

New cryogenic phase transitions in SrSnO_3

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 J. Phys.: Condens. Matter 22 095901

(<http://iopscience.iop.org/0953-8984/22/9/095901>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 07:24

Please note that [terms and conditions apply](#).

New cryogenic phase transitions in SrSnO₃

Manoj K Singh¹, J W Hong^{2,3}, N K Karan⁴, Hyun M Jang⁵,
R S Katiyar⁴, S A T Redfern² and J F Scott^{2,6}

¹ Center of Material Science, University of Allahabad, Allahabad 211002, India

² Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK

³ AML, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, People's Republic of China

⁴ Department of Physics and Institute of Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931, USA

⁵ Department of Material Science, Pohang University of Science and Technology, POSTECH, Pohang, Republic of Korea

⁶ Department of Physics, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

E-mail: jfs32@hermes.cam.ac.uk

Received 15 December 2009

Published 10 February 2010

Online at stacks.iop.org/JPhysCM/22/095901

Abstract

Strontium stannate is under study as an ultra-stable dielectric material for microelectronic applications at low temperatures. It is known to have a remarkably temperature-independent dielectric constant from 27 K to room temperature. However, we report anomalies in the Raman spectra, dielectric response, and differential thermal analysis of strontium stannate compatible with a structural phase transition at 160 K. Further anomalies are seen in calorimetric and Raman data (but not dielectric data) that suggest another phase transition at 270 K. A preliminary x-ray powder diffraction study confirms a small change in the pseudo-cubic lattice constant $a(T)$ at the lower transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Strontium stannate SrSnO₃ is a member of the perovskite family of compounds and is under active study from a microelectronics device point of view [1–4], notably because it has an ultra-low thermal change in its dielectric constant from 27 to 300 K. The stannate perovskites have attracted interest since the early structural studies of Megaw [5] who suggested that SrSnO₃ was primitive cubic. Half a century later it was shown by means of high resolution neutron diffraction that, at room temperature, SrSnO₃ adopts the D_{2h}¹⁶ *Pbnm* orthorhombic structure but with only a very small distortion from the cubic form, such that typical laboratory x-ray diffraction experiments do not resolve the lower symmetry distortion [6, 7]. It is well established that SrSnO₃ has two structural phase transitions: one at 909 K and one at 800 °C [8–13]. From a study of the structural stability and the phase transition in SrSnO₃ with varying temperature, Mountstevens *et al* [8] inferred a continuous orthorhombic *Pbnm* to *Imma* symmetry transition at 909 K and a first-order transition to a tetragonal *I4/mcm* phase at

1073 K. Goodwin *et al* [12] also reported an octahedral tilt distribution that reflects the displacive nature of the *Pbnm*–*Imma* transition at 905 K, together with the nature and distribution of planar ferroelectric domains and the associated real-space correlation functions. More recently we inferred a continuous or nearly continuous order–disorder transition from orthorhombic (pseudo-tetragonal) to orthorhombic structure on heating in SrSnO₃ at 650 K, and a discontinuous transition near 533 K [11]. High temperature phase transitions in SrSnO₃ have been of interest to both the geophysics and the ferroic materials communities: to the former because it is isostructural with MgSiO₃ perovskite (the most abundant silicate mineral in the Earth), and to the latter because there are indications that nanoferroelectric properties and relaxor phenomena become important as the structure approaches the cubic aristotype at high temperature [8–16]. It has further been suggested, on the basis of *ab initio* calculations, that doped SrSnO₃ may show semi-metallic properties and represent a new class of spintronic materials [17].

Despite the rather well developed characterization of the high temperature properties of SrSnO₃ it is, perhaps, surprising

to note that there appears to be a dearth of reports of its low temperature characteristics in the literature. Raman spectroscopy offers a unique opportunity of probing the structural instability due to the order–disorder transition and also due to displacive octahedral tilting, as well as finding some information on the effect of ferroelectric nanoscale domains on the corresponding microelectronic properties [11, 13, 14, 16]. Here, we discuss the results of studies using Raman, dielectric and x-ray diffraction methods below room temperature that reveal unexpected complexities in the behavior of SrSnO₃ at low temperature. The present study reveals two new phase transitions near 160 and 265 K, but it is important for electronics applications that this does not appear to adversely affect the rather temperature-independent dielectric constant or significantly modify the structure.

