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Structural and electrical properties of $La_{0.6}Sr_{0.2}Ca_{0.2}Fe_{0.8}M_{0.2}O_3$ (M=Al, Co, Ni, Cu, and Mn) perovskite type oxides

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ABSTRACT

Fine powders of $La_{0.6}Sr_{0.2}Ca_{0.2}Fe_{0.8}M_{0.2}O_3$(M=Al, Co, Ni, Cu, and Mn) were prepared by a co-precipitation method. The structural, morphological and thermal properties of fine powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermo gravimetric analysis (TGA). The electrical conductivity of cathode materials was increasing slightly with the increasing of dopant of Al, Co, Ni, Cu and Mn. The dielectric constant of the cathodes measured as a function of frequencies, it is seen that the doping of different oxides dielectric constant increases.

KEYWORDS

Oxides;
Chemical synthesis;
XRD;
Electrical properties.

INTRODUCTION

Intermediate temperature solid oxide fuel cells (IT-SOFCs) operating at 600-800^{0}C have attracted considerable interest in recent years[1-2]. Lowering the operation temperature can minimize various problems associated with high temperature operation, such as ionic interdiffusions between electrode/electrolyte interfaces, sintering of electrodes. In addition, advantages operating cost and fast starting time are also driving forces for research of IT-SOFCs. However, a major issue with the reduced operating temperature is the decrease in the catalytic activity of the cathode for oxygen reduction[3]. Thus, there is interest in identifying improved cathodes for IT-SOFCs.

Currently, $LaFeO_3$ is regarded as one of the most promising materials due to their innovative use in advance technologies[4-6]. These perovskite-type oxides are active oxidation catalysts, environmental monitoring films, can be employed as as cathodes and membranes in solid oxide fuel cells, as electrode materials, as magnetic materials, and as active materials for chemical sensors for the detection of humidity, alcohols, and gases such as oxygen, CO, NO and NO_2[7-11]. The primary object of this study was synthesize fine nano powders of $La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$(LSCF) and $La_{0.6}Sr_{0.2}Ca_{0.2}M_{0.2}Fe_{0.8}O_3$(M=Al, Cu, Co, Mn, Ni) compositions for applications as SOFC cathodes.

EXPERIMENTAL

$La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$(LSCF) and $La_{0.6}Sr_{0.2}Ca_{0.2}M_{0.2}Fe_{0.8}O_3$(M=Al, Cu, Co, Mn, Ni) was prepared by co-precipitation method using analytically pure La $(NO_3)_3.6H_2O$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, $Al(NO_3)_2.xH_2O$, $Co(NO_3)_2.xH_2O$, $Cu(NO_3)_2.xH_2O$, $Ni(NO_3)_2.xH_2O$, $Mn(NO)_3.xH_2O$ and $Fe(NO_3)_3{\cdot}4H_2O$ were mixed and dissolved in distilled water with the required molar ratio

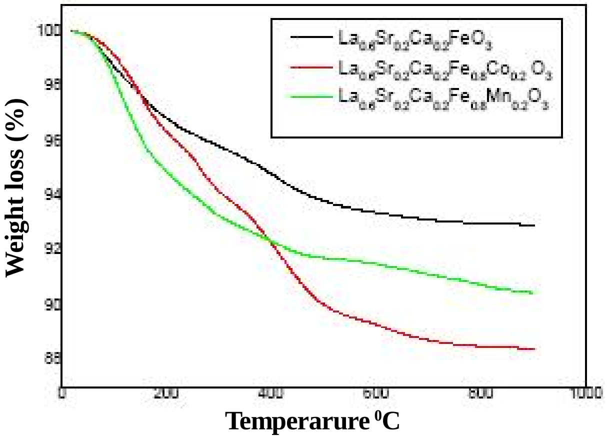

Figure 1: The TGA curve of the as synthesized powders recorded in air at a heating rate of 10^{0}C

