In situ high temperature X-ray diffraction studies of mixed ionic and electronic conducting perovskite-type membranes

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Abstract

Phase structure and stability of three typical mixed ionic and electronic conducting perovskite-type membranes, SrCo0.8Fe0.2O3/Co (SCF), Ba0.5Sr0.5Co0.8Fe0.2O3 (BSCF) and BaCo0.4Fe0.4Zr0.2O3 (BCFZ) were studied by in situ high temperature X-ray diffraction at temperatures from 303 to 1273 K and under different atmospheres (air, 2% O2 in Ar and pure Ar) at 1173 K. By analyzing their lattice parameters the thermal expansion coefficients (TECs) of BSCF, SCF and BCFZ are obtained to be 11.5/°C2x10/°C6 K1, 17.9/°C2x10/°C6 K1 and 10.3/°C2x10/°C6 K1, respectively. A relationship between phase stability and TEC was proposed: the higher is the TEC, the lower is the operation stability of the perovskite materials.

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1. Introduction

Perovskites (ABO3) are a prominent topic of research in materials science (high-Tc-electric conductor [1], ferroelectric [2] or high k dielectric [3], or magnetoresistance [4] material). Doping of these perovskites with multivalent cations on the A- and B-sites can lead to the simultaneous occurrence of ionic and electronic conductivities. For example, partial substitution of Sr and Co for La and Fe in A- and B-sites of LaFeO3 can result in a mixed conductor because oxygen vacancy defects (δ) are formed at elevated temperatures [5]. In recent years, such perovskite-type oxides with mixed ionic and electronic conductivities have attracted great interest, since they have large potential applications not only in the separation of oxygen from air [6–9] but also in the chemical process [10–18]. So far, most studies focused on the optimization of the oxygen fluxes, e.g., tube-type membranes [19]. However, there are only a few studies on the thermal expansion coefficient (TEC) and the phase stability of mixed ionic and electronic perovskites at high temperatures which could drastically affect their commercial applications.

In this paper, in situ high-temperature X-ray diffraction was used to study the TEC and phase stability of perovskite-type oxides at high temperatures. The purpose of this paper is to understand the relationship between high temperature phase structure, TEC and material stability, and to develop an effective way for choosing and estimating mixed ionic and electronic conducting perovskite-type materials. Three typical mixed electronic and ionic conducting perovskite membranes, SrCo0.8Fe0.2O3 (SCF) [21], Ba0.5Sr0.5Co0.8Fe0.2O3 (BSCF) [22] and BaCo0.4Fe0.4Zr0.2O3 (BCFZ) [23] were chosen because they are widely studied and have similar compositions but different properties. SCF has the highest reported oxygen permeation flux of 3.1 ml/(min cm2) at 1123 K, but its stability is poor. BSCF shows a high oxygen permeation flux (1.4 ml/(min cm2)) at 1223 K) and good stability (1000 h stable operation under air/He). BCFZ possesses...
a medium oxygen permeation flux (0.9 ml/(min cm²) at 1223 K) but the best stability reported so far.

2. Experimental

The SCF, BSCF and BCFZ oxides were synthesized using a combined citric and EDTA acid complexing method [22]. The stoichiometric amount of Sr(NO₃)₂, Ba(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃ and ZrO(NO₃)₂ were dissolved in EDTA-NH₃-H₂O solution. After stirring for a certain time, a proper amount of citric acid was introduced, with the mole ratio of EDTA acid: citric acid: total metal ions controlled at around 1:1.5:1. Precipitation might occur after citric acid addition. To avoid that, NH₃-H₂O was then added to adjust the pH value to around 6.0, and the solution became transparent immediately. EDTA-NH₃ and citrate formed a buffering solution, so the pH value of the system could be kept around 6.0 during the whole process. With the evaporation of water, a dark purple gel was obtained. The gel was then heated at 120–150 °C for several hours, followed by calcinations at 950 °C for 5 h to obtain the powders with final compositions of SCF, BSCF and BCFZ.

The crystal structures and lattice parameters of the three perovskites were characterized by in situ high-temperature X-ray diffraction (PHILIPS-PW1710) using Cu Kα radiation. The sample was tested in a high temperature cell (Bühler HDK 2.4 with REP 2000) with a heated Pt sample holder up to 1273 K under different atmospheres (air, 2% O₂ in Ar and pure Ar) and a Pt-Rh thermocouple connected with heated Pt strip sample holder was used to measure the temperatures. The heating and cooling rates amounted to 5 K/min. At each temperature step, the temperature was hold for 70 min. Data were collected in continuous scan mode in the range of 20–80° with interval 0.05°. The TEC for the Pt strip as an internal standard is 8.8 × 10⁻⁶ K⁻¹ that was used to calculate the correct peak positions of the perovskite oxides at examined temperatures. The lattice parameters refinements were performed using corrected peak positions.

3. Results and discussion

With increasing temperature, oxygen releases from the lattice. Accordingly, the metal ions could be reduced from a higher valence state to a lower one, and the oxygen vacancies were simultaneously formed. These effects may lead to phase transition. In situ high temperature X-ray diffraction technique provides an effective and direct way to trace the phase structure during the increasing and decreasing temperatures. Fig. 1 shows the XRD patterns of BSCF, SCF and BCFZ powders under air as the temperature was varied from 303 to 1273 K. Under air, the XRD patterns of BSCF, SCF and BCFZ oxides at different temperatures showed that these materials remained in their perovskite structure during the temperature range studied. This behavior is reversible since the XRD patterns during increasing and decreasing temperature, respectively, are almost the same. This means that the three perovskites exhibit good phase reversibility and structure stability under air.

