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| ESRF | **Experiment title:**<br>Resonant X-ray scattering of B-cation ordering in the microwave dielectric $BaZn_{1/3}Ta_{2/3}O_9$ | **Experiment number**:<br>Ch-1033 |
| **Beamline**:<br>BM16 | **Date of experiment**:<br>from: 28/03/01 to: 2/04/01 | **Date of report**:<br>18/2/02 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>Dr Andy Fitch | *Received at ESRF:* |


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## Introduction

$BaZn_{1/3}Ta_{2/3}O_3$ (BZT) and its modified doped ceramic oxides are used widely as microwave dielectric resonators in wireless communication industries. BZT is a perovskite that adopts the 2:1 ordered trigonal structure in which Zn and Ta cations alternate on the octahedral sites in a layered manner. Optimisation of the dielectric constant and microwave quality factor (Q) depends on the development of this cation order from a disordered cubic precursor formed in an initial calcination step, while controlling loss of ZnO at high (ca. 1500° C) sintering temperatures required for ordered domain growth. The effect of processing and cation ordering on the materials properties are understood empirically, however, the precise structure of these materials remains ambiguous. In particular, an understanding at the microscopic level of the extent of ordering realised at the elevated sintering temperatures has been elusive to date. Resonant X-ray scattering experiments are required in order to decipher unambiguously the extent of ordering of the Zn, Ta and Zr cations and possible vacancies over the two sites in the perovskite structure.

## Experimental

Data were recorded on BM16 for x = 0 and x = 0.022 samples of $BaZn_{1/3}Ta_{2/3}O_3$ + x $BaZrO_3$ at the Zn, Ta and Zr edges, λ = 1.283261, 1.256414 and 0.688819 Å respectively and under non-resonant conditions, λ = 0.62003 Å. Data were also collected on standard samples, from which values for *f'* were determined by refinement. The samples were ground in acetone and suspended on a non-background flat sample holder.

Data on standard samples were collected for some 1h 30min at the respective edges. By contrast for the BZT samples, data were collected

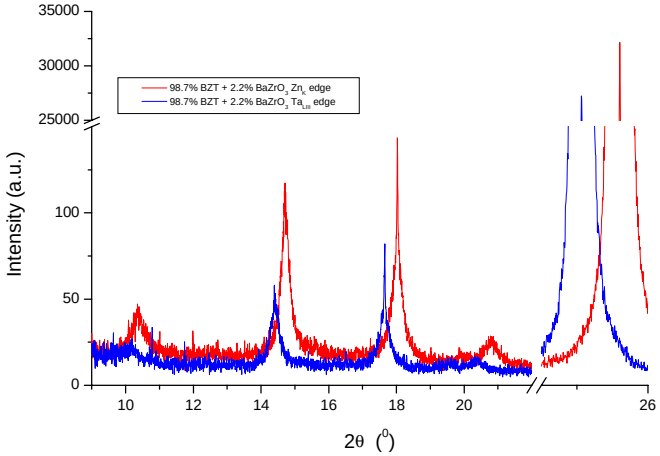


Figure 1 Comparison of data for 97.8% $BaZn_{1/3}Ta_{2/3}O_3$ + 2.2% $BaZrO_3$ at the Zn (red) and Ta (blue) edges

for at least 20h in order to have sufficient counting statistics, in particular for the weak superlattice reflections. Figure 1 shows a portion of the diffraction pattern of 0.978 $BaZn_{1/3}Ta_{2/3}O_3$ + 0.022 $BaZrO_3$ comparing the data collected at the Zn and Ta edges.

**Data Analysis**

i) Determination of *f'* using standard samples

$NiTa_2O_6$, $ZnTa_2O_6$, $BaZrO_3$ and $Ba_3ZnRu_2O_9$ were chosen as standards for refinement of the *f'* values. . Structural models taken from the literature [1, 2, 3, 4] were refined initially against recently collected neutron and X-ray data in order to provide accurate structural parameters for use in the determination of *f'*. The structure of the standard $Ba_3ZnRu_2O_9$ was that as reported by literature [4].

In order to determine the Ta *f'* at the Ta $L_{III}$ edge, the wavelength was refined against BZT data collected at this edge and the literature reported structure[5]. Sample scale factors were also pre-determined using non-resonant data and samples of known weight fractions of the standards and/or Si. These values were included as fixed parameters in the refinement. The wavelength refined to 1.256338(7) Å and the refined values of Ta *f'* using the various samples are summarised in Table 1. The wavelength at the Zn K edge was determined using a silicon standard. Zn *f'* was refined against the $Ba_3ZnRu_2O_9$ data. This value was subsequently used for the $ZnTa_2O_6$ standard in order to refine Ta *f'* at the Zn K edge. *f'* for both elements at the Zn K edge are summarised in Table 2.

The wavelength at the Zr K edge was refined using the structure of $BaZrO_3$ and determined as λ = 0.688929 Å. The refined value for Zr *f'* is given in Table 3.

