The flexibility of perovskite Solid Oxide Fuel Cell materials to accommodate oxyanion dopants, and the consequent influence on the structure and conductivity

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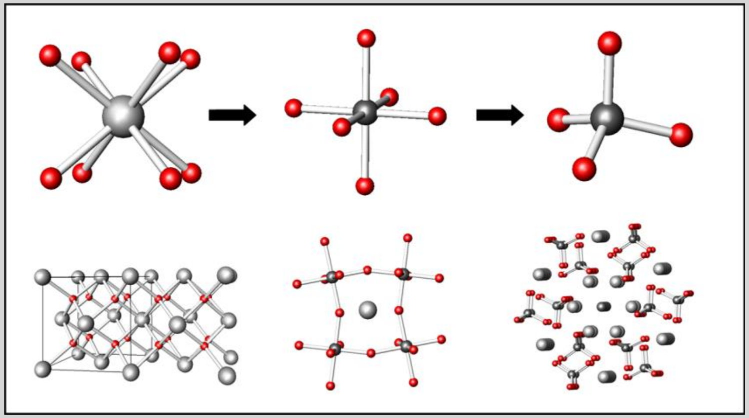


Outline

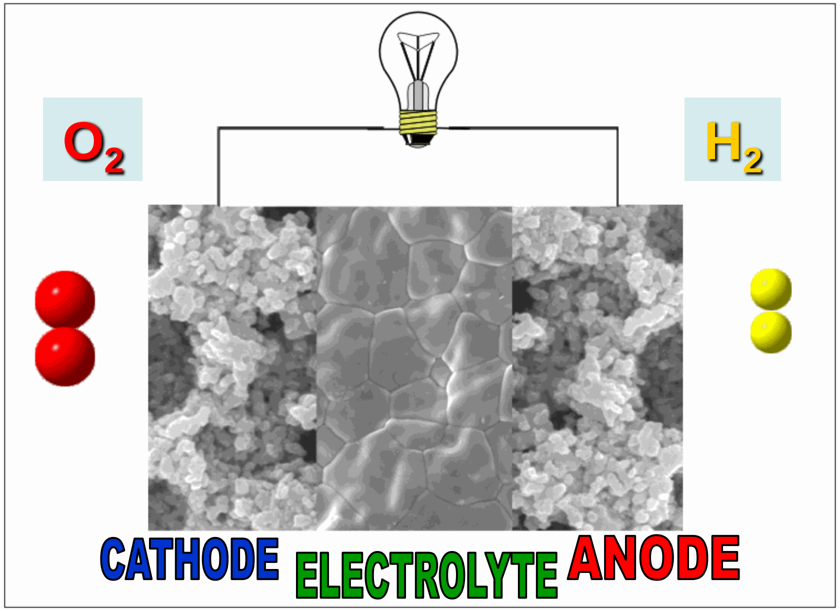
- Introduction: Solid Oxide Fuel Cells, Perovskite structure
- Oxyanion doping in Electrode Materials
- Carbonate – a “hidden” dopant

