Journal of the European Ceramic Society 38 (2018) 5030–5035

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Investigation on thermoelectric properties of screen-printed $La_{1-x}Sr_xCrO_3$-In_2O_3 thermocouples for high temperature sensing

Dan Liu[a], Peng Shi[a,*], Wei Ren[a,*], Yantao Liu[a], Ming Liu[a], Yijun Zhang[a], Qijing Lin[b], Bian Tian[b], Zhuangde Jiang[b,*], Zuo-Guang Ye[a,c]

[a] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, 710049, China
[b] The State Key Laboratory for Manufacturing System Engineering, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an, 710049, China
[c] Department of Chemistry and 4D LABS, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada

ARTICLE INFO

Keywords:
Lanthanum chromites
Thermocouple
Thermoelectric voltage
High stability
High reliability

ABSTRACT

$La_{1-x}Sr_xCrO_3$-In_2O_3 thick film thermocouples were fabricated by screen-printing method for high temperature sensing and the effects of Sr^{2+} content were investigated systematically. All $La_{1-x}Sr_xCrO_3$ thick films showed well crystallization with orthorhombic unit cell. Their average particle sizes showed the tendency of first increase then decrease gradually with the increase of Sr^{2+} content, and the maximum of average particle size was 1.76 μm. At the same time, the conductivities were improved with the increase of Sr^{2+} content. The thermoelectric properties of $La_{1-x}Sr_xCrO_3$ depended on the Sr^{2+} content and the average Seebeck coefficients had an exponential decay tendency with the increase of Sr^{2+} content. For $La_{1-x}Sr_xCrO_3$ (x = 0.1–0.4)-In_2O_3 thermocouples, excellent repeatability and stability were observed through multi-cycles and long-time usage testing at high temperature. The $La_{0.7}Sr_{0.3}CrO_3$-In_2O_3 thick film thermocouple with excellent thermal stability (drift rate: 0.81 °C/h) and reliability makes it become a promising candidate high sensitivity thermal sensor.

1. Introduction

With the development of modern propulsion systems, reliable data acquired from sensors are urgent, especially for the temperature of gas turbine engine [1–3]. The development of working temperature will benefit for higher fuel efficiency and lower harmful gas emissions, while make the acquirement of reliable temperature data more difficult in such harsh environment. In order to verify the structural model and propulsion, and promote health monitoring of gas turbine engine, film thermocouples have been directly deposited onto measured components with the thicknesses of a few micrometers in large quantities to measure in-time temperature, which have a minimal effect on the gas flow over the surface [4–8]. They can also offer excellent spatial resolution and exhibit faster response than wire or foil thermocouples because of the small thermal mass.

Conventional Type-*S* (Pt-Pt10%Rh) wire thermocouples have been used in the tail part of gas turbine engine to provide data for calculating the temperatures of blades or combustion chamber. This will lead to a large deviation between measuring value and true value. When the thermocouple turns into thin film form, it will suffer from reliability and stability issues, such as severe oxidation of rhodium at temperatures between 600 °C and 800 °C, and becoming thinner and poor adhesion on substrates [9,10]. At the same time, its output voltage is lower due to the intrinsic properties of composition materials, which makes the sensitivity poor. Transparent conducting oxides (TCO) In_2O_3 (*n*-type) and ITO (*n*-type) have been used to fabricate thin film thermocouples to improve the measuring temperature and output voltages due to their high melting point, excellent chemical stability, larger Seebeck coefficients and oxidation resistance at elevated temperatures. Although their fabricated thin film thermocouple could measure up to 1273 °C [11]. However, the fabricated principle is based on the thermoelectric potential of In_2O_3 electrode subtract that of ITO, leading to a lower output voltage because they are same type semiconductors just with different Femi levels. In order to both improve the output voltage and keep the stability of high temperature, ITO should be replaced by an appropriate *p*-type conducting oxide. $La_{1-x}Sr_xCrO_3$ (xLSCO) as a kind of *p*-type conducting oxides has been used as transparent conducting oxide [12], interconnect materials in solid oxide fuel cells (SOFC) [13,14] and electrodes for magnetohydrodynamic generators [15], due to their refractory nature and good conductivity. Meanwhile, the small-polaron hopping transport in $La_{1-x}Sr_xCrO_3$ will make their Seebeck coefficients almost do not change with temperature [16]. Therefore, the

* Corresponding authors.
E-mail addresses: spxjy@mail.xjtu.edu.cn (P. Shi), wren@mail.xjtu.edu.cn (W. Ren), zdjiang@mail.xjtu.edu.cn (Z. Jiang).

