Defects and electrical properties in Bi-doped calcium manganite

O V Merkulov, A A Markov, M V Patrakeev, I A Leonidov and V I. Kozhevnikov
Institute of Solid State Chemistry UB RAS, 620990 Ekaterinburg, Russia
E-mail: merkulov@ihim.uran.ru

Keywords: thermoelectric oxide, electrical conductivity, thermopower, Bi-doping

Abstract
The air synthesized samples Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$, where $x = 0.05$, 0.10 and 0.15, show the formation of fully oxidized solid solution, $\delta = 0$, with the orthorhombic structure (SG Pnma). It is shown that electrical properties at temperatures below 700 K are mostly governed by the charge disproportionation and local Jahn–Teller distortions of octahedral oxygen environment of Mn$^{3+}$ cations. The bismuth doping strongly affects the disproportionation enthalpy, charge carriers concentration and conductivity. The metallic-like temperature dependencies of electrical conductivity and thermopower are interpreted within frameworks of a small polaron mechanism of electron transport. The maximum power factor 250 $\mu$W·K$^{-2}$·m$^{-1}$ is observed in Ca$_{0.85}$Bi$_{0.15}$MnO$_{3-\delta}$ at 1120 K.

1. Introduction

Oxide thermoelectric materials are chemically and thermally stable at elevated temperatures in oxidative atmospheres and, therefore, very attractive for thermoelectric utilization of high-temperature waste heat. They are also cost efficient and nontoxic compared to the state-of-the-art chalcogenides, silicon germanium compounds, skutterudites, Heusler alloys, etc [1, 2]. In this connection and owing to inherently large thermopower perovskite-type calcium manganite CaMnO$_3$ has been identified as a promising material for the development of n-type thermoelectrics [3–5]. Considering rather low electrical conductivity a lot of efforts have been put into studies of different doping strategies aimed at conductivity enhancement and increase of the overall thermoelectric efficiency of CaMnO$_3$. The Ca-site substitutions by Y, La, In, Sn, Sb, Pb, Bi and rare-earth metals have been examined in works [3, 6–8]. The data on replacement of Mn by Mo, Ru, Nb and Ta are presented by authors [9–11]. Notice that the concentration dependent maxima of conductivity and thermoelectric efficiency do not coincide as a rule. This takes place because simultaneously with changes in the amount of charge carries doping cations influence the overlap of Mn3$d$ and O2$p$ orbitals and bending of O–Mn–O chemical bonds and, thus, impact the width of the conducting band [5, 8, 12, 13]. Another doping effect in case of replacement of manganese is related with disruption of conducting–Mn–O–Mn– chains in the structure, which usually results in decline of the mobility of electronic carriers [11, 14]. Though both types of doping may improve conductivity, the doping of Ca sites appears to be preferable.

Among numerous dopants bismuth, which is much heavier compared to calcium, attracts particular interest. The large mass difference is favorable for excitation of local phonon modes near doping centers, strong phonon scattering and reduction of thermal diffusivity of Ca$_{1-x}$Bi$_x$MnO$_3$. Several works are known where high-temperature conducting and thermoelectric properties of solid solutions Ca$_{1-x}$Bi$_x$MnO$_3$ have been studied [15–18]. However, significant disagreements are observed as to which composition is the best thermoelectric. For instance, authors [16] propose $x = 0.03$ as having the minimum thermal conductivity while a better properties combination in work [15] is found at $x = 0.04$. The divergence may possibly be related with differences in defect state and heterostructures at nanoscale [19, 20]. In this regard we can notice also that the parent manganite and its doped derivatives, though structurally robust, rather actively participate in oxygen exchange with the ambient atmosphere at elevated temperatures, and this process may considerably influence structural features and transport characteristics [21, 22]. Correspondingly, the formula of the solid solution may be more correctly presented as Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$, where symbol $\delta$ stands for oxygen non-stoichiometry.
In order to gain a deeper understanding of how temperature driven defect formation reactions, variations of bismuth content and oxygen non-stoichiometry may contribute to changes in concentration and mobility of electronic carriers we performed measurements of electrical conductivity and thermopower in Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$ at heating in air to 1250 K. For the data analysis we applied the earlier developed model of high-temperature polaron transport in CaMnO$_{3-\delta}$.[23]

