



High-temperature Thermoelectric Properties of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0 \leq x \leq 0.25$)

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2 **High-temperature thermoelectric properties**
3 **of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0 \leq x \leq 0.25$)**

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9 **Abstract** Polycrystalline compounds of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}$
10 Fe_xO_3 for $0 \leq x \leq 0.25$ were prepared by solid-state
11 reaction, followed by spark plasma sintering process, and
12 their thermoelectric properties from 300 to 1200 K were
13 systematically investigated in terms of Y and Fe co-doping
14 at the Ca- and Mn-sites, respectively. Crystal structure
15 refinement revealed that all the investigated samples have
16 the O' -type orthorhombic structure, and the lattice param-
17 eters slightly increased with increasing Fe concentration,
18 causing a crystal distortion. It was found that with
19 increasing the content of Fe doping, the Seebeck coefficient
20 of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ tended to increase, while the
21 tendency toward the electrical conductivity was more
22 complicated. The highest power factor was found to be
23 $2.1 \times 10^{-4} \text{ W/mK}^2$ at 1150 K for the sample with
24 $x = 0.05$ after annealing at 1523 K for 24 h in air. Thermal
25 conductivity of the Fe-doped samples showed a lower
26 value than that of the $x = 0$ sample, and the highest
27 dimensionless figure of merit, ZT was found to be
28 improved about 20 % for the sample with $x = 0.05$ as
29 compared to that of the $x = 0$ sample at 1150 K.
30

Introduction

With increasing the global energy demand, thermoelectric materials have recently gained much interest in both the theoretical and technological aspects due to the potential use of these materials in converting waste heat into electricity [1, 2]. In general, for a single thermoelectric material, the conversion efficiency can be evaluated by the dimensionless figure of merit ($ZT = \sigma S^2 T / \kappa$, where σ , S , T , κ are the electrical conductivity, the Seebeck coefficient, the absolute temperature, and the thermal conductivity, respectively). The requirements for practical application of high thermal-to-electrical energy conversion place on finding suitable thermoelectric materials, and are not easily satisfied. They should not only possess good thermoelectric performance, they must also be stable at high temperatures and be composed of nontoxic and low-cost elements, but also must be able to be processed and shaped cheaply. For this purpose, metal oxide-based materials are considered as good candidates.

CaMnO_3 , which is a perovskite oxide with orthorhombic structure at room temperature, has also been considered as a promising thermoelectric n-type material for high-temperature application [3–9]. Many attempts have been made in order to improve the thermoelectric performance of this type of material, mainly to enhance the electrical conductivity, reduce further the thermal conductivity, while avoiding degradation of the Seebeck coefficient. Most of these studies have been focused on doping, for example, Yb at Ca-site [4–7] or Nb at Mn-site [3, 8], while only few reports performed the research on dually doping, e.g., Sr and Yb at Ca-site [9]. Previous reports have showed that the substitution of Y for Ca resulted in a significant improvement in the thermoelectric performance of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ system in a wide temperature region, and the

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65 optimum doping level was found to be around $x = 0.1$ [5,
66 10]. Similar to other multi-valence systems such as cobaltites [11] or titanates [12], the interrelation between
67 Mn^{3+} and Mn^{4+} should be responsible for the transport
68 mechanism in the $CaMnO_3$ material. Therefore, doping of
69 trivalent ions such as Fe^{3+} or Co^{3+} at the Mn-site would
70 probably influence the transport properties of this material.

71
72 In this study, we have prepared the $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$
73 Fe_xO_3 system with $0 \leq x \leq 0.25$, in which Ca-site was
74 substituted with Y at a fixed concentration and Mn-site was
75 partly replaced by Fe. The structural and the thermoelectric
76 properties of these set of materials were investigated in
77 detail. The influence of Y and Fe doping at Ca- and Mn-
78 sites, respectively, on the crystal structure was carefully
79 studied by the Rietveld refinement analysis. The correlation
80 between the crystal structures and the thermoelectric
81 properties are discussed.