- Summary

Introduction:-Solid Oxide Fuel Cells

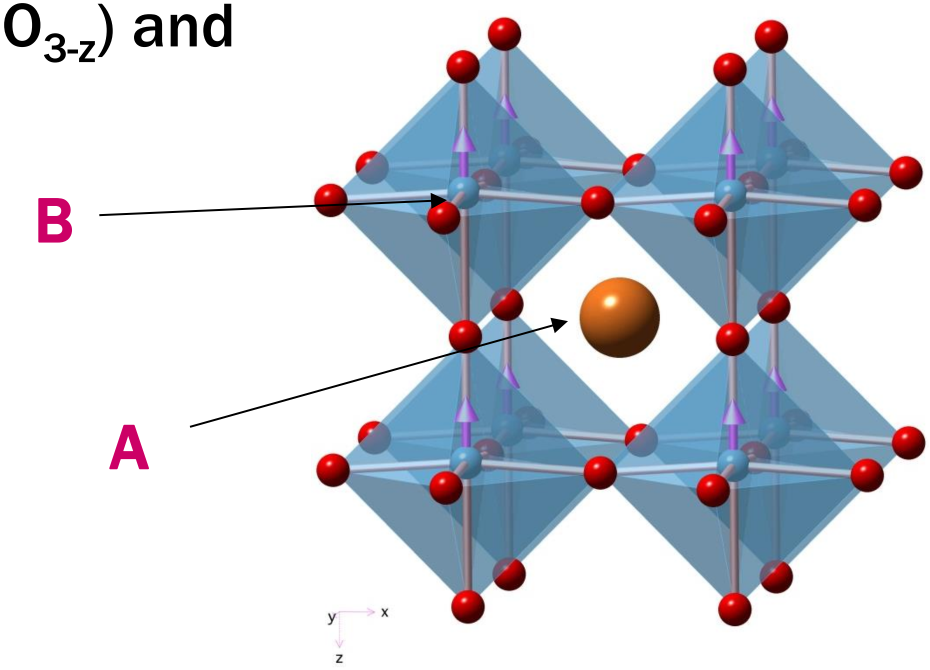
Solid Oxide Fuel Cells: Operate at high temperature (500-1000°C)

High temperature operation allows flexibility in the fuel used (hydrogen or hydrocarbon)



Solid Oxide Fuel Cell cathodes

Cathode: typically a composite of a transition metal containing perovskite (e.g. $La_{1-x}Sr_xMnO_{3-z}$) and the electrolyte.



Perovskite oxides:-

ideal formula: ABO_3

A is a large cation, e.g. Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+} (or other rare earth)

B is a smaller cation, e.g. transition metal

The Perovskite Structure (2)

Traditional doping strategies:- doping with aliovalent cation of similar size

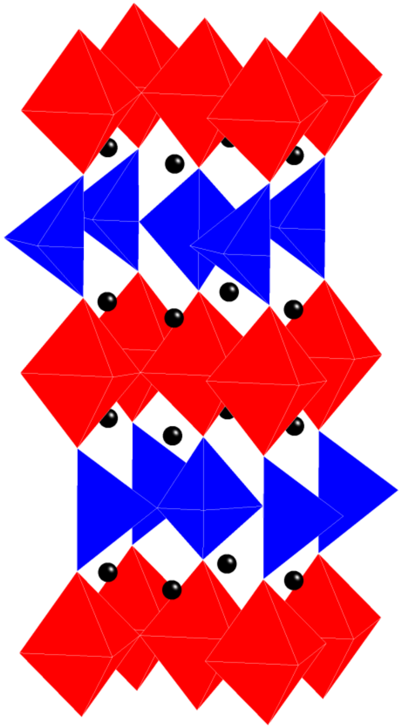
e.g. $La_{1-x}Sr_xMnO_3$

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-z}$

The structure has a ready ability to accommodate oxide ion vacancies

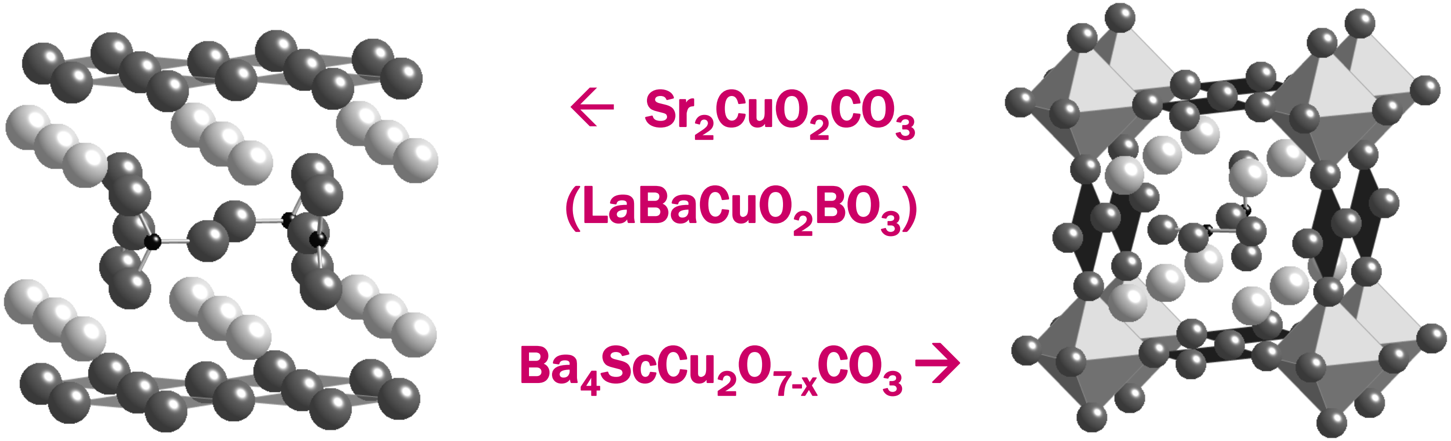
At high vacancy levels (e.g. $SrFeO_{2.5}$) ordering of vacancies can occur → brownmillerite structure