2. Methods

The samples in oxide series Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$, where $x = 0.05, 0.10$ and $0.15$, were obtained via organo-metallic precursors. For the synthesis, the starting powder reagents CaCO$_3$ (99.8%), Bi$_2$O$_3$ (99.8%) and Mn$_2$O$_3$ (99.9%) were weighed in desirable proportions, placed in a quartz beaker and dissolved in nitric acid, whereupon glycine $C_2H_5NO_2$ was added to the solution in 50 mol% excess to the total amount of metal cations. Gradual evaporation on a hot plate resulted in ignition and smooth burning of the desiccated gel. The resulting residue was carefully grinded with a mortar and pestle and calcined at 1173 K for 10 h in air for removal of trace organics and carbon. The resulting powder material was milled again and pelletized under uniaxial load of 200–300 MPa followed by sintering at 1573 K for 10 h in air. The pressed pellets were covered with the powdered material and placed in a crucible with the lid in order to avoid any changes of chemical composition at this stage of high-temperature treatment. The density of prepared ceramics was calculated from the geometric dimensions and mass of polished samples.

Powder x-ray diffraction (XRD) in Bragg-Brentano mode was utilized for phase purity control and structure analysis. XRD data were collected with the help of a XRD-7000 (Shimadzu) diffractometer ($CuK\alpha$ radiation) in the $2\Theta$ range $20^\circ$–$80^\circ$ with 0.03° step size and 3 s acquisition time. The calculations of the elementary cell parameters were performed using PCW 2.4 calculation package[24].

The scanning electron microscopy (SEM) with a secondary electron detector JEOL JSM 6390LA was used for the analysis of morphology and homogeneity of the sintered samples.

A Setaram TG–92 thermoanalyzer was used in order to collect weight changes of the samples equilibrated at 1223 K for half an hour and cooled down with the rate of 1 K min$^{-1}$ in air. This mode of thermal treatment results in fully oxidized samples with $\delta = 0$ at room temperature[5, 25] while the isobar of cooling is believed to coincide with temperature dependent variations of equilibrium oxygen content in the sample. Therefore, the changes of oxygen non-stoichiometry with temperature can be calculated as

\[
\delta = \frac{\Delta m(T)}{[m, M_O]},
\]

where $\Delta m(T)$ is the weight change relative to the state $\delta = 0$ of the initial sample with the weight of $m_i$ at room temperature, and $M_s$ and $M_O$ stand for the molar weight of the sample and oxygen, respectively. Typically, the weight $m_i$ was about 100 mg, and the uncertainties in determination of $\delta$ did not exceed 0.003.

Rectangular bars $2 \times 2 \times 12$ mm$^3$ were cut from the sintered pellets for electrical measurements from 300 to 1250 K in air. One specimen, equipped with butt S-type thermocouples, was used for measurements of thermopower. The temperature gradient in the furnace along the sample was about 15 K cm$^{-1}$. The Pt leads of the thermocouples were used as voltage probes. Thermopower data were corrected for the contribution of platinum [26]. Another specimen was used in four-probe measurements of d.c. conductivity. Current leads of Pt wire (0.3 mm) were tightly wound to the sample at 10 mm spacing while the spacing between the potential probes was 8 mm. The electrical parameters were measured with a high-precision Solartron 7081 voltmeter. More experimental details can be found elsewhere [27]. The uncertainties in the obtained results are estimated to be below 5%. The collected data were nalysed with the help of SigmaPlot V12.5 media[28].

3. Results and discussion

XRD patterns for the air synthesized samples Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$, where $x = 0.05, 0.10$ and $0.15$, show formation of single-phase perovskite-type oxides with orthorhombic structure (SG Pnma), figure 1. The replacement of Ca$^{2+}$ ($R_{Cn12} = 1.340$ Å) for larger Bi$^{3+}$ ($R_{Cn12} = 1.450$ Å) and charge compensating appearance of Mn$^{3+}$ ($R_{Cn6} = 0.645$ Å) in place of smaller Mn$^{4+}$ ($R_{Cn6} = 0.530$ Å) cations is accompanied with the increase of the crystalline structure parameters, table 1, in a good agreement with the available data[15, 16]. The representative SEM micrographs of the sintered materials $x = 0.10$ and $x = 0.15$ in figure 2 reveal pores in the sintered samples. The measured density of the samples is about 85%–88% of theoretical value, table 1. More important for reliable electrical measurements is to observe well sintered grains in figure 2 and a uniform distribution of the constituent elements as shown in figure 3.

The temperature dependent variations of oxygen content $(3-\delta)$ in Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$ are shown in figure 4 as calculated from TG measurements in air. It is seen that the oxygen depletion takes place at temperatures above
700 K, and the increase in bismuth content is followed with the decrease in the amount of oxygen released in air. The respective reaction can be represented as

\[ 2\text{Mn}^{2+}_{\text{Mn}} + O_2^- = 2\text{Mn}^{4+}_{\text{Mn}} + V^\text{Fe} + 0.5\text{O}_2, \]

where Kröger–Vink notations are used for defect species [29]. The bismuth doping results in the formation of electronic defects Mn\text{II}_{\text{Mn}} (Mn\text{III} cations) and, therefore, is favorable for the shift of the equilibrium (2) to the left hand side, i.e. for the decrease of the oxygen loss in accord with the experimental data in figure 4.

