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# New phase transitions in ceramic SrSnO<sub>3</sub>: Raman scattering analysis and differential thermal analysis

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## Abstract

We report a continuous or nearly continuous order–disorder transition from orthorhombic (pseudo-tetragonal) to orthorhombic structure on heating in SrSnO<sub>3</sub> at 377 °C, and a discontinuous transition near 260 °C. The transition at 377 °C is manifested in an order of magnitude increase in Raman linewidths and in a  $\lambda$ -shaped anomaly in the specific heat. Previous work (Mountstevens *et al* 2005 *Phys. Rev. B* **71** 220102R) has interpreted the *Pnma*–*Imma* transition at 636 °C as a continuous order–disorder transition and emphasized that this would be unique for an octahedron-tilting transition in oxide perovskite, as they have always been found to be displacive ('Glazer's rule'). Our work on Raman scattering and differential thermal analysis shows that the disorder sets in at much lower temperature 377 °C, so that the 636 °C transition is a disorder–disorder or a displacive transition within an already highly disordered structure. Hence it may not be as unusual as had been claimed, and Glazer's rule remains inviolate.

ABO<sub>3</sub> perovskite oxides generally exhibit a sequence of transition involving the tilting of oxygen octahedra. Even the mineral CaTiO<sub>3</sub> (Perovskite) undergoes several, including an orthorhombic to orthorhombic transformation. In the present work we show the existence of two new transitions in SrSnO<sub>3</sub>. These may have a general impact in mineralogy because the behavior of MgSiO<sub>3</sub> is of great geological importance; it is a primary constituent of the Earth's lower mantle. In addition, under real geophysical conditions it exhibits several phase transitions, including those now called 'post-perovskite'. Work up to 3500 K has been reported, and a very nice review is given by Wang *et al* [1]. However, because it is unstable under ambient conditions, much information about it has been inferred from the study of isomorphs. The tin compounds are useful in this respect [2–4] because the Sn<sup>4+</sup> ion is about the same size as Ti<sup>4+</sup> in well-studied titanates, yet it does not have Jahn–Teller or other electronically driven single-ion

distortions; consequently any phase transitions are apt to be lattice instabilities and not local distortions.

At room temperature, SrSnO<sub>3</sub> exhibits an orthorhombically distorted perovskite structure belonging to the space group  $D_{2h}^{16}$  (*Pbnm*) with the primitive cell containing four formula units. It is well established [1] that SrSnO<sub>3</sub> has two structural phase transitions: one at 636 °C and one at 800 °C. The lower transition was interpreted as order–disorder by Mountstevens *et al* [2], who noted that their interpretation was unusual or perhaps even unique, since an octahedron tilt transition in perovskite oxides is almost always displacive. They further pointed out that the *a*- and *b*-axis lattice constant divergence had a clear onset at ca 350 °C, but that there was no evidence of any phase transition at that temperature in their data; instead they interpreted the diverging lattice constants above 350 °C ( $b = a\sqrt{2}$  below 350 °C) as precursors to the transition at 636 °C, inferring that this divergence could 'sig-

nify the approaching transition'. We disagree with that interpretation; in our view the diverging lattice constants show that a transition has already occurred at lower temperatures, not that is one is approaching at higher temperatures.

## 1. Present work

In the present work we show via Raman spectroscopy that there is an abrupt and very large ( $\times 5$ ) change in the linewidth of some optical phonons at 377 °C, which we interpret as a clear sign of an order–disorder phase transition at 377 °C; thus, our new results strongly support the basic conclusion of Mountstevens *et al* [1] that the orthorhombic phase between 636 and 800 °C is disordered, but differ from their interpretation that the order–disorder transition is at 636 °C; instead we place it at 377 °C, and view the phase between 377 and 636 °C as disordered. The Raman results are supported by the dielectric measurements, which show anomalous increase in the dielectric loss near 260 and 377 °C and by specific heat (DTA) measurements, which reveal a  $\lambda$ -shaped anomaly near 377 °C indicative of a second-order, order–disorder transition. The entropy change at this transition is found to be comparable to that found at the 636 and 800 °C transitions. This transition is not found in SrZrO<sub>3</sub>, which manifests the higher-temperature transitions  $Pnma$ – $Imma$ – $I4/mcm$  [3]. The implications of the present work are that SrSnO<sub>3</sub> may be tetragonal below 377 °C (down to ca 260 °C) and that the 'accidental' equality of  $b = a\sqrt{2}$  is not accidental at all. Although phase transitions that increase point group symmetry or crystal class are unusual, many are known, including those that go from orthorhombic to tetragonal upon cooling: HoFe<sub>4</sub>Ge<sub>2</sub> is a good example [5], and others such as KNO<sub>3</sub> involve increasing point group symmetry via unit cell doubling upon lowering temperature [5]. In unpublished work Mountstevens noted in her thesis [4] that Raman anomalies in frequency, intensity, and linewidth suggested possible phase transitions near 260 and 440 °C.