In such cases, ionic conductivity is low



Oxyanions in perovskite cuprate systems

Prior studies of cuprate superconductors showed a great propensity for such materials to accommodate oxyanions (CO_3^{2-}, BO_3^{3-}, SO_4^{2-}, PO_4^{3-}).



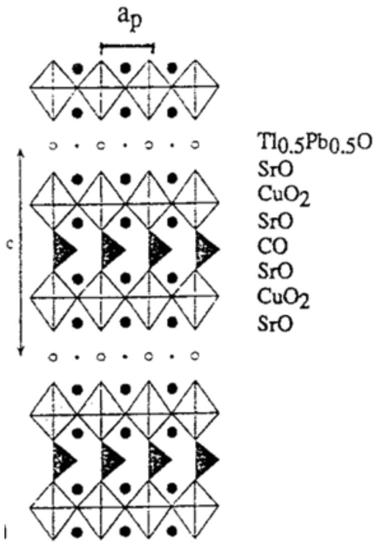
← $Sr_2CuO_2CO_3$

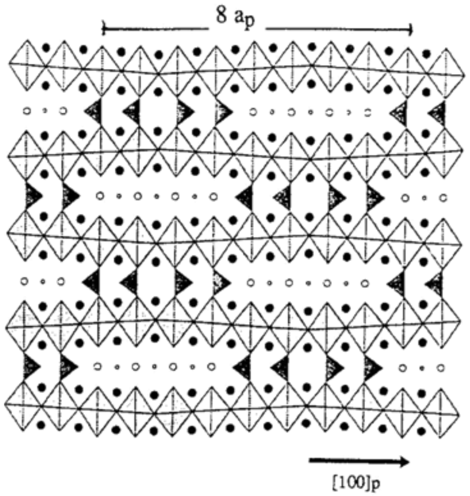
($LaBaCuO_2BO_3$)

$Ba_4ScCu_2O_{7-x}CO_3$ →

(The central cation of the oxyanion occupies the B cation site, with the oxide ions filling 3 or 4 of the 6 available anion sites surrounding the B site).

Wide range of compounds containing intergrowths of $Sr_2CuO_2CO_3$





Maignan et al; Physica C 249 (1995) 220

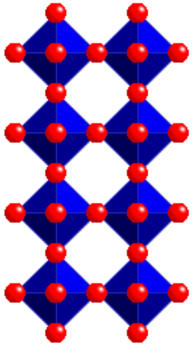
Can SOFC materials accommodate these oxyanions ?

1. Oxyanion doping in SOFC Electrode Materials

$Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-y}$

$Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-y}$ shows high electronic and oxide ion conductivity → applications as SOFC cathodes, oxygen separation membranes

Problem: Long term stability at intermediate (500-800°C) temperatures due to a structural transition to a hexagonal perovskite



