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Yttria-doping of $SmFeO_3$

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Introduction

Perovskites are chemical compounds with the general formula ABO_3 that have a well defined crystal structure (Figure 1). Typically, A is a large metal cation (usually a lanthanide) and B is a smaller metal cation (a transition metal). They are known for their semiconducting nature and stability in wide temperature ranges making them useful in electrochemical applications. The specific properties of a given perovskite can be tailored by partial substitution of other metal cations at the A-site, B-site, or both. The tunability of these structures makes them of great interest for various applications.

Motivation and Objective

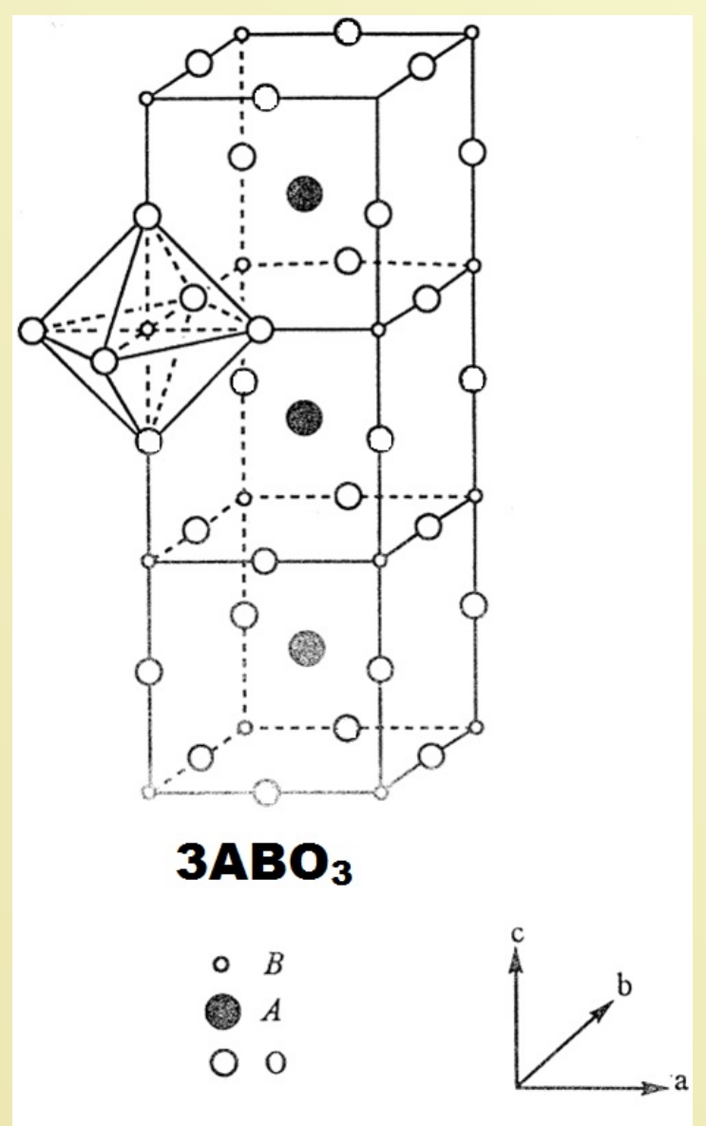


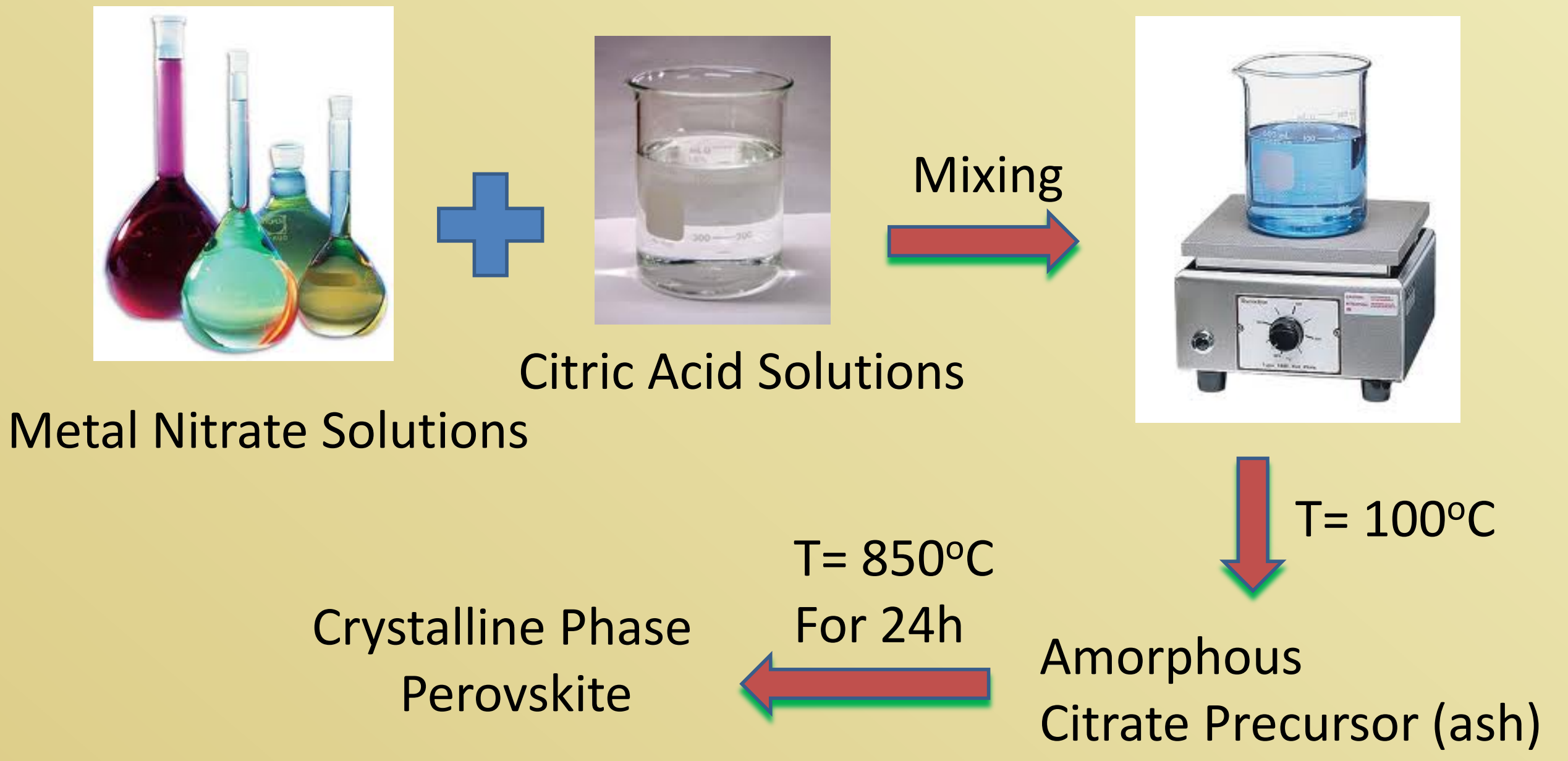
Fig. 1. General perovskite crystal structure.

This project is being conducted to study doping of samarium iron oxide ($SmFeO_3$) with yttrium. Yttrium has been predicted by calculations to have almost no energy preference for the A-site or B-site (Figure 3) and it is therefore predicted to produce an enhancement in the electrical properties of the perovskite. This project will experimentally determine the doping properties of yttrium in $SmFeO_3$ and its effects on stability, gas sensing, and conductivity properties.

Methods

Y-doped $SmFeO_3$ materials were prepared using the sol gel method which involves the thermal decomposition of amorphous citrate precursors.

- Nitrate salts of each metal cation were dissolved in de-ionized water in the desired stoichiometry where the sum of moles at the A-site and B-site were each set to one. The ratio of citric acid to metal ions is kept at one.
- The mixed solutions were dried at 100°C and the resulting amorphous citrates were ground and calcined at 850 °C for 24 hours to form the final perovskite phases.



Mixing

Citric Acid Solutions

Metal Nitrate Solutions

T= 100ºC

T= 850ºC
For 24h

Crystalline Phase
Perovskite

Amorphous
Citrate Precursor (ash)

Fig. 2. Process of creating perovskites via the sol gel method.

- The phase composition and crystallite sizes were determined using X-ray diffraction and the Powder Diffraction File database. Lattice parameters were determined using Jade 6.1 software.

- For conductivity measurements, the perovskite materials were pelleted by uniaxially pressing 2 g of powder to 15 000 lbs followed by sintering in air at 1350°C for 4 hours.
- Conductivities were measured using a four-probe DC method with a voltmeter and an ammeter over a room temperature to 400 C to room temperature cycle.

