Journal of Alloys and Compounds 731 (2018) 723–730

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Improving the thermoelectric properties of $SrTiO_3$-based ceramics with metallic inclusions

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ARTICLE INFO

Article history:
Received 6 July 2017
Received in revised form
4 October 2017
Accepted 5 October 2017
Available online 6 October 2017

Keywords:
Perovskite
Thermoelectric
Inclusions
Oxide
Grain boundary

ABSTRACT

High quality $Sr_{0.8}La_{0.067}Ti_{0.8}Nb_{0.2}O_{3-\delta}$ ceramics containing inclusions of Cu or Fe were prepared by the mixed oxide route and sintered under reducing conditions at 1700 K. Products were high density; Fe enhanced density (to 98% theoretical) and grain size (to 15 μm) whilst Cu tended to reduce both slightly. XRD and SEM analyses showed that the material is mainly composed of cubic $SrTiO_3$ phase, with rutile-structured minor phases and metallic inclusions along the grain boundaries. The inclusions increased carrier concentration and carrier mobility, leading to a reduction in electrical resistivity by a factor of 5 and increase in power factor by 75%. Both types of metallic inclusions were beneficial, increasing the thermoelectric figure of merit (ZT) from 0.25 at 1000 K for the control sample, to ZT of 0.36 at 900 K for the Cu-containing samples and to 0.38 at 1000 K for the Fe-containing samples.

1. Introduction

A range of potential applications for thermoelectric materials has been developed in recent decades. Not only have they been widely applied in niche applications such as radioisotope thermoelectric generators (RTGs), but plentiful prototypes for energy scavenging/harvesting, sensing and wearable devices have been developed as a result of extensive studies on these materials [1]. Oxides have been considered as promising materials since the demonstration of the thermoelectric properties of Na_xCoO_2 [2]. Oxides offer advantages over conventional materials on the basis of superior chemical and thermal stability [3].

Thermoelectric efficiency is dependent on the difference between the source and sink temperatures. Physical properties of the thermoelectric material affect the figure of merit, ZT which is given by Ref. [1]:

$$ZT = \left(\frac{S^2\sigma}{\kappa}\right)T \tag{1}$$

where, S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity and T is the mean operating temperature.

The requirement for high ZT, n-type material at temperatures over 600 K has driven research on oxides such as $SrCrO_3$, $CaMnO_3$, ZnO, In_2O_3 and $SrTiO_3$ [4]. Strontium titanate (STO) is a leading candidate and the undoped material has a large Seebeck coefficient ~ 850 μVK^{-1}, but low electrical conductivity and high thermal conductivity. There have been many approaches to improve the properties of $SrTiO_3$. A single crystal of La doped $SrTiO_3$ has been reported to have a similar power factor ($S^2\sigma$) to that of Bi_2Te_3 at room temperature (2800–3600 $\mu W/K^2m$) [5]. However the high thermal conductivity of undoped $SrTiO_3$, in the range 6–12 W/mK, from room temperature to 1000 K [6], remains an important factor limiting the improvement of overall ZT. The thermoelectric performance of the STO based ceramics has been addressed by simultaneously improving the power factor and introducing phonon scattering centres to reduce the thermal conductivity. The difficulty in this approach is further accentuated by the increased electronic component of thermal conductivity as the electrical resistivity is reduced (parameters being linked by the Wiedmann-Franz law [7]). Dehkordi et al. [8,9] have shown significant improvement in power factor of STO by using Pr doping and optimizing the presence of Pr-rich inclusions at grain

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https://doi.org/10.1016/j.jallcom.2017.10.033
0925-8388/

boundaries using non-equilibrium heating rates. The main factors that improve the properties are the influence of donor-type oxygen vacancies in bulk compositions and of cationic substitution. Doped $SrTiO_3$ prepared under reducing conditions has been particularly promising with ZT values as large as 0.41 at 1073 K being obtained [10]. Other work has demonstrated that A and B site doping and variation of processing conditions can enhance the thermoelectric properties of these perovskites [11–16]. Co-doping on the A/B sites and doping with heavy elements (in particular Dy [10,16] and W [15]) have been effective in reducing thermal conductivity by phonon scattering. In addition, the generation of oxygen vacancies, by processing the materials under reducing conditions, has been equally beneficial for STO, leading to the creation of additional charge carriers as the oxidation states of transition elements (particularly Ti/Nb) are adjusted [6,14,17–19]. The control of A-site cationic vacancies is also gaining attention as a route to improve thermoelectric properties. Popuri et al. [20] have demonstrated temperature independent thermal conductivity for STO where 27% A-sites are vacant. Related work has explored the effect of A-site vacancies generated by a range of co-dopants [19–23]. Notably, Lu et al. [22] also investigated vacancy ordering as the defect concentration is increased and its subsequent effect on crystal structure and thermoelectric properties; a maximum ZT of 0.41 at 1000 K was obtained for material containing 10–20% A-site vacancies. In the present work, we have investigated an optimized composition of $Sr_{0.8}La_{0.06}Ti_{0.8}Nb_{0.2}O_3$, which has 13.3% A-site vacancies, while processing under reducing conditions to create oxygen deficiency.