Table 1 - Ta *f'* at the Ta $L_{III}$ edge

| **Sample** | ***f'* (refined)** | ***f'* (literature)** |
|---|---|---|
| $NiTa_2O_6$ +Si | -18.30(6) | -16.515 |
| $ZnTa_2O_6$ +$BaZrO_3$ | -18.05(6) | -16.515 |

Table 2 - Zn *f'* and Ta *f'* at the Zn K edge

| **Sample** | ***f'* (refined)** | ***f'* (literature)** |
|---|---|---|
| $BaZnRu_2O_9$ | Zn -9.84(7) | -8.300 |
| $ZnTa_2O_6$ | Ta -13.99(9) | -11.049 |

Table - 3 Zr *f'* at the Zr K edge

| **Sample** | ***f'* (refined)** | ***f'* (literature)** |
|---|---|---|
| $BaZrO_3$ | -7.76(3) | -9.050 |

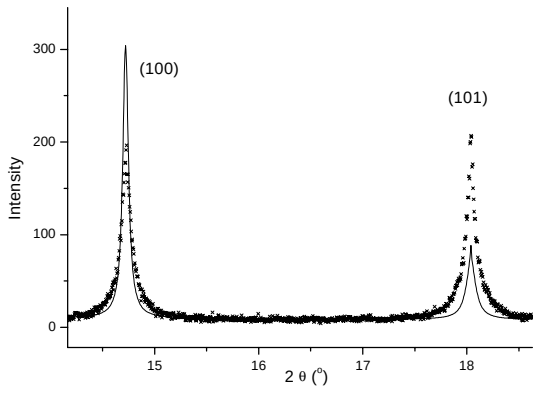


Figure 2 Portion of the $BaZn_{1/3}Ta_{2/3}O_3$ data collected at the $Zn_K$ edge. Crosses are observed data and solid line is that calculated using a single peakshape

These parameters were then used in the subsequent refinements of the BZT data against the three histograms of synchrotron data: at the Zn K edge, at the Ta $L_{III}$ edge and non-resonant. A section of the diffraction pattern collected on BM16 of pure BZT is shown in Figure 2. The portion of the pattern clearly illustrates that the superstructure peaks are considerably broader than the subcell peaks. The high-resolution diffraction data also revealed that the samples are intrinsically multiphase and comprise two similar trigonal BZT phases probably with different cation ordering. Data analysis is therefore extremely complex requiring multiphase and multi-histogram Rietveld refinement handling resonant scattering data in addition to the sub- and super-cell peak shape conditions. Furthermore we have valuable neutron diffraction data recorded on HRPD at ISIS introducing a multi-source requirement. To this end we have been utilising the Rietveld program PRODD[6] (Profile Refinement of Diffraction Data using the Cambridge Crystallographic Subroutine Library (CCSL)) modified successfully by Dr Jonathon Wright (ESRF) to accommodate these challenging analysis requirements. The analysis is on-going and good progress has been made on the $BaZn_{1/3}Ta_{2/3}O_3$ structure using the combined data sets. Figure 3 shows part of the refined diffraction patterns a) Zn K edge, b) Ta $L_{III}$ edge data, highlighting the good quality of fits obtained for the superlattice reflections.

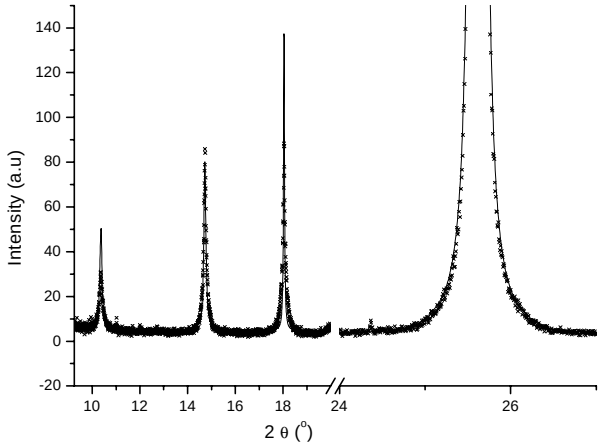


Figure 3 a) Part of the refined diffraction pattern at $Zn_K$ edge

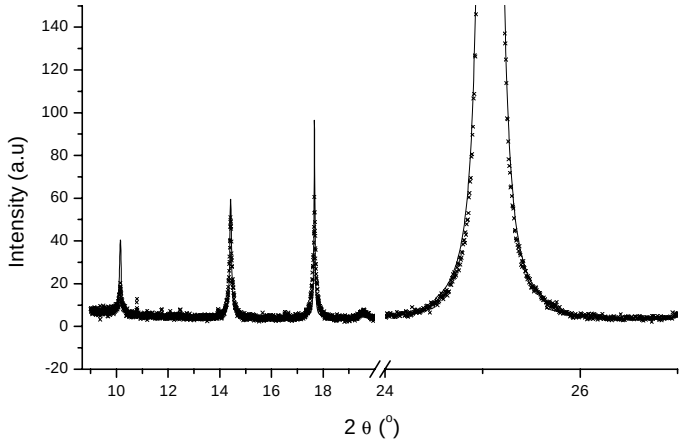


Figure 3 b) Part of the refined diffraction pattern at the $Ta_{LIII}$ edge

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