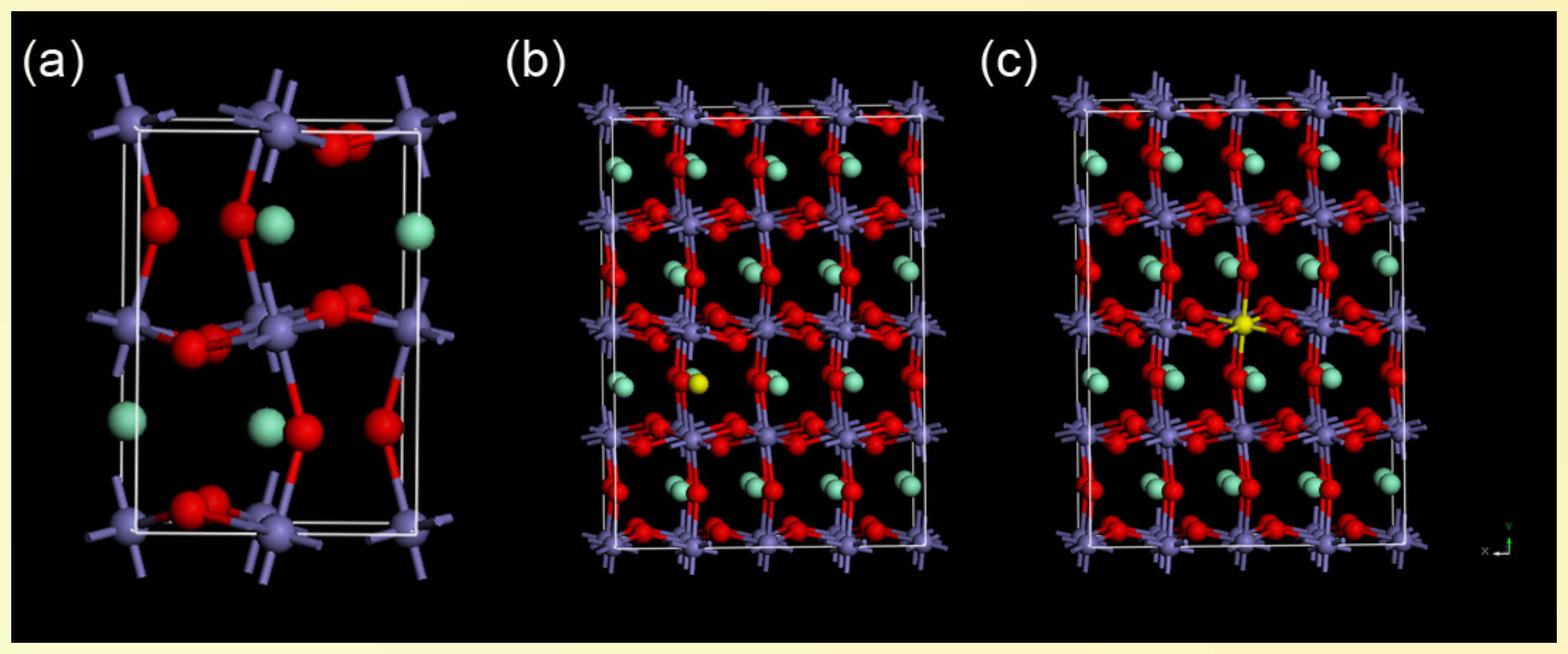


Fig. 3. The orthorombic structure of $SmFeO_3$. Samarium cations are shown in green, iron cations are shown in purple, oxygen anions are shown in red, and yttrium cations are shown in yellow. (a) Pure $SmFeO_3$. (b) 3.125 mole % Y-doping at the A-site. (c) 3.125 mole % Y-doping at the B-site. The energy difference between the A-site and B-site is almost negligible (0.26 eV preference for the B-site in an 8 unit cell structure). Images prepared by Arif Ismail.

Results

- XRD data shown in Figure 4 indicates the successful doping of $SmFeO_3$ by yttrium.
- The B-site has lower yttrium solubility than the A-site in $SmFeO_3$.

