Conducting mechanism of Sr\textsubscript{2}CoRO\textsubscript{6} (R=Mo, Nb) under different $P_{O_2}$

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The electrical conductivities of Sr\textsubscript{2}CoRO\textsubscript{6} (R=Mo, Nb) under different oxygen partial pressures and their crystal structures were investigated. Their conducting mechanisms were proposed. X-ray photoelectron spectra revealed that the dominated oxidation state of Co\textsuperscript{2+} was in Sr\textsubscript{2}CoMoO\textsubscript{6} but Co\textsuperscript{3+} in Sr\textsubscript{2}CoNbO\textsubscript{6}. The crystal lattice structures of Sr\textsubscript{2}CoRO\textsubscript{6} were identified by X-ray diffraction and their parameters were calculated by using Rietveld method. The refined crystal structures of Sr\textsubscript{2}CoRO\textsubscript{6} have been used to construct their own conducting channel model. And the electrical conductivities were measured by using an electrochemical workstation with four-terminals method through controlling the oxygen partial pressure of the testing environment. The results show that the electrical conductivity of Sr\textsubscript{2}CoMoO\textsubscript{6} is 0.36 S·cm\textsuperscript{-1}, much lower than that of Sr\textsubscript{2}CoNbO\textsubscript{6} (7.81 S·cm\textsuperscript{-1}) in air at 973 K, which is assigned to the difference of their conducting channels. And the electrical conductivity of Sr\textsubscript{2}CoMoO\textsubscript{6} increased linearly with the decrease in $P_{O_2}$, reaching 2.05 S·cm\textsuperscript{-1} when $P_{O_2} = 10^{-21}$ atm at 973 K, while Sr\textsubscript{2}CoNbO\textsubscript{6} presented an opposite trend. It was supposed that the different valences of cobalt in Sr\textsubscript{2}CoMoO\textsubscript{6} and Sr\textsubscript{2}CoNbO\textsubscript{6} lead to the different electron conducting channels and different changing trends of electrical conductivities with the decrease in oxygen partial pressure.

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1. Introduction

Materials with double perovskite structure exhibit various interesting physical properties, such as magnetoresistivity, superconductivity and dielectricity, which have received extensive concerns in many applied and fundamental areas of solid-state and advanced materials science. Double perovskite materials usually have a chemical formula of $A_2B_B O_6$ (A=alkali earths, B, B$'$= transition metals). However, it doesn’t mean that they only have one kind of crystal structure and tilt system. It is known that the crystal morphology is closely related to the physical and chemical attributes of (B') site atom. And it is generally accepted that if the charge difference between B and B$'$ cations reaches more than 2e, or their radii and electronegativity difference become large enough, then the solid solution formed by these two different octahedral cations may achieve an ordered octahedral cation sublattice. Double perovskite materials have a wide range of geometrical tolerance factor (0.77 $\leq t$ $\leq$ 1.1), indicating that the crystal structure can sustain a relatively severe deformation and distortion which will evolve in the varieties of tilt systems such as Fm$ar{3}$m (a$a$’a’), I4/m (a’a’c’), R3$\bar{m}$ (a”a”), and I2/m (a”b’b’$\bar{b}$’$\bar{b}$’) P2$_1$/n (a”$\bar{a}$”), respectively. And the geometrical tolerance factor can be defined as $t = (r_a + r_O)/\sqrt{2(r_B + r_O)}/2 + r_O$, where $r$ is the ion radius and subscript A, B, B$'$ and O represent ions of A-site, B-site, B$'$-site and oxygen, respectively.

In recent years, some double perovskite materials have been used as electrodes in solid oxide fuel cell (SOFC), presenting a high performance due to their high electronic conductivity, rapid oxygen ion diffusion and surface exchange kinetics, high coketransfer resistance and sulfur poisoning resistance, and so forth. For example, oxides of stoichiometry Sr$_2$MgMoO$_6$ and Sr$_2$MnMoO$_6$ have been used as high-performance anodes and their maximum power densities had respectively reached 838 and 658 mW·cm$^{-2}$ at 800°C with hydrogen as the fuel. Sr$_2$CoMoO$_6$ has been treated as anode material for SOFC and its maximum power densities were 1017 mW·cm$^{-2}$ in hydrogen and 634 mW·cm$^{-2}$ even in humid methanegasat 800°C, evidencing a high performance and stability in reductive conditions.