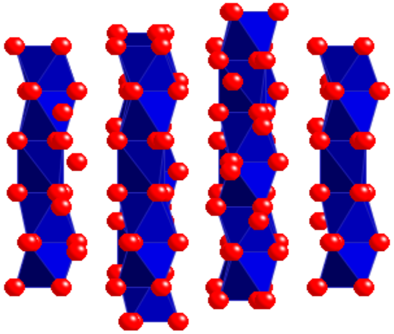
Cubic

Corner Sharing

→

Hexagonal

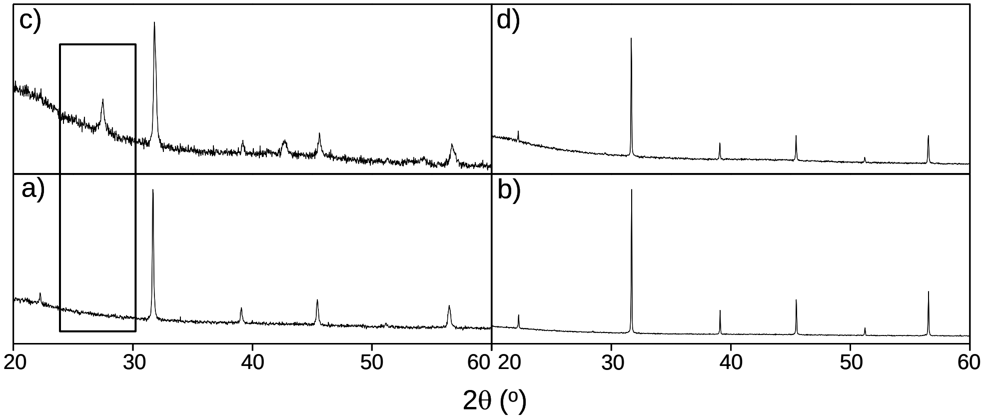
Face Sharing

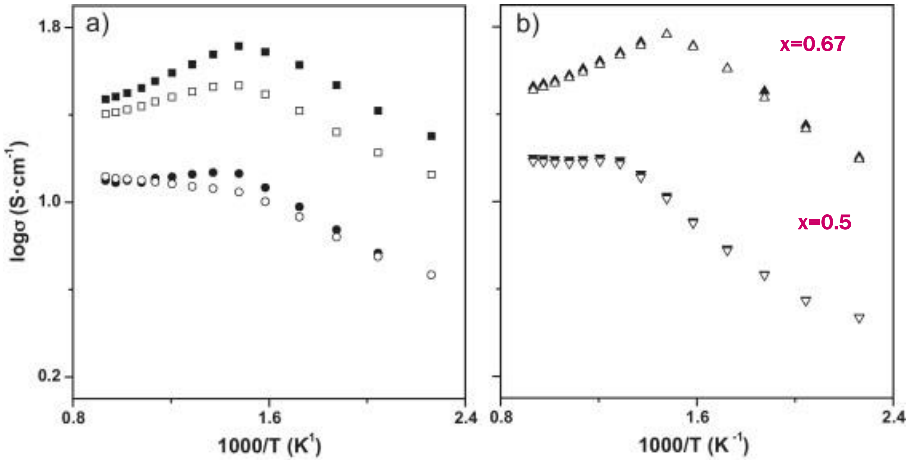


degradation of performance

Effect of Phosphate doping

$Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-y}$: **Introduction of 5% phosphate in place of Co/Fe leads to enhanced long term stability**





(a) no phosphate addition → reduction in conductivity after long term annealing at 750°C

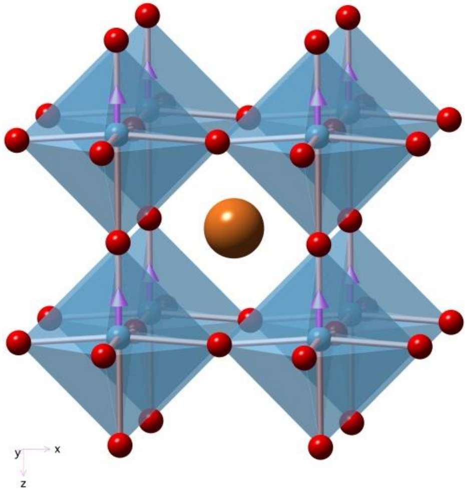
(b) phosphate added → negligible change in conductivity

J. Power Sources 209, 180, 2012

Silicate Doping in Electrode Materials

Silicon (as silica) is commonly considered as a poison for solid oxide fuel cells

e.g. it has been reported to collect at grain boundaries in fluorite (e.g. doped ZrO_2, CeO_2) electrolytes → reduction in conductivity.



