Experiment Report Form

	Experiment title: Induced microstrain on ferroelectric perovskite for properties modification	**Experiment number**: MA-3957
Beamline: ID22	**Date of experiment**: from: 27/07/2018 to: 30/07/2018	**Date of report**: 19/01/2020
Shifts: 9	**Local contact(s):** Mauro Coduri	*Received at ESRF:*

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Scientific background:

Ferroelectric and relaxor perovskites are and have been studied thank to their wide technological applications. Much attention has been paid on $BaTiO_3$ and its solid solutions which are environmental friendly ferroelectrics being lead-free materials. In particular the solid solution of $BaTiO_3$ with other $BaMIVO_3$ (M = Sn, Zr, Hf, Ce) perovskite shows interesting properties as an almost continuous variation of the ferroelectric behaviour with composition, from conventional ferroelectric, via diffuse ferroelectric transition to a clear relaxor state and further to dipolar glass behaviour. Many studies have been performed in order to find an explanation on the origin of this variation. Among the solid solutions above reported, $BaTi_{1-x}Ce_xO_3$ (BTC) has been deeply investigated by our group. BTC system presents many similarities with $BaTi_{1-x}Zr_xO_3$, but the large size of cerium (rTi=0.605Å and rCe=0.87Å) has made this case very interesting.
By our studies [1] [2], in BTC this difference in the ionic radius creates a great microstrain, which increases as a function of the doping. This is reflected in high RMS microstrain values and the high dislocation density, detected by TEM analysis. The polar behaviour variation seems then deeply link to the level of the microstrain to which the structure is exposed.
Another demonstration comes from the investigation of BTCs presenting nano grain size [3]. As well known, nano ferroelectric perovskites show, under a certain critical size, the so called 'size effect' which consists in the disappearance of ferroelectricity [5]. Once again, the strain seems to play an important role. In these samples indeed the reduced size and the high cerium amount produce a microstrain which is so high that seems to inhibit the ferroelectric properties. Reported studies have been then clarified the effect of the strain induced by doping and by doping coupled with reduced grain size. These previous results underline how microstrain could be a crucial factor in the material property modification. In this light, it is then important to study and explore the

effect of the strain on this type of oxide. Indeed, the strain manipulation, for example mechanically induced, could be a new way to modify the material properties.

Experimental:

For this investigation we selected compositions as follow: pure BaTiO3 and BaTi1-xCexO3 with *x*=0.02, 0.05, 0.1. The compositions of the BTC solid solution correspond to a different polar behaviours [1]: conventional ferroelectric (*xCe*=0.02 and 0.05) and diffuse phase transition (*xCe*=0.1). BaTiO3, whereas, shows a conventional ferroelectric behaviour. Samples were prepared by solid state reactions. This method was indeed proved to be suitable also in BTC preparation, previous analysis has demonstrated the right incorporation of cerium at the titanium site. The 4 samples obtained (1 pure BaTiO3 and 3 BTCs) was then treated to induce a "mechanical" microstrain. Samples were heated at high temperature (1200 K and 1000 K) and quenched in water. Heating temperatures were chosen dependently to the ceramic fragility and avoiding cracks.

Data collection was performed at different temperatures using a Cryostream (between 100 and 450K, 4 or 5 temperature for each sample). Lambda was set at 0.35455 (Å), data was collected through a multianalyser detector. For two samples also total scattering data was collected in situ in order to evaluate the microstrain effect on the local structure.

Results and Discussion:

Table 1, 2, 3 and 4 report results on phase stability of stressed and no stressed BT and BTC.

Table 1. Phase stability of stressed BaTiO3 (heated at 1000K and 2000K and then quenched) and no stressed.

BaTiCeO3	Stressed BT 1000 K	Stressed BT 12000 K	BT
150 K	Rhombodral	Rhombodral	Rhombodral
270 K	Orthorhombic	Orthorhombic	Orthorhombic
350 K	Tetragonal	Tetragonal	Tetragonal
450 K	Cubic	Cubic	Cubic

Table 2. Phase stability of stressed BaTi0.98Ce0.02O3 (heated at 1000K and 2000K and then quenched) and no stressed.

BaTi0.98Ce0.02O3	Stressed BTC 1000 K	Stressed BTC 12000 K	BTC [1]
150 K	Rhombodral	Rhombodral	Rhombodral
270 K	Rhombodral - Ortorhombic	Rhombodral - Ortorhombic	Rhombodral - Ortorhombic
350 K	Tetragonal	Tetragonal	Tetragonal
450 K	Cubic	Cubic	Cubic

Table 3. Phase stability of stressed BaTi0.95Ce0.05O3 (heated at 1000K and 2000K and then quenched) and no stressed.

BaTi0.95Ce0.05O3	Stressed BTC 1000 K	Stressed BTC 12000 K	BTC [1]
200 K	Rhombohedral	Rhombohedral	Rhombohedral
300 K	Rhombodral - Ortorhombic	Rhombodral - Ortorhombic	Rhombodral - Ortorhombic
350 K	Ortorhombic - Tetragonal	Ortorhombic - Tetragonal	Ortorhombic - Tetragonal
380 K	Cubic	Cubic	Cubic
420 K	Cubic	Cubic	Cubic

Table 4. Phase stability of stressed BaTi0.90Ce0.10O3 (heated at 1000K and 2000K and then quenched) and no stressed.

