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| | Experiment title: Exploring the competition of antiferrodistorsive and polar instabilities in Ba_{1-x}Eu_xTiO₃ system using EXAFS | Experiment number: CH-5039 |
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Report:

Combining the polar displacements and octahedra tilting of the ferroelectric BaTiO₃ and magnetoelectric EuTiO₃, the Ba_{1-x}Eu_xTiO_{3-δ} (BETO) solid solution displays very interesting physical properties, as recently shown in Ref. [1].

In experiment CH4799@ID22, we measured accurately the structure of BETO at long, medium, and short length scales, as a function of both temperature and composition, by means of high resolution powder diffraction measurements coupled with the real-space Pair Distribution Function (PDF) analysis.

The present experiment aimed to investigate the local structure of BaTiO₃ doped with Eu²⁺ in order to map the structural evolution as a function of dopant concentration and temperature, by performing EXAFS measurements at the Ba-K and Eu-K edges. These diffraction/absorption results supplied an accurate structural picture of the Ba_{1-x}Eu_xTiO_{3-δ} solid solutions.

Samples

$\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_{3-\delta}$ ($x = 0.3, 0.5, 0.7, 0.8, 0.9, 1.0$) was prepared using a Pechini method followed by annealing at 1273 K and sintering at 1473 K under reducing conditions as described in Ref. [1].

Data collection strategy

The EXAFS measurements of perovskite titanates $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_{3-\delta}$ (plus commercial BaTiO_3) were carried out in transmission geometry at both the Eu *K*-edge (48519 eV) and Ba *K*-edge (37441 eV) at the European Synchrotron Radiation Facility (ESRF) on beamline BM23, using a double Si(511) crystal monochromator. The measurements were performed at room temperature, 90 K, and 10 K.

The polycrystalline powders were dispersed in a cellulose matrix and pressed into pellets, adjusting the jump at the absorption edge. Each dataset consisted of five averaged scans, thus allowing to increase the signal to noise ratio and check reproducibility. EXAFS data were reduced using the Demeter package and the fits of the q^2 weighted EXAFS data were carried out in r space using theoretical functions from the FEFF9 code. High-quality q -space data were obtained up to 16 \AA^{-1} .

Results:

To include the first and further neighbours in the data, at the Eu (or Ba) *K*-edge (full fit range: $1.42\text{--}3.98 \text{ \AA}$), we have compared the results obtained from different fit models.

- The first model is the polar rhombohedral $R3m$ model [2] with a Eu-O (Ba-O) first shell bimodal distribution $N = 9+3$ (A1, A2), two Eu-Ti (Ba-Ti) coordination subshells, each with $N = 4$ (B1, B2) and the Eu-Eu (Ba-Ba) third shell with $N = 6$ (C).

- The second model tested assumes local tetragonal symmetry and accounts for coexistence of two tetragonal distortions of the perovskite cubic structure: the polar $P4mm$ [2] and the antiferrodistortive $I4/mcm$ [3]. Both models feature one single Eu-Ti (Ba-Ti) second shell peak with $N = 8$ (B) and the Eu-Eu (Ba-Ba) third shell with $N = 6$ (C).

The Eu/Ba environment of the two tetragonal distortions differ only in the 1st shell Eu/Ba-O distance distribution (A), this being divided into two subshells with coordination numbers $N = 8 + 4$ for $P4mm$ and three subshells with $N = 4 + 4 + 4$ for $I4/mcm$. Unfortunately, the r resolution reached in the experiment does not allow to distinguish between the $P4mm$ and $I4/mcm$ structural models despite the high q range (up to 16 \AA^{-1} at the Eu-K edge) [4]. As a consequence, to account for the tetragonal models we fitted the data using only two Eu/Ba-O subshells.

Rebus sic stantibus, the main difference between the tetragonal and rhombohedral models used for the fits lies in the Eu/Ba-Ti distance distribution of shell (B).