https://doi.org/10.1016/j.jeurceramsoc.2018.07.025
Received 27 March 2018; Received in revised form 16 July 2018; Accepted 16 July 2018
Available online 17 July 2018

output voltages of thermocouples made of xLSCO and In_2O_3 will have nearly linear increase with temperature as In_2O_3 itself. Based on this, we have fabricated a new 0.2LSCO *vs.* In_2O_3 thick film thermocouple with giant output voltage previously [17]. In addition, the La^{3+} is replaced by Sr^{2+}, the conductivity of xLSCO will be enhanced through increasing carriers (holes) and making the Seebeck coefficient variation [15]. Therefore, the dopant content of Sr^{2+} will strongly affect the properties of xLSCO-In_2O_3 film thermocouples, which need to investigate urgently.

In this work, $La_{1-x}Sr_xCrO_3$ (xLSCO, x = 0-0.4) and pure In_2O_3 were used to fabricate thick film thermocouples by screen-printing method. Effects of Sr^{2+} content on the microstructure and morphologies of xLSCO thick films were investigated. The thermoelectric properties of xLSCO were also tested by coupling with platinum reference electrodes. And the thick film thermocouples composed by xLSCO and In_2O_3 were statically calibrated for multiple cycles with temperature and the annealing effect was investigated.

2. Materials and methods

The $La_{1-x}Sr_xCrO_3$ (xLSCO, x = 0, 0.1, 0.2, 0.3, 0.4) precursor powders were prepared by Sol-Gel method. The raw materials Cr $(NO_3)_3{\cdot}9H_2O$ (AR, ≥ 99.0%), $La(NO_3)_3{\cdot}nH_2O$ (AR, ≥ 44.0%), $Sr(NO_3)_2$ (AR, ≥ 99.5%), $C_6H_8O_7{\cdot}H_2O$ (AR, ≥ 99.5%) and $H(OCH_2CH_2)nOH$ (CP, PEG 200) were purchased from Sinopharm Chemical Reagent Co. Ltd. In a typical procedure, $Cr(NO_3)_3{\cdot}9H_2O$, $La(NO_3)_3{\cdot}nH_2O$ and Sr $(NO_3)_2$ were dissolved in stoichiometric amounts in 60 ml deionized water by magnetic stirring to form a 0.04 mol $La_{1-x}Sr_xCrO_3$ solution. Then 0.08 mol $C_6H_8O_7{\cdot}H_2O$ and 20 ml $H(OCH_2CH_2)nOH$ were added in the solution. The mixed solution was heated at 80 °C and stirred continuously until a gel was formed. The gel was dried at 80 °C in an oven and then calcined in a furnace at 900 °C for 4 h. Then the xLSCO and In_2O_3 ((HeFei Crystal Technical Material Co., Ltd.) powders and the corresponding thermocouples were fabricated by the screen-printing method. The mass ratio of In_2O_3: glass powder (Commercial, 1000 meshes): ethyl cellulose (Sinopharm, CP)): terpilenol (Aladdin, CP) was 1:0.08:0.031:0.40. The mixture was stirred well to form a paste. Thick-films were printed by a screen printing plate with 250 meshes and L-form graphic width of 2.5 mm. The xLSCO thick films were prepared by the same procedure as for In_2O_3 but with no glass additives. The U-type thermocouples of xLSCO -In_2O_3 were screen-printed onto 200 mm × 20 mm × 2 mm alumina substrates, then calcined at 1250 °C for 2 h. Finally, the diameter of 0.15 mm copper lead wires were pasted onto the electrodes of thermocouples with silver paste, then the fabricated thermocouples were put in an oven under 200 °C for 2 h.

The structures of xLSCO powders and thick films were measured using an X-ray diffractometer (Dmax/1400, Rigaku, Cu-*K*α radiation) with the step of 0.02°. The surface SEM images were obtained by a field-emission scanning electron microscope (FEI Quanta, 250 FEG) equipped with an energy dispersive spectrometer for the film composition analysis. The sheet resistivity and conduction type of $La_{1-x}Sr_xCrO_3$ thick films were measured by Hall test system (Lake Shore, 7707A).