The measured data for electric conductivity \( \sigma \) and thermopower \( S \) in figure 5 agree with the literature data [15–18]. The porous morphology of the samples may result in about 15%–20% smaller values of the measured conductivity compared to perfectly dense ceramics [30]. At the same time, the porosity does not greatly affect the
conductivity activation energy, thermopower and other important characteristics. The appearance of bismuth in the crystalline structure is accompanied with a considerable increase of the conductivity from about 1 S cm$^{-1}$ at $x = 0$ [3, 31] to 300 S cm$^{-1}$ at $x = 0.15$ at near room temperature. The conductivity variations with temperature exhibit metal-like behavior in a wide temperature range from about 250 to 1100 K. On the other hand, the conductivity values are quite small even in comparison with poor metals, and at the same time,

**Figure 3.** The distribution of calcium (blue), manganese (green) and bismuth (red), and overlay at the surface of Ca$_{0.85}$Bi$_{0.15}$MnO$_3$, as obtained by EDAX microanalysis.

**Figure 4.** Oxygen content variation in Ca$_{1-x}$Bi$_x$MnO$_{3-\delta}$ at cooling in air.
The absolute values of thermopower are much larger than in metals. Notice additionally that the orthorhombic structure persists in the parent manganite at heating to about 1170 K, while donor dopants shift the ortho ↔ tetra transition to even higher temperatures [5, 21]. Therefore, the data in figure 5 reflect mainly temperature dependent changes of conductivity and thermopower in the orthorhombic structure. Only above 1150 K one can observe small upturns of the thermopower plots that can signal incipient transition to the tetragonal structure.

The electric properties combination observed in the experiment can be explained within frameworks of a polaron conduction mechanism in manganites [32–34]. Depending on the polarizability of the material, the charge carriers may be associated with either 'large' or 'small' polarons [35]. Authors [36] argue that electron-doped manganite compounds are near a large−to small−polaron crossover. At elevated temperatures, where the effects of dynamic disordering and localization [37] are especially pronounced, the picture of electron transport caused by the movement of small polarons seems preferable [22, 38]. In this relation we have to notice that apparently metallic transport characteristics can be observed in small-polaron systems with the activation energy of about \( k_B T \) so that the pre-exponential may overbalance in the expression for polaronic conductivity [39]

\[
\sigma = \frac{\sigma_0}{T} \exp \left( \frac{E_\sigma}{k_B T} \right),
\]

where \( \sigma_0 \) is a coefficient, \( k_B \) is the Boltzmann constant, and \( E_\sigma \) is the conductivity activation energy. Similarly to the other donor-doped manganites with \( E_\sigma = 10–40 \text{ meV} [3, 5, 16] \), the function \( \log(\sigma T) \) versus \( 1/T \) is increasing at heating to 700 K, figure 6, i.e. in conditions where \( \delta \) in \( \text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3 \) is near zero, figure 4. More expressed increase of the plots at further heating reflects commencement and intensification of oxygen exchange with ambient atmosphere, the increase of the formation of electronic defects in reaction (2) and respective enhancement of conductivity. Notice also that variations of \( \delta \) and, consequently, of electron concentration at \( T = \text{const} \) in figure 4 become smaller with the increase of bismuth content. In the result, the upward bends of the plots in figure 6 are less pronounced at \( x = 0.10 \) and 0.15 compared to \( x = 0.05 \).

Figure 5. Temperature dependent electrical conductivity and thermopower in \( \text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3 \) at heating in air. The solid lines show results of the fitting at temperatures below oxygen take-off.
The negative thermopower $S$ is in accord with $n$-type conductivity in Ca$_{1-x}$Bi$_x$MnO$_3$–$\delta$, figure 5(b). The thermopower changes with dopant concentration and temperature can be interpreted with the help of a general expression \[ S = \frac{k_B}{e} \left( \ln \frac{g}{n} + \frac{E_S}{k_B T} \right) \],

where $e$ is the elementary charge, $g$ and $n$ represent the amount of positions available for jumps and concentration of $n$-type charge carriers, respectively, and $E_S$ denotes the thermopower activation energy. First of all, it is seen from (4) that larger bismuth content, i.e. larger $n'$s, must favor smaller $|S|$ values as, indeed, is observed in the experiment, figure 5(b). The compositional changes due to oxygen loss (2) above 700 K also result in a decrease of the thermopower absolute values. At lower temperatures, where oxygen content is permanent, variations of thermopower may reflect changes caused by the charge disproportionation reaction