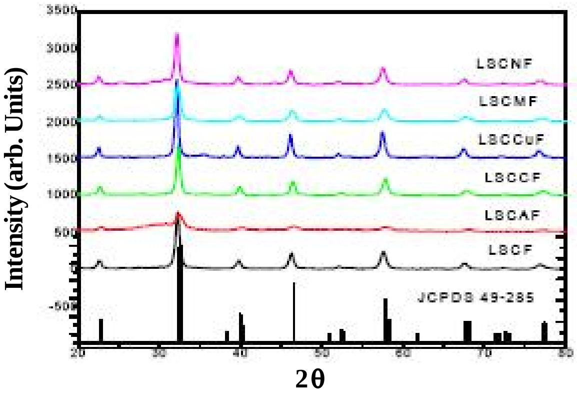

Figure 2: The powder X-ray diffraction pattern at temperature 600^{0}C calcined for 4hrs $La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$ (LSCF) and $La_{0.6}Sr_{0.2}Ca_{0.2}M_{0.2}Fe_{0.8}O_3$(M=Al, Cu, Co, Mn, Ni)(LSCMF)

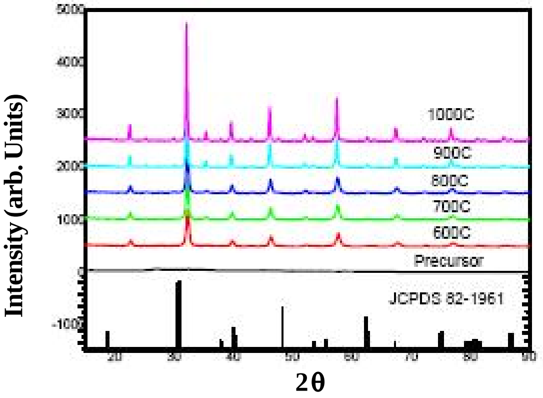

Figure 3: The powder X-ray diffraction pattern of $La_{0.6}Sr_{0.2}Ca_{0.2}Co_{0.2}Fe_{0.8}O_3$ (LSCCF) calcinated at temperatures of 600, 700, 800, 900 and 1000^{0}C

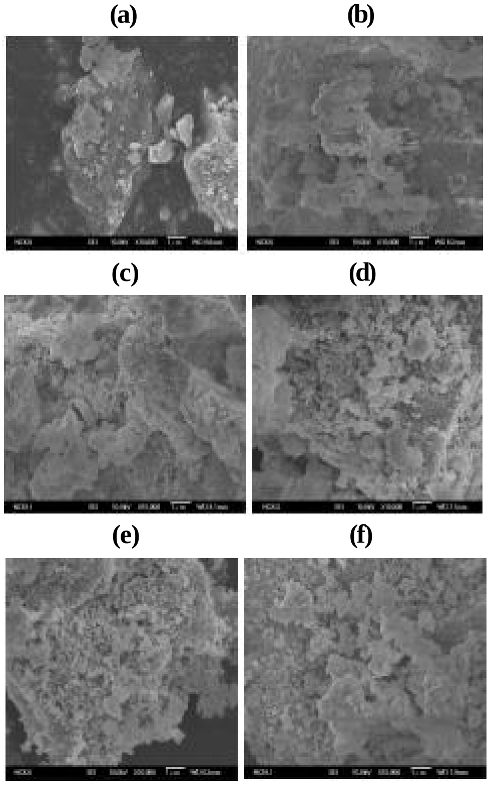

Figure 4: SEM micrographs of $La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$ powders calcined at temperatures (a) precursor (b) 600, (c) 700, (d) 800, (e) 900 and (f) 1000^{0}C

and excessive NaOH solution was added into the metal nitrates solution rapidly so that all the metal ions precipitated. Then the precipitate was washed with distilled water to remove the redundant OH^-. After that, the precipitate was dried at 80^{0}C to obtain the precursor powders. The as-dried precursor was ground and then calcined at the different temperature. The crystal phase of materials was identified by XRD.

The dielectric constant and ac conductivity measurements were carried out in the frequency range from 1M to 1K Hz at room temperature using LCR meter(HP 4824A).

RESULTS AND DISCUSSION

Figure 1 shows the weight loss of LSCF, LSCCF and LSCMF samples during heating up in air. As shown, there is a very slow weight loss from room temperature up to around 200^{0}C, which was attributed to the desorptions of physically adsorbed water and loss of residual[12].