2. Experiments

SrSnO₃ ceramics were prepared by the solid state reaction method [11]. To examine the structure of the SrSnO₃ powder, a theta/2-theta (θ – 2θ) x-ray diffraction (XRD) study was carried out; details of the preparation method and crystal structure have been discussed elsewhere [11]. Raman scattering data were obtained using a T64000 spectrometer (Horiba Inc.) equipped with a triple-grating monochromator and a Coherent Innova 90C Ar⁺ laser with an excitation wavelength of 514.5 nm. The measurements were performed with a micro-Raman option using a LN₂-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 the CCD. The spectral resolution was typically less than 1 cm^{−1}. A microscope-compatible thermal stage was used while recording the temperature-dependent spectra. Differential thermal analysis measurements were carried out at a rate of 10 °C min^{−1} in the temperature range 25–300 K using 10 mg of SrSnO₃ powder set in a platinum pan. In these measurements Al₂O₃ was employed as a reference material. Dielectric data for SrSnO₃ have been collected at temperatures below room temperature using pressed ceramic pellets and Ag electrodes. The dielectric properties were measured over a range of temperatures and frequencies of applied field using an HP4192 impedance analyzer.

3. Results and analysis

3.1. Raman spectroscopy at cryogenic temperatures

To study the structural instability due to octahedral tilting at cryogenic temperature and its effect on the optical phonons of the SrSnO₃, we performed micro-Raman scattering measurements as discussed above; the results are presented in figures 1(a) and (b). At room temperature SrSnO₃ is characterized [12] by orthorhombic symmetry with point group *mmm* (D_{2h}) and space group *Pbnm* (exactly equivalent to *Pnma*, D_{2h}¹⁶). The Raman active modes for this *Pbnm* structure are [11] $\Gamma_{\text{Raman}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$. These can be classified as two symmetric and four antisymmetric octahedral stretching modes, four bending modes, and six

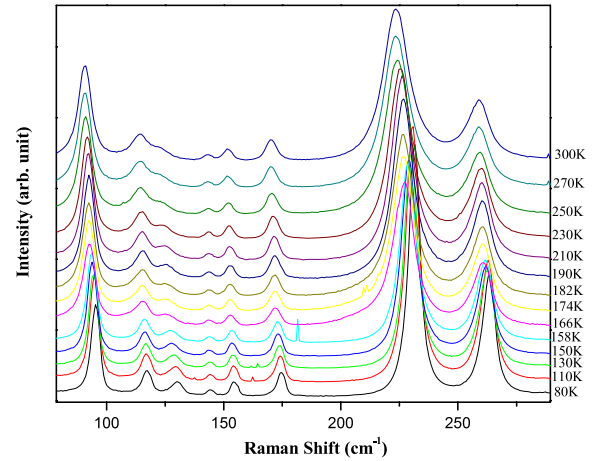


Figure 1. Raman spectra of SrSnO₃ in the temperature range 80–300 K.

rotation or tilt modes of the octahedra. The other eight modes are associated with the strontium cations. A detailed description of the room temperature Raman spectra is given elsewhere [11].

At room temperature we observed a total of 15 Raman modes: three relatively sharp peaks that appeared at 90, 223, 260 cm^{−1} and others relatively weak in intensity. The three observed Raman modes have been assigned as A_g modes by comparing these values with the observed Raman peaks in the SrZrO₃ spectra [16] and can be identified as corresponding to symmetrical vibrations of SnO₆ octahedra. In order to graph accurate values of the quasi-harmonic phonon frequencies of these Raman modes at different temperatures (i.e., correcting peak positions for damping) we used the damped harmonic oscillator model to fit the Raman profiles as $I(\omega) = \frac{\chi_0 \Gamma_0 \omega \omega_0^2 (\bar{n} + 1)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma_0^2}$, where $n = \exp(-\hbar\omega/k_B T) - 1$ is the phonon occupation number, ω_0 is the peak frequency, Γ_0 is the linewidth, and χ_0 is related to the peak intensity [18]. The values of ω_0 for the A_g modes were plotted as a function of temperature and are shown in figure 2(a); they show considerable softening between 80 and 300 K. In addition, we observe a rapid change in frequency of all three Raman modes near ~160 and ~265 K. Such an abrupt change in frequency shift (up to 20 cm^{−1}) of these A_g modes cannot be explained by thermal expansion. The linewidths (FWHM) of the three prominent Raman modes also change abruptly close to 160 and 265 K (figure 2(b)).

