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| ESRF | **Experiment title:**<br>Cation order in oxides studied in-situ on a timescale of seconds. | **Experiment number**:<br>CH-1655 |
| **Beamline**:<br>ID11 | **Date of experiment**:<br>from: 16-Jul-04 to: 19-Jul-04 | **Date of report**:<br>16 August 2004 |
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## Report:

The properties of complex oxides are controlled by high temperature reaction and processing. As such materials play a leading role in current technologies, understanding their evolution under formation conditions is of considerable importance. Microwave devices are widely used in communications equipment, waveguides and dielectric resonators, capacitors and frequency filters. Oxide ceramics are critical elements in these microwave circuits and a full understanding of their crystal chemistry is fundamental to future development. High temperature processing is crucial to the performance of these oxide materials in applications, due to the resulting control over both atomic scale structure and the domain size over which such ordered structures persist. For example, in the prototype microwave dielectric ceramic $Ba_3ZnTa_2O_9$ (BZT) processing to achieve the high Q (low loss) state required for applications involves the establishment of layered ordering of $Zn^{2+}$ and $Ta^{5+}$ cations on the octahedral sites of the perovskite structure from a disordered pseudocubic precursor. We have developed high resolution powder diffraction methods to study the development of the structure of BZT under industrial processing conditions[1] at temperatures of up to 1500°C. This has allowed us to demonstrate the separate stages of B site ordering (occurring at short times) and domain growth (at long times), with the Avrami-Erofeev kinetics indicating the importance of site saturation due to pre-existing nucleation sites in the pseudo-cubic precursor to the ordered material. The characteristics of ID31 are ideally suited to studying these ordering processes on this (~ hours) timescale, and the sample environment development has opened up the in-situ study of ceramic processing at high temperature.

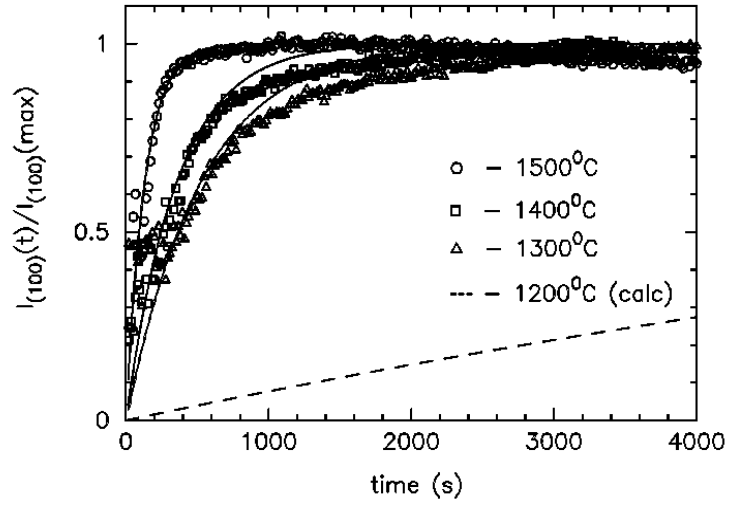


*Figure 1 - The evolution with time of the (100) superstructure reflection of BZT at 1500, 1400 & 1300 °C fitted to the Avrami-Erofeev equation with n = 1.0 and k = 7.6(1), 2.8(1), 1.9(1) x $10^{-3}$ $s^{-1}$ respectively. The curve for 1200 °C is based on a fit to previous data from ID31.*

In this experiment our aim was to harness the enhanced detector efficiency of ID11 to study the development of site order in these complex oxides on minute and second timescales. Growth of the ordered domains is monitored by the intensity and width of the superstructure reflections resulting from the ordering, measured on a BZT sample at various temperatures contained in a 0.52 mm OD, 0.44 mm ID Pt capillary at an energy of 36.0 keV ($\lambda$ = 0.347Å) (Figure1). The experiment is challenging since the Pt capillary absorbs around 90% of the X-rays and even when ordering is essentially complete, these superstructure reflections are less than 3% of the main reflection intensity. A 5 s measurement time plus 10 s read out time for the image plate provided the desired temporal resolution complementary to our previous measurements on ID31. Preliminary analysis has already broken new ground allowing us to quantitatively model the ordering of BZT at processing temperatures above 1200° C where ordering is complete in under an hour (Figure 1). These data should enable us to obtain activation energies for the short time site ordering and thereby gain the first insight into the kinetics governing the swapping of B sites essential for atomic ordering to proceed. Preliminary Rietveld refinement of the data is also showing promising results (see Figure 2) in modelling the ordering of Ta and Zn cations on to their repsective B sites in the perovskite structure. In addition, the resolution of the data are sufficient to discriminate variation in peak widths between the super- and sub-cell reflections.