Double perovskite materials with formula Sr$_2$BB’O$_6$ have been described as mixed ionic-electronic conductors, and the value of their mixed electrical conductivity has been usually unstable even at a fixed temperature. The mixed conductivities of Sr$_2$CoMoO$_6$ and Sr$_2$NiMoO$_6$ perovskites in different atmospheres (for instance, air, hydrogen and methane) had been investigated by Huang et al. The result showed that the conductivity in air was much lower than those in reductive conditions, due to the dropped oxygen partial pressure in reductive atmosphere, which was easily decreased down to 10$^{-17}$ atm in hydrogen. Then forced by the chemical potential, the lattice oxygen in the materials would run out and be substituted by an oxygen vacancy as well as two electrons around, both of which could be served as charge carriers that can increase the conductivity of materials. Similar result was found from NdBaFe$_2$As$_2$-Mn$_2$O$_{5+d}$ double perovskite, whose conductivity increased with the oxygen partial pressure decreasing from 0.2 to 10$^{-12}$ atm. However, in the present work, we found that lowering the oxygen partial pressure may also cause a negative impact on the conductivity of Sr$_2$CoNbO$_6$ perovskite. Because the response direction of conductivity of a material to the variation of oxygen partial pressure will influence the direction of application apparently, e.g., as anode or cathode in SOFC, so it is necessary to introduce the oxygen partial pressure as another key factor other than tem-
perature to evaluate the conductivity of Sr2BBO6 perovskite family.

In this paper, the crystal structures of Sr2CoRO6 (R=Mo, Nb) and their conductivities under different oxygen partial pressures have been systematically investigated. And a conducting channel model has been introduced to explain their conducting mechanisms.

2. Experimental

Polycrystalline samples of Sr2CoRO6 were synthesized by solid-state reaction using raw powders of SrCO3, Co(NO3)2·6H2O (cobalt source for Sr2CoMoO6), CoCO3 (cobalt source for Sr2CoNbO6), (NH4)6Mo7O24·4H2O and Nb2O5 stoichiometrically. All the chemical reagents are of analytical grade purity. During typical processing, the raw powders were mixed thoroughly and milled in ethanol medium by a planet mill for 24 h to form uniform mixtures. After drying, the mixtures were first calcined at 1100°C for 10 h, then cooled down to room temperature. After grinding, second calcination was carried out at 1300°C for 10 h to achieve a pure phase. After re-grinding, the obtained powders were pressed into rectangular green bodies and then sintered at 1300°C for 24 h. The whole calcination process above was carried out in air. Finally, the prepared rectangular sintered bodies were processed in to a size of about 4 × 4 × 25 mm for electrochemical test.

The phase properties of Sr2CoMoO6 (SCM) and Sr2CoNbO6 (SCN) were characterized by X-ray diffraction (XRD) with a D8-advance diffractometer operating with Cu Kα radiation. The measurements were executed at room temperature in step scanning mode with a step size of 0.02° and a scanning speed of 1.5°/min. Rietveld method was used to analyze the X-ray powder diffraction data in order to obtain accurate crystal structure information of SCM and SCN. Surface analysis was performed on an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi).

The microstructures were observed by scanning electron microscopy (SEM). The electrical properties were measured on a solartron SI1287 & SI1260 electrochemical workstation using four-probes DC method. The measurements were performed in an airright alumina ceramic container, where the oxygen partial pressure could be maintained by controlling the mixing flow of hydrogen and nitrogen. The oxygen partial pressure was detected by a device of Oxygen Transmitter 1632.

3. Results and discussion

3.1 Stability and morphology

The stabilities of SCM and SCN were investigated by XRD after thermally processing their powders at 700°C with a flow of 5% H2/Ar for 2 h. The results were shown in Fig. 1. From this figure, no additional phase can be found from the XRD patterns of SCM and SCN after thermal treatment, which means that both SCM and SCN were stable at low oxygen partial pressure atmosphere created by the flow of 5% H2/Ar. Furthermore, it can be found from Fig. 1(a) that the peaks at about 27.6 and 30.7°, which could be assigned to the impurity phase (marked by *) of SrMoO4,11) are weakened and would disappear after thermal treatment. It is because that the SrMoO4 phase may not be stable under low oxygen partial pressure. The similar phenomenon was also found in Ref.14) The SEM images of SCM and SCN ceramics after final sintering process are shown in Fig. 2. It can be seen that both SCM and SCN ceramic bodies are relatively dense and present almost similar microstructure both in crystal morphology and grain size, implying that the effect of crystal morphology on their electrical conductivity might be negligible.