82 Experimental

83 Polycrystalline samples of $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$ with
84 $x = 0, 0.05, 0.15, 0.2, \text{ and } 0.25$ were synthesized by a
85 solid-state reaction. A mixture of commercially available
86 $CaCO_3$ (98 %), MnO_2 (99.9 %), Fe_2O_3 (99.9 %), and Y_2O_3
87 (99.9 %) precursors were thoroughly mixed by ball milling
88 with ethanol for 24 h. The mixtures were dried and then
89 calcined at 1273 K for 24 h in air with an intermediate
90 grinding procedure. The densify processing was carried out
91 using a spark plasma sintering (SPS) system (SPS Syntex
92 Inc., Japan). The samples were heated to 1123 K, while a
93 uniaxial pressure of 50 MPa was applied for 8 min in Ar
94 atmosphere. During the experiment, the temperature,
95 applied pressure, and displacement of the sample were
96 recorded continuously. The as-prepared samples were then
97 polished in order to remove the graphite foil used during
98 the SPS processing. The pellets were then cut into bar
99 ($3.5 \times 3.5 \times 12 \text{ mm}^3$) and plate ($10 \times 10 \times 1.4 \text{ mm}^3$)
100 shapes for the thermoelectric properties and thermal con-
101 ductivity measurements, respectively. XRD analysis was
102 carried out on the powders after calcining and after the SPS
103 processing using a Bruker robot diffractometer with Cu-K α
104 radiation. Structural refinement was carried out using the
105 Rietveld method with TOPAS 4.1. Microstructures of the
106 samples were observed using scanning electron microscopy
107 (SEM) with a Hitachi TM-1000 system. The electrical
108 resistivity and the Seebeck coefficient were measured
109 simultaneously from room temperature to 1200 K using an
110 ULVAC-RIKO ZEM3 measurement system in a low-
111 pressure helium atmosphere. The thermal conductivity, κ ,
112 was determined from the measured thermal diffusivity, α ,
113 the heat capacity, C_p , and the density, d , using the formula:
114 $\kappa = d \times \alpha \times C_p$. The densities of the samples were

measured by an AccuPyc-1340 pycnometer. The thermal
diffusivity was measured by a LFA-457 laser flash system.

117 Results and discussion

118 Figure 1 shows powder X-ray diffraction (XRD) spectra
119 measured at room temperature for pure $CaMnO_3$ and for
120 $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$ samples with $x = 0, 0.05, 0.1, 0.15,$
121 $0.2, \text{ and } 0.25$ after they were calcined at 1273 K for 24 h in
122 air. All the visible XRD peaks can be indexed as the pure
123 phase of $CaMnO_3$, indicating that all the investigated
124 samples are single phase.

125 Figure 2 displays XRD patterns of a typical sample with
126 $x = 0.05$ for the calcined powder (a), spark plasma sintered
127 pellet (b), and the SPS sample after further heat treatment
128 at 1523 K for 24 h in air (c). As indicated by this figure
129 regardless of heat treatment, the structure remained the
130 same. The structure refinement for the calcined powders
131 $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$ system was conducted using Topas
132 4.1 Rietveld refinement software with input parameters
133 which were taken from Poeppelmeier et al. [13] using
134 space group $Pnma$ (No.62), and the refined results are
135 summarized in Table 1. The profile R value (R_p), weighted
136 profile R -factor (R_{wp}), and Goodness of fit (GOF) values
137 obtained in this analysis are of high quality, and is clearly
138 illustrated in Fig. 2 for a typical $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$
139 sample with $x = 0.05$ as an example. This result implies
140 that Y and Fe most likely substituted on the Ca- and Mn-
141 sites of $CaMnO_3$, respectively. It can be judged from the
142 data in Table 1, that the lattice parameters follow a relation
143 of $c/\sqrt{2} \leq a \leq b$, confirming that the polycrystalline