Note that the lattice constant data [2] suggest that the crystal class changes from tetragonal at low temperatures to orthorhombic above  $T_0 = 377$  °C. Lowering of crystal symmetry upon heating often requires a change in the size of the primitive unit cell [5]. Therefore our suggestion is that the unit cell doubles below 377 °C; however, this has not been observed in any superlattice reflections in x-ray or neutron scattering data published to date [2–4]. It seems equally likely that the transition at 377 °C could be orthorhombic–orthorhombic, as in CaTiO<sub>3</sub> [4, 6], or SrHfO<sub>3</sub> [7], or SrZrO<sub>3</sub> [8]. In this view the equality of  $a\sqrt{2} = b$  would be accidental.

### 1.1. Sample preparation

SrSnO<sub>3</sub> was prepared by employing a solid-state reaction method [3]. The nominal composition of powder SrCO<sub>3</sub> (99.99%) and SnO<sub>2</sub> (99.99%) was mixed by mechanical ball milling process for 24 h. The mixture obtained was pressed into a disc-shaped pellet. The disc was sintered at 1380 °C for 24 h. To examine the structure, theta–2-theta ( $\theta$ – $2\theta$ ) x-ray diffraction (XRD) experiments were carried out, and their

results are shown in figure 1(a). As expected, polycrystalline SrSnO<sub>3</sub> has been found to be a single-phase orthorhombic perovskite structure with the space group  $Pbnm(D_{2h}^{16})$ .

### 1.2. Raman spectroscopy

Raman scattering data were obtained using a T64000 spectrometer equipped with a triple-grating monochromator and a Coherent Innova 90C Ar<sup>+</sup>-laser at 514.5 nm. The measurements were performed with a micro-Raman option using a LN<sub>2</sub>-cooled charge coupled device (CCD). The Raman signal was analyzed by employing normal backscattering geometry, and scattered light dispersed by the spectrometer was detected by CCD. The spectral resolution was typically less than 1 cm<sup>-1</sup>. A microscope-compatible thermal stage was used while recording the temperature-dependent spectra.

