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Detecting CO_2 at ppm level in synthetic air using mixed conducting double perovskite-type metal oxides

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ABSTRACT

Here, we report a novel double perovskite-type $BaCa_{0.33}Nb_{0.34}Fe_{0.33}O_{3-\delta}$ (Fe–BCN) as a CO_2 sensor at ppm level in a mixture of 21% O_2 in N_2 (dry synthetic air) working at 500–700 °C. Powder X-ray diffraction (PXRD) was used to confirm the formation of cubic double perovskite-type structure. In situ PXRD measurement under CO_2 showed excellent chemical stability in the temperature range of 25–800 °C. A significant decrease in total impedance (resistance) was observed upon exposure to CO_2 (ppm level) in synthetic air using AC impedance spectroscopy. Fe–BCN showed a fast response ($t_{90} \sim 4$ min) when 1500 ppm CO_2 was introduced. The sensor response was found to be linear over the investigated range in the log I vs. log pCO_2. Fe-substitution in $BaCa_{0.33}Nb_{0.67}O_3$ (BCN) is critical for the observed CO_2 sensor properties since BCN exhibited a poor response under the identical sensor measurement conditions. The CO_2 sensor mechanism was established using mass spectrometry (MS) in combination with DC measurements. The long-term sensor performance was studied for Fe–BCN and re-assured high sensitivity, stability and reliability.

1. Introduction

The detection of greenhouse CO_2 is gaining attention because of increasing global warming and environmental pollution. Monitoring CO_2 in residences, industries, agricultural fields, and CO_2 sequestration plants is primary concern for public security [1]. Reliable gas sensors are necessary for continuous on-site monitoring of greenhouse CO_2 emitted by power plants and solid oxide fuel cells (SOFCs), if these SOFCs are powered by hydrocarbons and integrated with CO_2 capture and storage (CCS). Also, continuous detection of CO_2 is important in enhanced oil recovery (EOR) [2] as well as carbon capture and storage (CCS) [3]. Therefore, it is essential for such applications to detect in situ CO_2 concentration at high temperatures, under high pressure and other harsh environmental conditions.

The power plant industries consider solid state sensors, which can detect in situ CO_2 concentration in real-time, as a potential low cost, high-sensitive, high-selective monitoring system [4–8]. CO_2 is commonly detected by spectroscopic method, known as non-dispersive infrared (NDIR) sensor. Not only are they expensive, but they are large and may not be ideal for real-time CO_2 detection in a combined CCS and SOFCs. Optical, semiconductor, and electrochemical CO_2 sensors, in development, could detect wide range of CO_2 concentrations [9–13]. However, they are not applicable for in situ measurements at elevated temperatures because their gas sensor properties become unstable [14].

Metal oxides, such as SnO_2 [15] and In_2O_3 [16], are possible high operating temperature gas sensors; however, semiconductor-based sensors are unsuitable for CO_2 detection at trace ppm level because the detection limit is too high and the sensors display cross-sensitivity to humidity [17]. Although, the fast Na^+ ion conducting $Na_3Zr_2Si_2PO_{12}$ and Na-β-alumina were found to detect CO_2 down to ppm level [18–20], these sensors have a reduced life-time because of gas leakage through the sealing and electrolytes, formation of reaction products at interfaces, and use of extra auxiliary electrode [21]. Major challenges for these sensors also include selectivity, response time, and degradation of electrodes [22]. Transition metal substituted double perovskite-type $BaCa_{0.33}Nb_{0.67-x}M_xO_{3-\delta}$ (M–BCN) has been widely studied as mixed ionic and electronic conductors (MIECs) for SOFCs [23–25]. Fe-substituted $BaCa_{0.33}Nb_{0.34}Fe_{0.33}O_{3-\delta}$ (Fe–BCN) is explored as a potential solid state resistance-type CO_2 sensor in synthetic air at 500–700 °C because of its high thermal and chemical stability in CO_2 atmosphere. In addition, Fe–BCN is less likely to deteriorate in humid conditions, offering a wider range of applications.

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2. Experimental

2.1. Sample preparation

Required stoichiometric amounts of $Ba(NO_3)_2$ (99+%, Alfa Aesar), $CaCO_3$ (99% Fisher Scientific Company), Nb_2O_5 (99.5%, Alfa Aesar) and Fe_2O_3 (99+%, Alfa Aesar) were mixed to prepare double perovskite-type structure $BaCa_{0.33}Nb_{0.67}O_3$ (BCN) and $BaCa_{0.33}Nb_{0.34}Fe_{0.33}O_{3-\delta}$ (Fe–BCN) using conventional solid-state (ceramic) reaction. The desired amount of 2-propanol was added to these starting powder materials in a zirconia bowl and ball milled for 12 h at 200 rpm using zirconia balls with reversed rotation every hour to ensure proper mixing. The mixed powders were then dried and calcinated at 1000 °C for 12 h. The resulting powders were ball-milled again for 6 h after adding 2-propanol, dried and pressed into the pellets using an isostatic pressure, and sintered in air at 1400 °C for 24 h. Re-crystallized alumina crucibles were used for sintering the pellets.

2.2. Characterization of structure and chemical stability

The sintered pellets were crushed into powders for the phase characterization by powder X-ray diffraction (PXRD) using a Bruker D8 powder X-ray diffractometer (Cu Kα, 40 kV; 40 mA) at room temperature with a 2θ step scan width of 0.02° and a counting time of 6 s per step. The structure was characterized using the Rietveld refinement with PXRD data. In situ chemical stability test was performed from 25 to 800 °C with the continuous flow (100 sccm) of 1% CO_2 (balanced in dry synthetic air, 21% O_2 in N_2) using the PXRD equipped with the Anton Par HTK2000 high temperature stage. The temperature was raised from room temperature to 800 °C at the rate of 6 °C/min and was kept for an hour to equilibrate after reaching the target temperature at 100–800 °C with the difference of 200 °C for each measurement.