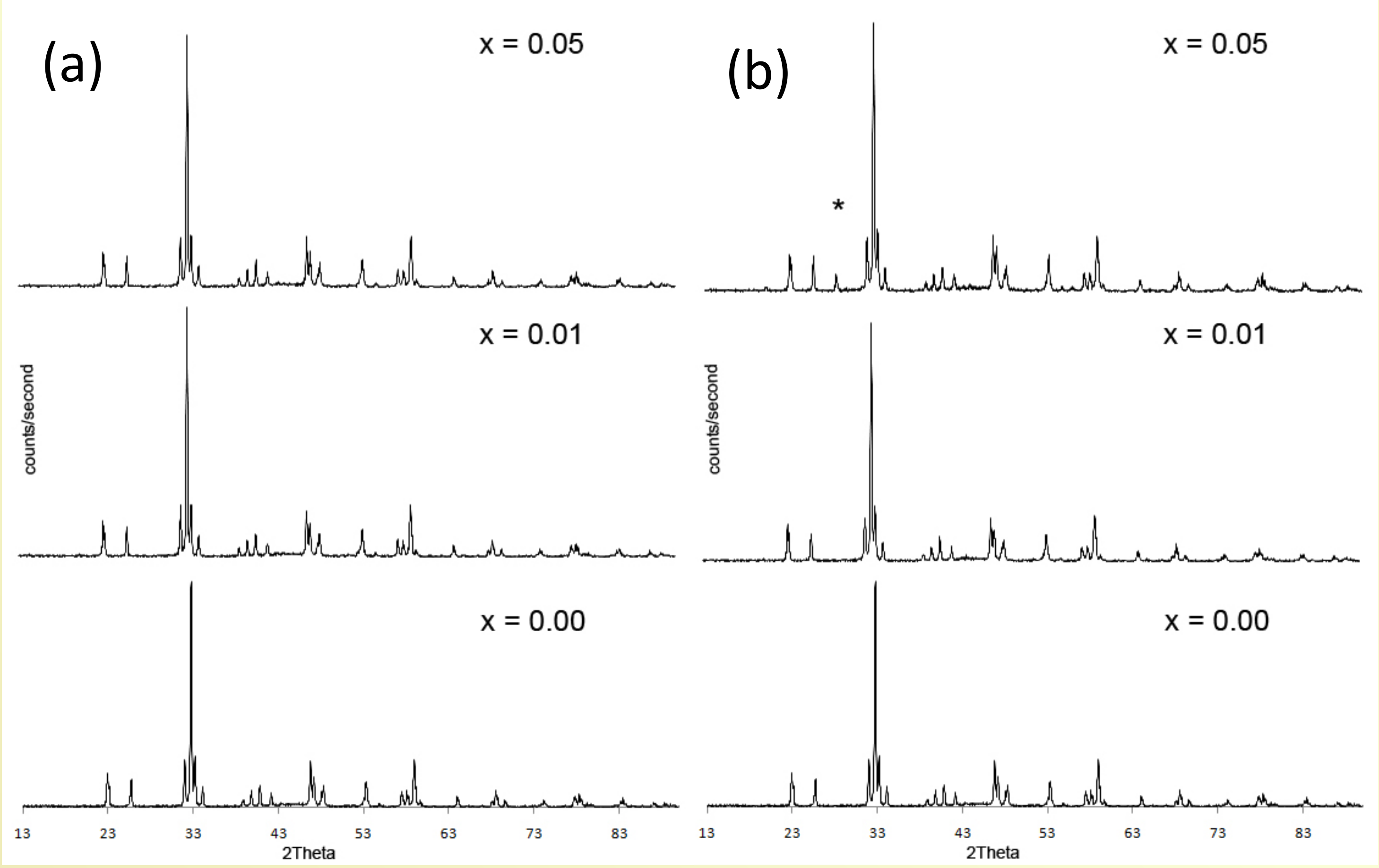


Fig. 4. XRD patterns of Y-doped $SmFeO_3$ at the (a) A-site making $Sm_{1-x}Y_xFeO_3$ and at the (b) B-site making $SmFe_{1-x}Y_xO_3$. * indicates the primary peak for Sm_2O_3 showing the creation of a second phase. Yttria is not completely soluble at the indicated concentration.

