Effects of the atmosphere and Mn doping on the electrical properties of Sr2Fe1−xMnxNbO6 and their mechanisms

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Abstract
Double-perovskite composite oxides (A2BB′O6) usually have excellent functional properties and are widely studied and applied. Its electrical, magnetic or other properties can be optimized by doping transition metal elements at its B or B′ site. In this paper, the effects of Mn doping and testing atmosphere on the crystal structures and the electrical conductivities of Sr2Fe1−xMnxNbO6(SFMN) were systematically investigated. The experimental results demonstrate that the conductivities of SFMN will increase in air while decrease under H2/H2O(g) atmosphere with Mn content rise. Doping Mn can enlarge the interplanar spacing of SFMN which increases the resistance of electron conduction across the crystal. First-principles calculations and XPS analysis results reveal that the chemical adsorption of H2 on the surface of SFMN is a key reason for its conductivity increase under H2/H2O(g) atmosphere. The forbidden band width of the reduced state of Sr2FeNbO6 (1.177 eV) is much smaller than that of the oxidation state (1.426 eV). The analysis results suggest that Fe 3d electron transition and exchange interaction between Mn−O−Mn are mainly two possible mechanisms contribute to the electrical conductivity of SFMN.

1. Introduction
There has been a spectacular increase in research activities related to double-perovskite oxides (A2BB′O6) in recent years [1–3]. In A2BB′O6, A sites are occupied by rare earth or alkaline earth ions, B and B′ site cations are transition metal ions. Normally, BO6 and B′O6 octahedras are arranged alternately by corner-sharing [4, 5]. With different radii of A site and B (B′) site cations, the crystal system of double-perovskites can be cubic (which is the ideal one), tetragonal, orthorhombic, even triclinic. These complex crystal structures of double-perovskites result in their many excellent electromagnetic properties, such as metal-insulator phenomena [6], superconducting characteristic (Sr2YRuO6) [7], giant magnetoresistance (GMR) performance (Sr2FeMoO6) [8], etc.

Many double perovskite materials exhibit higher electrical conductivity at higher temperatures. Childs found that Sr2−xVMoO6−δ (x = 0.0, 0.1, 0.2) double perovskites exhibited metallic like conduction with electrical conductivities of 1250 S cm−1 (Sr2VMoO6−y), 2530 S cm−1 (Sr1.9VMoO6−y), and 3610 S cm−1 (Sr1.7VMoO6−y) at 800 degrees C in 5% H2/95% N2 [9]. However, in addition to having a higher electrical conductivity, solid oxide fuel cell electrode materials also need to have a higher ionic conductivity. Recently, it has been proved that some double-perovskite oxides have high mixed ionic–electronic conductivities and catalytic activities, and have been used as electrode materials in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs). Early in 2006, Huang succeeded to introduce Sr2MgMoO6−δ into SOFC as an anode material for the first time [10]. After doping Mn, Huang found that Sr2−xMnxMoO6−δ meet the...
requirements for long-term stability with tolerance to sulfur and show a superior single-cell performance in hydrogen and methane [11]. Subsequently, studies on applications of double-perovskites in SOFC became a hot spot [12–15]. Some other double-perovskite electrode materials also show good cell performances, such as Ba2CoMnO6/3Nb2O5 [16], Sr2FeMoO6 [17, 18], YBaCo2–xFeO δ+delta [19], SmBaCuCoO5+delta [20], etc [21–24]. Moreover, we have introduced Sr2FeNbO6 to SOEC and proved that it can be used as the hydrogen electrode and its electrochemical performance is better than that of Ni under the same operation conditions [25].

However, research on double perovskites applied in solid oxide fuel and electrolysis cells is still at the initial stage. Notably, there are only a few reports about double-perovskites applied in SOFC [26, 27]. Moreover, many literatures have found that the conductivities of double-perovskites will show very large differences with the amount of element doping and testing environment changing [9, 28], but the mechanism is not yet very clear. Thus, R&D of new double-perovskite electrode materials and study on their electrochemical mechanisms are the current research directions. On the basis of previous studies [25, 29], a modification of Sr2FeNbO6 is made herein. It should be noted that this article is an extension of the previous work in depth and breadth. In particular, the internal mechanisms of the influence of doping and different material service environments on the electrical performance of Sr2Fe1–xMnxNbO6 (SFMN) was studied based on both experimental results analysis and first-principle calculations.