\[ 2\text{Mn}^{3+} = \text{Mn}^{4+} + \text{Mn}^{2+} \]

or

\[ 2\text{Mn}^{3+} = \text{Mn}^{4+} + \text{Mn}^{2+} \]

in trivial notations. In writing (5) we follow authors \[40–42\] who consider temperature dependencies of resistivity and thermoelectric power as a striking evidence of the disproportionation. Reaction (5) results in a decrease in the concentration of Mn$^{3+}$ cations associated with $n$-type polarons. The concentration of manganese cations per formula unit can be expressed as

$\text{Mn}^{4+} = x$, $\text{Mn}^{3+} = n$ and $\text{Mn}^{2+} = m$. Assuming $\delta = 0$ and introducing concentrations of manganese charged states according to Ca$_{1-x}$Bi$_x$MnO$_3$–$\delta$ we can write the structure conservation and electro-neutrality requirements as

\[ g + n + m = 1 \]

\[ x = n + 2m \]

Supplementing these relations with the equilibrium constant for reaction (5)

\[ K_D = \frac{mg}{n^2} \]

we obtain a system of equations that can be resolved as

\[ g = \frac{x + 8K_D - 4xK_D}{8K_D - 2} - 1 - \sqrt{\text{det}} \]

\[ m = x - 1 + g \]

\[ n = 2 - x - 2g \]

where

\[ \text{det} = x^2 - 2x + 8xK_D - 4x^2K_D + 1 \]
thermopower at different bismuth content in Ca$_{1-x}$Bi$_x$MnO$_3$.

\[ K_0(T) = \exp\left(\frac{\Delta S_0^0}{R}\right) \exp\left(-\frac{\Delta H_0^0}{RT}\right) \]

\( \Delta H_0^0 \) and \( \Delta S_0^0 \) represent changes of standard enthalpy and entropy in reaction (5), respectively, and \( R \) is the gas constant. It follows from (9) and (10) that a decrease in the concentration \( n \) of Mn$^{3+}$ cations with the increase of temperature may take place only when \( \Delta H_0^0 > 0 \), which is consistent with the endothermal character of reaction (5). For quantifying calculations we have to notice that polaron jumps from Mn$^{3+}$ to Mn$^{4+}$ cations are energetically favorable on condition of equal multiplicities of the initial Mn$^{3+}$ and final Mn$^{4+}$ spin configurations [12]. Therefore, Mn$^{4+}$ cations that do not satisfy this requirement are not available for the jumps, and must be considered as excluded from the transport process while equation (4) ought to be modified as

\[ S = -\frac{k_B}{|e|} \ln \left( \frac{g - g_{ex}}{n} \right) + \left( \frac{E_s}{k_B T} \right) \]

Unfortunately, direct computations of the concentration \( g_{ex} \) of the excluded sites are difficult because exact statistics of spin distribution over manganese cations must be known. However, the backward estimation can be made by fitting experimental data in figure 5(b) with the help of (12) and \( g \) and \( n \) taken from (9). For simplicity, fitting parameters \( g_{ex}, E_s, \Delta H_0^0 \) and \( \Delta S_0^0 \) can be assumed temperature independent. The trial attempts to treat the data in figure 5(b) below 700 K showed that \( E_s \) can be safely set to zero. Notice here that the observation of the thermopower activation energy smaller compared to the conductivity activation energy gives additional confirmation to the small polaron character of charge transport in the manganites [39]. The obtained values of \( g_{ex}, \Delta H_0^0 \) and \( \Delta S_0^0 \) in table 2 make it possible to describe with a good precision the experimental polythermal for thermopower at different bismuth content in Ca$_{1-x}$Bi$_x$MnO$_3$, figure 5(b).

