X-ray powder diffraction characterization of perovskite oxides prepared by auto-combustion.

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Perovskite oxides ABO_3 and related compounds are a vast and very flexible family of oxides [1]. They are, not only the broadest solid-state chemistry sandbox, but also a huge test-bank for properties, since they are known for a myriad of applications, notably piezoelectrics, superconductors, mixed ionic-electronic conductors, catalysts, etc. Additionally, perovskites play a key role in our current understanding of strongly correlated materials [2].

In the search for the simple and cheap preparation of large amounts of nanostructured perovskite oxides for solid oxide fuel cell applications, we have adapted the gel-combustion method for a rapid one or two-step preparation of a wide variety of perovskite oxides. The auto-combustion methods proceeds with the dissolution of metallic precursors, EDTA (ethylenediaminetetraacetic acid -$C_{10}H_{16}N_2O_8$) and ammonium nitrate (NH_4NO_3) in a 1:1.1:n molar proportion at pH=10 (achieved by addition of NH_4OH). The solvent is evaporated at 120°C until a dry paste is obtained. The paste is heated at 300-350 °C in the same beaker, where NH_4NO_3 fusses and later decomposes, in a controlled combustion that yields the final nanostructured perovskite, when this is the thermodynamically stable phases at the combustion temperature. This was observed for $LaMO_3$ with M=Cr, Mn, Fe, Co and mixed M with V and Cu, $SrMO_{2.5}$ (M=Fe, Co) and ammonium nitrate proportion n=6-10. Alternatively, when the desired phase is not formed in the combustion step, an amorphous precursor could be obtained by reducing n in the initial dissolution. The solid formed for a combustion with lower amounts of NH_4NO_3 (n=3) is later fired in air to yield the desired perovskite, as observed in $(La,Sr,Ba)(Fe,Cu)O_{3-d}$ [3-4]. The phases obtained from the direct combustion procedure, in batches of up to ~10 g in a short time of less than 4 hours, show an unexpected oxygen-reduced form, as confirmed by X-ray diffraction and thermogravimetric analysis. The phases obtained in the two-step procedure show normal oxygen content for air-fired oxides and could be obtained in ~20 g amounts in less than 24 hours. We have also explored the preparation of more complex perovskite phases such as double $Sr_2(Ni/Fe)WO_6$, layered $LnBa_2Cu_3O_{7-d}$ (Ln=lanthanoid) and Ruddlesden-Popper $La_{2-x}Nd_xCuO_4$ perovskites phases for magnetic studies and catalysis with success.

This presentation will describe the preparation method and the X-ray powder diffraction characterization results of some of the mentioned phases, including Rietveld structural analysis and analysis of phase purity.

[1] “Perovskites modern and ancient” By Roger H. Mitchell. Almaz Press, 2002. ISBN 0-9689411-0-9.
[2] “Transition metal compounds” by Daniel I. Khomskii. Cambridge University Press, 2014. ISBN 978-1-107-02017-7.
[3] S. Vázquez, et al. J. Solid State Chem. 228 (2015) 208-213.
[4] S. Vázquez, et al. J. Power Sources 274 (2015) 318-323.