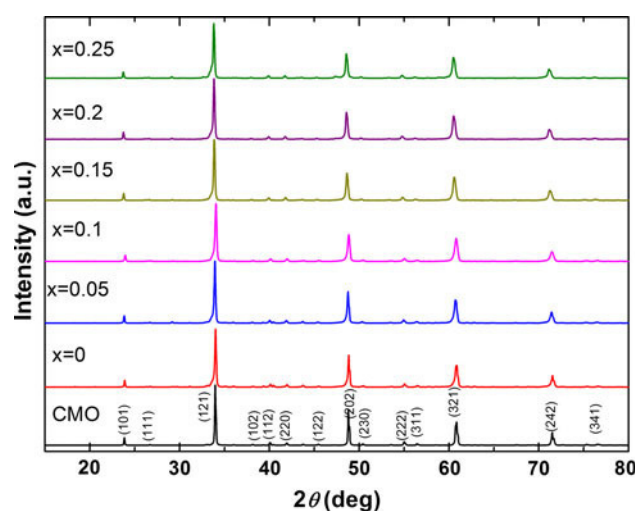


Fig. 1 XRD patterns of $CaMnO_3$ and $Ca_{0.9}Y_{0.1}Mn_{1-x}Fe_xO_3$ with $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$ samples after calcining at 1273 K for 24 h in air

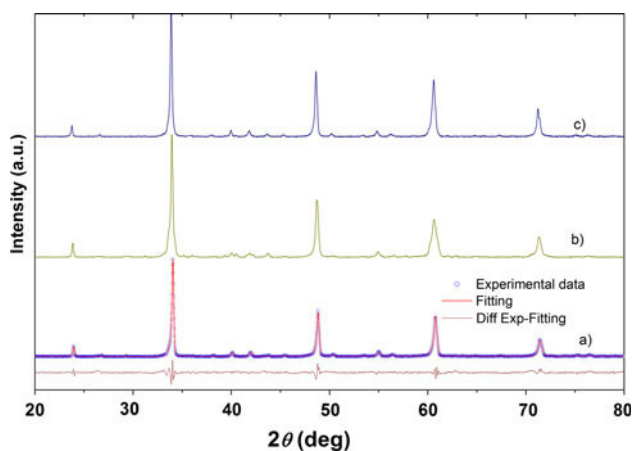


Fig. 2 XRD patterns of a typical sample $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3$: (a) Rietveld refinement profile of the calcined powder, (b) pellet sample sintered by SPS at 1173 K under pressure 50 MPa for 8 min under Ar atmosphere, (c) SPS sample after annealing at 1523 K in air for 24 h

144 compounds $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ of our samples have O' -
145 type orthorhombic structure [9, 14].

146 The dependence of the lattice parameters and the cell
147 volumes of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ on the amount of Fe
148 substituent are presented in Fig. 3. The result shows that
149 the lattice parameters slightly increased with the increasing
150 Fe concentration, resulting in an expansion in the unit cell
151 volume. The increase in lattice parameters may be asso-
152 ciated with the substitution of Fe^{3+} with a larger ionic
153 radius (0.55 Å) for smaller Mn^{4+} (0.53 Å) ion [15]. In the
154 case if Fe^{3+} substitutes for Mn^{3+} (0.58 Å), which has
155 larger ionic radius, one would expect a slight contraction of
156 the unit cell volume. The geometric distortion of ABO_3 -
157 type perovskites can be explained by Goldsmith tolerance
158 factor, which is defined as

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O) \quad (1)$$

160 where r_A , r_B , and r_O are the ionic radii of A, B, and O
161 atoms, respectively [15]. For $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ com-
162 pounds, calculation of Goldsmith tolerance factors
163 (t) showed that the highest t value was 0.988 in the case of
164 Fe^{3+} substitutes for Mn^{4+} and the smallest t value was

0.963 with Fe^{3+} substitutes for Mn^{3+} . It implies that the
orthorhombic structure is stable for all $\text{Ca}_{0.9}\text{Y}_{0.1}$
 $\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds.

Figure 4 depicts the temperature dependence of the
electrical conductivity for $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with
 $x = 0, 0.05, 0.1, 0.15, 0.2,$ and 0.25 spark plasma sintered
samples. The result points out that the electrical conduc-
tivity of the entire samples exhibit a semiconducting-like
behavior over the whole measured temperature range.
However, the electrical conductivity of the spark plasma
sintered samples does not show a clear tendency with the
increase of Fe doping concentration. σ tends to decrease
with increasing Fe concentration for $x > 0.1$, while
increases for the samples with $x \leq 0.1$. It should be noted
here that those samples were sintered under a high pressure
at high temperature and in inert gas atmosphere. The
oxygen content or even the microstructure may be varied
from the samples, causing the different behaviors of the
electrical conductivity as a result.