2. Experimental and computational details

Sr2Fe1–xMnxNbO6 powders were synthesized by the solid state reaction method. Analytically pure SrCO3, Fe2O3, MnO2 and Nb2O5 powders were stoichiometrically mixed by ball-milling for 4 h using alcohol as the milling medium. After dried and sifted, the mixed oxide powders were calcined at 1200 °C for 12 h in air to form a pure phase of double-perovskite structure. Obtained powders were pressed into bulks, sintered at 1450 °C for 24 h in air, and then machined to disks with diameter of 8 mm and thickness of 1 mm for conductivity testing under different conditions. XRD analysis was carried out on a Bruker D8-ADVANCE diffractometer at room temperature using Cu Kα1 (λ = 0.154 06 nm) radiation in Bragg-Brentano geometry, with acceleration voltage of 40 kV, and current of 40 mA.

All calculations were performed based on density functional theory (DFT) by the CASTEP (Cambridge Serial Total Energy Package) module [30] of materials studio software. The exchange-correlation energy was described using the revised Perdew–Burke–Ernzerhof exchange-correlation density functional (PBESOL) within the generalized-gradient approximation (GGA). A 400 eV plane-wave kinetic energy cutoff was chosen. The Brillouin zone was sampled with 4 × 4 × 4 and 2 × 2 × 3 Monkhorst–Pack grids for SFMN bulk and surfaces calculations. A 15 Å thick vacuum layer was used to avoid the interaction between top and bottom surfaces. The atomic positions were fully relaxed until a maximum energy difference and residual force on atoms, respectively, converged to 10−6 eV and 0.01 eV Å−1. In addition, we used the DFT + U approach to correct self-interaction error by including the onsite Coulomb interaction for standard GGA exchange correlation based on the Hubbard model approach. The values setting of Hubbard U of related transition metal elements (UFe = 7 eV, U>Mn = 9 eV, U>Nb = 9 eV) refers to our previous work and literatures [31, 32]. The valences of Fe, Mn and Nb are set to +3, +3 and +5, respectively. The system was set to a vacuum environment.

3. Results and discussion

3.1. Conductivities of SFMN in different atmospheres

The conductivities of Mn-doped Sr2Fe1–xMnxNbO6 (SFMN) in air were studied. The results are shown in figure 1 (also can be seen from figure S1 is available online at stacks.iop.org/MRX/7/056302/mmedia). According to the comparison of the curves, the conductivities of SFMN in air enhance with the increase of doped Mn, revealing that doping Mn is helpful to improve the conductivity of Sr2FeNbO6 in air. When Mn content (x) is greater than or equal to 0.4, ‘ln(σT)’ and ‘1000/Τ’ are approximately linear in the entire temperature range; when Mn content is less than 0.4, it is approximately a polyline, and the slopes in low and high temperature region are different. It may be attributed to the fact that the materials correspond to different conductive mechanisms in the low temperature region and the high temperature region, respectively. It is found that circular arcs in the AC impedance spectrum of Sr2FeNbO6 appear at low temperature (<700 °C) without Mn doping (figure 2), which indicates that the sample has a certain ionic conductivity in this temperature range. However, there is no obvious arc in the high temperature region (> 700 °C), which is mainly dominated by electronic conductance.

The mixture of hydrogen and steam is the working environment on the hydrogen electrode side of the solid oxide electrolysis cell (SOEC), so the properties of SFMN were investigated under this working atmosphere.
Figure 3. (and figure S2) shows the conductivities of SFMN at different temperature under H₂/H₂O(g) atmosphere (80 vol.% H₂O(g), 20 vol.% H₂). It can be seen that, contrary to the case in air, the conductivity of SFMN gradually decreases with the increase of Mn content. In addition, there exists an ideal linear relationship between $\ln(\sigma T)$ and $1000/T$ for SFMN in the entire temperature range, indicating that conductivities of SFMN in this condition can be well fitted by adiabatic small polaron hopping model \[33–35\]. It can be further known from table 1 that the conductance activation energy increases with the increasing of the Mn content under H₂/H₂O(g) atmosphere, but the change is not large. In addition, it can be seen that when the Mn doping amount is less than 0.5, the conductance activation energy in the air is larger than that under H₂/H₂O(g) atmosphere; when the Mn doping amount is equal to 0.5, the two are approximately equal, about 0.5 eV; when the doping amount of Mn is greater than 0.5, the conductivity activation energy in air is smaller than that under H₂/H₂O(g) atmosphere.

