

**Experiment title:**

Local structure of acceptor-doped barium zirconates

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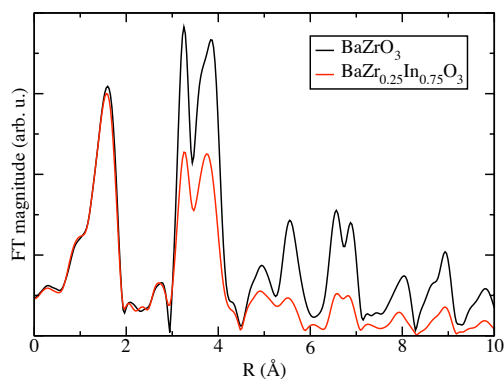
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We have performed EXAFS measurements on Y, Zr and In K-edges (17, 18, and 28 keV, respectively) on ceramic powders of In:BaZrO₃ and Y:BaZrO₃ with different doping degrees (from 2 to 75% in the case of In-doping, and from 1 to 15% in the case of Y-doping) and both in the hydrated and dry states. The samples were pressed in self-sustaining pellets with boron nitride, and all the spectra were taken at 25K in transmission mode. For comparison, also undoped BaZrO₃ and brownmillerite-structured Ba₂In₂O₅ were measured. The monochromator was equipped with two Si(311) crystals and the storage ring was filled in multibunch mode. The data were extracted and modeled with Viper, using scattering amplitudes and phases generated with FEFF8.4.



While in the case of Y K-edge the presence of the subsequent Zr K-edge limited the useful data range to about 14 Å⁻¹, in the case of both In and especially Zr K-edges the very high signal to noise ratio allowed us to achieve excellent data quality beyond 18 Å⁻¹. Thanks to the many colinear paths in the cubic perovskite structure, the signals are very sharp and defined also in R-space, where one can highlight correlations up to 10 Å over the whole composition series BaZrO₃:Ba₂In₂O₅. In general, we did not observe local deviations from the cubic perovskite structure on Y and Zr environments: the reluctance to release the size mismatch strain through octahedral tilting could be the reason for the low Y³⁺ solubility limit in

zirconates. In the analysis of the In K-edge, very high-k data were decisive to resolve two different In-Ba distances (3.57 and 3.73) arising in In-doped samples above the 20% limit.

The outcome of the preliminary analysis is in agreement with the expected results: the ionic radius of In^{3+} is shown to be strongly dependent on the host matrix, while Zr^{4+} maintains more or less always the same size. As what concerns Y^{3+} , we have not evidenced any Y-Y segregation in zirconates up to the 15% doping, nor any sign of distortion of the YO_6 first shell octahedron, as we had for $\text{Y}:\text{BaCeO}_3$. The distortion in the dopant environment are then attributed to the peculiar interaction with an orthorhombic matrix.

The normal and dry forms of $\text{Ba}_2\text{In}_2\text{O}_5$ were compared, to verify claims of a possible structural water intercalation in the lattice. Since the In K-edge spectra for the two compounds were found to be the same, some other mechanism must be held responsible for the water uptake.

As we had already observed in $\text{Gd}:\text{BaCeO}_3$ and $\text{Y}:\text{BaCeO}_3$, the presence of protonic defects significantly increases the overall disorder in the lattice. This applies to both the Zr and the dopant environment. Since the measurements were taken at 25K, we argue that the disorder is positional in nature, rather than vibrational.