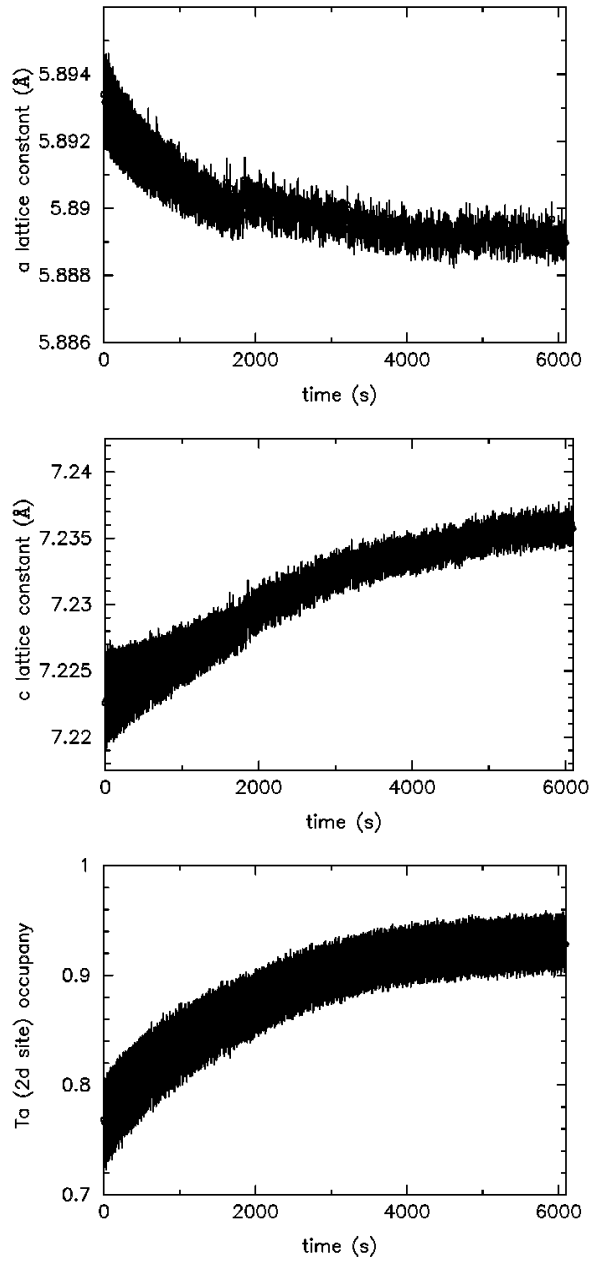


*Figure 2 – Refined BZT lattice constants and Ta fractional site occupancy vs annealing time at 1300º C. Data are plotted as error bars determined by Rietveld refinement*

We have recently shown that ordering in niobates appears even faster than tantalates, contrary to accepted ideas in the materials processing community and measurements on $Ba_3CoNb_2O_9$ (BCN) were also recorded. Despite these sample being generally less ordered, having smaller domains and with less scattering contrast the ordering process could be clearly monitored following the data collection strategy used for BZT. BCN is less prone to materials loss at high temperatures thus enabling extended measurements to be made on a single sample. For the first time, it was possible having first produced an ordered sample 'in-situ' to then heat above the order-disorder transition temperature ($T_{O/D}$) and follow the disordering process then subsequently quench below $T_{O/D}$ and re-order. This promises to be a highly effective experimental technique to accurately determine 'in-situ' the order-disorder temperature and probe both the thermodynamics of ordering and the kinetics of the related order-order, order-disorder and disorder-order processes.

1 – S.M. Moussa, R.M. Ibberson, M. Bieringer, A.N. Fitch, M.J. Rosseinsky, Chemistry of Materials **15** (2003) 2527-2533.

2 - S.M. Moussa, J.B. Claridge, M.J. Rosseinsky, S. Clarke, R.M. Ibberson, T. Price, D.M. Iddles, D.C. Sinclair, Applied Physics Letters **82** (2003) 4537-4539.