Figure 4. Conductivities of SFMN in different atmospheres at 850 °C, which is the typical operating temperature of SOEC, is compared in figure 4. Without Mn doping, Sr₂FeNbO₆ has the highest conductivity under H₂/H₂O(g) atmosphere, approximately 2.21 S·cm⁻¹. In contrast, its conductivity in air is the lowest, about 0.05 S·cm⁻¹. However, Sr₂MnNbO₆ has the highest conductivity in air, about 1.37 S·cm⁻¹. The conductivities of
Sr$_2$Fe$_{0.5}$Mn$_{0.5}$NbO$_6$ in both two atmospheres are basically the same, about 0.5 S·cm$^{-1}$. These data illustrate that: The conductivity of Sr$_2$FeNbO$_6$ will increase in air and decrease under H$_2$\slash H$_2$O(g) atmosphere by doping Mn in its B-site.

3.2. XRD analysis of SFMN crystal structure change

According to the basic theory of materials science, property change must come from structural reasons. Similarly, the performance of perovskite also depends on its microstructure [36]. Especially the structural changes caused by element doping will lead to corresponding changes in the electrical properties of double perovskite [13, 37]. XRD testing were used to study the phase formation and crystallinity of SFMN, after calcining at 900 °C for 24 h both in air and under H$_2$\slash H$_2$O(g) atmosphere. The results are shown in figure 5. The following conclusions can be drawn accordingly: (1) first, the raw material powders with different Mn doping

![Figure 3. Arrhenius curve of SFMN in a hydrogen-steam atmosphere (80 vol.% H$_2$O(g), 20 vol.% H$_2$).](image)

| Doping amount of Mn | Temperature range (°C) | Conductivity activation energy (eV) | Air | Hydrogen-steam |
|--------------------|------------------------|-------------------------------------|-----|----------------|
| 0                  | 500 ~ 650              | 0.39                                | 0.30|                 |
|                    | 800 ~ 900              | 1.33                                |     |                 |
| 0.1                | 500 ~ 650              | 0.57                                | 0.36|                 |
|                    | 700 ~ 900              | 0.92                                |     |                 |
| 0.2                | 500 ~ 600              | 0.36                                | 0.63|                 |
|                    | 600 ~ 900              | 1.01                                |     |                 |
| 0.3                | 500 ~ 600              | 0.39                                | 0.60|                 |
|                    | 600 ~ 900              | 0.81                                |     |                 |
| 0.4                | 500 ~ 900              | 0.61                                | 0.57|                 |
| 0.5                | 500 ~ 900              | 0.59                                | 0.54|                 |
| 0.6                | 500 ~ 900              | 0.56                                | 0.64|                 |
| 0.8                | 500 ~ 900              | 0.35                                |     |                 |
| 1                  | 500 ~ 900              | 0.19                                |     |                 |

* The missing data is due to the embrittlement of SFMN with high Mn content when exposed to H$_2$\slash H$_2$O(g) at high temperature (>800 °C) (see figures S3, S4).

Sr$_2$Fe$_{0.5}$Mn$_{0.5}$NbO$_6$ in both two atmospheres are basically the same, about 0.5 S·cm$^{-1}$. These data illustrate that: The conductivity of Sr$_2$FeNbO$_6$ will increase in air and decrease under H$_2$\slash H$_2$O(g) atmosphere by doping Mn in its B-site.
amounts can be calcined in air to form a relatively ideal perovskite structure without obvious impurity phases. (2) The intensity of the XRD diffraction peaks decreased with the increase of Mn doping amount in air, indicating that it is difficult to form the pure perovskite phase of SFMN with high Mn content. However, the peak position was basically unchanged, which indicates that doping will not change the crystal structure of Sr$_2$FeNbO$_6$ in air. At the same time, the decrease in peak intensity indicates that Mn doping tends to amorphize the crystal. Theses local disorders may be one of the reasons for conductivity increase of SFMN in air. (3) The influence of H$_2$/H$_2$O(g) atmosphere on the crystal structure of SFMN with lower Mn content is not significant. However, as the Mn content increases, the effect becomes more pronounced. As a result, the high-angle peak shifts to the left, indicating that the lattice spacing becomes larger and the crystal expands. (4) It can be seen from figure 5(b) that Sr$_2$Fe$_{0.2}$Mn$_{0.8}$NbO$_6$ coexisted with many trace impurity phases in air. The impurities disappeared after being treated in the hydrogen-steam atmosphere, but the diffraction peaks moved towards a lower angle. According to the Bragg equation, the value of the interplanar spacing $d$ becomes larger, which may be due to the doping of Mn. The larger lattice spacing means that the resistance of electron conduction across the lattice becomes larger, which may also be a cause of the conductivity decrease of SFMN with the increase of Mn content under H$_2$/H$_2$O(g) atmosphere.

