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RESEARCH ARTICLE

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Solid-state synthesis and properties of $SmCoO_3$

Abstract In this paper, perovskite oxide $SmCoO_3$ was prepared by the solid-state reaction method using Co_2O_3 and Sm_2O_3 as raw materials. The structure and properties of the samples were investigated by XRD, Raman spectral techniques, and DC measurements and so on. The results of XRD and Raman spectra showed that the mixtures of Co_2O_3 and Sm_2O_3 can react to produce a single phase perovskite oxide $SmCoO_3$ around 1353 K. The single-phase $SmCoO_3$ changes from an insulator to a semi-conductor and transition occurs around 470 K. The thermal expansion coefficient (2.17×10^{-5} K^{-1}) of the single-phase $SmCoO_3$ is approximately equal to that of doped $LaGaO_3$, but much bigger than that of SDC($Ce_{0.85}Sm_{0.15}O_2$) above 873 K.

Keywords $SmCoO_3$, solid-state reaction, cathode material, structure characteristic, conductivity

Perovskite-type oxides of $SmCoO_3$ system are of particular interest in the study and application of fuel cells. On the one hand, proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) both use Pt as electrode, which will be seriously oxidized after a time, with efficiency being decreased greatly. The solution to this problem is to make a mixed electrode made up of oxides having higher electrical conductivity as catalyst with Pt. $SmCoO_3$ is the most promising among the choices of compounds. On the other hand, new moderate dielectric materials have been developed to decrease the work temperature of solid oxide fuel cells (SOFCs) and the potential electrolyte are doped $LaGaO_3$ and CeO_2 compounds, with $SmCoO_3$ as the favorite cathode material for them [1,2].

The electronic property of $SmCoO_3$ perovskite is mainly decided by the 3d electron of Co, which exhibits Mott phase transition (an electronic transition deduced by temperature), i.e., it turns into metal from an insulator with increasing temperature. [2,3] Some established study has indicated that different synthesis methods can greatly affect the material properties, but the cause is not yet known [4]. Obtaining a stable material by studying the effect of the synthesis method on the property needs to be solved at present. In this paper, $SmCoO_3$ is prepared by solid-state reaction method and the influence on the structure and properties of the material is investigated by structure and property measurements.

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1 Experiments

1.1 Solid-state synthesis of $SmCoO_3$

$SmCoO_3$ is prepared by Sm_2O_3 and Co_2O_3 at high temperature under normal pressure in a furnace, the process is as follows: the weighed raw materials are mixed evenly in an agateware and grinded with alcohol. The prepared mixture is crumbled into a tablet that has a 13 mm radius and a 1 mm thickness by 200 Mpa pressure. The tablet is later put into a muffle furnace and sintered for 10 h at several different temperatures.

1.2 Presentation of structure and property

The XRD patterns were recorded with a diffractometer (Model Bede D') using CuKα radiation (λ=0.15418 nm) and silica powder (99.99%) scale. Raman spectra were measured at room temperature (Model JY-Hr800, France) using He–Ne laser (resolution ratio: 1 cm^{-1}). DC current measurement was done by model KEITHLEY 2400 series Source Meter on a four-probe arrangement. Polarization curve is obtained by Electrochemical Interface (Model SI 1287). And thermal expansion was measured by apparatus (Model Netzsch DIL 402C/3/G) using vitreous silica as sample frame in air (by a rate of 5 K/min).

2 Results and discussion

2.1 The effect of reaction temperature on sample

Figure 1 shows the XRD patterns of samples synthesized under several temperatures. The result indicated that, when the sample was subjected to the treatment at 1173 K, some peaks caused by the orthorhombic $SmCoO_3$ were observed, but the strongest peak (200) coincided with the second strongest peak, which showed the raw materials did not react completely. These two peaks were divided when the temperature increased to 1353 K and 1473 K. At these temperatures, only the peaks due to the orthorhombic $SmCoO_3$ were observed. The calculated crystal parameters are as follows: a=0.5278 nm, b=0.53391 nm and c=0.74762 nm, V =0.21068 nm^3, which coincided with the standard card. However, when the sample was heated up to 1573 K, peaks due to $SmCoO_3$ were slightly observed, together with those due to unreacted Sm_2O_3 and Co_2O_3 and other oxides, which showed the $SmCoO_3$ perovskite was unstable at this temperature. The above analysis shows that the relationship between the formation of $SmCoO_3$ perovskite and raising the temperature is not simple.