The enthalpy change \( \Delta H_0^0 \), which is the parameter that most strongly affects temperature variations of thermopower, is increasing with bismuth content, table 2. The similar trend was observed earlier for the charge disproportionation reaction in Ca$_{1-x}$Pr$_x$MnO$_3$ [23]. In perovskite-type manganites this value is approximately equal to the energy splitting \( \Delta \varepsilon \) of manganese \( \varepsilon_z: 3d_{z^2} \) and \( \varepsilon_{\pm}: 3d_{\pm} \) states. The component \( \varepsilon_z: 3d_{z^2} \) is lower on energy scale, and Mn$^{3+}$O$_6$ octahedra are elongated along \( z \) – axis due to the Jahn–Teller effect [12]. The donor doping of CaMnO$_3$ is accompanied with partial transformation of highly symmetrical Mn$^{4+}$O$_6$ to less symmetrical and larger Mn$^{3+}$O$_6$ octahedra. In turn, the appearance of large and stretched Mn$^{3+}$O$_6$ octahedra results in the overall expansion of crystalline structure and local deformations of Mn$^{4+}$O$_6$ octahedra so that the gap between \( \varepsilon_z: 3d_{z^2} \) and \( \varepsilon_{\pm}: 3d_{\pm} \) states tends to increase with the doping. Notice also that at equal dopant content the enthalpy \( \Delta H_0^0 \) for Ca$_{1-x}$Bi$_x$MnO$_3$ in table 2 is larger compared to Ca$_{1-x}$Pr$_x$MnO$_3$ [23]. It is because larger size of Bi$^{3+}$ results in larger local deformations in the crystalline structure.

The thermodynamic parameters \( \Delta H_0^0 \) and \( \Delta S_0^0 \) in table 2 can be used further in order to calculate the equilibrium constant \( K_0(T) \) according to (10) and find the temperature driven variations in the concentration of different manganese species from (9). The respective plots for Mn$^{3+}$ and Mn$^{4+}$ are shown in figure 7 where one can see that the disproportionation reaction (5) noticeably affects relative concentrations of manganese states above room temperature. Accordingly, at lower temperatures where \( n = x \), the concentration of Mn$^{3+}$ cations depends only on the concentration of bismuth donors in Ca$_{1-x}$Bi$_x$MnO$_3$ [23, 45]. At the same time, the heating is favorable for a slight increase of [Mn$^{4+}]_{av} = g - g_{ex}$ and a decrease of \( n \) so that these simultaneous changes result in the apparently \( << \text{metallic} >> \) increase of the absolute values of thermopower in figure 5(b) up to the temperatures of oxygen depletion.

The temperature dependent changes in the concentration of mobile charge carries \( n \) and positions \( g - g_{ex} \) available for polaron jumps in figure 7 can be applied for calculations of the coefficient \( \sigma_0 \) in equation (3) and

\[ \sigma_0 = \frac{e^2 \nu_0 \cdot n \cdot (g - g_{ex})}{k_B} N, \]

where \( r \) is the length of polaron jumps, \( \nu_0 \) is the characteristic frequency of jump attempts, and \( N \) is the amount of formula units per cubic centimeter. Neglecting weak temperature dependence of \( r \) and \( \nu_0 \) we can represent equation (3) in the form more convenient for calculations.
\[
\sigma T = \frac{e^{2/3} N/k_B}{m^*} \cdot \exp \left(-\frac{E_m}{k_B T}\right),
\]

where \(\sigma^0 = e^{2/3} n_0 N/k_B\) and \(E_m\) is the mobility activation energy. Parameters \(\sigma^0\) and \(E_m\) can be derived from the plots \(\log(\sigma T/n \cdot (g - g_{\alpha})) \) versus \(1/T\), and the respective values in table 2 result in a quite satisfactory coincidence of the calculated and experimental plots of the conductivity in figure 5(a) up to the temperatures of oxygen take-off.

The obtained multiplier \(\sigma^0\) can be utilized for the estimation of the frequency \(\nu_0 = 3.8 \times 10^{14}\) s\(^{-1}\) of polaronic jumps, which is consistent with the earlier data for \(\text{Ca}_{1-x}\text{Pr}_x\text{MnO}_3\) \([31]\) and characteristic frequency \(\sim 10^{14}\) s\(^{-1}\) of optical phonons in similar perovskites \([44]\). Therefore, the small polaron model gives correct and consistent description of electron transport in \(\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3\) at temperatures up to at least 700 K. The temperature dependent plots for the mobility of \(n\)-type charge carriers

\[
\mu = \frac{\sigma}{enN}
\]

