

AFeO_{3-δ} Perovskites for SOFC Cathode Materials Applications. Effect of A-site Parameters.

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For the AFeO_{3-δ} perovskites the properties can be turned by the size and charge of the cations occupying the A sites (A = Ln_{1-x}M_x). The A-size can be parameterised through the mean A-cation radius, $\langle r_A \rangle$, and the size variance or size disorder, $\sigma^2(r_A)$, which describes the mismatch in ionic radii of the cations at the A-site [1]. For two or more A site species with fractional occupancies, y_i ($\sum y_i = 1$), the variance of the ionic radii, r_i , about the mean $\langle r_A \rangle$ is given by the formula:

$$\sigma^2 = \sum_i y_i r_i^2 - \langle r_A \rangle^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$$

where $\langle r_A \rangle = \sum y_i r_i$ and r_i is the standard ionic radii tabulated by Shannon [2].

This work summarises the independent studies on the separate effects of x [3,4] $\langle r_A \rangle$ and $\sigma^2(r_A)$ in the properties of AFeO₃ perovskites. In order to separate their contribution to the changes in properties, Perovskites of general formula Ln_{1-x}M_xFeO_{3-δ} (Ln= La, Pr and/or Nd; M= Sr, Ca and/or Ba) with $0.2 \leq x \leq 0.8$; $1.21 \leq \langle r_A \rangle \leq 1.25 \text{ \AA}$ and $0.0021 \leq \sigma^2(r_A) \leq 0.0155 \text{ \AA}^2$ have been synthesised by conventional ceramic solid state reaction under identical synthetic conditions. For each series, one parameter has been varied independently keeping the other two constant. The AFeO₃ system has been chosen due to the potential properties and stability of these materials as cathodes for Solid Oxide Fuel Cells [5].

The compounds have been characterised by means of X-ray powder diffraction and Rietveld analysis, elemental ICP-AAS analysis, dc 4-probe conductivity measurements and SEM. The synthesised powders were processed and applied as cathodes on electrolyte supported button cells with a SDC barrier layer to prevent reaction with the SSZ electrolyte and a Ni-SSZ anode was used as counter electrode. EIS and I-V measurements were performed at 700 and 800 °C. Systematic trends upon doping, average A size and size variance have been observed in structure, conductivity and electrochemical properties. Overall, best results correspond to samples with doping $x=0.5$, the highest mean A size and the smallest A size variance.

Figure 1 shows a summary of SEM images at the same magnification on bulk materials. There is a marked increase in grain growth as x increases, $\langle r_A \rangle$ decreases and

$\sigma^2(r_A)$ increases. The trend upon doping may be related to increasing alkaline-earth cation content, which lowers the melting point of the materials. Amongst the alkaline-earth cations, Ca seems to have a larger influence on grain growth, as shown in the $\langle r_A \rangle$ series, where grain growth decreases as $\langle r_A \rangle$ increases and Ca content decreases. The reason for an increase in particle size as $\sigma^2(r_A)$ increases is not clear as there is a simultaneous progressive substitution of Ca by Ba and an increase of the latter element across the series.

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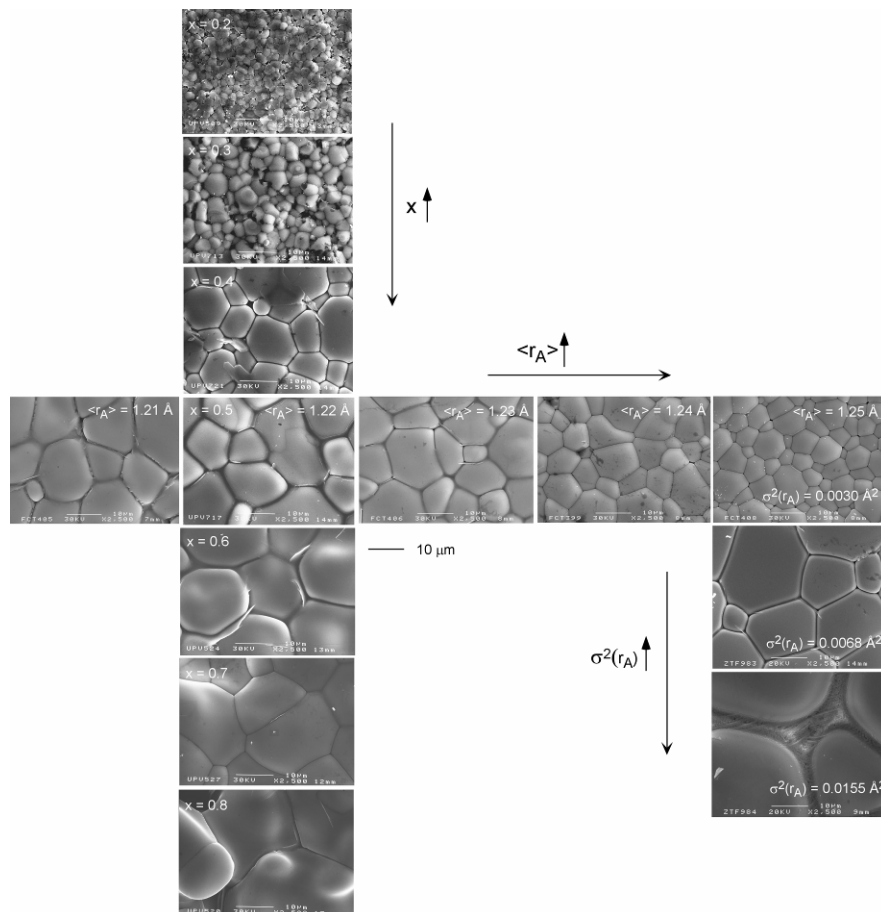


Figure 1. SEM images of polycrystalline surfaces at the same magnification of perovskite materials corresponding to the x , $\langle r_A \rangle$ and $\sigma^2(r_A)$ series.