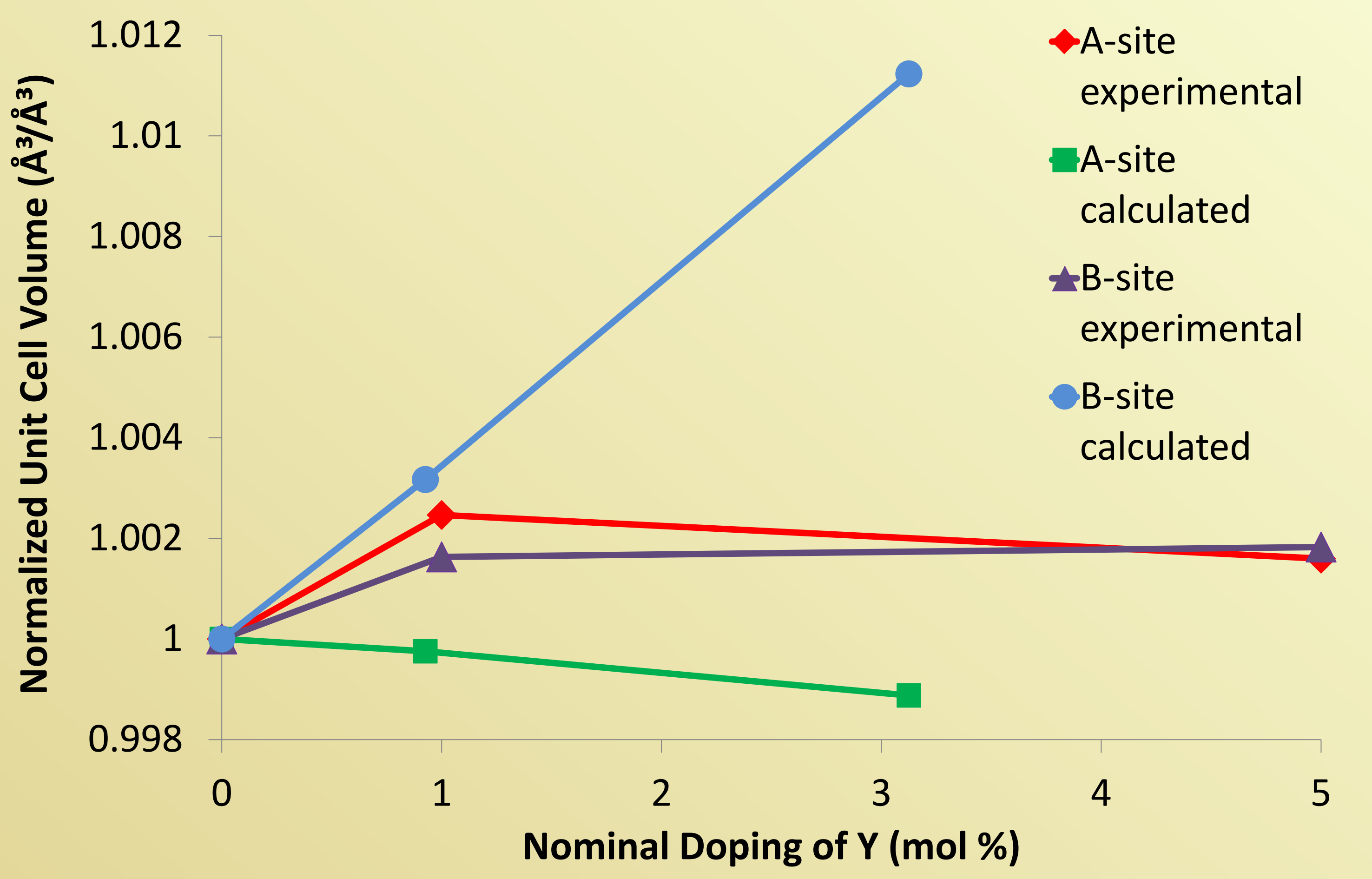


Fig. 5. Orthorhombic crystal volume of Y-doped $SmFeO_3$ as concentration changes. Calculated volumes (using DFT) by Arif Ismail and experimental volumes are presented.

Data obtained regarding lattice parameters of the doped material do not exhibit any obvious trends or follow the calculated data. Based on the data presented, the current hypothesis is that doping occurs at the B-site regardless of the designed stoichiometry until saturation which is followed by doping at the A-site.

Conductivity of the $Sm_{0.99}Y_{0.01}FeO_3$ (1 mol% yttria A-site doped) material was tested and the maximum conductivity achieved was approximately 0.039 S/cm at 400°C (Figure 6).