Si is known in the perovskite structure,

e.g. $CaSiO_3$, $MgSiO_3$, but these phases

require very high pressures to form

Can we accommodate Si as tetrahedral SiO_4^{4-} ?

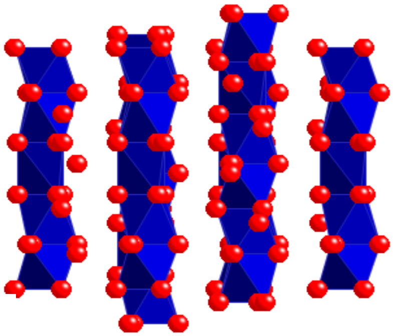
Silicate Doping in Electrode Materials

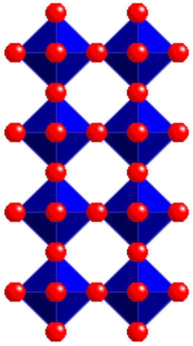
$SrCoO_3$ and $SrMnO_3$ are hexagonal perovskites:- low electronic and ionic conductivity:- unsuitable for SOFC applications

Dope with SiO_4^{4-} → a "cubic" perovskite and a substantial increase in the conductivity

Hexagonal

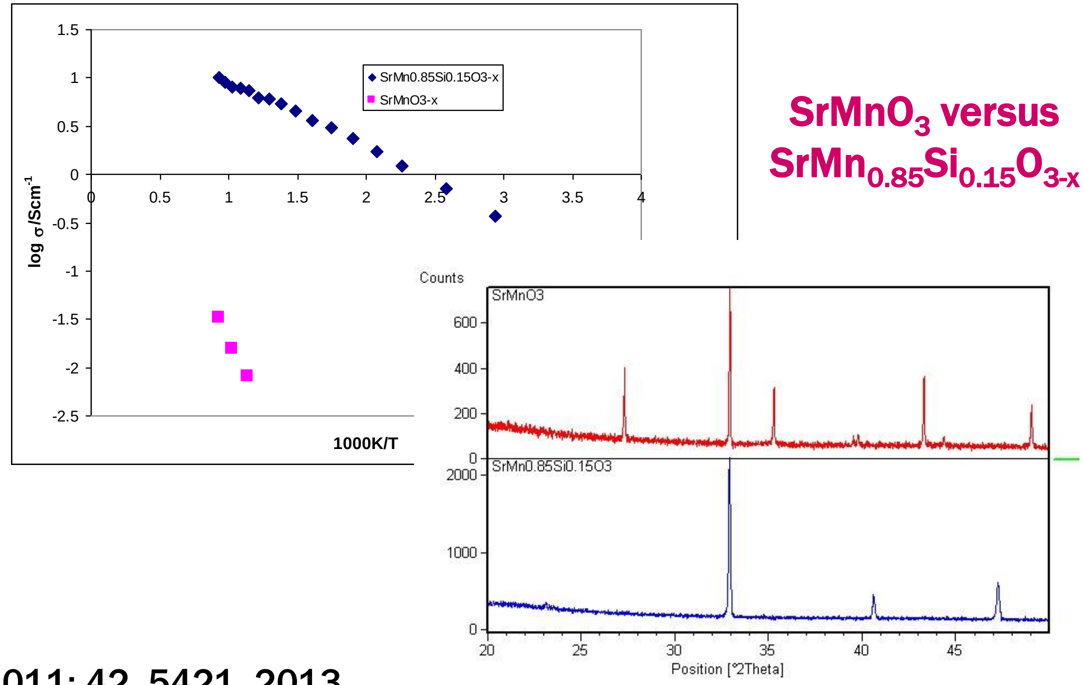
Face Sharing





Cubic

Corner Sharing



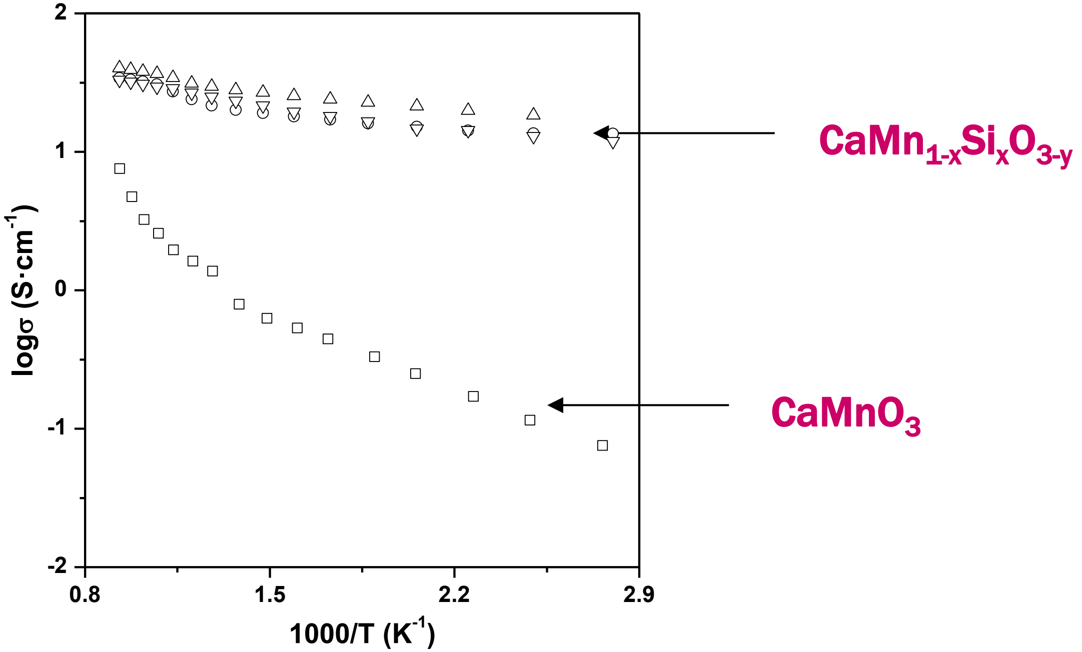
