ESRF	**Experiment title:** IN-SITU STUDY OF B-CATION ORDERING IN THE MICROWAVE DIELECTRIC $Ba_3ZnTa_2O_9$	**Experiment number**: CH-1139
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Introduction

Modified $Ba_3ZnTa_2O_9$ (BZT) is used as a microwave dielectric for wireless communication technologies. The material can be thought of as a simple perovskite (ABO_3) with Zn/Ta disorder on the B-cation site (space group *Pm3-m*). Zn/Ta cation ordering can be achieved at high temperature resulting in a trigonal unit cell (space group *P-3m1*). The disordered cubic and ordered trigonal structures are illustrated in figure 1.

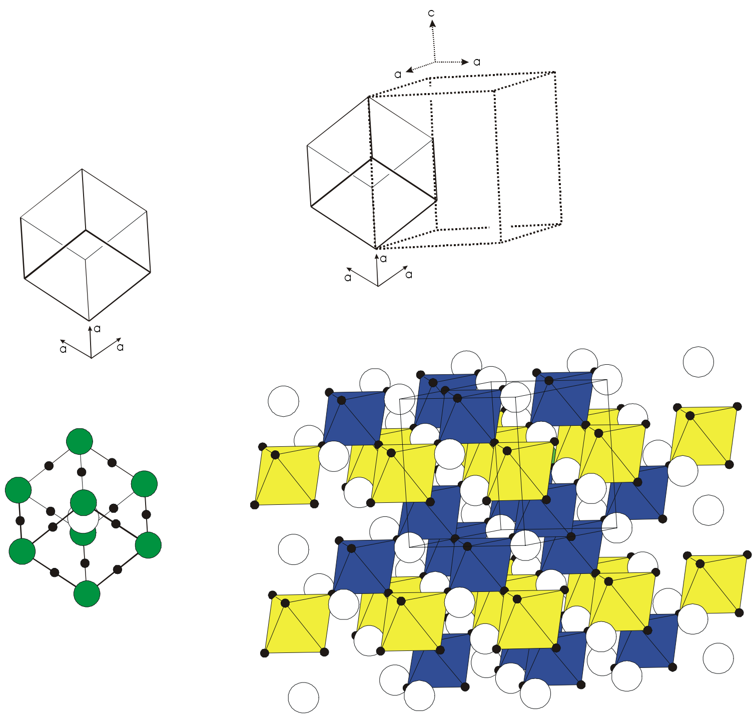

Figure 1: *left, disordered Zn/Ta (green) in cubic $Ba_3ZnTa_2O_9$, right: ordered trigonal structure (Zn =yellow, Ta = blue).*

The B-cation ordering process at high temperature is not understood todate. In particular details regarding phase separation, domain size growth and the extent of cation ordering as a function of preparation conditions can not be fully understood from ex-situ studies. We therefore carried out an in-situ study on the ordering process of BZT at 1500^0C in air.

Experimental

The in-situ study of Zn/Ta ordering in the trigonal perovskite $Ba_3ZnTa_2O_9$ was carried out on powder diffractometer BM16 using a wavelength of $\lambda = 0.336117$Å. The calcined material was loaded into Pt capillaries ($d_{inner} = 0.52$ mm, 0.04 mm wall thickness) and heated (within 1 hour) to approximately 1500^0C. A newly designed optical furnace[(1)] consisting of 3 focussing halogen lamps was used for this experiment. The sample temperature stability was determined by monitoring the variation of the (420) Pt peak position with time. The unit cell parameter variations of Pt over 24 hours are consistent with a temperature variation of less than 50^0C for the duration of the experiment.