Temperature dependence of the Seebeck coefficient
(S) for the spark plasma sintered samples of $\text{Ca}_{0.9}\text{Y}_{0.1}$
 $\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15, 0.2,$ and 0.25 are
shown in Fig. 5. S of all investigated samples show a
negative values over the whole measured temperature
range, indicating n-type conduction. Contrastingly to the
electrical conductivity, the absolute S values increase with
increasing Fe concentration, and the effect was more sub-
stantial in low temperature region.

In order to understand further the influence of the Fe
doping on the thermoelectric properties, four SPS samples
with $x = 0, 0.05, 0.1,$ and 0.15 were selected and further
annealed at 1523 K for 24 h in air. Figure 6a shows the
electrical conductivity and the Seebeck coefficient as a
function of temperature after annealing at 1523 K for 24 h
in air. As seen from Fig 6a, a clear tendency showing the
decrease of σ , while S increases with increasing Fe con-
centration from $x = 0, 0.05, 0.1$ to 0.15 . The value of
electrical conductivity was found to increase more than two
times as compared with post samples, while the Seebeck
coefficient remained almost the same.

In general, the conduction mechanism of CaMnO_3 can
be interpreted by hopping conduction [16] where hopping

Table 1 Structural refinement factors, lattice parameters, and cell volumes of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$

Compositions (x)	0	0.05	0.1	0.15	0.2	0.25
R_{wp} (%)	8.42	9.33	9.39	11.27	10.62	10.62
R_p (%)	6.68	6.70	6.42	7.67	7.45	6.63
GOF	1.73	1.90	1.71	1.83	1.92	1.85
a (Å)	5.28233(2)	5.27480(3)	5.3018(3)	5.3004(1)	5.29596(2)	5.29999(3)
b (Å)	7.46185(3)	7.45797(4)	7.4846(6)	7.4806(2)	7.48990(3)	7.49067(5)
c (Å)	5.26841(2)	5.27498(5)	5.2899(2)	5.3035(3)	5.28405(2)	5.28344(3)
V (Å ³)	207.659(2)	207.514(2)	209.914(2)	210.284(3)	209.598(3)	209.755(2)

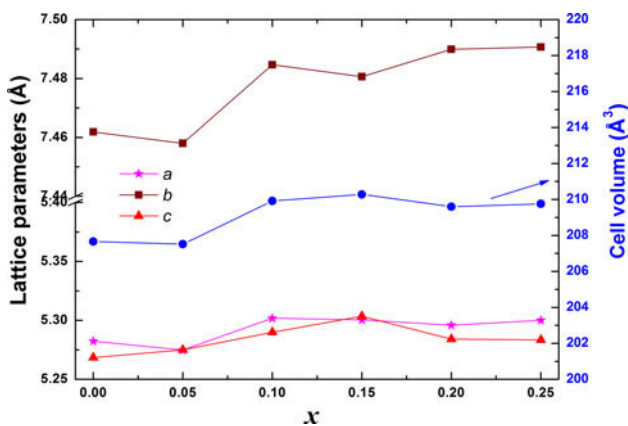


Fig. 3 Lattice parameters and cell volume of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ as function of Fe content (x)

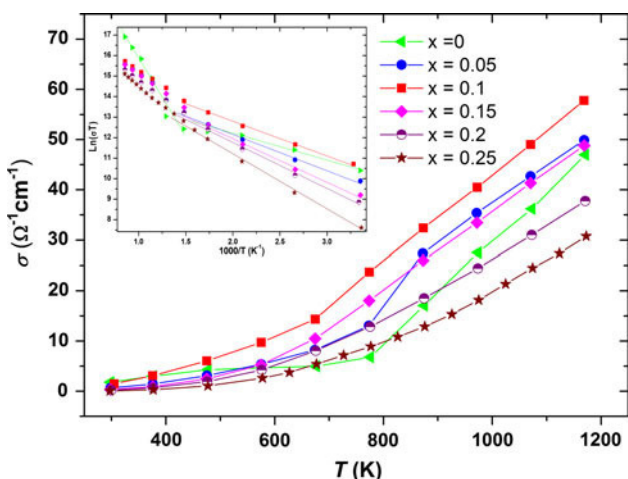


Fig. 4 Temperature dependence of the electrical conductivity for $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$ spark plasma sintered samples; Inset, the activation energies were fitted from experimental data