Figure 4. Conductivities of SFMN in different atmospheres at 850 °C.

Figure 5. XRD patterns of samples after calcining at 900 °C for 24 h (a) SFMN (b) Sr$_2$Fe$_{0.2}$Mn$_{0.8}$NbO$_6$. 

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3.3 Effect of surface adsorption states on electrical conductivity in different atmosphere

If the changes in conductivity with increasing Mn content can be explained from the perspective of microstructural, then how to explain the changes in conductivity in different atmospheres? For instance, the conductivity of Sr$_2$FeNbO$_6$ under H$_2$/H$_2$O atmosphere is much higher than that in air (figure 4).

In order to study whether atmosphere change caused valence change of some elements of SFMN, which in turn affected the electrical conductivity, the x-ray photoelectron spectroscopy (XPS) was used to study the changes of chemical elements before and after the atmosphere change (Powders treated under H$_2$/H$_2$O(g) atmosphere were not exposed in air before XPS tests). The test results show that the XPS peak of element O shows obvious peak position and shape changes (figure 6), however, Sr, Fe, Mn, and Nb do not show significant peak shifts and deformations (figure S5). The results had reproducibility. According to the literature [38], after samples were activated by H$_2$/H$_2$O(g) atmosphere, the absorption peak of the element O in the form of O$^-$ and OH$^-$, which came from the chemical adsorption of H$_2$, became much stronger (figure 6). Therefore, it is speculated that the surface adsorption layer of the sample under H$_2$/H$_2$O(g) atmosphere may be the cause of the conductivity increase.

3.4 Mechanism explanations given by first-principle calculations

The Sr$_2$Fe$_{1-x}$Mn$_x$NbO$_6$ (SFMN) supercell calculation models were built based on XRD experimental results (figure S6). In order to simplify the model, we selected several special Mn doping ratios (0, 0.25, 0.5, 0.75, 1). The geometric structure of the supercells was firstly optimized, and then the band structure, the density of states (DOS), the electron density and the electron density difference were calculated.

DFT calculation results show that cell volume increases with Mn content rise (the curve in figure 7), which validates the experimental results of SFMN (figure 5(a)). Further analysis suggests that the bond length of Mn–O is longer than that of Fe–O and Nb–O, and becomes much longer with the increase of Mn content, this should be the reason for the cell volume increasing of SFMN. The chemical bonds are all in the direction of [010]. The symmetry of the unit cell changes with the amount of Mn doped, and the bond length in different directions is slightly different, forming dipole moments, which also affect the electromagnetic performance of the material to a certain extent.

The cross-sectional color maps of the electron density and the electron density difference in figure 7 are from the (100) plane of the cell, and all B-sites elements are displayed on this plane as much as possible. It can be seen that the charge density between Mn and O atoms is the smallest, which corresponds to the longer bond length and weaker bond formation. The comparison of the electron density difference also indicates that the bond between Mn and O is relatively weak. In addition, there is a significant increase in the charge density between Fe and O, indicating that Fe3d electrons have a strong bond with O2p electrons, which can give a possible explanation for the higher conductivity of SFMN under lower Mn content in hydrogen atmosphere.

Figure 8 is results of the total and partial density of states of SFMN. First, as the amount of Mn doping increased, the spin-up electron states near the Fermi level increased (mainly 2p orbital electrons of O), and the valence band moved across the Fermi level to a higher energy direction; However, the spin-down electron energy did not change much, and even had a tendency to move to a lower energy direction. This indicates that the spin polarization phenomenon of the SFMN system intensifies with the increase of Mn content. The valence band
moves through the Fermi level to a higher energy direction, making the forbidden band narrower and reducing the energy required for electronic transitions, which may be the direct cause of the increase in the conductivity of SFMN in air.

Figure 7. Cell volumes and bond lengths of SFMN calculation models and their electron density, electron density difference diagrams (All the graphs are divided into 5 columns, corresponding to Mn doping ratios 0, 0.25, 0.5, 0.75, 1 from left to right).

