

PEROVSKITES. FROM PIGMENTS TO MULTIFERROICS, TO THE DISCOVERY OF THE LOCKED-TILT PEROVSKITES

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Superconductors, non-toxic inorganic pigments, sensitizers in dye-sensitized solar cells (DSSCs), semiconductors, and multiferroics are just a few examples of the broad range of uses for which ceramics with perovskite structure are employed. In its aristotype form the ABO_3 perovskite structure is cubic (s.g. $Pm-3m$) with A cations located at the center of dodecahedral sites defined by a three-dimensional array of corner-sharing BO_6 octahedra. This polyhedral arrangement makes the perovskite structure extremely flexible. Indeed, due to changes in the chemical nature of A and B cations as well as on temperature and pressure conditions, the ideal cubic symmetry is often lowered, and the resulting structure is described by a combination of tilts and distortion of the BO_6 octahedra (Mitchell, 2002).

In this contribution, a series of case studies on the interplay among structural characterizations, coloration mechanisms, and technological prospects of ceramics with perovskite structure are outlined. Starting from the Cr-doped (Y,REE)AlO₃ (YAP) case, *i.e.* the only system manufactured at the industrial scale and currently used as ceramic red pigment (Ardit *et al.*, 2016), the first case study (*i.e.*, a X-ray powder diffraction and electronic absorption spectroscopy combined investigation) is focused on the effects due to the Al \leftrightarrow Cr substitution at the B octahedral site of the YAP structure, which cause a degree of structural relaxation around Cr³⁺ that, whether compared with other Cr-bearing structures, is relatively low (Cruciani *et al.*, 2009). The concept of crystal field stabilization energy CFSE, closely related with that of structural relaxation (Burns, 1993), will lead to the second case study where *in situ* high-pressure synchrotron XRD measurements coupled with *ab initio* simulations of the electronic population of the orthorhombic NdCrO₃ perovskite are compared with the compressional feature of NdGaO₃ (high-tech ceramics applied as interconnector of solid oxide fuel cells (SOFC), substrate for high- T_c superconductors (HTSC), colossal magnetoresistive (CMR) film epitaxy, and so on). The different electronic configuration of octahedrally coordinated Cr³⁺ and Ga³⁺ ions that leads to a redistribution of electrons at the $3d$ orbitals for Cr³⁺ allows the CFSE at octahedral sites to act as vehicle of octahedral softening in NdCrO₃ or it turns octahedra into rigid units when CFSE is null as in NdGaO₃. The third (and last) case study deals with the first finding of a perovskite characterized by absence of changes in the octahedral tilting and a volume reduction with pressure exclusively controlled by an isotropic polyhedral compression (Ardit *et al.*, 2017). A synchrotron structural investigation at high-pressure sets YAl_{0.25}Cr_{0.75}O₃ as the prototype of the so-called *locked-tilt* perovskites. Besides to reveal a new P - T thermodynamic scenario in the world of perovskite compounds, such a freezing of the octahedral rotations offers a new (and antithetic, keeping in mind that oxygen rotations are strongly coupled to the functional properties of perovskite compounds) perspective on the research of new functional materials (*e.g.*, ferroelectrics and multiferroics). For example, the mutual interaction between layers of octahedrally tilted perovskites subjected to an external perturbation can be easily tuned whether one of the layers is a *locked-tilt* perovskite.

REFERENCES

- Ardit, M., Cruciani, G., Dondi, M., Zanelli, C. (2016): Pigments based on perovskite. *In*: "Perovskites and related mixed oxides: Concepts and applications", P. Granger, V. Parvulescu, S. Kaliaguine, W. Prellier, eds. Wiley-VCH, 259-288.
- Ardit, M., Dondi, M., Cruciani, G. (2017): Locked octahedral tilting in orthorhombic perovskites: At the boundary of the general rule predicting phase transitions. *Phys. Rev. B*, **95**, 024110.
- Burns, R.G. (1993): Mineralogical application of crystal field theory. 2nd Ed. Cambridge University Press, 551 p.
- Cruciani, G., Ardit, M., Dondi, M., Matteucci, F., Blosi, M., Dalconi, M.C., Albonetti, S. (2009): Structural relaxation around Cr³⁺ in YAlO₃-YCrO₃ perovskites from electron absorption spectra. *J. Phys. Chem. A*, **113**, 13772-13778.
- Mitchell, R.H. (2002): Perovskites: Modern and Ancient. Almaz Press., Thunder Bay, Ontario, 316 p.