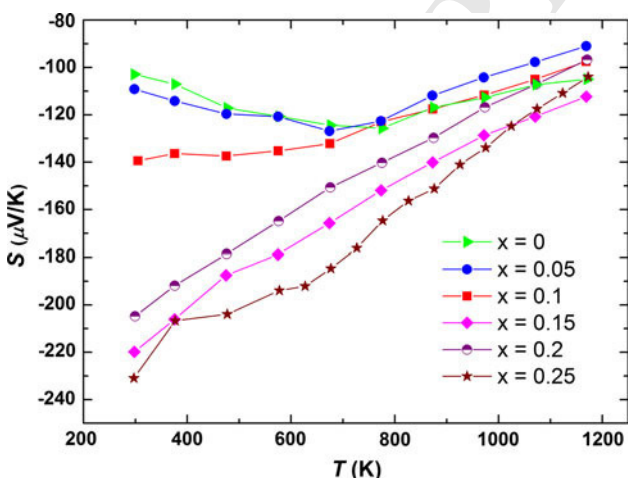


Fig. 5 Temperature dependence of the Seebeck coefficient for $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15, 0.2, \text{ and } 0.25$ spark plasma sintered samples

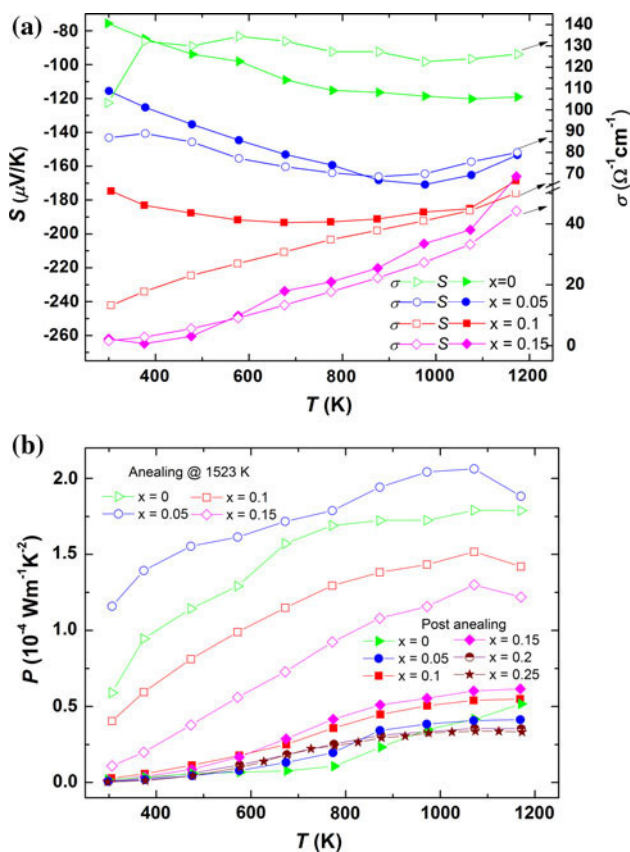


Fig. 6 Temperature dependence of **a** the Seebeck coefficient (*solid symbols*) and the electrical conductivity (*open symbols*), and **b** the PFs for all the spark plasma sintered samples $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$ and selective samples with $x = 0, 0.05, 0.1, 0.15$ after annealing at 1523 K for 24 h in air

of the charge carriers is thermally activated with the activation energy E_a , the temperature dependence of the electrical conductivity is given as

$$\sigma = C/T \exp(-E_a/k_B T) \tag{2}$$

where T is absolute temperature, k_B is the Boltzmann constant, and C is a constant depending on the charge carrier concentration. The activation energy could be estimated from the Arrhenius plot of $\text{Ln}T$ versus $1/T$ as shown in the inset in Fig. 4. The calculated activation energy, E_a is listed in Table 2 for all investigated samples, showing that E_a is linearly increasing with the increase of Fe substituent. However, the relationship between E_a is only obeyed the hopping conduction's equation at temperatures below 700 K, as shown in Fig. 4 inset as well as in Table 2. As for the $x = 0$ and 0.05 samples, the $\text{Ln}T$ versus $1/T$ curve showed two different slopes in the temperature regions of $T < 700$ and $T > 700$ yielding two activate energies (see Table 2), which is similar to the observation by Vecherskii et al. [17] on the oxygen non-stoichiometry $\text{CaMnO}_{3-\delta}$ system.

