

# Phase Transformations in the $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ Perovskite System

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Mixed perovskite samples,  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ , a constituent phase in Synroc, were studied using dynamic modulus and internal friction, to resolve aspects of the phase diagram for this system. An elastic instability for an  $x = 0.7$  sample, provides evidence for a transformation which is supported by a structural transition from space group Pbnm to Pbcm, revealed by neutron diffraction.

## 1. Introduction

The mixed perovskite  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$  is one of the major constituent phases of Synroc, a synthetic rock form proposed for the long-term immobilisation of Purex-type, high-level nuclear waste [1]. A detailed understanding of the crystal structures formed, and transitions within, each of the constituent phases is of vital importance to gaining a complete knowledge of the overall structural stability of Synroc. This study investigated the transition temperatures of and the temperature dependences of the space group symmetries for several samples having  $x = 0.6$  to  $0.8$ .

There have been many previous studies of the  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$  phase diagram [2-7] and a summary of these data was reported elsewhere [8]. There are general trends to some of the phase boundaries while there are also conflicting data concerning others. The discrepancies in previously observed data are here ascribed to the variety of sample preparation techniques employed. This study has attempted to produce samples using techniques closely related to those used in bulk Synroc manufacture and to analyse these samples in their polycrystalline form as they would exist in Synroc.

## 2. Experimental Details

Powders of the correct stoichiometry were prepared via the alkoxide method [1]. The calcined powders were then hot pressed at  $1400^\circ\text{C}$  and  $21\text{MPa}$  in a graphite die and cooled slowly to give the final product.

The main technique used for the study was that of dynamical mechanical analysis using the piezoelectric ultrasonic composite oscillator [9]. This technique allows for continuous monitoring of the Young's modulus and internal friction of a sample over a range of temperatures, with a modification to the experimental set-up to enable automated data collection as a function of temperature [10].

Neutron scattering studies were carried out at a series of temperatures using the High Resolution Powder Diffractometer (HRPD) at the Lucas Heights Research Reactor. A solid section of the polycrystalline sample was machined in order to contain as much sample as possible inside the thin-walled vanadium cylinder used to contain the sample in the displacive cryostat on the HRPD. It is again emphasised (see above) that it was important to use a solid piece of material for the neutron scattering experiment so that the diffraction and mechanical property studies were undertaken on specimens of identical preparation methods. Initial HRPD data were collected at a neutron wavelength of  $1.88384\text{\AA}$ . In a second experiment with improved temperature stability and control, the neutron wavelength was  $1.49384\text{\AA}$ . Diffraction data were analysed by the Rietveld method, using the package Rietica [11].

### 3. Results

#### 3.1 Young's Modulus and Internal Friction

The dynamic Young's modulus and internal friction results are shown in Fig. 1. It is clear that there are two distinctly different types of anomalies occurring. The first anomaly (at low temperature) is characterised by a large V-shaped dip in Young's modulus and the second by a sharp break in the trend of the Young's modulus as well as an internal friction peak. The sample of composition  $x = 0.7$  shows both types of anomalies while the 0.6 and 0.8 samples show only one.

Activation energies were calculated for the peaks in internal friction by plotting the natural log of internal friction as a function of the reciprocal temperature. The gradient of such a plot is the activation energy divided by the gas constant. Activation energies of 0.51eV, 0.55eV, and 0.38eV were found for samples of composition  $x = 0.6$ , 0.7 and 0.8, respectively.

#### 3.2 Neutron Diffraction

For the  $x = 0.7$  sample, the room temperature phase refined equally well in both the tetragonal  $I4/mcm$  and the orthorhombic  $Pbnm$  space groups. Patterns taken between the temperatures of 120K and 250K all refined very well using the orthorhombic  $Pbnm$  space group while the low-temperature phase was concluded to be an orthorhombic  $Pbcm$  structure doubled along the  $c$  direction. This doubling along the  $c$  direction was characterised by the appearance of superlattice reflections within the diffraction pattern, as shown in Fig. 2. The