The addition of conductive second phases can also improve the electrical conductivity by reducing grain boundary resistance. Previous work has included the addition of graphene at concentrations less than the percolation level as a means to enhance electrical conductivity [24]. In the case of $Sr_{0.9}La_{0.1}TiO_{3,}$ the addition of 15% silver as a second phase was shown to increase the ZT through an increase in the electrical conductivity and a decrease in the thermal conductivity [25]. The latter was associated with increased phonon scattering at the second phase grain boundaries. Zheng et al. [26] prepared $Sr_{0.9}La_{0.1}TiO_3$ ceramics containing up to 15% Ag in the matrix by hydrothermal synthesis and reported significant improvement in electrical conductivity and modest improvement in the Seebeck coefficient. There was also a reduction in thermal conductivity, but that may have been related to density and microstructure changes. Additions of silver have also been employed to improve the electrical and thermal properties of $Ca_3Co_4O_9$. Wang et al. [27], and Mikami et al. [28] added silver both as a second phase and as a dopant; the latter was more effective in reducing thermal conductivity with the Ag acting as a phonon scatterer in the lattice. In $BaTiO_3$ ceramics the addition of silver has been shown to improve the strength and electrical properties [29,30]. However, in some materials the presence of silver may cause problems. For example, Iwagami et al. [31] found that the use of silver as an electrode for $Bi_{1/2}Na_{1/2}O_3$ ceramics led to rapid diffusion along grain boundaries causing the properties to degrade. The low melting point of silver (1235 K) tends to promote diffusion during sintering, making microstructural control more difficult. The use of other metallic inclusions may overcome the limitations of silver. Qin et al. [32] investigated the effect of including up to 20 wt % metallic Ti particles in $SrTiO_3$. They found that metallic Ti is not a very effective additive as it results in formation of non-stoichiometric TiO_{2-x} and properties that depend sensitively on sintering conditions.

The candidate metallic inclusions chosen for this study were iron and copper, having melting points of 1811 K and 1358 K respectively. The melting temperature of iron is above that used for sintering strontium titanate whilst copper has a melting temperature below the sintering temperature [19,23,24]. The doping of $SrTiO_3$ by Fe and Cu has previously been studied for application in magnetic fields [33], photocatalysis [34] and oxygen sensors [35]. However, in these cases the metals were introduced as dopants within the structure of the perovskite lattice and not as separate inclusions. The presence of iron within the strontium titanate lattice has been shown to significantly increase the conductivity especially near the strontium ferrite end of the phase diagram [36]. However, because of the presence of high concentrations of oxygen vacancies the conduction is ionic [37]. The solubility of copper in $SrTiO_3$ is limited and any excess is present as CuO [38,39] which can be readily reduced to Cu. These additives are relatively cheap compared to Ag, have high electrical conductivity compared to many other prospective metal additives and moderate electronegative values, which allows their oxides to be easily reduced to the metallic state under reducing sintering conditions.

2. Experimental

The starting powders were: $SrCO_3$ (Sigma Aldrich, UK); La_2O_3 (Molycorp Inc, USA); Nb_2O_5 (Solvay, UK); TiO_2 (Sachtleben Chemie GmbH); all had >99.9% purity. They were mixed in the appropriate molar ratios to produce the base formulation $Sr_{0.8}La_{0.06}Ti_{0.8}Nb_{0.2}O_3$, denoted as L2. The mixed powders were milled for 24 h with yttria-stabilized zirconia balls and propan-2-ol in a weight ratio of 1:1:1. The homogeneous slurry was dried overnight and then calcined in air at 1425 K. These mixing and calcination stages were repeated.

Metal nitrate solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $(Cu(H_2O)_6](NO_3)_2)$ were individually mixed with batches of L2 powder to give an additional 2.5 wt% of Fe or Cu. The powders were mixed homogeneously using the incipient wetness technique, which exploits capillary forces [40]. The appropriate volumes and concentrations of the solutions needed for incipient wetness were determined prior to mixing. The powders were dried in an oven at 350 K and then heated in air at 750 K to decompose the starting nitrates to their corresponding oxides. The powders were then milled using an agate mortar and pestle and pressed uniaxially in a hardened steel die to produce cylindrical pellets 20 mm diameter and 5 mm thick. The pellets were sintered in a Vecstar tube furnace (model No. VTF7 SP) at 1700 K for 24 h under 1 bar total pressure, with reducing atmosphere of Ar-5% H_2.

The densities of the sintered ceramics were determined using the Archimedes method. Circular cross-sections of individual specimens were cut using a diamond wheel, then ground and polished down to a 1 μm diamond paste followed by silica solution (OPS) ready for phase and microstructural analysis. X-ray diffraction (XRD) was carried out using a Philips X'pert diffractometer with Cu source; the 2θ scan angle was 10°–85° with step of size 0.030° and a dwell time of 10 s at each step. The XRD spectra were refined using the Rietveld program Topas [41].

Scanning electron microscopy (SEM) was undertaken on a Phillips XL30 FEGSEM equipped with a Rontec EDX, energy dispersive spectroscopy system. The samples were polished using OPS solution to obtain mirror like finish. Grain sizes were determined by the linear intercept method. Electron Backscatter Diffraction (EBSD) analysis was undertaken on a Quanta 85 650-FEGSEM microscope, equipped with an Oxford Instruments EBSD detector (Nordlys II).

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra instrument with a monochromated Al Kα X-ray source. Samples were polished cross-sections. Detailed scans of electronic transitions of core levels were performed with a resolution of 0.05 eV; data were collected for areas of 700 × 300 μm. Charge compensation was performed for all samples and peak fitting was carried out using CASAXPS software. The carbon 1*s* peak