Table 2 Relative densities and electrical characteristics of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$

Compositions (x)	0	0.05	0.1	0.15	0.2	0.25
Relative density (%)	94.36	94.86	97.40	96.65	95.60	93.39
E_a (meV)	117.46	146.15	155.28	181.33	189.69	227.47

227 For an extrinsic n -type semiconductor with negligible
 228 hole conduction, the thermoelectric power can be given by
 229 [18, 19]:

$$S(T) \approx -\frac{k_B}{e} \left[\ln\left(\frac{N_V}{n}\right) + A \right] \quad (3)$$

231 where e is the electric charge of the carrier, k_B the Boltz-
 232 mann constant, N_V the density of states (DOS), n the carrier
 233 concentration, and A is a transport constant. Equations 2
 234 and 3 clearly show that the decrease in carrier concentra-
 235 tion (n) will result in an increase in the thermoelectric
 236 power (S) and vice versa. This can well explain the tenden-
 237 cy of the Seebeck coefficient and the electrical conduc-
 238 tivity as a function of temperature observed for the
 239 investigated samples after annealing with the increasing Fe
 240 concentration (see Fig. 6). Increasing the Fe content
 241 decreases the conductivity and increases the Seebeck
 242 coefficient which is also related to the carrier concentration
 243 via Eq. 3. However, further investigation on the carrier
 244 density and the mobility by means of the Hall measure-
 245 ments is currently ongoing to evidently support this
 246 interpretation.

247 Figure 6b shows the power factor (PF) as a function of
 248 temperature for all the spark plasma sintered samples and
 249 the selected ones after annealing. It is obvious that the PF
 250 values were remarkably improved by further heat treatment
 251 in air. The $x = 0.05$ sample showed the highest PF values
 252 over the whole measured temperature region, and the
 253 maximum PF attained was $2.1 \times 10^{-4} \text{ W/mK}^2$ at about
 254 1150 K.

255 To understand the reason which led to the finding
 256 interesting effect on the thermoelectric properties of the
 257 samples after heat treatment, the microstructure of the
 258 samples after SPS and after further annealing was studied
 259 using SEM, and the results are shown in Fig. 7a, b. Fig-
 260 ure 7 shows an obvious difference in the grain size before
 261 and after the annealing. The small grains size structure
 262 observed for the spark plasma sintered sample means to be
 263 more grain boundaries, leading to the increase in electron
 264 scattering at the grain boundaries, and thus decreasing the
 265 electrical conductivity. This result well explained the
 266 behavior of the electrical conductivity for the samples
 267 before and after heat treatment.

268 Figure 8 shows the total thermal conductivity (κ_{total}) for
 269 all investigated samples. It can be seen that κ decreases