Figure 8. (a) The total and partial density of states of SFMN (b) partial enlargement near the Fermi level.
Figure 8(b) shows that the DOS increase of spin-up electrons near the Fermi level is due to the chemical bond formed between O2p and Mn3d electrons. The peak shape of the DOS is gentle, indicating that the chemical bond is a delocalized bond, and the electrons can move freely, so that exchange interaction between Mn–O occurs [39, 40]. The larger the amount of Mn, the more intense the exchange interaction, which in turn improves the electrical conductivity of the material. The conclusions can provide a theoretical explanation for the conductivity increase of SFMN in air with the increase of Mn content.

In addition, it can be seen from figure 8(a) that the spin-down electronic state of Fe in the conduction band (there is no electron occupation in the ground state) is the closest to the valence band, which can provide the lowest energy consumption path for the electron transition in the valence band. Therefore, Fe also plays a key role in the conductivity of SFMN.

When Mn replaced Fe completely, the 3d electronic state of Fe in the conduction band disappeared, and the forbidden band width became larger (figure 8(a), Sr2MnNbO6), which is difficult to explain why the conductivity of Sr2MnNbO6 has not decreased but increased. Through careful analysis, the possible reasons are as follows: for SFMN, there are mainly two possible mechanisms that contribute to electrical conductivity. Firstly, when Fe content is high, the 3d electronic state of Fe provides a lower energy barrier for the transition of electrons, and the conduction is mainly dominated by electron transitions. Secondly, as the Mn content increases, Mn–O bond increases. As previously analyzed, the electron exchange interaction between Mn–O increases significantly. When the Mn content is sufficiently high, the conductance is dominated by electron exchange interaction between Mn–O–Mn.

According to the previous XPS analysis conclusions, it can be seen that the difference in conductivity under different atmospheres is mainly due to changes in the surface adsorption state of the material. Therefore, we established two kinds of surface calculation models ([110] plane), in which the surface of the air atmosphere model relaxed normally, and the model of H2/H2O(g) atmosphere introduced the adsorption of hydrogen in order to construct OH– adsorption state. Here, Sr2FeNbO6 was taken as the calculation research object. The calculated results of the band structure and the DOS of the two models are compared. The results are shown in figures 9 and 10, respectively.

From the comparison of the band structure results in figure 9, it can be seen that the spin polarizations of the two atmospheres are different, and the forbidden band width of the reduced state model (1.177 eV) is much smaller than that of the oxidation one (1.426 eV). In combination with figure 10, the spin-down Fe3d electron state in the conduction band of the reduction state model moved to a lower energy direction, and became closer to the Fermi level, which results in a reduction of the forbidden band width. In addition, both the band structure diagram and DOS diagram show that the DOS near the Fermi level in the reduction state model is greater than that of the oxidation state, mainly due to the DOS increase of O2p electronic states and Fe3d electronic states in the valence band. These conclusions can reasonably explain why the conductivity of SFMN increases under H2/H2O(g) atmosphere.

4. Conclusions

The relationship between the electrical conductivities of SFMN and the Mn content in air and under H2/H2O(g) atmosphere was investigated. The analysis results show that: (1) the conductivity of Sr2FeNbO6 will increase in air and decrease under H2/H2O(g) atmosphere by doping Mn in its B-site. (2) Doping Mn will enlarge the interplanar spacing of SFMN, which will increase the resistance of electron conduction in the crystal, and leading to conductivity decrease under H2/H2O(g) atmosphere with the increase of Mn content. (3) The chemical adsorption of H2 on the surface is an important reason for the conductivity increase under H2/H2O(g) atmosphere. (4) The spin polarization phenomenon becomes more intense with the increase of Mn content. The valence band moves across the Fermi level to a higher energy direction, which narrows the forbidden band width and reduces the energy required for electronic transitions, which may be the direct cause of conductivity increase of SFMN in air. (5) There are mainly two possible mechanisms that contribute to electrical conductivity of SFMN. When Fe content is high, as Fe3d electronic state can provide a lower energy barrier for the electron transition, the conduction is mainly dominated by electron transitions. When the Mn content is sufficiently high, Mn–O bonding increases, the conductance is dominated by electron exchange interaction between Mn–O–Mn. (6) First-principle simulation results reveal that the forbidden band width of the reduced state model (1.177 eV) is much smaller than that of the reduction one (1.426 eV). The forbidden band narrowing and the DOS enhancement near the Fermi level are the reasons for conductivity increase of SFMN under H2/H2O(g) atmosphere.
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