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Materials Research Bulletin 40 (2005) 507–520
Materials Research Bulletin
www.elsevier.com/locate/matresbu

High temperature structural phase transitions in $SrSnO_3$ perovskite

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Received 13 April 2004; accepted 24 November 2004

Abstract

Three high temperature structural phase transitions have been identified in the perovskite-structured phase $SrSnO_3$ using differential scanning calorimetry and dilatometry, and have subsequently been structurally characterised using high-resolution neutron powder diffraction. Between 298 and 905 K, $SrSnO_3$ is orthorhombic, space group *Pmcn* before undergoing a continuous phase transition to a second orthorhombic phase in space group *Incn*. At 1062 K there is a first order phase transition to a tetragonal phase in space group *I*4/*mcm* before finally transforming to the aristotype phase at 1295 K. Using the magnitude of the anti-phase tilt as a measure of the order parameter for the transition from *I*4/*mcm* to $Pm\bar{3}m$ suggests this transition is tricritical in nature. Crystal structures are reported for the three hettotype phases.

Keywords: A. Oxides; C. Differential scanning calorimetry; D. Phase transitions

1. Introduction

There remains a continuing interest, both theoretical and applied [1], in the structural phase transitions exhibited by the perovskite-structured family of oxides and halides. The wide diversity of structures

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0025-5408/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2004.11.004

exhibited by the perovskites and their closely related compounds, such as the Ruddlesden-Popper, Dion-Jacobson and Aurivillius phases have recently been brought together in an excellent monograph by Mitchell [2]. Despite the extensive studies carried out on the temperature-dependent structural phase transitions exhibited by non-ferroelectric perovskites, the ability to predict the probable sequence of phase transitions for any particular compound remains elusive. For example, at least five sequences of phase transitions from the hettotype *Pnma* to the aristotype $Pm\bar{3}m$ have been identified and studied in sufficiently small temperature intervals and crystallographic detail to be considered as well-characterised.

$$Pnma \rightarrow P4/mbm \rightarrow Pm\bar{3}m, \mathrm{NaMgF_3}[3]$$

$$Pnma \rightarrow R\bar{3}c \rightarrow Pm\bar{3}m, \mathrm{LaGaO_3}[4]$$

$$Pnma \rightarrow Cmcm \rightarrow P4/mbm \rightarrow Pm\bar{3}m, \mathrm{NaTaO_3}[5,6]$$

$$Pnma \rightarrow Imma \rightarrow R\bar{3}c \rightarrow Pm\bar{3}m, \mathrm{BaCeO_3}[7,8]$$

$$Pnma \rightarrow Imma \rightarrow I4/mcm \rightarrow Pm\bar{3}m, \mathrm{SrZrO_3}[9]$$

Although there is growing evidence that many Sr-containing perovskites ($SrZrO_3$, $SrHfO_3$, $SrRuO_3$, $Sr_{1-x}Ba_xZrO_3$) undergo the last of the listed sequences, high resolution, high-temperature powder X-ray diffraction has found no phase transitions in $SrPbO_3$ up to 1033 K [10] and similar work, using medium resolution powder neutron diffraction, has shown $SrCeO_3$ to have the *Pnma* space group from 4.2 to 1273 K and from ambient pressure to 7.9 GPa [11]. It is therefore clear that it is necessary to perform simple, in-house characterisation of perovskites to ascertain whether structural phase transitions do in fact occur before embarking on a detailed structural survey using high-resolution neutron or synchrotron powder diffraction.

$SrSnO_3$ has become of technological interest because of its potential application as a dielectric material for use in capacitors [12] and, more recently, for its use as a humidity sensor [13,14].The room temperature, structural crystallography of $SrSnO_3$ has been studied many times in the past using both single-crystal X-ray and powder diffraction techniques. Using powder diffraction, Megaw [15] and Coffeen [12] both found it to have the aristotype structure, whilst the later single-crystal investigation of Smith and Welch [16] found it to be cubic with a unit cell doubled over the aristotype phase. In the most recent single crystal study by Vegas et al. [17], the compound was found to be orthorhombic in space group *Pbnm* with the structure being derived from geometrical considerations due to the presence of heavy twinning. The nature of the twinning, studied by transmission electron microscopy [17], provided the first evidence for the likely existence of high temperature structural phase transitions in $SrSnO_3$. Three different twin domains were observed in a single crystal identical to that used in the X-ray diffraction study. The micrograph shown by Vegas et al. [17] is suggestive of ferroelastic twin domains produced on cooling from a high-temperature, higher symmetry phase.

In this study we have used differential scanning calorimetry (DSC) and dilatometry to prove the existence of structural phase transitions in $SrSnO_3$ and have characterised the hettotype phases by high-resolution, powder neutron diffraction. The results from the DSC and dilatometry study have been reported earlier in the thesis of Glerup [18] and a preliminary account of the identification of the hettotype phases has also been made in the ISIS Facility Annual Report for 2001–2002 [19]. In this paper we give more detailed information on the identification and characterisation of the hettotype phases with information on the likely thermodynamic order of the observed structural phase transitions.