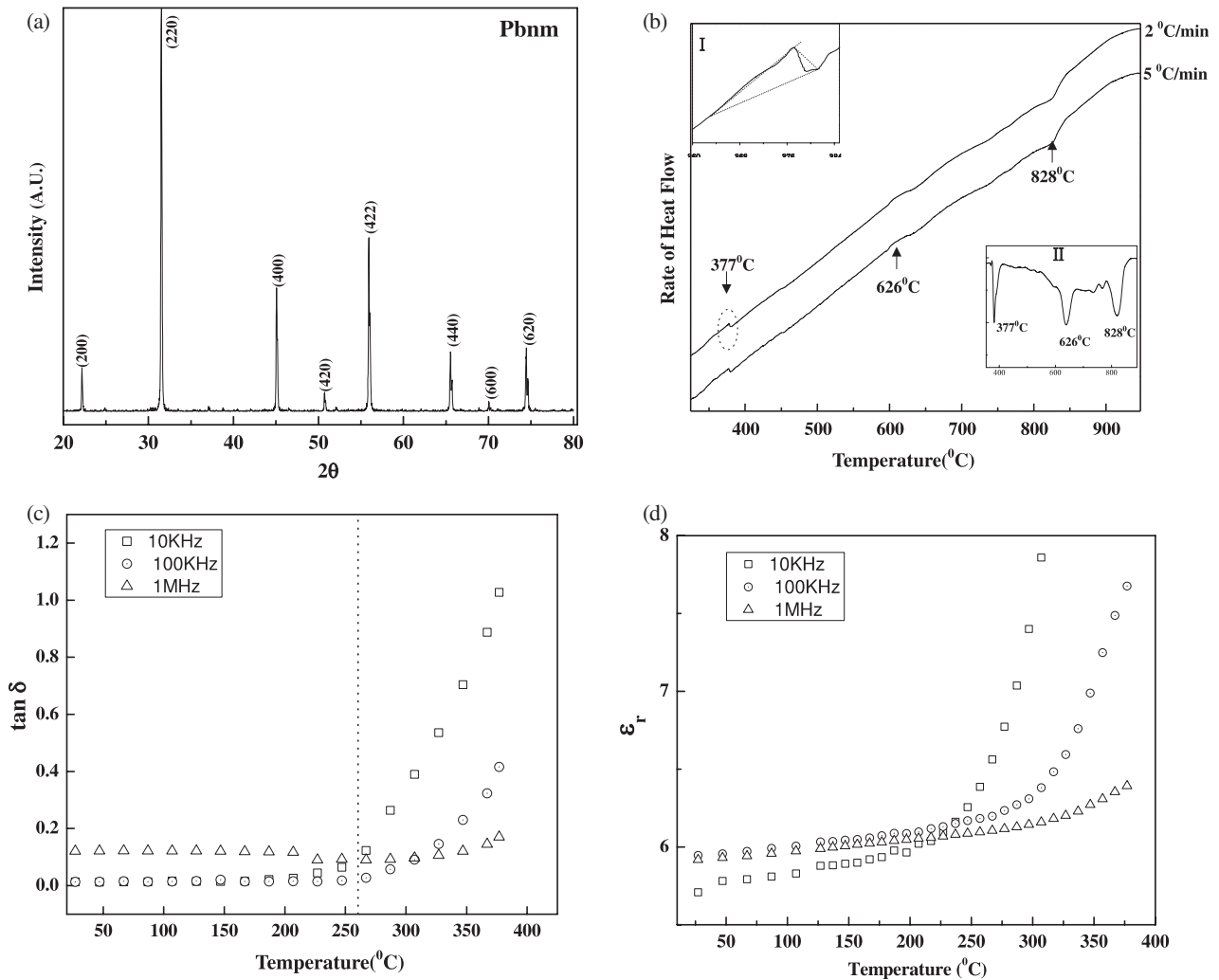
## 2. Differential thermal analysis

Phase transition behavior in SrSnO<sub>3</sub> was also analyzed with a quantitative differential thermal analysis (DTA). These measurements were carried out at a rate of 2 and 5 °C min<sup>-1</sup> in the temperature range 25–1000 °C using 10 mg of SrSnO<sub>3</sub> powder set in a platinum pan. In these measurements Al<sub>2</sub>O<sub>3</sub> was employed as a reference material.

On the DTA curve of pure SrSnO<sub>3</sub> shown in figure 1 we note three anomalies in the rate of flow of heat at 377, 628 and 828 °C respectively, where the slope of measurement change indicates three consecutive phase transitions, which are nearly the same as the transition temperatures reported [1]. At 377 °C, DTA measurement shows a  $\lambda$ -shaped anomaly, which is shown in the inset (I) of figure 1(b), this reveals a new second-order, order–disorder transition, whereas the other two transitions indicate first-order phase transitions. In DTA measurement, background has been carefully subtracted off using interpolated values far below and far above the apparent transition temperature and shown in inset (II) of figure 1(b). The remaining anomaly has the size and shape of the well-known order–disorder transition in tri-glycine sulfate (TGS), a paradigm in many textbooks (e.g., figure 5.16, p 152 of [9]). The difference between the inserts I and II shows that the background subtraction is rather subtle, and more work will be done to resolve the question of first- or second-order for this transition.