3.2. Differential thermal analysis

It can be seen that in the DTA curve of pure SrSnO₃ shown in figure 3 there is a sharp peak at 160 K where a new phase transition occurs. Unlike the exothermic transition near 265 K, this anomaly is endothermic. DTA measurements at low temperatures reveal two consecutive phase transitions; however the modest change in specific heat and Raman linewidth at 160 K suggests a displacive transition associated with octahedral tilting, whereas the large linewidth change near 265 K implies an order–disorder transition. (The other

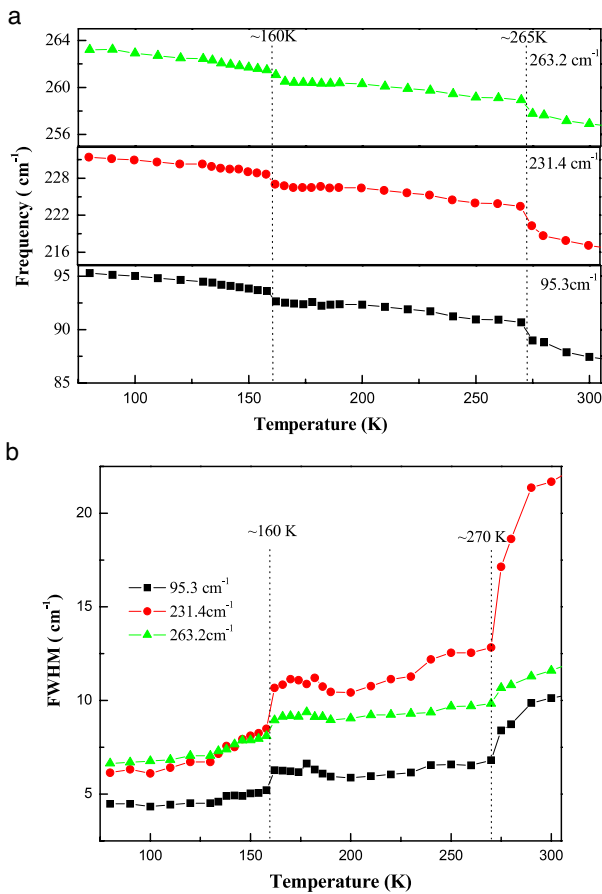


Figure 2. (a) Raman peak frequencies versus temperature for SrSnO₃. (b) Raman mode linewidths at low temperatures for SrSnO₃. Spectral slit-width resolution: 1 cm⁻¹.

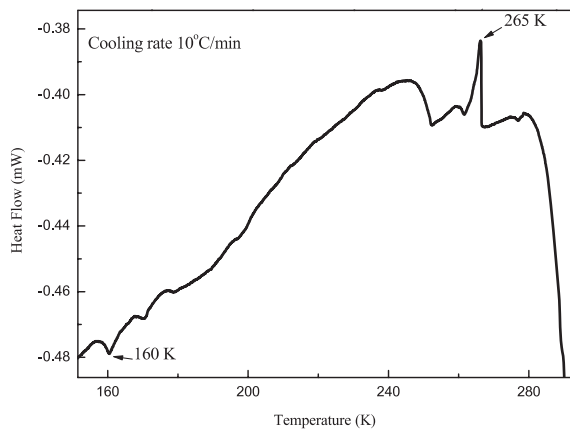


Figure 3. The DSC (differential scanning calorimetry) measurement for SrSnO₃ ceramics at low temperatures (the cooling rate is 10 K min⁻¹).

anomalies in the DTA curve shown, either small sharp peaks or broad curves, arise from noise and instrumental drift, respectively, and are not reproducible.)

The Glazer criterion discussed elsewhere suggests that octahedral tilt transitions in oxide perovskites are always displacive [8, 11].