are shown in figure 8 as obtained from the experimental results for the conductivity in figure 5(a) and calculated data for \(n\), i.e. the concentration of \(\text{Mn}^{3+}\) cations, in figure 7. The mobility values below the characteristic threshold \(\sim 1\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) \([3]\) separating narrow and broad band conduction types corroborate polaronic conductivity in \(\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3\). The maxima in figure 8 take place because the mobility exponent in (14) is increasing with heating below \(\sim 400\) K. Further decline of the mobility with heating is due to the decrease of the pre-exponent \(\sim (g - g_{\alpha})/T\). Generally, the mobility plots are similar to those for \(\text{Ca}_{1-x}\text{Pr}_x\text{MnO}_3\) \([31]\).
The power factor $PF = S^2/\sigma$ can be obtained from the measured data for thermopower and conductivity, figure 9. In difference with $x = 0.05$ and 0.10, where $PF$ varies rather weakly even at temperatures of intensive oxygen exchange, the power factor values in $x = 0.15$ appreciably increase with temperature showing no anomalies at heating above 700 K. This difference in temperature dependent behavior may possibly reflect enhancement of local deformations of Mn$^{3+}$O$_6$ octahedra and respectively induced increase of $D_{H0}$ at deep doping. Consequently, the power factor in $x = 0.15$ attains about 250 $\mu$W·K$^{-2}$·m$^{-1}$ at 1120 K. This value is not record high yet as shown in figure 10. However, efforts towards improved microstructure and sintering may result in further enhancement of thermoelectric properties of the bismuth doped manganites.

4. Conclusion

The samples Ca$_{1-x}$Bi$_x$MnO$_3$, where $x = 0.05, 0.10$ and 0.15, with the orthorhombic structure (SG Pnma) are obtained via organo-metallic precursors. The measurements of oxygen content, electrical conductivity and thermopower are carried within 298–1223 K in air. The oxygen take-off temperature at heating in air is found to increase with bismuth content. It is argued that metallic-like temperature dependencies of the conductivity and thermopower can be interpreted within frameworks of a small polaron model of electron transport in Ca$_{1-x}$Bi$_x$MnO$_3$. The bismuth doping is favorable for the increase of the charge carriers concentration and conductivity. At the same time, the conductivity tends to decrease with the temperature increase due to intensification of charge disproportionation of Mn$^{3+}$ cations. The disproportionation enthalpy is shown to depend rather strongly on bismuth content. As a result, the power factor in Ca$_{0.85}$Bi$_{0.15}$MnO$_{3-\delta}$ is a function noticeably increasing with temperature and attaining the largest value of 250 $\mu$W·K$^{-2}$·m$^{-1}$ at 1120 K.
Acknowledgments

Authors appreciate the support of this work under government assignment AAAA-A19–119031890026–6.