$SrMnO_3$ versus $SrMn_{0.85}Si_{0.15}O_{3-x}$

Dalton Trans 40, 5599, 2011; 42, 5421, 2013

$CaMnO_3$

Similar doping strategies can be employed for other perovskite systems, e.g. $CaMnO_3$ (here no change in cell symmetry on doping)

Low level Silicate, doping leads to enhanced conductivity due to electron doping (creation of O vacancies)



$$SiO_2 + 3Mn_{Mn}^{X} + O_O^{X} \rightarrow Si_{Mn}^{X} + \boxed{2Mn_{Mn}'} + \boxed{V_O^{\bullet\bullet}} + \tfrac{1}{2} O_2 + MnO_2$$

Note: other isovalent dopants (e.g. Ti) do not give an enhancement in conductivity

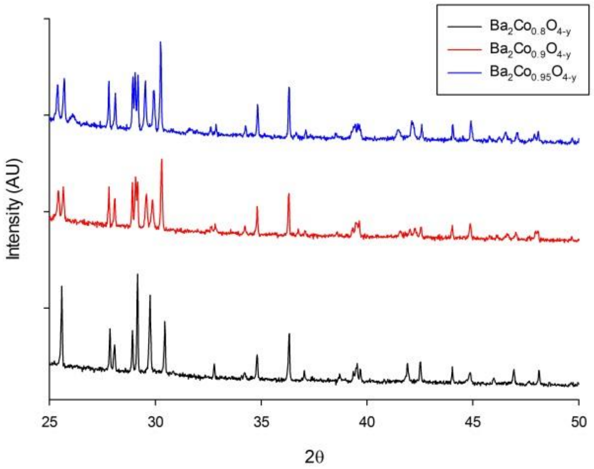
2. Carbonate: a “hidden” dopant ?