Data Collection:

Diffraction data were collected in 30 minute increments. This was adequate for basic analysis, for example determination of *c/a* ratio, but in order to have sufficient counting statistics for full Rietveld analysis, data sets over a 2 hour range were added together. Here we report the preliminary diffraction results for $Ba_3ZnTa_2O_9$ annealing at approximately

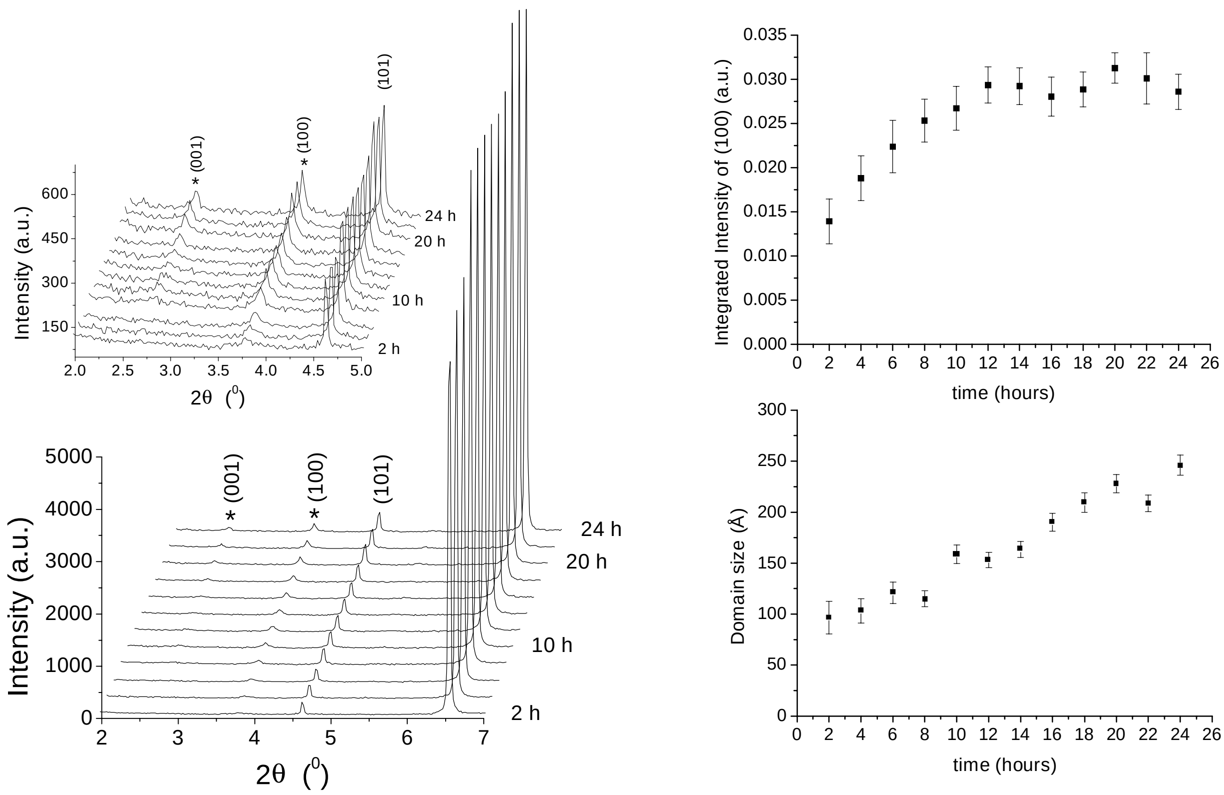

Figure 2: *Powder X-ray diffraction patterns obtained at 1500^0C in a Pt capillary. Left: time evolution of powder diffraction patterns, the superstructure peaks are labelled with *. Right: Evolution of the integrated intensity of the (100) reflection and the trigonal domain size as a function of the annealing time.*

1500^0C. The left hand side of figure 2 shows the powder diffraction patterns of BZT as a function of annealing time at 1500^0C. The inset emphasises the growth and sharpening of the (001) and (100) superstructure peaks. The (100) reflection is already present at room temperature as a broad feature, which sharpens significantly with increasing annealing time. The (001) peak is first observed after 8 hours of annealing at 1500^0C. The upper right of figure 2 shows the integrated intensities of the (100) reflection, after 10 hours of annealing a plateau is reached. The increase of the (100) and (001) intensities indicate cation ordering, the data show that the Zn-Ta ordering process comes to a halt after 8 to 10 hours. The lower graph in figure 2 shows growth of trigonal domains, determined using the Scherrer equation, as a function of time. Clearly the (100) reflection sharpens with time and appears to still sharpen after 24 hours of annealing. The peak sharpening indicates domain size growth for the trigonal superstructure. It appears that the growth of trigonal domains takes place without further Zn/Ta cation ordering. The analysis of the data is still at an early stage however, the data clearly indicate that the in-situ study of cation ordering in $Ba_3ZnTa_2O_9$ is feasible.