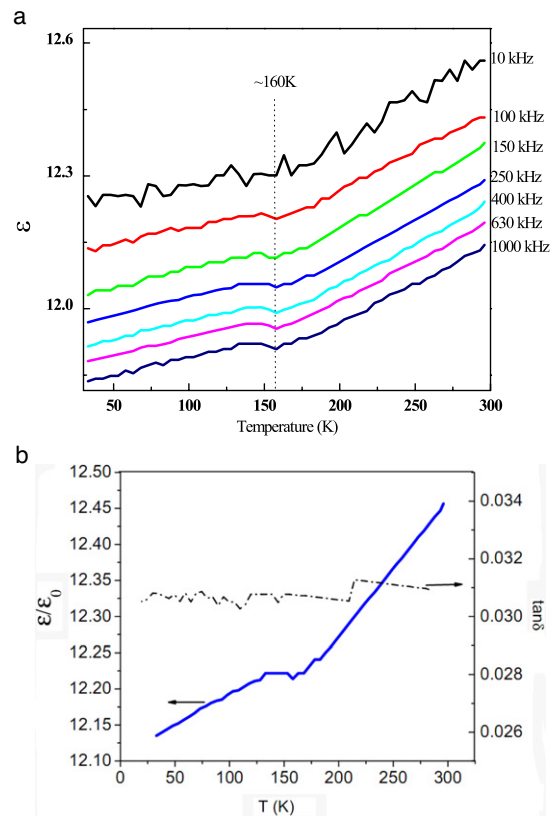


Figure 4. (a) Dielectric constant at different frequencies versus temperature in SrSnO₃; (b) real and imaginary parts at 250 kHz versus temperature.

3.3. The dielectric constant

Further support for low temperature disorder is shown in figure 4, where the dielectric loss tangent of SrSnO₃ has been plotted as a function of temperature at different frequencies. At all frequencies measured we find a subtle but unambiguous anomaly in the dielectric constant at around 160 K. The temperature at which the real part of the dielectric constant shows this anomaly is independent of frequency over the range of our measurements, indicating that a new structural phase transition is occurring in SrSnO₃ at this temperature. However this change in susceptibility is less than 1%, appears continuous, and is most evident in the change in slope $d\epsilon/dT$ above and below the transition temperature. The slopes are slightly frequency dependent but numerically approximate $d\epsilon/dT = 0.66 \times 10^{-3} \text{ K}^{-1}$ below 160 K and $2.3 \times 10^{-3} \text{ K}^{-1}$ above. In addition there is a small but reproducible dip at the transition temperature. Furthermore, we note that, for all frequencies, the dielectric losses remain low ($\tan \delta < 0.1$) and show no obvious anomaly at the transition temperature. These data therefore imply that the transitions near 160 and 265 K are not ferroelectric.

3.4. Lattice parameter analysis

We attempted to characterize this behavior further at low temperatures by means of laboratory x-ray measurements. X-ray diffraction patterns were collected between room

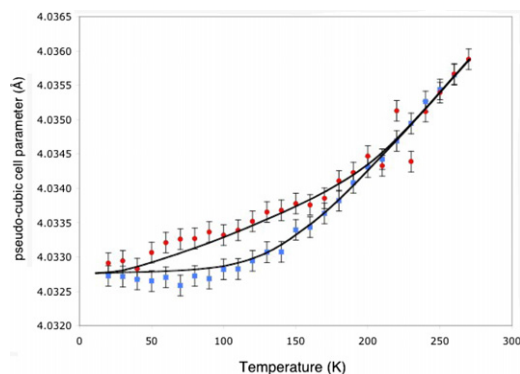


Figure 5. Pseudo-cubic lattice parameter $a(T)$ for SrSnO_3 ; cooling (upper curve) and heating (lower curve). Note the small discontinuity near 155 K on the heating run. The large thermal hysteresis in this temperature region obscures further details. Note also the anomaly near 240 K; this may be the same transition as is observed near 265 K in figures 1 and 2(a), shifted by thermal hysteresis.

