected to have anisotropic thermal expansion for full range of composition. However the volume expansion coefficient is expected to change sign for $x = 0.82$. This can be confirmed from temperature dependent X-ray diffraction or dilatometric studies.

Summary and conclusions

$\text{Al}_{2-x}\text{Sc}_x(\text{WO}_4)_3$ solid-solutions have been synthesized in the orthorhombic structure over the complete range of composition x using solid-state reaction method. The unit cell

parameters are found to vary monotonically between those of the end-members. Raman spectroscopic investigations of this mixed crystal system reveal a systematic evolution of the mode frequencies from one compound to the other suggesting ‘one-mode’ behavior for the phonons.

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