## 3. Dielectric measurements

Further support for low temperature disorder is shown in figure 1(c), where the dielectric loss tangent of SrSnO<sub>3</sub> has been plotted as a function of temperature at different frequencies. And in figure 1(d) we show the real part  $\epsilon'(T)$  over the same temperature range at three different frequencies; the real and imaginary parts are rather proportional to each other. The increase in  $\epsilon'(T)$  is too small to indicate ferroelectricity. These data indicate a probable transition near 260 °C and a disorder induced loss that is already large by 377 °C, the limit of our dielectric facilities. Because these are ceramic samples, the dielectric analysis is not trivial, and a



**Figure 1.** (a) Theta–2 theta ( $\theta$ – $2\theta$ ) XRD pattern of polycrystalline SrSnO<sub>3</sub>. (b) Differential thermal analysis (DTA) of SrSnO<sub>3</sub> presented as different rate of heat of flow with temperatures between 25 and 1000 °C. The inset (I) presents the abrupt change in DTA slope (like  $\lambda$  shape) at 377 °C and inset (II) presents the DTA curve after subtracting the base line effect. (c) Dielectric loss tangent ( $\tan\delta$ ) of SrSnO<sub>3</sub> as a function of temperature at different frequencies. (d) Real part of the dielectric constant in the same temperature and frequency range as (c).

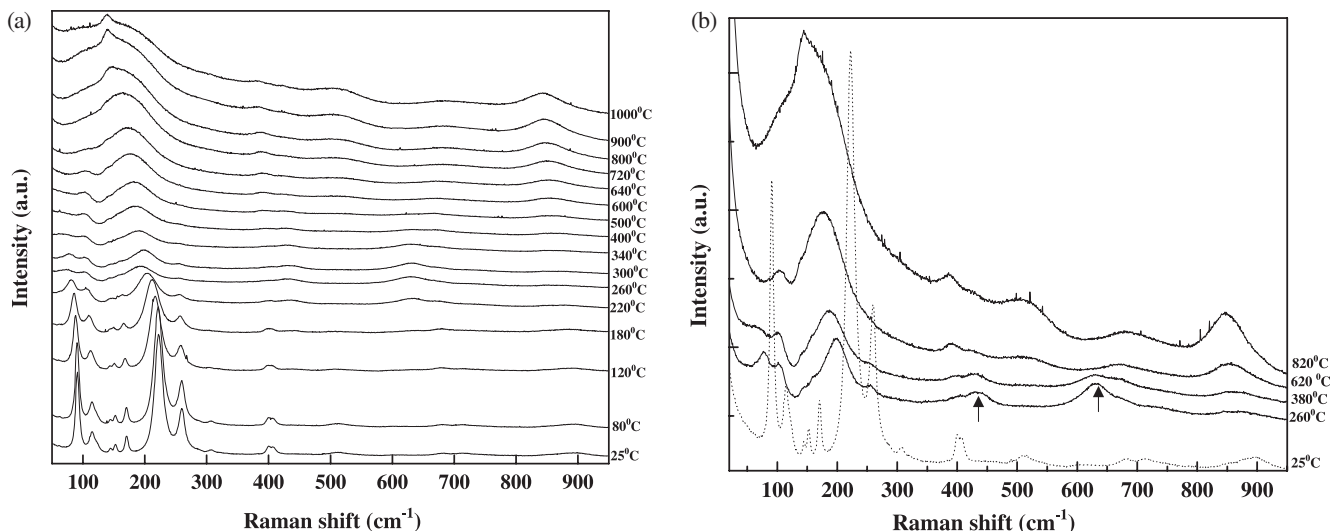
full impedance analysis of dielectric data near these transition temperatures using a constant phase element analysis (CPE) will be provided in a separate paper.

