Crystal structure, local atomic order and metastable phases of zirconia-based ceramics for Solid-Oxide Fuel Cells

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ZrO_2-based ceramics are widely used because of their high ionic conductivity at high temperatures and their excellent mechanical properties. For example, they are usually employed as solid electrolytes in Solid-Oxide Fuel Cells (SOFCs). Differently, ZrO_2-CeO_2 solid solutions are used as SOFC anodes and in three-way catalysis due to their excellent oxygen-storage capability. Pure ZrO_2 exhibits 3 polymorphs of monoclinic (m), tetragonal (t) and cubic (c) symmetries. The m phase is stable at room temperature and transforms to the t one at 1170°C during heating, while this phase transforms to the c one at 2370°C. The cubic phase can be fully stabilized at room temperature by doping with other oxides (Y_2O_3, CaO, etc.). The t phase can not be fully stabilized, but it can be retained, in a metastable condition, in nanopowders and fine-grained ceramics. The high-temperature phases are the relevant ones for applications, since the m phase has poor properties.

In the last years, our research groups have investigated the crystallographic features of a number of ZrO_2-based systems (ZrO_2-CeO_2, ZrO_2-CaO, ZrO_2-Y_2O_3 and ZrO_2-Sc_2O_3). We mainly focused on the retention of metastable tetragonal forms in nanocrystalline compositionally homogeneous zirconia-based solid solutions. These materials exhibit three tetragonal forms, all belonging to the $P4_2/nmc$ space group. The stable tetragonal form is called the t-form, which is restricted to the solubility limit predicted by the equilibrium phase diagram. There is also a t'-form with a wider solubility, but unstable in comparison with the mixture of the t-form and cubic phase. Finally, the t''-form has an axial ratio c/a of unity, but with the oxygen atoms displaced along the c axis from their ideal sites of the cubic phase (8c sites of the $Fm3m$ space group).

In this presentation, we will review our main investigations on this matter, performed by XPD and XAFS at the LNLS. We will show that the use of a high intensity synchrotron source in XPD experiments allows the detection of small Bragg peaks, which are related to the displacement of oxygen atoms in the tetragonal lattice. By analyzing selected compositions in high-temperature XPD experiments, we investigated the influence of the crystallite size on the phase diagram of these ZrO_2-based systems. It is particularly interesting the ZrO_2-Sc_2O_3 system, which exhibits low-conductivity rhombohedral phases that can be avoided in nanocrystalline powders and fine-grained ceramics. We will also discuss our results regarding the local atomic structure of these materials, which gives a new insight on their disorder in the oxygen sublattice, and the mechanism for the retention of the metastable phases in nanomaterials.

Acknowledgements: This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS), Agencia Nacional de Promoción Científica y Tecnológica (Argentina), CONICET (Argentina), CNPq (Brazil, PROSUL Program), CLAF and CAPES-MinCyT and CNPq-CONICET cooperation agreements between Brazil and Argentina.