Scanning electron microscopy (SEM) (Philips XL30 SEM) was used to study the microstructure of the Fe–BCN pellet. Microstructure and phase purity were further studied using a high-resolution transmission electron microscopy (HRTEM) coupled with selected area electron diffraction (SAED) (FEI Tecnai F20 FEGTEM equipped with a Gatan Imaging Filter and a Gatan 860 GIF 2001 CCD of 1024 × 1024 resolution). HRTEM was done at magnifications between 940,000 and 1,350,000. The diffraction patterns were taken at a camera length of 400 mm and directly after taking each individual diffraction pattern of the sample, it was exchanged by a reference sample of Au without changing any settings on the microscope. The diffraction rings of Au were used to confirm a proper calibration in diffraction mode of the equipment.

2.3. Characterization of electrical transport properties

Electrical conductivity of sintered pellets was measured under different pCO_2 (0–1500 ppm CO_2 balanced in dry synthetic air) at 500–700 °C. Au paste (Heraeus Inc., LP A88-11 S Germany) was painted on both sides of the sintered pellets and cured at 600 °C for 1 h in air to remove the organic binders. Moreover, Au wires as a current collector were kept in contact with the surface of the pellet using a spring-loaded contact. The cell with the pellet was heated to the desired temperature (500–700 °C) using Barnstead tubular furnace (model No. 21100). The furnace temperature was held constant for a minimum of 2 h and a maximum of 24 h before each measurement. A two probe electrochemical cell was employed for the electrical characterization, where conductivity was measured by AC electrochemical impedance spectroscopy (Solartron; model no.: SI 1260, 0.1 V; 0.01 Hz–1 MHz).

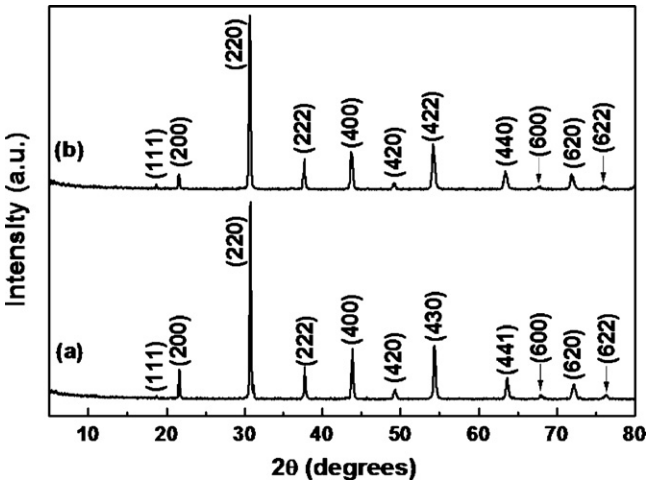

Fig. 1. PXRD of as-prepared $BaCa_{0.33}Nb_{0.34}O_3$ (a), and $BaCa_{0.33}Nb_{0.33}Fe_{0.33}O_{3-\delta}$ (b) at room temperature.

2.4. CO_2 sensor studies

A typical conventional gas flow apparatus using computer regulated mass flow controllers (MCS-100 SCCM-D/5M, 5IN) was used to prepare desired pCO_2. The concentration of CO_2 was controlled in the range between 0 and 1500 ppm by mixing N_2 (99.99%) and CO_2 balanced by dry synthetic air (Praxair, Inc., Canada). The total gas flow rate of gas passing through the cell was 100 sccm. The CO_2 sensors were located in the middle of a quartz tube inside the Barnstead tubular furnace and measurements were conducted at 500–700 °C. A two probe electrochemical cell was employed. DC measurements were done by applying a constant voltage of 0.1 V (Solartron, SI 1287). Sensor measurements were performed at constant current of 0.2 mA, 0.5 mA, and 1 mA at 700 °C. In order to investigate the effect of humidity on the sensing behavior, the sensing characteristics were examined in both dry and wet atmospheres (3% H_2O). For wet atmosphere, the mixed gas was passed by bubbling through water at ~25 °C. The Au electrodes with surface area of 0.049 cm^2 were used for measuring the surface sensitivity and the distance between two electrodes was kept at 0.55 cm. Mass spectrometer (MS) (Pfeiffer Vacuum) was used to analyze the gases coming out of the operating cell.

3. Results and discussion

3.1. Structure and phase stability studies using ex situ and in situ PXRD, HRTEM and SAED

Fig. 1 shows the powder X-ray diffraction (PXRD) patterns of as-prepared parent $BaCa_{0.33}Nb_{0.67}O_3$ (BCN) (Fig. 1a) and Fe-substituted $BaCa_{0.33}Nb_{0.34}Fe_{0.33}O_{3-\delta}$ (Fe–BCN) (Fig. 1b). All observed diffraction lines for both compounds can be assigned to single-phase double perovskite structure. Rietveld refinement of Fe–BCN PXRD pattern is shown in Fig. 2a, which further confirmed double perovskite-type structure (space group: *Fm*-3*m* (No. 225)) with a lattice constant of $a = 8.3257(2)$ Å, akin to parent $BaCa_{0.33}Nb_{0.67}O_3$ (BCN) [23,24]. The detailed structural models and the Rietveld refinement results are summarized in Table 1. Furthermore, HRTEM and SAED studies were done on as-prepared parent compound BCN (Fig. 2b) as well as on Fe–BCN (Fig. 2c) to validate our proposed structure. The assigned diffraction lines in the SAED patterns shown in Fig. 2b (ii) and c (ii) for BCN and Fe–BCN respectively, are consistent with their corresponding PXRD.