#### 4. Symmetry discussion

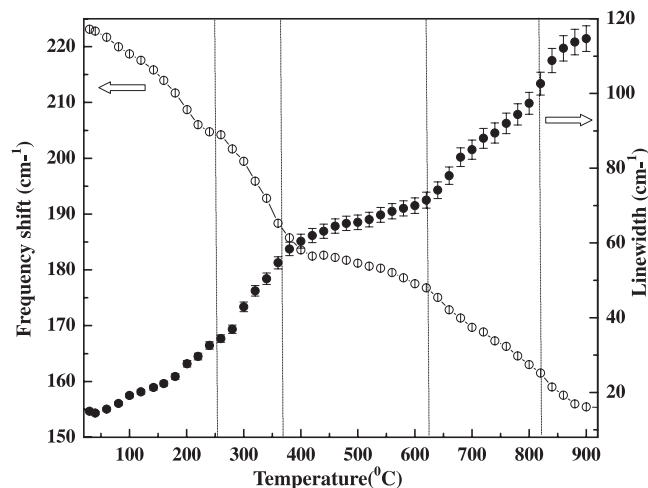
At room temperature SrSnO<sub>3</sub> is characterized [3] by orthorhombic symmetry with the point group  $mmm(D_{2h})$  and the space group  $Pbnm(D_{2h}^{16})$ . The distribution of ions in crystallographic positions can be summarized using the Wyckoff notation: Sr<sup>4+</sup> ions in 4(c), Sn<sup>4+</sup> ions in 4(b), and O<sup>2-</sup> ions in 4(c) and 8(d). The B-site Sn<sup>4+</sup> ion is surrounded with the six neighboring O<sup>2-</sup> ions in a SnO<sub>6</sub> octahedron. The orientation of the corner-sharing SnO<sub>6</sub> octahedra in SrSnO<sub>3</sub> can be described by using the tilting Glazer system [9]  $a^+a^-c^+$  with in-phase tilting about the direction of the  $c$ -axis. The group-theoretical analysis by considering the site symmetry for the  $\Gamma$ -point phonons of orthorhombic SrSnO<sub>3</sub> indicates that the following 24 modes are Raman-active

among 60 zone-center ( $\Gamma$ -point) phonon modes in the  $Pbnm$  structure [11]:  $\Gamma_{\text{Raman}} = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$ . Raman scattering data of the orthorhombic SrSnO<sub>3</sub> were obtained by employing backscattering geometries at temperature range room temperature to 1000 °C, and their results are presented in figure 2(a) and Raman spectrum at transition temperature are presented in figure 2(b). At room temperature we observed a total of 15 Raman modes: three relatively sharp peaks appeared at 90, 223, 260 cm<sup>-1</sup> and others peaks are relatively weak in intensity. Comparing these values with the observed Raman peaks in the SrZrO<sub>3</sub> spectrum [12], one can conclude that the most intense Raman peaks at 90 and 223 and 260 cm<sup>-1</sup> in the room temperature spectrum are the A<sub>g</sub> modes. Raman modes at 223 and 260 cm<sup>-1</sup> can be identified as corresponding to O–Sn–O bending [13], whereas the peak near 90 cm<sup>-1</sup> is similar to the lowest mode in cassiterite [14] SnO<sub>2</sub>.

The phonon modes in figure 2(a) show remarkable change in their linewidths at three different temperatures. As temperature increases from ambient to 377 °C, these peaks broaden dramatically and then disappear around 377 °C, which



**Figure 2.** (a) Temperature-dependent Raman spectra of ceramic SrSnO<sub>3</sub> in the temperature range 25–1000 °C. (b) Raman spectra of ceramic SrSnO<sub>3</sub> at different transition temperatures 260, 380, 620 and 820 °C.



**Figure 3.** Temperature-dependent frequency shift and linewidth change of A<sub>g</sub> Raman mode (223 cm<sup>-1</sup>) of SrSnO<sub>3</sub>.