In figure 3 three diffraction patterns collected at 1500^{0}C are compared at different annealing times. The peak shape becomes very complex for prolonged heating and Rietveld refinements show that phase separation occurs. The peaks are well fitted using a model comprising two BZT phases with different degrees of cation ordering and different unit cell constants and peak widths. Results of the refinement of ambient temperature data (table 1) recorded post annealing shows the major phase refines as fully ordered. Cation vacancies were not considered in this model.

Table 1: Refined parameters (RT) for a two-phase model of 24 h /1500 ^{0}C annealed BZT. (A fully disordered phase has occupany factors of 0.66 and 0.33 for Ta and Zn respectively on the 2d and 1b sites.)

				cation occupancies			
	wt %	a (Å)	c (Å)	Ta (2d)	Zn (2d)	Ta (1b)	Zn (1b)
Phase 1	56(1)	5.7844(1)	7.1074(3)	1.00(1)	0.00(1)	-0.01(3)	1.01(3)
Phase 2	44(1)	5.7917(8)	7.0854(2)	0.82(3)	0.18(3)	0.36(6)	0.64(6)

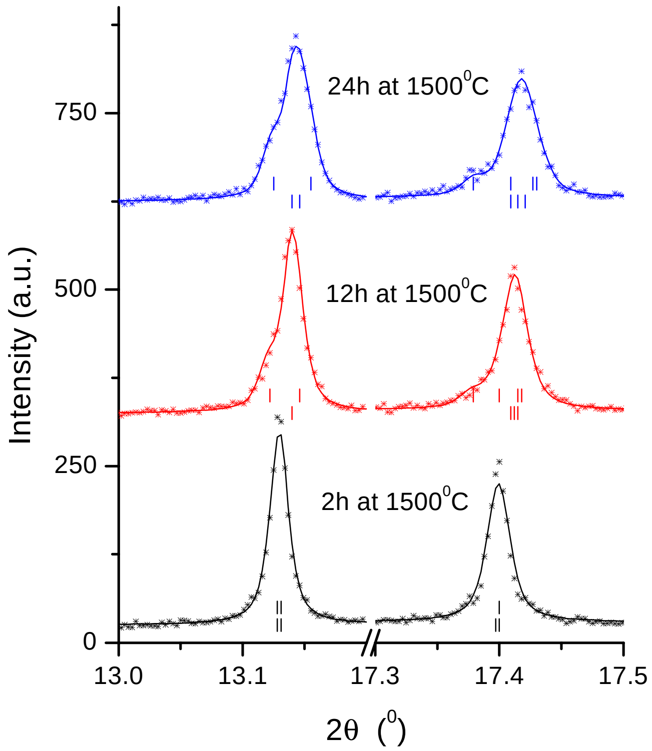

Figure 3: *Phase separation in $Ba_3ZnTa_2O_9$ as a function of annealing time. The solid lines are best fits from Rietveld refinements, the vertical tick marks indicate Bragg positions*

Future

The current data indicate a complex relationship between the extent of cation order within a domain and the rate at which the size of the domain increases. This can be explored by studies with improved time resolution and intensity. The installation of the powder diffractometer on an insertion device will allow the use of much harder X-ray radiation, thus decreasing the X-ray absorption by the Pt capillary as well as the sample. We plan therefore to continue in-situ cation ordering experiments on ID31.

Reference

1. furnace designed and constructed by M. Olivier Grimaldi, beamline technician for BM16/ID31.