ORCID iDs

O V Merkulov https://orcid.org/0000-0002-8275-4126

References

[1] Awad D K, Basu R and Singh A 2016 Key issues in development of thermoelectric power generators: high figure-of-merit and materials
and their highly conducting interfaces with metallic interconnects Energy Convers. Manage. 114 59–67
[2] Cohen I, Kaller M, Kornisarchik G, Faks D and Gelbstein Y 2015 Enhancement of the thermoelectric properties of n-type PbTe by Na
and Cl co-doping J. Mater. Chem. C 3 9559–64
[3] Ohtaki M, Koga H, Tokunaga T, Eguchi K and Ariai H 1995 Electrical transport properties and high-temperature thermoelectric
performance of (Ca_{n-1}Mo_n)O_3 (M = Y, La, Ce, Sm, In, Sn, Pb, Bi) J. Solid State Chem. 105 105–11
[4] Wang Y, Sui Y, Wang X and Su W 2009 Effects of substituting La^{3+}, Y^{3+} and Ce^{4+} for Ca^{2+} on the high temperature transport and
thermoelectric properties of CaMnO_3 J. Phys. D: Appl. Phys. 42 055010–055010
[5] Thiel P, Eikerse J, Populoh S, Saucke G, Dobeli M, Shikhalo A, Sagarna I and Karvonen I 2013 Influence of tungsten substitution and
oxygen deficiency on the thermoelectric properties of CaMnO_3 J. Appl. Phys. 114 243707–9
[6] Kobayashi T, Tazakiwa H, Endo T, Sato T, Shimada M, Taguchi H and Nagoa M 1991 Metal-insulator transition and thermoelectric
properties in the system (R_{i-1}Ca_{i}Mn_{i}=\ldots) (R: Tb, Ho, Y). J. Solid State Chem. 92 116–29
[7] Cong B T, Taiji X, Thao P X, Thank P Q and Yamamura Y 2004 High temperature thermoelectric properties of Ca_{1-x}Pr_{x}MnO_{3–δ}
(0 < x < 1) Phys. BCondens. Matter 352 18–23
[8] Caspi E N, Avdeev M, Short S, Jorgensen J D, Lobanov M V, Zeng Z, Greenblatt M, Thiyagarajan P, Botez C E and Stephens P W 2004
Structural and magnetic phase diagram of the two-electron-doped (Ca_{1-x}Ce_x)MnO_3 system: effects of competition among charge,
obital, and spin ordering Phys. Rev. B 69 10402–17
[9] Kolesnik S, Dabrowski B and Chmaissem O 2008 Structural and physical properties of SrMn_{1–x}Ru_x perovskites Phys. Rev. B 78
214425–9
[10] Pi L, Hebert S, Martin C, Maigan N and Raveau B 2003 Comparison of CaMn_{1–x}Ru_x and CaMn_{1–x}Mo_x perovskites Phys. Rev. B
67 244430–7
[11] Xu G, Funahashi R, Pu Q, Liu B, Tao R, Wang G and Ding Z 2004 High-temperature transport properties of Nb and Ta substituted
CaMnO_3 system Solid State Ionics 171 147–51
[12] Lokev V M and Pogorelov Y G 2000 Peculiar physical properties and the colossal magnetoresistance of manganeseites (review) Low Temp.
Phys. 26 231–61
[13] Bocher L, Aiguier M H, Logvinovich D, Shikhalo A, Robert R, Trottmann M and Weidenkaff A 2008 CaMn_{1–x}NbO_3 (x < 0.08)
perovskite-type phases as promising new high-temperature n-type thermoelectric materials Inorg. Chem. 47 8077
[14] Wang C, Shi L, Xu X, Zhou S, Zhao J, Guo Y, Liu H, He L, Cai X and Xu G 2013 High-temperature thermoelectric characteristics of
B-site substituted Y_{0.6}Ca_{0.4}Mn_{1–x}NbO_3 system (0 < x < 0.1) Appl. Phys. A 112 1003–13
[15] Xu G, Funahashi R, Matsubara I, Shikano M and Zhou Y 2002 High-temperature thermoelectric properties of the Ca_{1–x}Bi_{x}MnO_3
system J. Mater. Res. 17 1092–5
[16] Kabir R, Tian R, Zhang T, Donelson R, Tan T J and Li S 2015 Role of Bi doping in thermoelectric properties of CaMnO_3 J. Alloys and
Compounds 628 347–51
[17] Bhaskar A, Yuan J and Liu C J 2013 Thermoelectric properties of n-type Ca_{1–x}Bi_{x}MnO_3 (0.00, 0.02, and 0.05) system J. Electroceram.
31 124–8
[18] Fujimoto K, Gibu M, Yamaguchi Y, Aimi N, Nishio K, Rabin O and Takeuchi I 2017 Thermoelectric properties of bismuth-substituted
calcium manganite Ca_{1–x}Bi_{x}MnO_3 prepared via the electrostatic spray deposition method J. Ceram. Soc. Japan 125 308–12
[19] Gorisse S, Bauer Pereira P, Decourt R and Sellier E 2010 Microstructure engineering design for thermoelectric materials: an approach
to minimize the thermal diffusivity Chem. Mater. 22 988–93
[20] Patraevsky M V, Markov A A, Shaleaev E V, Tyutyunnik A P, Tsipis E V, Waarenborgh J C, Kharton V V, Leonidov I A and
Kozhevnikov V I 2013 Phase separation-promoted ion conduction in SrFe_{0.67}Ta_{0.33}O_3 perovskites Solid State Ionics 244 17–22
[21] Goldevry E I, Leonidov I A, Patraevsky M V and Kozhevnikov V I 2012 Oxygen non-stoichiometry and defect equilibria in CaMnO_{3–δ}
J. Solid State Electrochem. 16 1187–91
[22] Goldevry E I, Leonidov I A, Patraevsky M V and Kozhevnikov V I 2014 Temperature activated electron transport in CaMnO_3 Solid
State Ionics 262 678–81
[23] Leonidov I A, Konstantinova E I, Patraevsky M V, Markov A A and Kozhevnikov V I 2017 Seebeck coefficient of Ca_{1–x}Pr_{x}MnO_{3–δ}
paramagnetic manganites Inorganic Material 53 583–8
[24] http://powdercell-forwindows.software.informer.com/2.4
[25] Chmaissem O, Dabrowski B, Kolesnik S, Maass J, Brown D E, Kruk R, Prior P, Pyles B and Jorgensen J D 2001 Relationship between
structural parameters and the Néel temperature in Sr_{1–x}Ca_{x}MnO_3 (0 ≤ x ≤ 1) and Sr_{1–x}Ba_{x}MnO_3 (y ≤ 0.2) Phys. Rev. B 64 134412–9
[26] Csak N and Kendall P 1958 The absolute scale of thermoelectric power at high temperature Proc. Phys. Soc. 72 896–901
[27] Patraevsky M V, Leonidov I A, Kozhevnikov V I and Poeppelemeier K R 2005 p-Type electron transport in La_{1–x}SrFeO_{3–δ} at high
temperatures J. Solid State Chem. 178 921–7
[28] Systat Software Inc. (http://sigmaplot.co.uk/)
[29] Kroger F A and Vink H J 1956 Relations between the concentrations of imperfections in crystalline solids Solid State Phys. 3 407–435
[30] Montes J, Cevas F G, Cintas J, Ternero F and Caballero E S 2018 Electrical resistivity of porous powders compacted in electrical and
electronic properties of materials Ed. Md. Kawsar Alam Ch. 2 111–34
[31] Leonidov I A, Konstantinova E I, Patraevsky M V, Markov A A and Kozhevnikov V I 2017 Electrical conductivity and carrier mobility in
Ca_{1–x}Pr_{x}MnO_{3–δ} manganites Inorganic Material 53 589–94
Zhao G-M, Conder K, Keller H and Muller K A 1996 Giant oxygen isotope shift in the magnetoresistive perovskite La$_{1-x}$Ca$_x$MnO$_3$ Nature 381 676–8