3.2 XPS analysis

The element chemical environment of SCM and SCN ceramic bodies sintered at 1300°C in air was detected by the XPS spectra. The chemical environments of Co, Mo and Nb ions were estimated by curve-fitting of the Co 2p, Mo 3d and Nb 3d spectra, as shown in Fig. 3. The asymmetric Co 2p core-level spectra of SCM and SCN samples are shown in Fig. 3(a). Two different valences of Co2+ and Co3+ appear in both SCM and SCN. The doublet peaks with binding energy at 780.1 and 795.2 eV can be assigned to the Co2+ 2p3/2 and 2p1/2 states, respectively. And the other doublet peaks can be assigned to the Co3+ 2p3/2 and 2p1/2 states whose binding energies are at 781.0 and 796.1 eV, respectively. By comparing the peak area of Co2+ and Co3+, it can be found that the content of Co2+ is much higher than that of Co3+ in SCM. However, the situation in SCN is just the opposite. Figure 3(b) shows the symmetrical Mo 3d 3d and Nb 3d core-level spectra, indicating that both of them are in a single valence state, or the relative content of main valence state is very high. The
doublet peaks located at 232.5 and 235.6 eV belong to the Mo$^{6+}$ 3d$5/2$ and 3d$3/2$ states, and the other doublet peaks with binding energy at 206.4 and 209.1 eV are attributed to Nb$^{5+}$ 3d$5/2$ and 3d$3/2$ states. In summary, the dominant valence states of cobalt and molybdenum ions in SCM are $3d^7$ and $3d^3$, respectively, while the cobalt and niobium ions are mainly presented in the form of Co$^{3+}$ and Nb$^{5+}$ in SCN. These results are consistent with other reports in Refs.16,17.

### 3.3 Electrical conductivity

As can be seen in Fig. 4, both SCM and SCN exhibit a semi-conducting behavior in air, and both of their electrical conductivities ($\sigma$) present a positive temperature coefficient. It can be also obviously found that the electrical conductivity of SCM in air is far less than that of SCN in the whole applied temperature range. When the ambient temperature is 973 K, the conductivity of SCM is only 0.36 S·cm$^{-1}$, while that of SCN reaches 7.81 S·cm$^{-1}$.

For most double perovskites, their electrical conductivities are sensitive not only to the environmental temperature but also to the oxygen partial pressure ($P_{O_2}$). In defect chemistry, the equilibrium relationship between the concentration of oxygen vacancies inside the crystals and the environmental oxygen partial pressure will exist at a fixed temperature for most materials. The defect equation can be described as $O_0^\cdot = 1/2O_2 + V_0 + 2e^\cdot$, from which one can find that two free electrons will emerge inside the crystals with the formation of an oxygen vacancy and the equilibrium of the defect reaction will change with $P_{O_2}$. Thus the concentration of free electron and oxygen vacancy inside the crystals, which can serve as charge carriers, would always change with $P_{O_2}$. For most materials, the relationship between electrical conductivity and oxygen partial pressure can be deduced as follows:18

$$K = \frac{P_{O_2}}{[O_0]} = \frac{P_{O_2}}{P_{O_2}^{\frac{1}{2}} |e^\cdot|^2} \quad (1)$$

$$\sigma \propto |e^\cdot| = (2K)^{\frac{1}{2}} \cdot P_{O_2}^{\frac{1}{2}} \propto P_{O_2}^{\frac{1}{2}} \quad (2)$$

$$\log \sigma = (-1/6) \cdot \log P_{O_2} + C \quad (3)$$

where $K$ is the constant of defect equilibrium reaction, and $C$ represents another constant related to material and temperature.