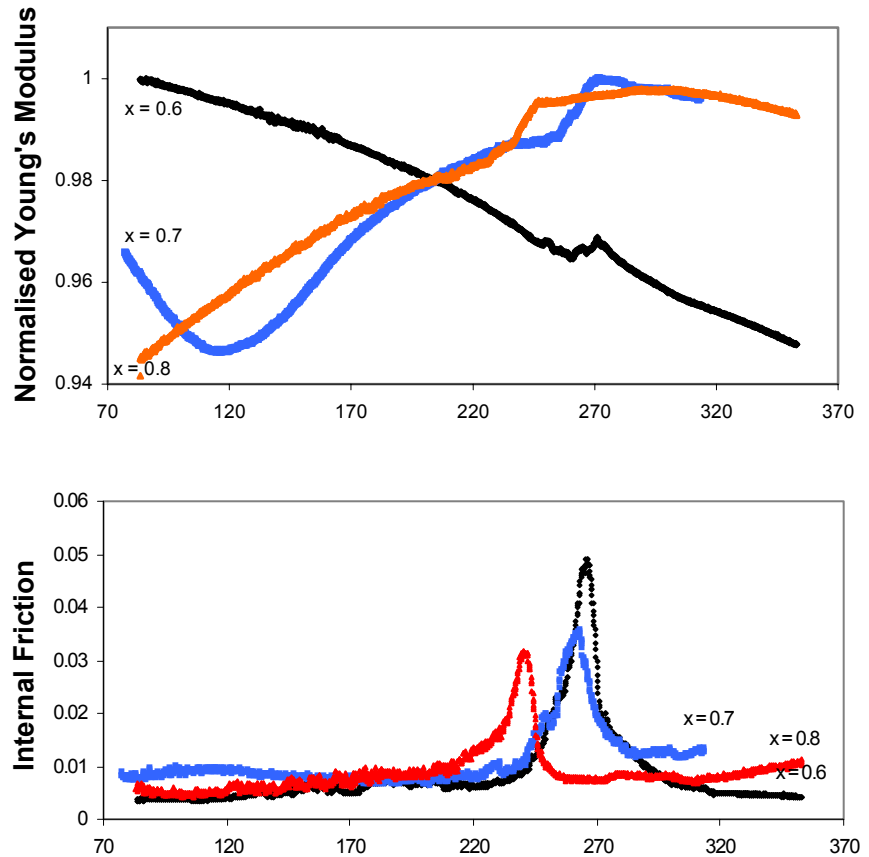


Fig. 1. Modulus and internal friction for  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ .

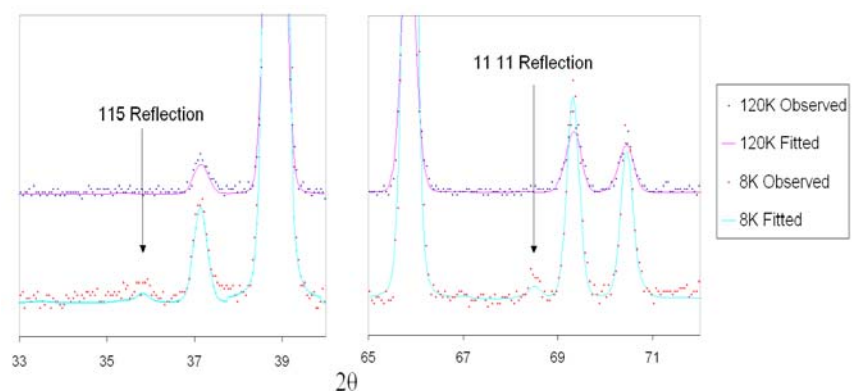


Fig. 2. Observed and calculated intensity profiles above and below the low temperature transition for  $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ .

temperature of the Pbnm to Pbcm transition correlated well with the large V-shaped dip in Young's modulus, as shown in Fig. 3.

#### 4. Discussion and Future Work

While there appears to be a good correlation between the large V-shaped dip in Young's modulus observed in the  $x = 0.7$  strontium sample and the structural transition from the space group Pbnm to Pbcm at about 110K, the transition temperature differs by about 90K from that reported in the literature

[4] for this particular structural change at this composition. These large discrepancies in results can only be attributed to the various sample preparation and analysis techniques used throughout the literature. Indeed, it will be of interest to examine the neutron diffraction data from a powder prepared by crushing the present solid sample (as has been the nature of the sample used by some other authors) or to study the Young's modulus for solid samples prepared under different ceramic processing conditions. Such experiments are planned for the future.

The internal friction peaks seen in Fig. 1 do not appear to be associated with a structural transition, as the temperature at which they are observed does not vary greatly with composition. Possible origins of these peaks include twin boundary motion or oxygen vacancy diffusion [12], although in both of these cases activation energies of greater than 0.9eV would be expected.

Further work is proposed for this study, including an increased temperature range for the dynamic mechanical analysis apparatus and more thorough neutron scattering on all samples.

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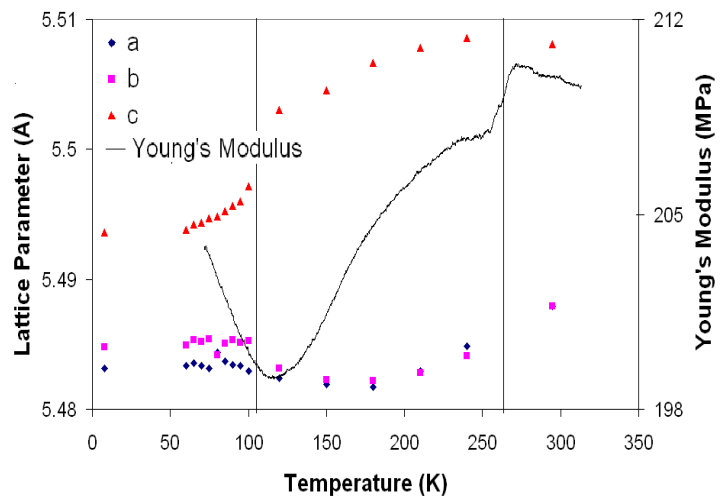


Fig. 3. Comparison of refined lattice parameters and modulus for  $Ca_{0.3}Sr_{0.7}TiO_3$ .