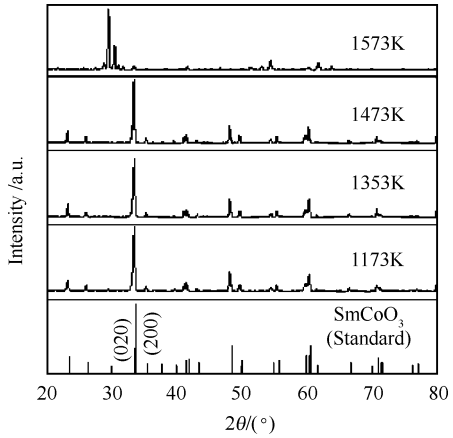

Fig. 1 XRD patterns of the samples prepared at different temperatures

The Raman spectra for the samples are shown in Fig. 2. The figure shows that the peaks of samples synthesized at 1353 K and 1473 K are the same but greatly different from those at 1173 K and 1573 K. The $SmCoO_3$ has an orthorhombic perovskite structure with space group D_{2h}^{16} (Pnma), which has 24 activated patterns. The Raman spectra of $LaFeO_3$ and $BaCeO_3$, which has the same space group, were studied although that of $SmCoO_3$ was still not reported. In Refs. [4,5], three Raman scattering bands of $BaCeO_3$ and $LaFeO_3$ are all observed: $BaCeO_3$: 80–150 cm^{-1}, 320–370 cm^{-1}, 620–660 cm^{-1} and $LaFeO_3$: 150–200 cm^{-1}, 400–450 cm^{-1}, 600–660 cm^{-1}, respectively. The band of low-frequency corresponds to the stretching and bending vibration of A ion and O ion (A–O,O–A–O), and the other two bands correspond with the vibration of Octahedron, which is made up of B ion and O ion (BO_6). Besides, the micro-structure difference due to Raman laser beam powers and kinds and synthesis method can also lead to the lack of bands. The peaks of samples at 1173 K and 1573 K do not exhibit an orthorhombic character but the samples at 1353 K and 1473 K exhibited only one Raman and at the range of 140–175 cm^{-1}. This is due to the stretching vibration of Sm-O and bending vibration of O-Sm-O, which coincide with the result of XRD in Fig. 1. The lost of Raman band of Octahedron of Co-O is yet to be studied.

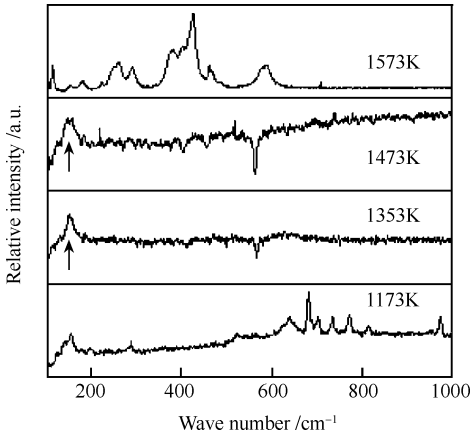

Fig. 2 Room temperature Raman spectra of the samples at different temperatures

2.2 Electrical conductivity

Figure 3 shows the temperature dependence of the electrical conductivity of $SmCoO_3$ synthesized at 1353 K and 1473 K from normal temperature to 1123 K, respectively. Figure 4 shows the logarithm of electrical conductivity ($\ln \sigma T$) vs. reciprocal temperature (1000/T) for the above two samples. The samples are both insulators with low electrical conductivity below 600 K. When it is above 600 K the conductivity increases with increasing temperature and samples behave

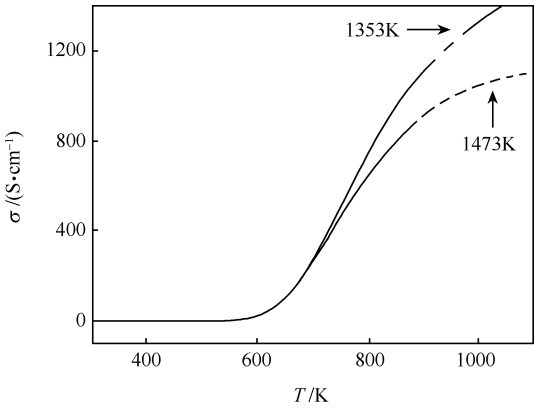

Fig. 3 Conductivity–temperature dependences of the two samples prepared at 1353 K and 1473 K, respectively

like a semiconductor. The structure of the two samples is the same by the result of XRD and Raman while the conductivity varies differently. The sample synthesized at 1353 K has high conductivity and coincides with that found in the literature [2].

Three regions can be found in the curve at 1353 K. From 300 K to 470 K the activation energy was 0.36 ev and it was 0.81 ev and 0.28 ev from 470 K to 750 K and above 750 K, respectively, which was consistent with the results in the literature [2]. These results indicated the mechanism of conduct electricity from insulator to semiconductor to metal (Mott transition induced by temperature). At 470 K, transition from insulator to semiconductor occurs and to metal transition above 470 K. In this range of temperature a semiconductor phase would coexist with a metallic phase (small polaron hole hopping mechanism). [2,6] For the sample at 1473 K, only two regions can be found in the curve from 300 K to 750 K and above 750 K, there was no insulator-to-semiconductor transition. From XRD results we can conclude that the sample synthesized at higher temperature (1573 K) is mainly single oxides of Sm and Co, which are resolved from $SmCoO_3$, so the electrical conductivity decreases.

