Interstitial Oxygen in Oxy-apatites

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Oxide ion conductors are an important group of materials utilized as electrolytes in solid oxide fuel cell´s (SOFCs), oxygen sensors, etc. Several families of oxide materials are being actively investigated including: i) fluorite-type (f.i. $Y_{0.16}Zr_{0.84}O_{1.92}$ and $Gd_{0.2}Ce_{0.8}O_{1.9}$); ii) perovskite-type (f.i. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$); and iii) oxy-apatite-type (f.i. $La_{9.33}(SiO_4)_6O_2$).

Lanthanide oxy-apatites display very high pure oxide ion conductivity likely due to an interstitial oxygen conduction mechanism instead of the common oxygen vacancy mechanism that operates in fluorite and perovskite oxide ion conductors.

We have used neutron powder diffraction (both constant-wavelength and time-of-flight data) [1,2] to determine the crystal structures of several lanthanum oxy-apatites at room and high temperatures. Some compositions have been analyzed by the Rietveld method including oxygen-stoichiometric materials ($La_{9.33}(SiO_4)_6O_2$, $La_{9.33}(Si_{0.5}Ge_{0.5}O_4)_6O_2$, $La_{9.50}(Ge_{0.916}Al_{0.083}O_4)_6O_2$, $La_8Sr_2(SiO_4)_6O_2$ and $La_8Sr_2(GeO_4)_6O_2$) and oxygen-excess materials ($La_{9.55}(SiO_4)_6O_{2.32}$ and $La_{9.60}(GeO_4)_6O_{2.40}$). The presence of the interstitial oxygen for some compositions will be highlighted including its structural consequences. Finally, the relationship between the interstitial oxygen and the high-oxide ion conductivity properties will be emphasized.

[1] Leon-Reina L., et al., *J. Mater. Chem.,* 2004, **14**, 1142. [2] Leon-Reina L., et al., *J. Mater. Chem.,* 2005, **15**, *submitted*.

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