Figure 2 Shows the X-ray diffraction (XRD) patterns of the $La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$(LSCF) and $La_{0.6}Sr_{0.2}$

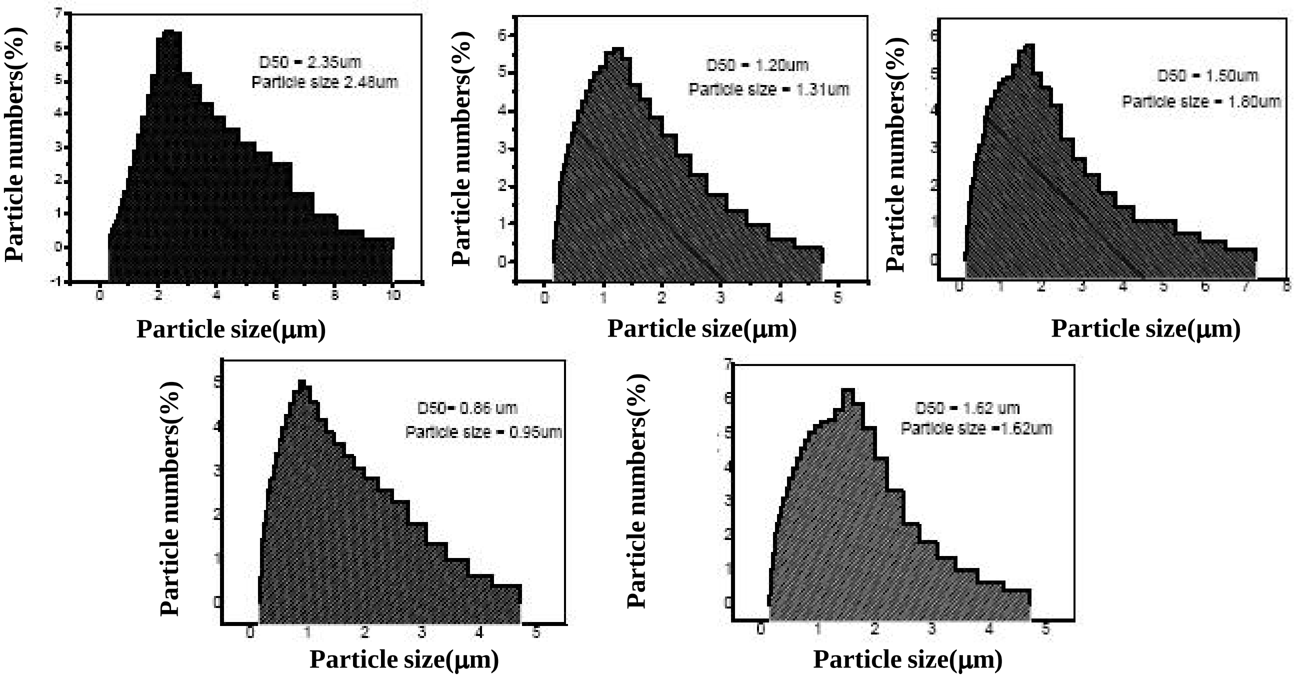

Figure 5: Particle size distribution of as calcinated at 1000°C powder samples (a) $La_{0.6}Sr_{0.2}Ca_{0.2}FeO_3$(LSCF), (b) $La_{0.6}Sr_{0.2}Ca_{0.2}Al_{0.2}Fe_{0.8}O_3$(LSCAF), (c) $La_{0.6}Sr_{0.2}Ca_{0.2}Co_{0.2}Fe_{0.8}O_3$(LSCCF), (d) $La_{0.6}Sr_{0.2}Ca_{0.2}Mn_{0.2}Fe_{0.8}O_3$(LSCMF), and (e) $La_{0.6}Sr_{0.2}Ca_{0.2}Ni_{0.2}Fe_{0.8}O_3$(LSCNF)