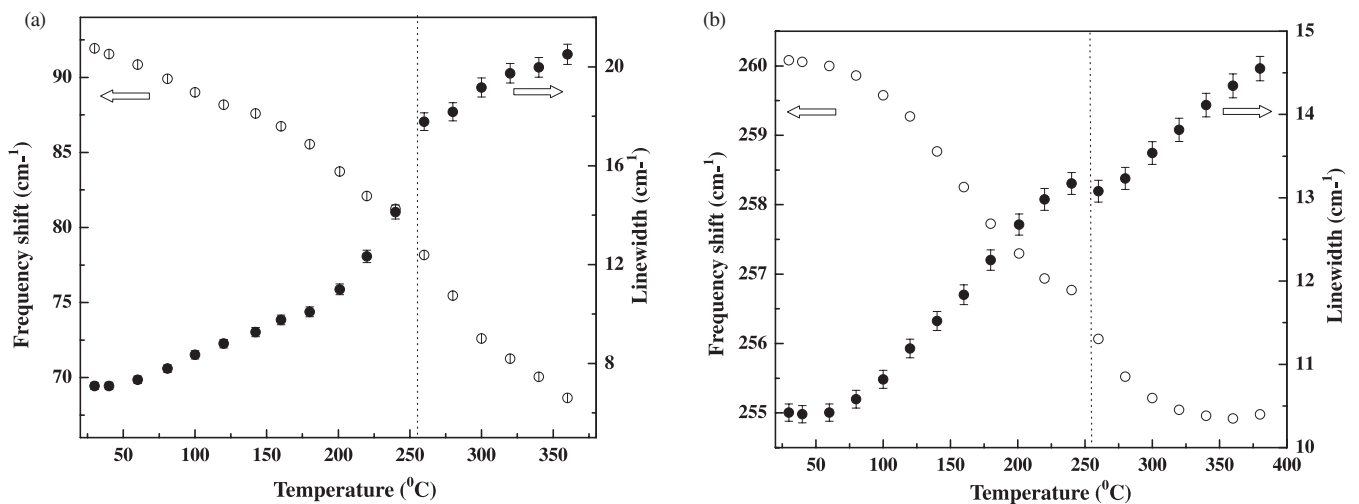
reveals an order–disorder phase transition in SrSnO<sub>3</sub> at 377 °C. In addition we also observe a rapid change in frequency and lineshape in most of the Raman modes around 260 °C; a brief mention of anomalies was also reported in Mountstevens’ thesis [4]. In figure 2(b), we observed two new Raman modes appearing at 423 and 632 cm<sup>-1</sup> and these two relatively sharp Raman modes, which disappear above 380 °C, indicating an unknown phase (Orthorhombic or tetragonal) of SrSnO<sub>3</sub> between 260 and 377 °C. The high-temperature Raman spectra also show remarkable changes in the lineshape and the frequency shifts in Raman modes at 628 and 828 °C, which are very close to the transition temperatures in SrSnO<sub>3</sub> reported earlier [1].

In order to account for the accurate value of the phonon frequencies and the line width of three sharp Raman modes at different temperatures, we used the damped harmonic

oscillator (DHO) model to fit the Raman profiles [15]. In figure 3, the values of the A<sub>g</sub> mode frequency located at around 223 cm<sup>-1</sup> and the corresponding linewidth are plotted as a function of temperature. The optical mode (~223) shows considerable softening between ~260 and ~377 °C but then becomes nearly temperature independent between 377 and 636 °C, and also exhibits a considerable change around 800 °C. A similar change in the linewidth for this Raman mode was observed and is shown in figure 3. The Raman shifts and the linewidths of other two sharp optical modes, namely at 90 and 260 cm<sup>-1</sup> are plotted as a function of temperature and are shown in figures 4(a) and (b). The changes in linewidth and frequency shift with temperature of an optical mode near 260 cm<sup>-1</sup> are like that at 223 cm<sup>-1</sup>; and this mode disappears around 377 °C, whereas the behaviors of linewidth and Raman shift of the optical mode at 90 cm<sup>-1</sup> are not anomalous. This fact suggests that the phase transition at 377 °C is strongly related to the tilting of SnO<sub>6</sub> octahedra.

## 5. Summary

In conclusion, differential thermal analysis (DTA), dielectric loss measurements, and Raman linewidth measurements on ceramic SrSnO<sub>3</sub> samples reveal two new phase transitions. That at 377 °C is second-order (or very nearly) and order–disorder. Both the entropy change and Raman linewidth change arising from this transition show it to be order–disorder and hence that about as much disorder sets in at 377 °C as reported earlier at 636 °C. This gives us a revised view on the disorder–disorder characteristics of the 636 °C transition. Our analysis confirms ‘Glazer’s Law’ in this material—that oxygen octahedron tilt transitions are always displacive in perovskites. A possible additional transition occurs at nearly 260 °C. This could be first-order and it results in the abrupt disappearance of some Raman lines. The structures of the lower phases



**Figure 4.** (a) Temperature-dependent frequency shift and linewidth of  $A_g$  Raman mode ( $90\text{ cm}^{-1}$ ) with temperature. (b) Temperature-dependent frequency shift and linewidth of  $A_g$  Raman mode ( $260\text{ cm}^{-1}$ ) with temperature.

are unknown and the phase between  $260$  and  $377\text{ }^\circ\text{C}$  could be orthorhombic or tetragonal.

### Acknowledgments

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