The thermoelectric properties of xLSCO thick films *versus* calibrated Pt wires and xLSCO-In_2O_3 thermocouples were measured by using the home-made test measurement system. The hot junction of the thermocouples was put into a high-temperature furnace (LHT 02/17/P310, Nabertherm, Germany) monitored by Type-S thermocouple and the cold junction was in the outside of the furnace monitored by Type-K thermocouple. The measured temperatures and thermal voltages were monitored using a USB Data Acquisition system (LR8431-30, HIOKI, Japan) with "Logger Utility" software.

3. Results and discussion

Fig. 1 shows the XRD patterns of xLSCO thick films annealed at 1250 °C for 2 h. All samples show a pure perovskite phase with orthorhombic unit cell (JCPDS:71-1231), indicating that the Sr^{2+} ions are dissolved perfectly into the LCO lattices to stable the valance of Cr^{3+} to Cr^{4+}. The major peaks (112) have a slightly tendency to shift toward higher diffraction angles with the increase of Sr^{2+} content due to that La^{3+} ions with a relatively large radius (0.136 nm) are substituted by Sr^{2+} ions with a smaller radius (0.118 nm) [18], resulting in reducing the lattice parameters of LCO as listed in Table 1. The relative intensities of Al_2O_3 substrates are increasing with Sr^{2+} content especially for x ≥ 0.2, which may be ascribed to reduce the stability of xLSCO that makes the thicknesses of thick films become thinner.

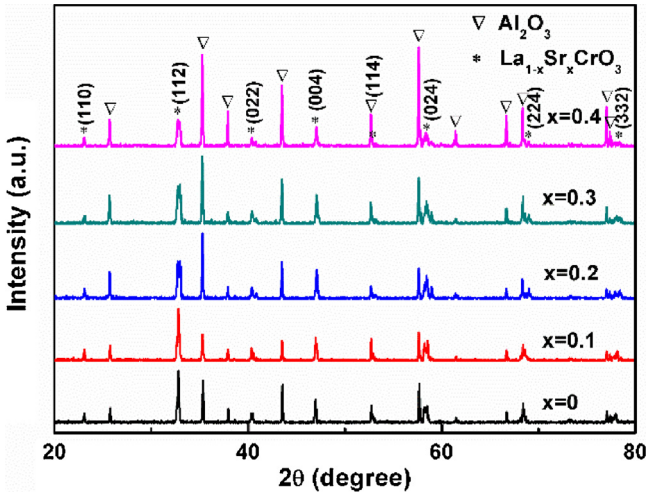

Fig. 1. XRD patterns of xLSCO (x = 0–0.4) thick films treated at 1250 °C for 2 h.

SEM images of xLSCO are shown in Fig. 2 to help us to understand the effect of Sr^{2+} content on the morphologies of xLSCO thick films. As the xLSCO thick films were annealed at higher temperature (1250 °C) than that of their precursor powders, which made the particle sizes becoming bigger. The average particle size has a tendency of increase first and then decrease with the increase of Sr^{2+} content, especially for the sample with 30% which showed the maximum particle size. The porous morphologies and partially melting particles were observed for all samples, especially for 0.4LSCO. It is mainly attributed to the activation effect of the doped Sr^{2+} ions, which promotes the structural diffusion and lattice distortion of LCO crystal and then leads to the deviation of structural units from the equilibrium position. Therefore, an increase in the free energy of the system enhances the driving force of atomic diffusion [19].

The resistivity of xLSCO thick films is shown in Fig. 3. The resistivity of xLSCO is decreased with the increase of dopant Sr^{2+} content and has lager values than that of reported thin films or ceramics due to their porous morphologies [12,15]. For LCO, as a typical intrinsic p-type conducting oxide with fewer carriers, the oxygen vacancies enter the charge balance relations by presenting a charge compensation to create Cr^{4+} [15]. While for LCO doped with Sr^{2+} ion, the electrical conductivity will be improved by forming shallow impurity energy level and additional free carriers, and enhanced with the increase of Sr^{2+} content. If the content of Sr^{2+} ion reaches up to 100%, the metallized $SrCrO_3$ is even obtained [20]. In addition, the grain size and porosity will effect on the conductivity of xLSCO thick films. When the grain size become bigger, the transport of the carriers will be enhanced due to the reduction of the scattering between grain boundary. At the same time, the porosity of xLSCO thick films will be reduced due to the improved densification by doping Sr^{2+}, which can enhance their conductivity [21]. While for 0.4LSCO, the negative impact of its grain size is very small so that its better conductivity mainly comes from the doping of Sr^{2+} and the reduction of porosity. In a word, it is beneficial to the conductivity of LCO by increasing the dopant content of Sr^{2+}.