temperature and 20 K using an INEL position sensitive detector based system and $\text{Cu K}\beta$ radiation. As noted in the introduction, the unit cell of SrSnO_3 is thought to be orthorhombic, $Pbnm$, at room temperature, but with only a very slight distortion from the metrically cubic structure. Indeed, SrSnO_3 was assumed to be cubic for many decades. We are unable to distinguish any non-cubic splitting of powder lines in our data, as such splitting is below the resolution of the diffractometer, so we have analyzed the data in terms of the pseudo-cubic cell parameter (effectively a measure of the cell volume). Figure 5 shows the SrSnO_3 lattice constant (pseudo-cubic) with lowering temperature, and there are no anomalies observed that are greater than the experimental uncertainties. (There is a very small kink at around 160 K in the lower curve for the heating run only.) This shows that the phase transition at 160 K is more easily seen in dynamical measurements than in static data. No attempt has been made yet to determine the space group symmetry of the low temperature phase, which will require detailed synchrotron or neutron investigation. Since the room temperature phase is thought to be orthorhombic, a small monoclinic distortion may be involved, or an orthorhombic–orthorhombic transition. Since the former would be ferroelastic and the latter non-ferroelastic, stress–strain measurements, in the future, could be useful.

4. Conclusions

Two new structural phase transitions in strontium stannate at 160 and 270 K are suggested. These low temperature transitions were not predicted and are unexpected for this oxide

perovskite, and indicate the need for further study of SrSnO_3 at low temperatures, by additional structural methods. All three major optical phonon modes of A_g symmetry exhibited anomalous frequency shifts near 160 and 265 K. Differential thermal analysis (DTA), dielectric anomalies, and the change in lattice parameter also support the two new phase transitions. The transition at 160 K may be second order and is likely to be displacive due to octahedral tilting. Since this has a negligible effect on the temperature-independent dielectric constant and loss, it does not diminish the device appeal of this material. However, such a low temperature transition was not predicted and is unexpected for this oxide perovskite, which raises questions about its lattice dynamics. The transition near 265 K appears to be an order–disorder one, on the basis of its large increase in Raman linewidth.

Acknowledgments

We thank Professor A M Glazer for discussions and the DOD (grant W911NF-05-1-0340) for financial support.

References

- [1] Chen D and Ye J 2007 *Chem. Mater.* **19** 4585
- [2] Wang S, Lu M, Zhou G, Zhou Y, Zhang A and Yang Z 2007 *J. Alloys Compounds* **432** 265
- [3] Wakana H, Kamitani A, Adachi S, Nakayama K, Ishimaru Y, Tarutani Y and Tanabe K 2005 *Adv. Supercond.* **17** 1495
- [4] Azad A M, Pang T Y and Alim M A 2003 *Act. Passive Electron. Compon.* **26** 151
- [5] Megaw H D 1946 *Proc. Phys. Soc.* **58** 122
- [6] Vegas A 1986 *Acta Crystallogr. B* **42** 167–72
- [7] Green M A, Prassides K, Day P and Neumann D A 2000 *Int. J. Inorg. Mater.* **2** 35–41
- [8] Mountstevens E H, Redfern S A T and Attfield J P 2005 *Phys. Rev. B* **71** 220102
- [9] Mountstevens E H, Attfield J P and Redfern S A T 2003 *J. Phys.: Condens. Matter* **15** 8315–26
- [10] Daraktchiev M, Harrison R J, Mountstevens E H and Redfern S A T 2006 *Mater. Sci. Eng. A* **442** 199–203
- [11] Singh M K, Karan N K, Katiyar R S, Scott J F and Jang H M 2008 *J. Phys.: Condens. Matter* **20** 055210
- [12] Goodwin A L, Redfern S A T and Dove M T 2007 *Phys. Rev. B* **76** 174114
- [13] Glerup M, Knight K S and Poulsen F W 2004 *Mater. Res. Bull.* **40** 507
- [14] Wang Y, Guyot F and Liebermann R C 1992 *J. Geophys. Res.* **97** 12327
- [15] Aydi A, Khemakem H, Simon A, Michau D and von der Muhll R 2009 *J. Alloys Compounds* **484** 356–9
- [16] Kamishima O, Hattori T, Ohta K, Chiba Y and Ishigame M 1999 *J. Phys.: Condens. Matter* **11** 5355
- [17] Shein I R, Kozhevnikov V L and Ivanovskii A L 2006 *Semiconductors* **40** 1261–5
- [18] Samanta K, Bhattacharya P and Katiyar R S 2007 *Phys. Rev. B* **75** 035208