To demonstrate the relationship between the electrical conductivity and oxygen partial pressure, the electrical test was carried out at a self-regulating container where the partial pressure of oxygen could be controlled as well as being detected. The electrical conductivities for SCM and SCN varying with $P_{O_2}$ at 973 K presented a great difference, which can be seen in Fig. 5. For SCM, the conductivity increases with the decrease in oxygen partial pressure and a linear relation with a slope of about 0.14 can be established between log $\sigma$ and $P_{O_2}$, presenting a good fitting with Eq. (3), over the $P_{O_2}$ range of $10^{-21} \leq P_{O_2} \leq 10^{-14}$ atm. And the relationship between $\sigma$ and $P_{O_2}$ is reversible. The conductivity of SCM is 2.05 S·cm$^{-1}$ when $P_{O_2}$ reached 10$^{-21}$ atm, about 6 times higher than that in air. This result indicates that SCM has a typical characteristic of n-type semiconductor. However, it presents an opposite trend for SCN with a relatively more complicated function relationship between $\sigma$ and $P_{O_2}$. From Fig. 5(b), it can be obviously found that the decreasing of $P_{O_2}$ would cause a great attenuation for the conductivity of SCN. Compared with the value in air, it presents almost three orders of magnitude deterioration when $P_{O_2} = 10^{-19}$ atm. As discussed from XRD patterns, the phase of SCN is stable at low oxygen partial pressure atmosphere created by the flow of 5% H$_2$/Ar, so the reason for the dramatic decrease of conductivity in SCN while $P_{O_2} = 10^{-16}$ atm is probably not caused by the phase variation but by some other reasons.

The conducting properties of SCM and SCN are further explored in Fig. 6. The small-polaron formula $\sigma = (A/T)\exp(-E_a/kT)$ can be introduced to describe the temperature dependence of $\sigma$ over the whole applied temperature range, 573 $\leq T$ $\leq 973$ K. In the formula, $A$, $T$ and $k$ represent the pre-exponential factor, absolute temperature and Boltzmann’s constant, respectively, and $E_a = \Delta H_m + (\Delta H_f/2)$ is the sum of the polaron motional enthalpy $\Delta H_m$ and the enthalpy $\Delta H_f$ to free a polaron from the oxygen vacancy that creates it.19 According to the experimental data obtained in air, the Arrhenius plots [ln($\sigma$) vs $T^{-1}$] of SCM and SCN achieve a good linear fit within the whole test temperature range and give an $E_a$ of 0.205 and 0.339 eV, respectively. However, when the conductivity was measured under $P_{O_2} = 2.0 \times 10^{-18}$ atm, an inflection point (at 773 K) can be observed in the Arrhenius plot of SCM, which is absolutely impossible to be
found when it was measured in air. This result indicates that the conducting mechanism of SCM begins to change at the inflection point. According to the defect equation, the amount of oxygen vacancy increased with the decrease in \( P_{\text{O}_2} \). When \( P_{\text{O}_2} \) becomes relatively small, for example \( 2.0 \times 10^{-18} \text{ atm} \), the concentration of oxygen vacancy \( \{\text{O}_1\} \) will be high enough to produce distinct oxygen ion conductance in the crystals when it was activated at certain temperature. For SCM, the activating temperature of oxygen ion conductance is about 773 K, after which it shows apparent mixed conductance.

3.4 Crystal structure and conducting channel

As already introduced, double perovskites have one distinguished feature that the tilt system, the presence or absence of certain type of reflections must be carefully examined. The XRD patterns of SCM and SCN are shown in Fig. 7. The superstructure reflections at about 19.5 and 37.8° of \( 2\theta \) can be apparently observed in the XRD pattern of SCM, indicating that CoO\( _{6/2} \) and MoO\( _{6/2} \) octahedras have developed into an alternately orderly arrangement in three dimensional lattice to a certain degree, i.e. rock salt arrangement. The space group 14/m has been used as the fitting model, which can induce an excellent matching as is evident from Fig. 7(a). The reliability parameters from the fitting were \( R_p = 3.86\% \) and \( R_w = 6.34\% \). A tiny amount of SrMoO\(_4\) were identified as impurity phases (marked by *). For SCN, the space group 14/m was also the best model according to the diffraction data. The reliability parameters were \( R_p = 2.75\% \) and \( R_w = 3.95\% \), demonstrating an excellent fitting. As is shown in Fig. 7(b), almost no super cell diffraction peaks, produced by the orderly arrangement of CoO\( _{6/2} \) and NbO\( _{6/2} \) octahedras, can be observed, which indicates that BB’ cations may just turn into partial ordering or even out-of-order.