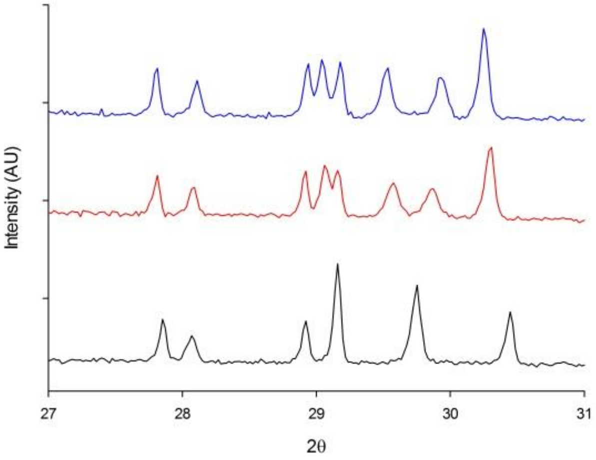
Perovskites containing large levels of carbonate (e.g. $Sr_2CuO_2CO_3$ (50% carbonate on B cation site) are known, but with growing focus on low temperature (e.g. sol gel) synthesis routes, do we have low levels of carbonate present, that may be affecting performance ?

Fe/Co Containing Systems: Ba_2MO_4 (M=Fe, Co)

Preparation of Ba_2MO_4 (M=Fe, Co) tends to lead to impure samples

Lowering the Fe, Co content (i.e. $Ba_2M_{1-x}O_y$) → improved purity, plus significant changes in cell parameters

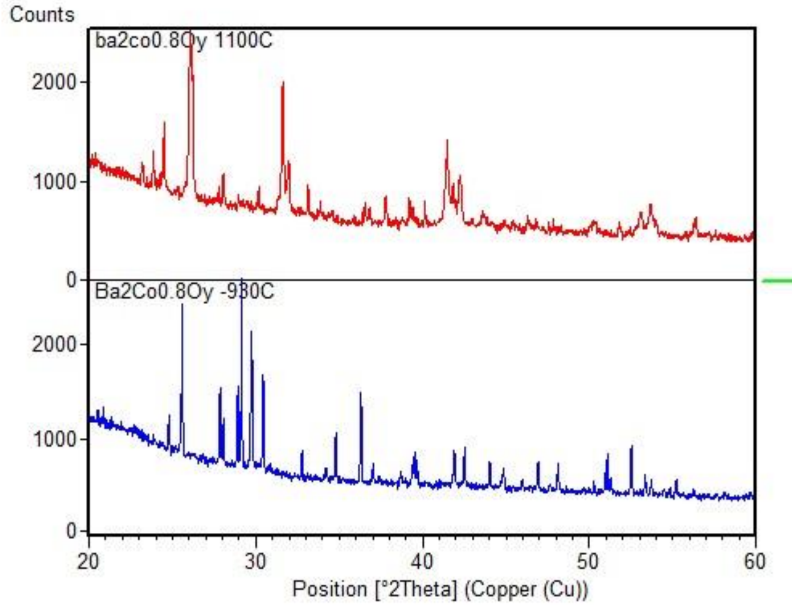




$Ba_2M_{1-x}O_{4-y}$ (M=Fe, Co)

Changes as a result of carbonate incorporation: Composition actually $Ba_2M_{1-x}C_xO_{4-x}$ ($x<0.33$)