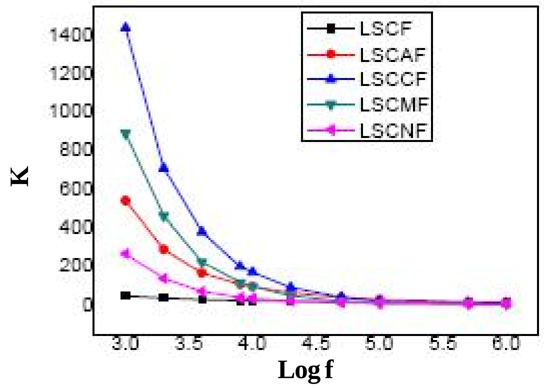

Figure 6: Dielectric constant vs. frequency for LSCF series sintering temperature at 1200°C

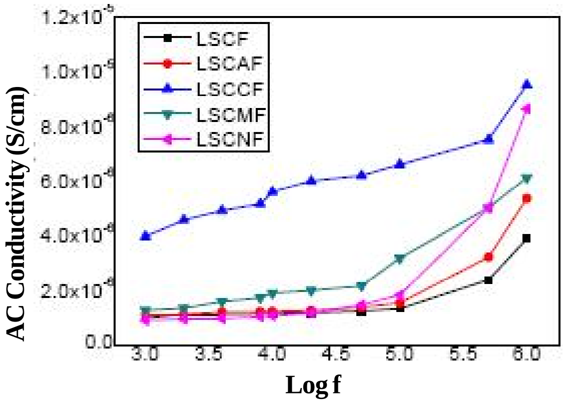

Figure 7: AC Conductivity vs. frequency for LSCF series sintering temperature at 1200°C

$Ca_{0.2}M_{0.2}Fe_{0.8}O_3$(M=Al, Cu, Co, Mn, Ni) powders calcinated at 600°C. Single phase powders with a cubic ABO_3 perovskite type structure similar to that of LSCF were obtained[13]. X-ray diffraction patterns for different heat treated LSCCF powders are shown n figure 3. The X-ray patterns before calcination show an amorphous phase. After calcinations the orthoferrite $LaFeO_3$ can observe in samples calcinated at 600, 700, 800, 900, and 1000°C. The as prepared LSCCF powders shows weak crystallinity of the perovskites phase. Formation of the perovkite phase is completed at 600 °C as observed by XRD results in figure 3.

The SEM micrographs of the LSCF prepared powder are shown in figure 4. The as-prepared agglomerates, Substantial particle growth was observed upon calcinations for 4 h at 600 to 1000°C[14]. The particle size distributions of the 1000°c temperature powder samples were presented in figure 5.

The room temperature dielectric constant versus frequency is shown in figure 6. They have relatively high dielectric constant, ε_r in the range 100-1400 at 1 KHz. The dielectric constant shows very little variation in the frequency range 20K Hz–1 MHz for all doping cathodes. It is seen that the dielectric constant increases progressively with the substitution for B-site. The dielectric constant decreases with the increase in frequency and at high frequency[15-16]. The AC conductivity with respect to frequency is shown in figure 7. The low frequency region corresponds to the dc conductivity where the inter-well hopping responsible for dc conduction completely dominates over the intra-well hopping associated with pure ac conduction[15].

The phenomenon of the conductivity dispersion in solids is generally analyzed using jonschers law[16] $\sigma(\omega) = \sigma 0 + A\omega^n$, where σ_0 is the DC conductivity fr a particular temperature, A is a temperature dependent constant and n is the power law exponent which generally varies between 0 and 1 depending on temperature. The exponent n represents the degree of interaction between mobile ionics with the lattice around them. The prefactor A determines the strength of polarizability.

CONCLUSIONS

Perovskite-type mixed oxides, such as $La_{0.6}Sr_{0.2}Ca_{0.2}Fe_{0.8}M_{0.2}O_3$ (M=Al, Co, Ni, Cu, and Mn) cathode materials for intermediate temperature solid oxide fuel cell (IT-SOFCs) were prepared and characterized. The TGA results, it was associated with the loss of lattice oxygen. The decrease in dielectric constant with frequencies shows the dielectric dispersion at low frequency regions.

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