X-ray photoelectron (XPS) and Diffuse Reflectance Infra Fourier Transformation (DRIFT) study of $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ (BSCF: $x=0$–0.8) ceramics

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ABSTRACT

The X-ray photoelectron spectra (XPS) of sintered BSCF ceramics ($Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}, 0 \leq x \leq 0.8$) were measured at room temperature (RT). Peak areas of Fe_{2p1}, Fe_{2p3}, Fe_{3p} and Co_{3p} increased systematically with increasing cobalt concentration, while their binding energies (BEs) remained the same (723.3, 710.0, 55.0 and 60.9 eV, respectively). However, the BEs of lattice oxygen in O_{1s} (528.1 eV) and Ba_{4d} for the BaO bond (87.9V and 90.2 eV) increased with increasing cobalt concentration. The shoulder peak of Ba_{3d}/Co_{2p} increased from 778.0 to 778.7 eV, which implies that this peak can be attributed to another Ba XPS peak (described as Ba_{2nd} in this study) due to the overlapping area between barium cations and oxygen anions. The overall peak areas of Ba_{4d} increased up to $x=0.4$, and then decreased, which coincides with the behavior of the Diffuse Reflectance Infrared Fourier Transform (DRIFT) bands representing adsorbed CO_3^{2-} (vCO_3^{2-}) and structurally bonded CO_3^{2-} (v_2, v_3) (800–1200 and 862/1433 cm^{-1}, respectively).

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1. Introduction

The perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) has attracted considerable attention for its potential application as a cathode material in the intermediate temperature solid oxide fuel cells (IT-SOFCs) and oxygen separation membranes [1,2]. BSCF as a mixed ionic-electronic conductor (MIEC) exhibits a high oxygen-ionic transport rate via oxygen vacancies, with the oxygen self-diffusion coefficient and ionic conductivity on the order of 10^{-6} cm^2/s and 0.018 S/cm at 700 °C [3]. Such outstanding conducting properties as well as relatively high phase stabilities make it possible for BSCFs to be applied as semipermeable membranes and catalytic converter of hydrocarbons [4]. The substantial analyses of the surfaces of BSCF in diverse aspects such as crystalline structure and ionic binding energy can be helpful in designing BSCFs for the future applications.

BSCF possesses a cubic perovskite structure. B-site metal ions (Co, Fe) are coordinated by six oxygen ions to form close packing of BO_6 octahedral sites. A-site ions (Ba^{2+}(1.61 Å), Sr^{2+}(1.44 Å)) are coordinated by 12 adjacent oxygen ions and fitted between the BO_6 octahedra. The ideal lattice parameter, a, can be obtained with $a=\sqrt{2}(R_A+R_O)$ or $2(R_B+R_O)$ on the ground that R_A (Ba^{2+})=1.61 Å,

R_B (Fe^{4+})=0.59 Å and R_O (O^{2-})=1.40 Å. If the lattice parameter, a, is equal to $\sqrt{2}(R_A+R_O)$, the calculated lattice parameter can be about 4.25 Å. On the other hand, the calculated lattice parameter with $a=2$ (R_B+R_O) will be about 3.97 Å.

The BO_6 octahedral determines lattice constant with $a=2(R_B+R_O)$, implied by the measured lattice constant by XRD analysis (around 3.95 Å) [5]. Therefore, it is expected that the electron clouds surrounding A-site cations could be overlapped with those of oxygen anions because of the shortened distance between A-site cations (especially Ba^{2+}) and oxygen anions in BSCF. Particularly, the bonding states between Ba cations and oxygen anions influence the BE of e$^-$ using XPS spectra [6]. Also, the non-ideal crystal structure keeps a significant concentration of oxygen vacancies, which would also affect the unit cell volume size. In addition to the unit cell volume expansion, the calculated tolerance factor (t_f) increases from 1.042 to 1.052 as cobalt concentration increases from $x=0$ to 0.8 in $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ according to [7]

$$t_f = \frac{(0.5*r_{Ba^{2+}} + 0.5*r_{Sr^{2+}} + r_{O^{2-}})}{\sqrt{2}(x*0.4*r_{Co^{3+}} + x*0.6*r_{Co^{4+}} + (1-x)*r_{Fe^{4+}} + r_{O^{2-}})} \quad (1)$$

where $r_{Ba^{2+}}$=1.61 Å, $r_{Sr^{2+}}$=1.44 Å, $r_{Co^{4+}}$=0.53 Å, $r_{Co^{3+}}$=0.61 Å, $r_{Fe^{4+}}$=0.59 Å, $r_{Fe^{3+}}$=0.65 Å and $r_{O^{2-}}$=1.40 Å [8]. The comparison between the increases of lattice parameter and tolerance factor according to cobalt concentration increase is summarized in Table 1. Reaney et al. reported that the dielectric permittivity of

Ba- and Sr-based perovskite deviates significantly from the temperature referenced values when tolerance factor (t_f) are between 0.95 and 1.06 [9]. When t_f deviates from this range, the crystal structure is prone to be unstable. Therefore, the change of bonding state due to unit cell expansion and the increase of t_f with increasing cobalt concentration can affect the binding energy (BE) of e^- to each atom of BSCF.