The detailed information of Sr\(_2\)CoRO\(_6\) perovskites, including lattice parameters, bond length and bond angle obtained by Rietveld refinement, is listed in Table 1. The lattice cell volume of SCM is larger than that of SCN. The mean Co–O bond length in SCM is longer than that in SCN. It is known that the length of bond is related to the ion radius. And the main valence state of cobalt in SCM is +2 and the corresponding radius of Co\(^{2+}\) (HS, six folds coordination) is 0.745 Å, while the main cobalt ion in SCN is Co\(^{3+}\) (HS, six folds coordination) and its radius is 0.61 Å. Also the length of Mo–O bond is shorter than that of Nb–O because the ionic radius of Mo\(^{6+}\) (0.59 Å) is smaller than that of Nb\(^{5+}\) (0.64 Å). All of the ionic radii above were based on Shannon’s ionic radii. In addition, Co–O1–R bonds are connected in a straight line, while Co–O2–R bond angles are less than 180°, implying that CoO\( _{6/2} \) and RO\( _{6/2} \) octahedras have a small angle of twist, taking e axis as the rotation axis. The crystal structure model of Sr\(_2\)CoRO\(_6\) is displayed in Fig. 8.

However, the conducting properties of SCM and SCN showed great difference, although their crystal structures and elemental compositions were bearing a close resemblance. Firstly, the conductivity of SCN in air was much higher than that of SCM, in excess of an order of magnitude. Secondly, the conductivity of SCM gave out a negative oxygen partial pressure coefficient, i.e. its conductivity decreased with the increase in the partial pressure of oxygen, while the conductivity of SCN presented a positive one. The electron conductivity occupies the dominant position in the entire conducting behavior in most double perovskites such as SCM and SCN. The differences of the conducting characteristics between the present two double perovskites can be possibly ascribed to the differences of the conducting mechanism of electrons.

In order to explain these differences, a conducting channel model based on crystal structure has been proposed here. The electron conduction (including electrons and holes) proceeds via charge exchanging among mixed-valent ions, mainly BB’ transition cations, which have incomplete \( d \) shells to exchange electrons between the possible neighboring atoms. The lattice arrangement as shown in Fig. 9 is a top view from (001) crystal plane of Sr\(_2\)CoRO\(_6\), which was used to display the conducting channels of electrons and holes. C1, C2 and C3 represented the transition path of electrons (or holes): Co–R, R–R and Co–Co, respectively. The electron transition paths were established via classical electron exchange theories of direct exchange, in which there was coupling between the adjacent neighbor cations but not involving in an intermediary oxygen ion, i.e. electron exchange.

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Fig. 5. The relationship between the electrical conductivities (\( \sigma \)) and oxygen partial pressure (\( P_{\text{O}_2} \)) for (a) Sr\(_2\)CoMoO\(_6\) and (b) Sr\(_2\)CoNbO\(_6\) at 973 K.

Fig. 6. The Arrhenius plots of ln(\( \sigma T \)) vs \( T^{-1} \) for Sr\(_2\)CoMoO\(_6\) and Sr\(_2\)CoNbO\(_6\).
exchanges through the incomplete \( d \) shells between positive ions nearby. The distance of separation between the incomplete \( d \) shells (as well as ions) is related to the difficulty degree of electron exchange to some extent. For example, the neighboring Mn ions in MnCl\(_2\) are comparatively far apart, 40\% further than in metallic Mn, leading to a small direct exchange so as to produce hardly any conduction electrons.\(^{21}\) The distance of the single jump of electrons (or holes) could be represented by the distance between the adjacent two ions qualitatively in each conducting channel. The average length of ions in each channel is listed in Table 2, from which one could find that the length in C1 was more than 40\% shorter than that of the others, indicating it was the most effective conducting channel among them.

In SCM, the poly-valent ions, which could be used to form a conducting channel, are cobalt and molybdenum. However, most cobalt ions are difficult to accept another electron because the main valence state of cobalt is +2, the lowest one in cobalt ions. This phenomenon is similar to the reported results that Nb\(^{5+}\) or Sb\(^{3+}\) can hardly play the role of hole transfer in the hole conducting materials in Refs.\(^{22,23}\) So the conducting channel for electrons across cobalt ions will be blocked, which means that the channels of C1 and C3 are null and void for electron transfer. However, the conducting channel of C2 constituted by molyb-denum plays an important role in the overall electron conduction.

![Fig. 7](image1.png)

**Fig. 7.** The recorded (circles), fitted (full line) and differential (at the bottom) data of XRD patterns: (a) Sr\(_2\)CoMoO\(_6\) and (b) Sr\(_2\)CoNbO\(_6\).