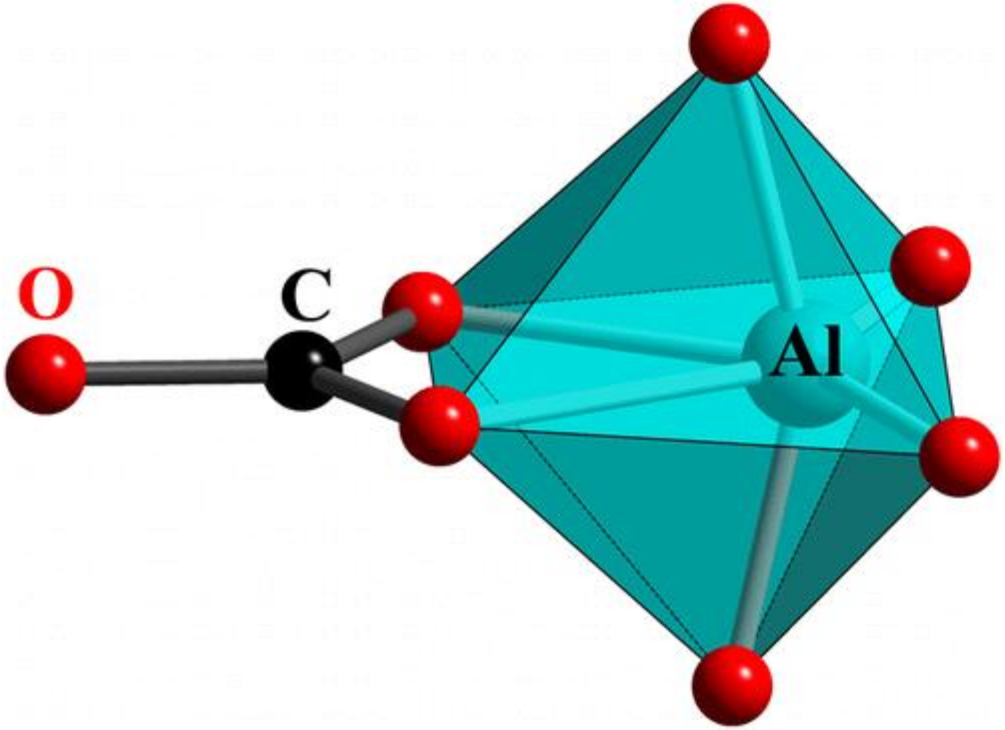
Requires synthesis below 1000°C. Above 1000°C, carbonate loss observed, and decomposition occurs



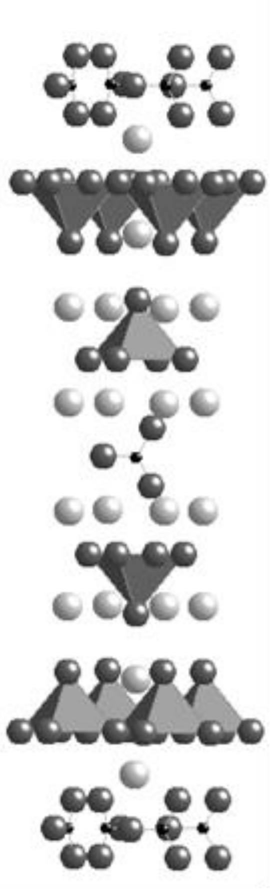
Similar systems can be prepared with Sr/La doping ($Ba_{2-x}Sr/La_xM_{1-y}C_yO_{4-z}$ (M=Fe, Co))

Carbonate in other systems:

Hexagonal “$YAlO_3$” recently shown to be $Y_3Al_3O_8CO_3$ (Subramanian et al.; Inorg. Chem 2015, 54, 837)



Doping In Ruddlesden Popper Phases



Carbonate has been shown to be incorporated into Ruddlesden Popper systems;

e.g. $Sr_4(Fe/Co/Cr)_{3-x}(CO_3)_xO_{10-4x}$ (Maignan et al., Cava et al.)

(Stabilises n=3 R-P phase)

Recently we have demonstrated that SO_4^{2-} will also stabilise such n=3 R-P phases

(straightforward synthesis in air)

(see Abbey Jarvis poster)

Summary

1. Oxyanion (carbonate, borate, silicate, phosphate, sulphate) doping offers an alternative strategy to the control of the electrical properties/stability of perovskite SOFC electrolyte/electrode materials

2. Carbonate, in particular, may be incorporated in materials through low T routes: some literature reported “oxide” systems are actually oxide carbonates.

Review article: Dalton Trans. 44, 10559-10569, 2015.

Acknowledgements

University of Birmingham; Cathryn Hancock, Abbey Jarvis

Universidad de Málaga: Enrique Losilla, Jose Porras

Funding:

UNIVERSITY OF BIRMINGHAM

The Leverhulme Trust

Science & Technology Facilities Council

EPSRC

investing in your future
European Regional Development Fund
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Advantage West Midlands
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