The XPS BE (eV) shift is the chemical shift which changes according to differences in formal oxidation state, molecular environment, lattice site and so forth. The chemical shift effect

Table 1
Tolerance factor (t_f) and lattice parameter (a) as x increases in $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$.

	Tolerance factor (t_f)	Lattice parameter (a), Å
0	1.042	3.931
0.2	1.044	3.951
0.4	1.047	3.968
0.6	1.049	3.978
0.8	1.052	3.986

can be explained with the charge potential model as shown in

$$E_i = E_i^o + kq_i + \sum_{i \neq j} \frac{q_i}{r_{ij}} \qquad (2)$$

where E_i is the BE of a particular core level on atom i, E_i^o is an energy reference, q_i is the charge on atom i and the final term sums the potential atom at atom i due to 'point changes' on surrounding atoms j, which is also referred to as a Madelung potential [10]. The change in the valence electron density of Δq_i changes the potential inside the sphere by $\Delta q_i/r_v$, and the BE as well, where q_i has the opposite charge to atom. For an example, the decrease in valence electron density on atom i will cause the increase of BE, which can be achieved by the increase of bond length between atoms. Vasquez et al. reported that, as the XPS BE of $Ba_{4d5/2}$ increases from 87.2 to 88.0 eV, the Ba–O bond length linearly increases from 2.802 to 2.818 Å in Tl–cuprate system, which is expected from the Madelung energy change [6]. Borca et al. reported that the main two O_{1s} peaks observed in $La_{0.7}Ca_{0.3}MnO_3$ can be assigned to the perovskite structure (i.e., the peak at lower binding energy (528.7–529.0 eV) to the O_{1s} of the Mn–O layer, and the peak at 531.0 eV to O_{1s} of the La/Ca–O)
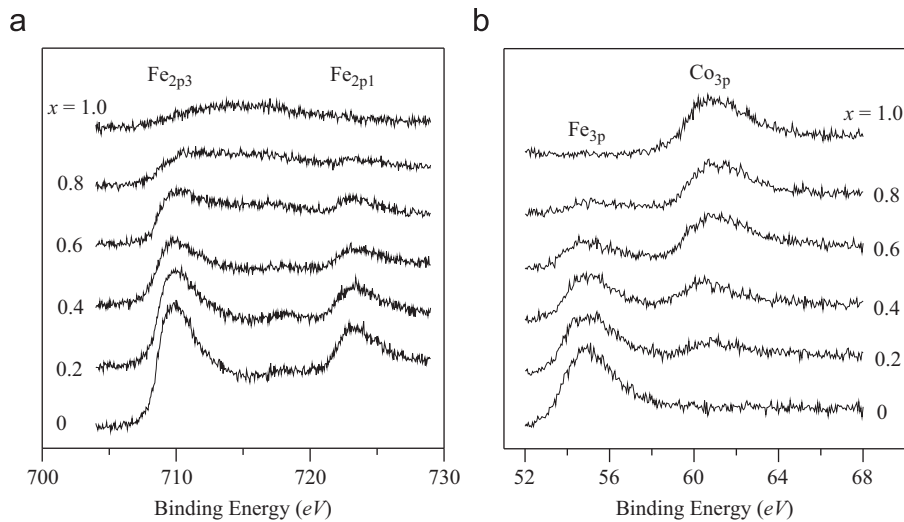

Fig. 1. The XPS spectra of (a) Fe_{2p} and (b) Co_{3p}/Fe_{3p} for the fractured surfaces of sintered $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ samples.

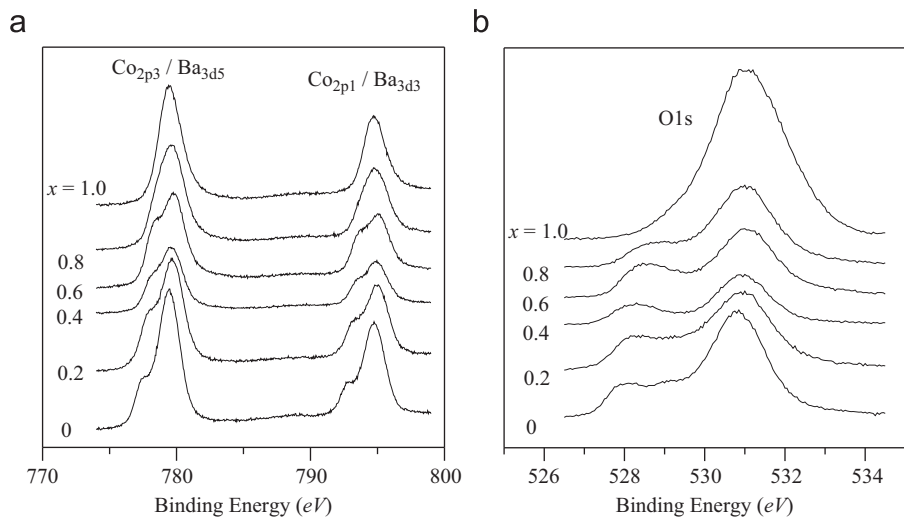Fig. 2. The XPS spectra of (a) Co_{2p}/Ba_{3d} and (b) O_{1s} for the fractured surfaces of sintered $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ samples.