SYNTHESIS AND CRYSTAL STRUCTURE ANALYSIS OF PEROVSKITE AND SPINEL BASED OXYGEN CARRIES

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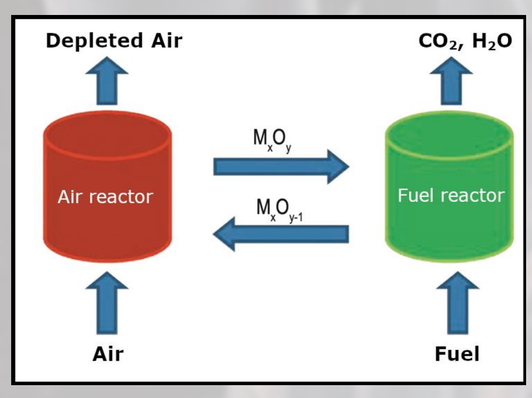
Introduction



Oxygen carrier (OC) is a material composed of one or multiply metal oxides. It is capable for releasing oxygen in certain conditions, as when changed oxygen partial pressure.
OCs are used in Chemical Looping Combustion technology (CLC), for transporting purposses of oxygen from an air to fuel reactor. Therefore, an oxygen released from OC structure is used to combust a fuel. That approach is significantly competitive to fuel combustion in pure oxygen atmosphere (oxy-fuel combustion).

Synthesis of oxygen carriers

- Although many routes of synthesis of OC are used, synthesis from solid state oxygen precursors is considered as one of the most promising methods due to its simplicity and easiness to scale-up to an industrial level.
- The spinel and perovskite-based OCs were synthetized using solid state and calcination method. As precursors metal oxides were used.
- The OCs were tested using powder XRD to check if a sample was monophasic and no byproducts were observed.
- XRD was also used to comprehensively examine the crystal structure.
- To determine crystal structure of the sample FullProf software was applied.
- Two different spinel and perovskite-based oxygen carriers were obtained and examined: $Mg_{0.625}Cu_{0.375}Fe_2O_4$- spinel and $SrFeO_3$- perovskite.

Synthesis route

Mechanical mixing
- Metal oxides as precursors

Tabletting
- Hydraulic press ~100 bar

Calcination
- 900-1000°C /12-24h dependent on composition

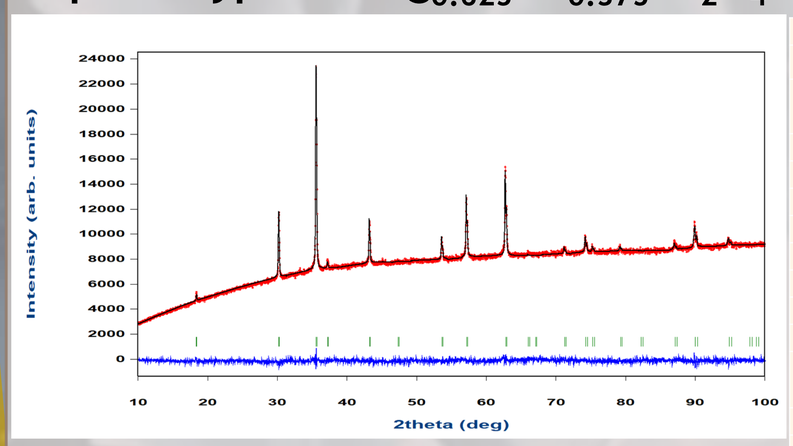
Grinding
- Obtaining small granules of OCs

Sieving
- 120-180 μm fraction is desired

XRD analysis
- Examination of phase and crystal structure

Results

Spinel-type OC $Mg_{0.625}Cu_{0.375}Fe_2O_4$



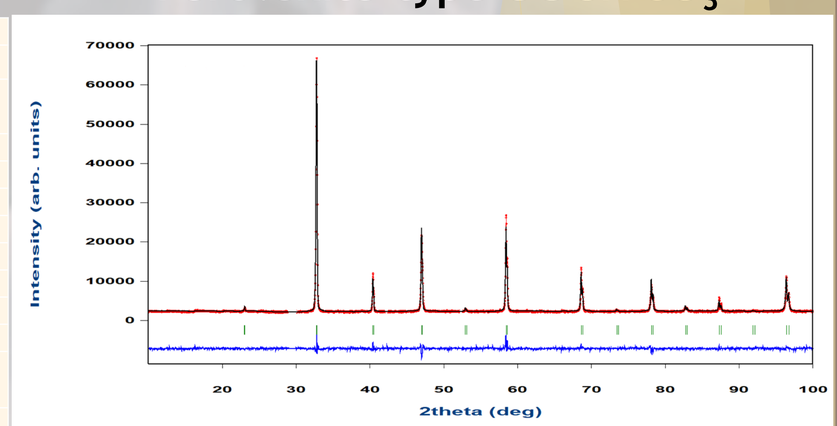
$Mg_{0.625}Cu_{0.375}Fe_2O_4$ 298K *Fd-3m*
a=8.36899(0)Å V=586.1Å^3

