

Electronic and local structure of $\text{CaBaCo}_{4-x}\text{M}_x\text{O}_7$ (M= Fe, Zn) revealed by X-ray absorption spectroscopy.

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Magnetoelectric materials attract a great interest due to their wide applications in spintronics. Most of them are based on transition metal oxides with polar structures showing magnetic frustration. This is the case for $\text{CaBaCo}_4\text{O}_7$, which is ferrimagnetic below $T_c=64\text{K}$ and also shows a linear magnetoelectric coupling below this temperature [1]. *Ab-initio* calculations proved that the material is pyroelectric, and the large pyroelectric currents observed were ascribed to exchange-striction effects. It adopts an orthorhombic unit cell (space group $Pbn2_1$). The crystallographic structure of $\text{CaBaCo}_4\text{O}_7$ consists of a stacking of alternating triangular (T) and kagomé (K) layers of CoO_4 tetrahedra along the *c* axis. There are four different crystallographic sites for Co: Co1 stays at the T layer, while Co2, Co3, and Co4 are in the K layers [1] and ferrimagnetism appears because the magnetic moments at the Co1 and Co4 sites are larger than those at the Co2 and Co3 sites. The stoichiometric formula corresponds to $\text{CaBaCo}_2^{2+}\text{Co}_2^{3+}\text{O}_7$ and therefore the nominal oxidation state for Co is 2.5+. Furthermore, the substitution of Co with another transition metal may be useful to increase the transition temperature and magnetic coupling.

To fully characterize the tetrahedral distortion on $\text{CaBaCo}_4\text{O}_7$ and the effects of doping with Fe and Zn on Co sublattice, we performed XAS measurements as a function of temperature on Co, Fe and Zn K edges at BM23 at the ESRF (Grenoble, France). $\text{CaBaCo}_{4-x}\text{Fe}_x\text{O}_7$ ($x=0.5, 1, 1.5, 2$) and $\text{CaBaCo}_{4-x-y}\text{Fe}_x\text{Zn}_y\text{O}_7$ ($x=0, 1, 2$ and $y=1$) samples were synthesized by solid state chemistry reactions and the resulting powders were pressed into pellets mixed with cellulose for optimized XAS transmission measurements.

From XANES, we conclude that a mixed-valence oxidation state is found for Co atom in all the studied $\text{CaBaCo}_{4-x}\text{M}_x\text{O}_7$ (M=Fe or Zn) samples, with a combination of Co^{2+} and Co^{3+} in their formal ionic species. Fe and Zn are incorporated as Fe^{3+} and Zn^{2+} in the whole series. The analysis of EXAFS measurements show that the largest Debye-Waller factors are found for the intermediate $\text{Co}^{3+/2+}$ valences, indicating either a larger distortion or the occupation of different crystallographic sites (disordered distribution).

EXAFS measurements as a function of temperature show the presence of a local disorder highly localized in the CoO_4 tetrahedra that remains unchanged for all the samples except for the parent $\text{CaBaCo}_4\text{O}_7$ compound. A small but appreciable increase in the local distortion of the CoO_4 tetrahedra is observed at the magneto-electric transition temperature for this sample. This reveals the occurrence of a local magneto-elastic coupling at the ferrimagnetic phase that may be related to the observation of the pyroelectric effect in this composition.

[1] V. Caignaert et al., Phys. Rev. B. **81**, 094417 (2010).

The authors acknowledge the ESRF for granting beamtime and the financial support of the Spanish Ministerio de Economía y Competitividad, Project MAT2015-68760-C2-1-P.