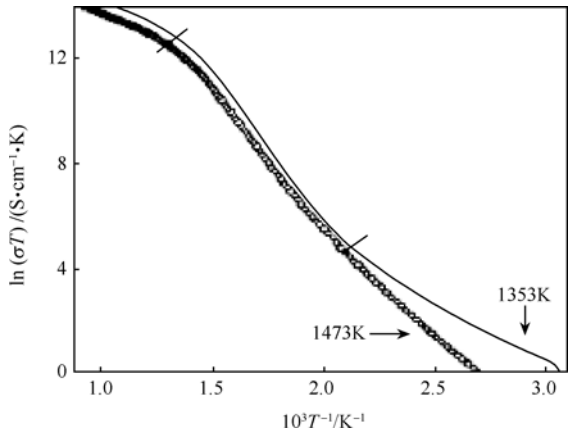

Fig. 4 Arrhenius plots of the two samples prepared at 1353 K and 1473 K, respectively

2.3 The curve of thermal expansion and electrochemical property

It is important that the thermal expansion coefficient of the electrode should match with the electrolyte. The thermal expansion coefficient of sample (1353 K) is measured by apparatus (Model Netzsch DIL 402 C/3/G) at 373 K–1073 K (shown in Fig. 5). Three regions can be found, which is consistent with the results of the curve ($\ln \sigma T$) -1000/T, showing that the change of thermal expansion coefficient comes along with the transition from insulator to semiconductor to conductor. The potential electrolytes are doped $LaGaO_3$ and CeO_2 compounds; the thermal expansion coefficient (2.17×10^{-5} K^{-1}) of the single-phase $SmCoO_3$ is approximately equal to that of doped $LaGaO_3$, but bigger than that of SDC ($Ce_{0.85}Sm_{0.15}O_2$) above 873 K[7].

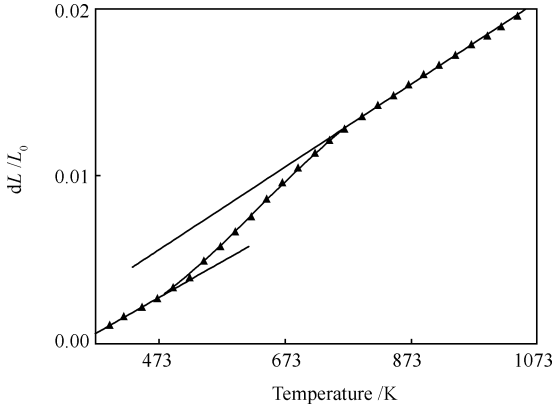

Fig. 5 Thermal expansion curve of the sample prepared at 1353 K

The electrochemical property directly influences the power output of fuel cells and the electrochemical property is related to the synthesis method. The sample of single phase $SmCoO_3$ was made into an electrode on SDC and its over potential–temperature dependence curve is shown in Fig. 6. The current density does not change with the temperature below 973 K but increases greatly when the temperature is above 973 K, which shows that the work temperature of fuel cell is above 973 K when its electrode is $SmCoO_3$.

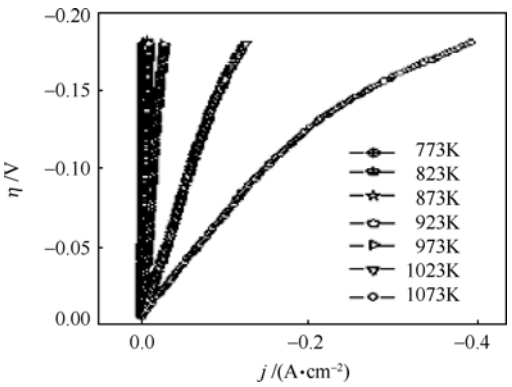

Fig. 6 Over potential-temperature dependence of the sample prepared at 1353 K

From the above analyses, we have made four conclusions: (1) The single phase perovskite oxide $SmCoO_3$ is synthesized from precursors Sm_2O_3 and Co_2O_3 at 1353 K by solid-state reaction. (2) The logarithm of electrical conductivity ($\ln \sigma T$) vs. reciprocal temperature (1000/T) curve shows that an insulator-to-semiconductor transition occurs and to metal transition when it is above 470 K; from 470–750 K a semiconductor phase would coexist with a metallic phase. (3) The clearly observed band in the room temperature Raman spectra of single-phase $SmCoO_3$ is at 140–175 cm^{-1}. (4) The thermal expansion coefficient of the single-phase $SmCoO_3$ is approximately equal to that of

doped $LaGaO_3$, but bigger than that of SDC ($Ce_{0.85}Sm_{0.15}O_2$) above 873 K, and the electrical property is well above 973 K. Therefore, the perovskite oxide $SmCoO_3$ is a kind of potential pre-material for fuel cell cathode electrode.

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