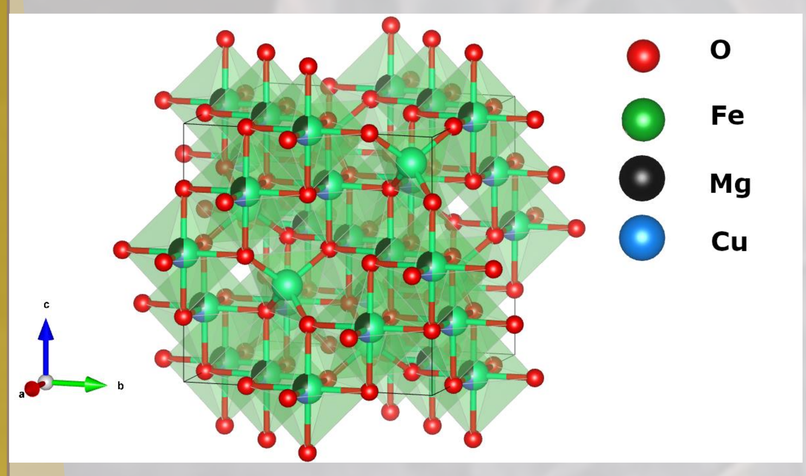
Ion	Wyckhoff position	X	Y	Z	B (temp.)	SOF
Fe^{+3}	16d	0.500(0)	0.500(0)	0.500(0)	0.82(3)	0.25(0)
Fe^{+3}	8a	0.125(0)	0.125(0)	0.125(0)	0.19(3)	0.25(0)
Cu^{+2}	16d	0.500(0)	0.500(0)	0.500(0)	0.02(4)	0.10(0)
Mg^{+2}	16d	0.500(0)	0.500(0)	0.500(0)	0.25(9)	0.15(0)
O^{-2}	32e	0.252(6)	0.252(6)	0.252(6)	0.82(3)	0.48(4)

$SrFeO_3$ 298K *Pm-3m*
a=3.8663(3)Å V=57.8Å^3

Ion	Wyckhoff position	X	Y	Z	B (temp.)	SOF
Sr^{+2}	3d	0.500(0)	0.500(0)	0.500(0)	0.55(6)	0.98(5)
Fe^{+4}	1a	0.000(0)	0.000(0)	0.000(0)	0.17(7)	0.33(3)
O^{-2}	1b	0.500(0)	0.000(0)	0.000(0)	0.54(8)	0.50(0)

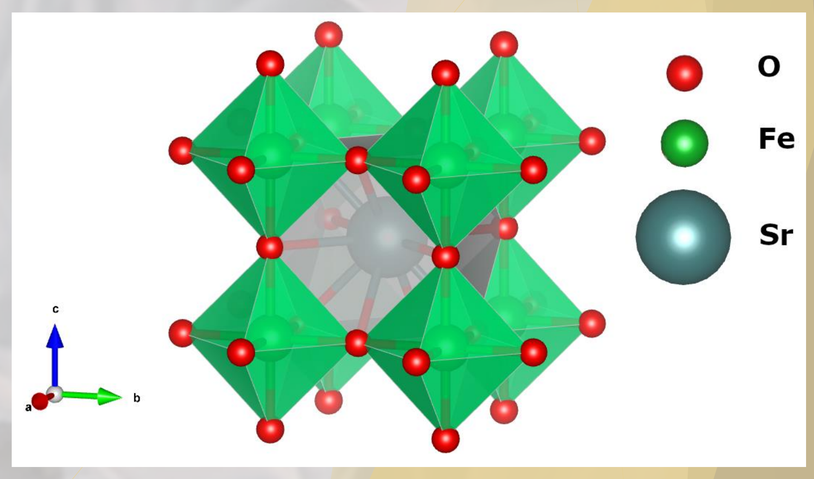
Perovskite-type OC $SrFeO_3$





Conclusions

- Solid state synthesis of OCs is a perfect alternative to wet synthesis methods
- Monophase spinel and perovskite OCs were succesfully obtained using a mechanical mixing and calcination methods
- Obtained OCs were also further positively tested for their oxygen transport capabilities with TGA-QMS
- The type of the Me-O binding, togheter with a distortion of crystal structure enable prediction of oxygen transport properties for fuels CLC and CLOU applications as observed in our study



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