Figure 1 shows, as an example, the fits of the sample EuTiO_3 collected at 90 K at the Eu-*K* edge. The *R*-factors of the rhombohedral and tetragonal fits are 0.022 and 0.034, respectively, showing that a

rhombohedral local distortion gives the best fit. The fitted parameters for the rhombohedral model are reported in Table 1.

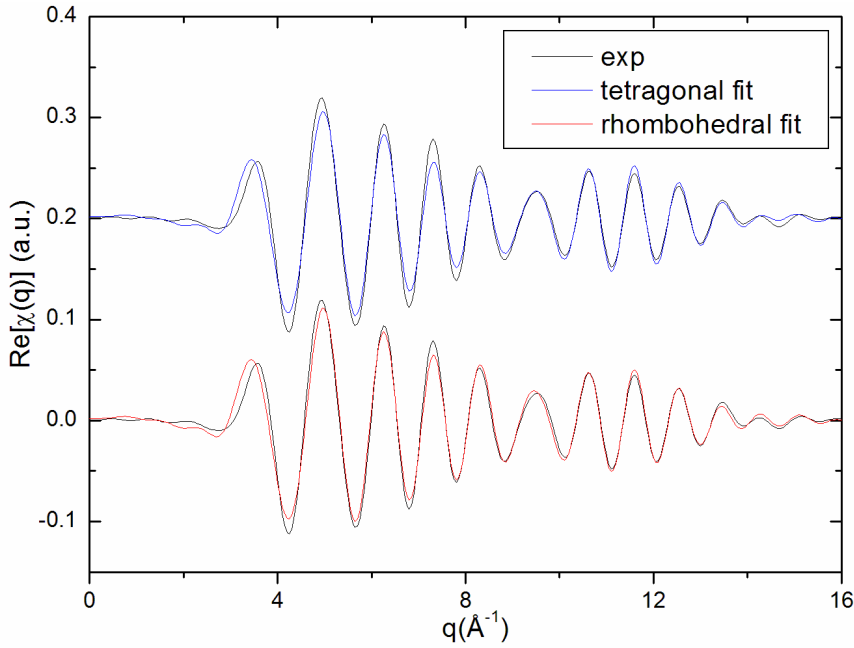


Figure 1. EuTiO₃ sample at 90 K at the Eu-K edge. Comparison between the Back Fourier transform best-fit curves obtained from a tetragonal model (upper curves) and a rhombohedral one (lower curves). The two fit curves have been shifted for clarity.

Table 1. Eu-K edge of EuTiO₃ at 90 K. Fitted parameters for the rhombohedral model. Model includes two Eu-O subshells (A1+A2), two Eu-Ti subshells (B1+B2) and a single Eu-Eu distance (shell C).

| EuTiO ₃ 90 K | Eu-O(2) (A1) | Eu-O(1) (A2) | Eu-Ti(2) (B1) | Eu-Ti(1) (B2) | Eu-Eu (C) |
|-------------------------|-----------------|-----------------|------------------|------------------|--------------|
| N | 3 | 9 | 4 | 4 | 6 |
| $r(\text{Å})$ | 2.638(5) | 2.744(5) | 3.326(5) | 3.427(5) | 3.883(5) |
| $\sigma^2(\text{Å}^2)$ | 0.01044(2) | 0.01044(2) | 0.00064(3) | 0.00064(3) | 0.00384(2) |

Further data analysis details

The initial fitting parameters were the Debye-Waller factors σ^2 , the interatomic bond lengths R , the E_0 shift in the edge energy with respect to the theoretical value and the amplitude reduction factor S_0^2 from multi-electron effects, generally between 0.8 and 1.0. At low T , the lattice is well ordered and a value $S_0^2 = 0.95$ was determined from the average of several fits of scans at 90 K on the reference titanate composition and fixed. The E_0 shift was also constrained to a single value for all the shells included in the fits. The coordination numbers were fixed to the previously reported values for the first shell or subshells and to the crystallographic values for all the other shells and paths employed in the fits [2]. In this way, the experimental uncertainty on the Debye-Waller factors σ^2 was reduced.

References

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- [4] The PDF results will help to distinguish between the two tetragonal models.