![Fig. 8](image2.png)

**Fig. 8.** Two views of the structure of Sr\(_2\)CoRO\(_6\) (R=Mo, Nb): (a) along the \( c \) axis; and (b) with the \( c \) axis vertically.

![Fig. 9](image3.png)

**Fig. 9.** Schematic diagram of the conducting channel model for Sr\(_2\)CoRO\(_6\) (R=Mo, Nb).

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<th>Sr(_2)CoNbO(_6)</th>
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Table 1. Room-temperature lattice parameter, bond length, bond angle and density (\( d \)) obtained by rietveld refinement from XRD patterns of Sr\(_2\)CoRO\(_6\) (R=Mo, Nb).

Table 2. Average distance of each conducting channel.
denum also plays an important role in electron conduction. Mo$^{6+}$ ions across the conduction path complete a dynamic electron transfer by continuously absorbing and releasing electrons. The main channel for holes transfer is C3, for which the analytical method is opposite to that of electron, i.e., when the ions reach the highest valence state, they cannot accept vacancies. In SCM, the most effective conduction channel C1 is not involved in electron (or hole) transfer, which may be an important factor for the low conductivity of SCM in air. It is worth mentioning that oxygen nonstoichiometry also plays an important role in enhancing the conductivity of SCM, especially under a reducing atmosphere. The concentration of free electrons will be constantly increasing with the reduction of oxygen partial pressure, which will effectively enhance the efficiency of transporting electrons from C2.

In SCN, the main valences of cobalt and niobium are +3 and +5, respectively, neither of which reaches its correspondingly lowest one. This fact implies that a dynamic electron transfer between Co$^{3+}$ and Nb$^{5+}$ ions can be easily established, i.e., the conducting channel C1 is the dominant conducting path for electrons. Although BB$^+$ cations in SCN have not formed a long range ordered arrangement, but it does not affect the formation of C1. The transfer of electrons in SCN in air will be more efficient than that of SCM, which could explain the higher conductivity of SCN to some extent. According to the experimental facts from Fig. 2(b), the conductivity of SCN decreased with the descending of oxygen partial pressure, which may be contradictory with the theoretical deduction from the defect equation. Here, we give a possible explanation. Free electrons produced through the defect equation are trapped in CoO$_6$ (or NbO$_6$)$_2$, leading to the reduction of trivalent cobalt ions to bivalent (or the reduction of Nb$^{5+}$). The C1 channel will be broken when the concentration of Co$^{3+}$ is high enough, thus leading to a sharp drop in conductivity. Similar phenomenon has been reported in Ref. 26 where the authors indicated that the conductivity of Sr$_2$Fe$_{1-x}$Nb$_x$O$_{6+x}$ decreases with increasing amount of Nb$^{5+}$, which turns Fe$^{3+}$ into Fe$^{2+}$ in order to maintain the charge equilibrium in crystals.

The difference in conducting property between Sr$_2$CoMoO$_6$ and Sr$_2$CoNbO$_6$ can be attributed to their different valence states of cobalt ions. The conducting channels of electrons through Co$^{2+}$ will be broken, but promoted through Co$^{3+}$. Thus, the conductivity gives a negative oxygen partial pressure coefficient while the content of Co$^{3+}$ is dominant. Nevertheless, its reverse process will present an opposite trend.

4. Conclusions

The crystal structures of double perovskites Sr$_2$CoMoO$_6$ and Sr$_2$CoNbO$_6$ were refined by using Rietveld method via powder X-ray diffraction data. The result shows that both of them are tetragonal and have the same space group of I4/m. The refined crystal structures of Sr$_2$CoMoO$_6$ and Sr$_2$CoNbO$_6$ have been used to construct their own conducting channel model. For Sr$_2$CoMoO$_6$, the electrons (or holes) transfer through Mo$^{6+}$—Mo$^{5+}$ (or Co$^{3+}$—Co$^{4+}$) pair, and its conductivity increases with the decrease in oxygen partial pressure. For Sr$_2$CoNbO$_6$, the electrons have a more efficient transfer channel, i.e., Co$^{3+}$—Nb$^{5+}$ pair, in air. However, its conductivity decreases as the oxygen partial pressure decreases, because Co$^{3+}$ will be reduced to Co$^{2+}$ by capturing free electrons produced by the defect equation and break the electron transfer channel Co$^{3+}$—Nb$^{5+}$.

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