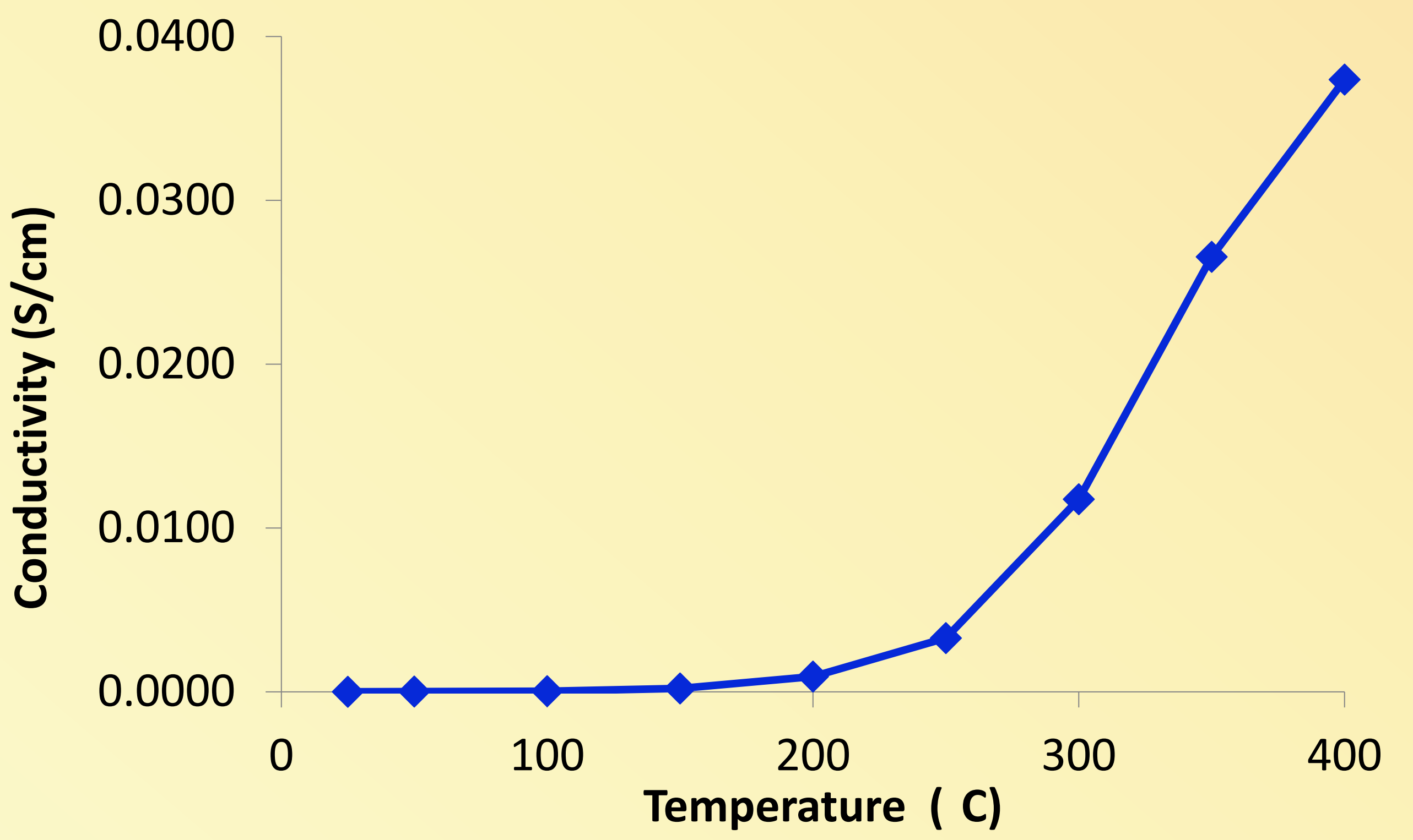


Fig. 6. Conductivity of $Sm_{0.99}Y_{0.01}FeO_3$ as a function of temperature.

Table 1. Conductivities of samarium iron oxide based materials at 400 C in air for comparison.

Material	Conductivity (S/cm)
$SmFeO_3$	≈ 0.030 [1]
$Sm_{0.99}Y_{0.01}FeO_3$	≈ 0.039
$Sm_{(1-x)}Ce_xFeO_3$ (x = 0.01, 0.03, 0.05)	≈ 0 [1]
$Sm_{0.95}Ce_{0.05}Fe_{(1-x)}Co_xO_3$ (x = 0.01, 0.03, 0.05, 0.07, 0.10)	≈ 0 [2]
$Sm_{0.95}Ce_{0.05}Fe_{0.90}Ni_{0.10}O_3$	≈ 1.00 [3]

The next steps

- Testing the hydrogen gas sensing abilities of the doped $SmFeO_3$ at different Y-concentrations at room temperature (25°C).

- Testing the conductivity of the doped $SmFeO_3$ at different Y-concentrations over a wide temperature range to determine optimal concentration and thermal stability.

- Testing the doped $SmFeO_3$ as anodic materials in solid oxide fuel cells (SOFCs) for use in practical applications.

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