During the oxygen permeation operation, one side of the membrane is exposed to air (high oxygen partial pressure side); the other side of the membrane is exposed to Ar or He (low oxygen partial pressure side). Thus the phase stability of the perovskite oxides under air alone is not enough to reflect the actual stability when they are selected as candidates for oxygen separation membranes. Therefore, it is necessary to study the high temperature phase stability of the mixed ionic and electronic conducting perovskite-type oxides under low oxygen partial pressures, e.g. 2% O₂ in Ar and pure Ar. Fig. 2 shows the XRD patterns of BSCF and BCFZ powders at 1173 K under different atmospheres (2% O₂ in Ar, pure Ar and air). New XRD peaks appeared in the XRD patterns of SCF when the atmosphere was 2% O₂ in Ar or pure Ar. Further analysis showed that a part of the perovskite has been decomposed to SrO, CoO and Fe₂O₃, as shown in Fig. 2(a). This means that SCF exhibits poor phase stability at low oxygen partial pressures although it has good phase stability under air. It was found that the perovskite structure of SCF is thermodynamically stable only at higher oxygen pressures (>0.1 atm) and this material has very limited chemical and structure stability at low oxygen partial pressures [24]. Pei et al. [24] found that the membrane reactor made from SCF broke into pieces when methane was fed to the reactor. These results are in accordance with our XRD results.

However, BSCF and BCFZ oxides can remain their perovskite structure under both air and 2% O₂ in Ar, and even under a pure Ar atmosphere with oxygen partial pressure ≤1 × 10⁻⁵ atm (shown in Fig. 2(b) and (c)). These results indicate that BSCF and BCFZ possess good phase stability at high temperatures not only under air but also under low oxygen partial pressures, e.g. pure Ar. By oxygen temperature-programmed desorption technique (O₂-TPD) Shao et al. [22] found that the substitution of strontium ions in SCF by larger barium ions could effectively suppress the oxidation of Co³⁺ and Fe³⁺ to Co⁴⁺ and Fe⁴⁺ in the lattice and stabilize the perovskite structure under low oxygen partial pressures, e.g. pure Ar. Consequently, it is reasonably understood that BSCF and BCFZ membranes can be steadily operated for a long time as reported in Refs. [22,23].

Fig. 3 shows the lattice parameters of BSCF, SCF and BCFZ perovskites at various temperatures calculated based on the XRD data under air. Koster and Mertins [25] had reported X-ray powder diffraction data for BSCF. The Rietveld refined unit cell parameter is 3.9830 Å at room temperature which is similar to our value of 3.9793 Å as shown in Fig. 3. This means our calculation method and measurement is believable. Among the three perovskites, the lattice parameter of BCFZ is the largest while that of SCF is the smallest. The lattice parameter of BSCF is larger than that of SCF because Ba²⁺ is larger than Sr²⁺. For the same reason, substitution of Co³⁺ by the larger Zr⁴⁺ should lead to an increase in the lattice parameter of BCFZ. From Fig. 3 it can be seen that the lattice parameters of the perovskites increase linearly with temperatures. Within the examined temperature range, the variation percents of BSCF, SCF and BCFZ were 1.1%, 1.7% and 1.0%, respectively. The TEC was calculated following the definition d[Δa/ΔT] = 2a₀/ΔT (a₀: lattice constant, ΔT: temperature difference). By analyzing their lattice parameters as shown in Fig. 3, the TECs of BSCF, SCF and BCFZ are obtained to be 11.5 × 10⁻⁶, 17.9 × 10⁻⁶ and 10.3 × 10⁻⁶ K⁻¹, respectively.

The highest TEC is found for SCF (17.9 × 10⁻⁶ K⁻¹), i.e. the material with the highest Co and the lowest Ba content. The high
Fig. 1. XRD patterns of the three perovskites under study during increasing and decreasing temperatures. Heating rate and cooling rate: 5 K/min, equilibration time at each temperature: 70 min, (a): BSCF, (b) SCF, (c) BCZF. P: perovskite.
Fig. 2. XRD patterns of the three perovskites under study in different atmospheres at 1173 K. Equilibration time: 70 min, (a): SCF, (b): BSCF, (c): BCZF. P: perovskite.
TEC of SCF was caused by the high concentration of cobalt and iron which can easily change their valences in this composition. It can be assumed that the higher the TEC of the perovskite is, the more easily the B-side ions can change their valences. The relationship between reducibility and the TEC is also validated by comparing the BSCF and BCFZ materials. It is found that doping the B-site of perovskites with metal cations exhibiting a constant oxidation state, such as Zr$^{4+}$, can suppress oxygen nonstoichiometry variations and lattice expansion induced by changes in temperatures or oxygen chemical potentials and increase the phase structure stability [26]. From our experiments it was found that the TEC of BCFZ ($10.3 \times 10^{-6}$ K$^{-1}$) is slightly lower than that of BSCF ($11.5 \times 10^{-6}$ K$^{-1}$). This finding is in agreement with the fact that the membrane reactor made of BCFZ is more stable during the POM reaction than that made of BSCF. Thus it can be understood that a high reducibility of metal ions in the perovskite leads to a high TEC which results in poor operation stability when it was used as membrane material for oxygen separation and membrane reactors for POM at high temperatures.

4. Conclusions

Structure and stability of the mixed ionic and electronic conducting perovskite-type oxides can be effectively studied by in situ high-temperature X-ray diffraction. It is a fast method to estimate the phase stability of new mixed ionic and electronic conducting perovskite-type oxides by determining by-phases, lattice constants and TEC. In this study a relationship between phase stability and TEC was proposed: the higher is the TEC, the lower is the phase stability of the perovskite materials.

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References