Mollah S, Anjum G and Yang H D 2009 Non-adiabatic polaron hopping conduction in CaMn$_{1-x}$Cr$_x$O$_3$ (0 ≤ x ≤ 0.3) J. Phys. Chem. Solids 70 489–94

Meskine H, Saha-Dasgupta T and Satpathy S 2004 Does the self-trapped magnetic polaron exist in electron-doped manganites? Phys. Rev. Lett. 92 056401–4

Kittel C 2004 Introduction to Solid State Physics (New York: Wiley)

Mollah S, Anjum G and Yang H D 2009 Non-adiabatic polaron hopping conduction in CaMn$_{1-x}$Cr$_x$O$_3$ (0 ≤ x ≤ 0.3) J. Phys. Chem. Solids 70 489–94

Cohn J L, Chiorescu C and Neumeier J J 2005 Polaron transport in the paramagnetic phase of electron-doped manganites Phys. Rev. B 72 024422–6

Sadovskii M V 1981 Electron localization in disordered systems: critical behavior and macroscopic manifestations Sov. Phys. Usp. 24 96–115

Schrade M, Kabir R, Li S, Norby T and Finstad T G 2014 High temperature transport properties of thermoelectric CaMnO$_{3.8}$– indication of strongly interacting small polarons J. Appl. Phys. 115 103705–7

Bosman I G and van Dau H J 1970 Small-polaron versus band conduction in some transition-metal oxides Adv. Phys. 19 1–117

Raffaelle R, Anderson H U, Sparlin D M and Parris P E 1991 Transport anomalies in the high-temperature hopping conductivity and thermopower of Sr-doped La(Cr,Mn)O$_3$ Phys. Rev. B 43 7991–9

Zhou J S and Goodenough J B 1999 Paramagnetic phase in single-crystal LaMnO$_3$ Phys. Rev. B 60 R15002–4

Buch J J U, Pathak T K, Lakhani V K, Vasoya N H and Modi K B 2007 High temperature thermoelectric power study on calcium substituted lanthanum manganites J. Phys. D: Appl. Phys. 40 5306–12

Leonidov I A, Konstantinova E I, Patrakeev M V, Chukin A V and Kozhevnikov V L 2017 Electron transport and mobility analysis in La/Sr co-doped CaMnO$_{3.8}$ J. Solid State Electrochem. 21 2099–108

Jaime M, Salamon M B, Rubinstein M, Trece R E, Horwitz J S and Christey D B 1996 High-temperature thermopower in La$_{2-x}$Ca$_x$MnO$_3$ films: evidence for polaronic transport Phys. Rev. B 54 11914–7

Merkulov O V, Politov B V, Yu C K, Markov A A, Leonidov I A and Patrakeev M V 2018 Fabrication and testing of a tubular thermoelectric module based on oxide elements J. Electron. Materials 47 2808–16

Taguchi H, Kugi T, Kato M and Hirota K 2010 Fabrication of (Ca$_{1-y}$La$_y$)MnO$_3$ Ceramics with a high relative density and their power factor J. Am. Ceram. Soc. 93 3009–11

Park J W, Kwak D H, Yoon S H and Choi S C 2009 Thermoelectric properties of Bi, Nb co-substituted CaMn$_3$O$_7$ at high temperature J. Alloys Compd. 487 550–5

Kosuga A, Ise Y, Wang Y, Koumoto K and Funahashi R 2009 High-temperature thermoelectric properties of Ca$_{0.9-x}$Sr$_x$Yb$_{0.1}$MnO$_3$–δ (0 ≤ x ≤ 0.2) J. Appl. Phys. 105 093717