BaTi0.90Ce0.10O3	Stressed BTC 1000 K	Stressed BTC 12000 K	BTC [1]
100 K	Rhomboedral	Rhomboedral	Rhomboedral
200 K	Rhomboedral	Rhomboedral	Rhomboedral
300 K	Rhomboedral	Rhomboedral	Rhomboedral
400 K	Cubic	Cubic	Cubic

Figure 1 and 2 show two examples of peak evolution as a function of the temperature for BaTiO3 and BaTi0.90Ce0.10O3. The visual inspection confirms the symmetry determined by Rietveld refinements (reported in Tables 1-4), according to the best agreement between calculated and observed profile in terms of Rietveld goodness-of-fit parameter R$_{wp}$.

Comparing obtained results with those of non stressed pure BaTiO3 and BTC, it is possible to notice no differences on phase stability.
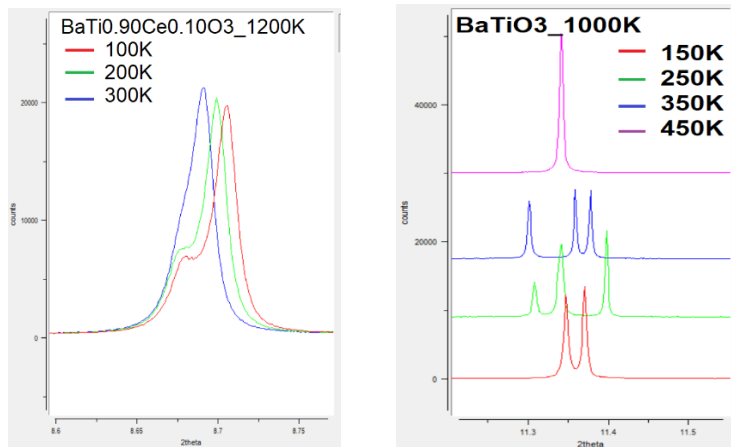
Figure 1. Left panel. Comparison of peak (111) at 100, 200 and 300 K for the BaTi0.90Ce0.10O3. The split clearly visible at 100 and 200 K proves the stability of the rhombohedral phase as well as the shoulder at 300K.

Figure 2. Right panel. Comparison of peak (211) at 150, 250, 350 and 450 K for the BaTiO3. The evolution of the peak is a clear signal of the phase transitions occurring as a function of the temperature. At 150 K rhombohedral phase is stable, orthorhombic at 250 K, tetragonal at 350 and cubic at 450 K.

Unfortunately, the stress originated by quenching seems not sufficient to modify the stability field of the phases and therefore the ferroelectric properties of the material.

Indeed, as shown in Figure 3 and 4 no differences in the peak broadening is observable between stressed and no stressed samples, therefore no modification of the RMS microstrain seems to occurs due to the quenching process. As well as the average structure, also local structure is not affected by the quenching treatment.
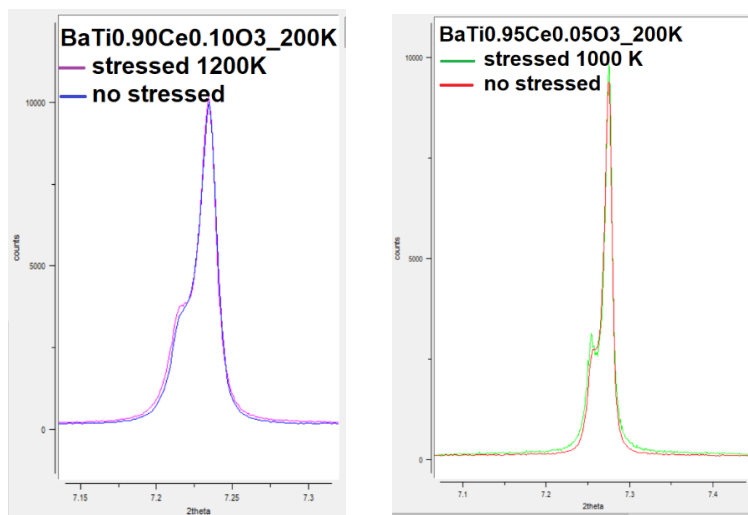

Figure 4. Left panel. Comparison of peak (111) at 200 K for the stressed and no stressed BaTi0.90Ce0.10O3. Peak broadening appears the same for both samples. Data are re-scaled to obtain a fair comparison.

Figure 5. Left panel. Comparison of peak (111) at 200 K for the stressed and no stressed BaTi0.95Ce0.05O3. Peak broadening appears the same for both samples. Data are re-scaled to obtain a fair comparison.

Conclusion:

Results show that the used method did not succeed to increase the stress of BTC samples and consequently we were not able to change the property of the material. Due to the subtle phase transitions occurring in this type of material, it was not possible to check them before synchrotron data collection. Despite we were not able to manipulate the microstrain, we can not exclude that the eventual manipulation of the microstrain can effectively change the ferroelectric properties of the material.

Bibliography

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[3] G. Confalonieri, V. Buscaglia, G. Canu, M.T. Buscaglia, M. Dapiaggi, J Synchrotron Radiat, 26 (2019) 1280-1287.