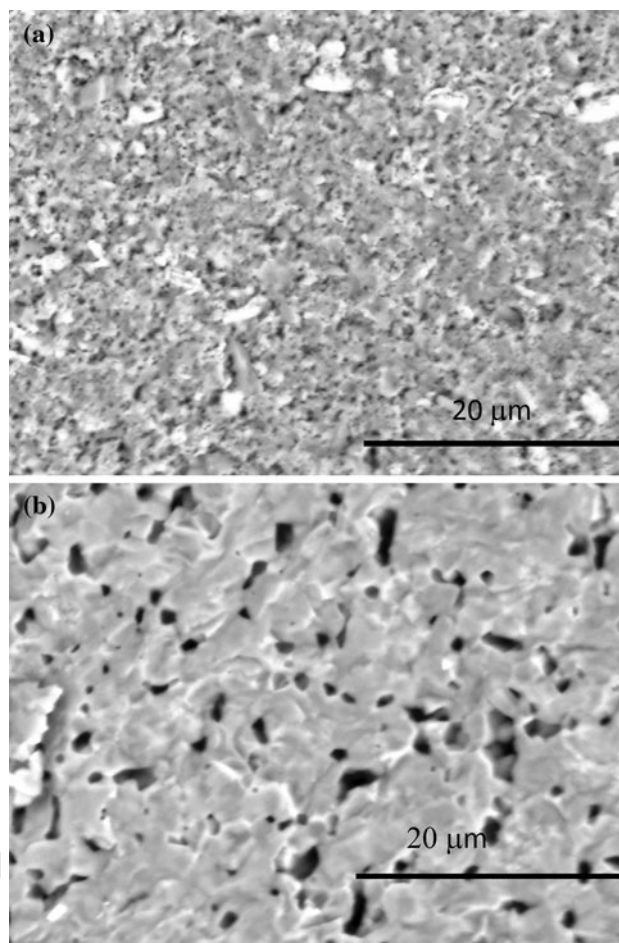


Fig. 7 SEM images from fractured surfaces of a typical $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.05$ sample: **a** sample was sintered by SPS, **b** sample was annealed at 1523 K for 24 h in air flow

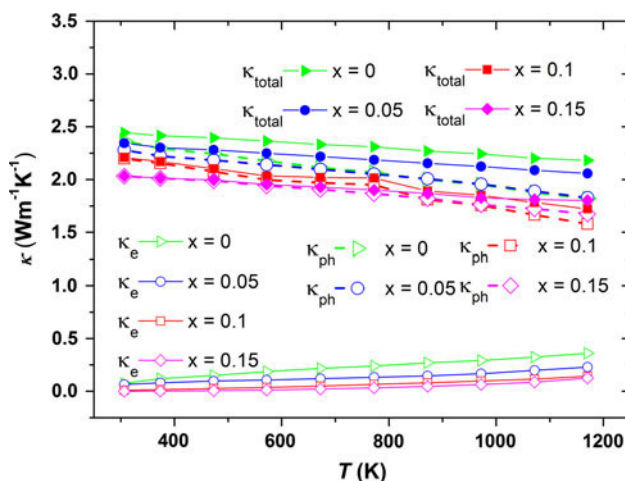


Fig. 8 the total thermal conductivity (κ_{total}), the electronic and phonon components (κ_e and κ_{ph}) of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ samples with $x = 0, 0.05, 0.1, 0.15$ as a function of temperature

Author Proof

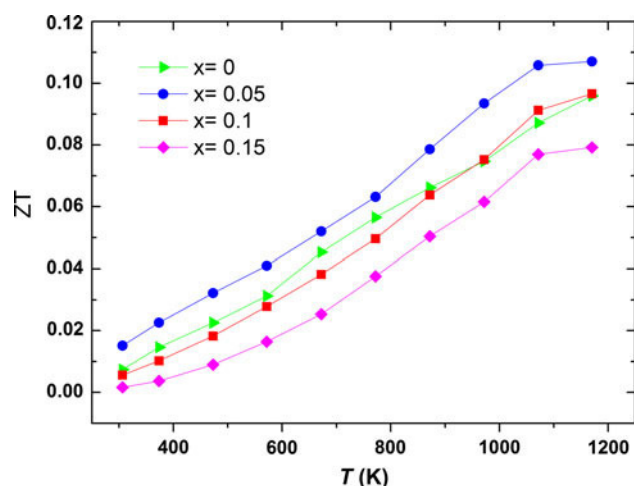


Fig. 9 The dimensionless figure of merit (ZT) as a function of temperature for $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15$ selective SPS samples after heated treatment at 1523 K for 24 h in air

with increasing temperature. The substitution of Fe at Mn-sites generally decreases the thermal conductivity. The total thermal conductivity can be expressed by the sum of a lattice component (κ_{ph}) and an electronic component (κ_{e}), i.e., as $\kappa_{\text{total}} = \kappa_{\text{ph}} + \kappa_{\text{e}}$. In this case, the contribution of κ_{e} to κ_{total} , estimated from the Wiedemann–Franz relation, is small, indicating the major contribution of the phonon term κ_{ph} , as clearly illustrated in Fig. 8. Finally, using the measured thermoelectric data, the dimensionless figure of merit of these compositions was calculated. Figure 9 presents the dimensionless figure of merit, ZT , versus temperature for the $x = 0, 0.05, 0.1$, and 0.15 samples, showing that ZT increased for the $x = 0.05$ and then decreased again with increasing x over the whole temperature range. The maximum ZT value reached a value of 0.11 at about 1150 K for the $x = 0.05$ samples.

286 Conclusion

287 The effect of Fe substitution on the structure and the high-
 288 temperature thermoelectric properties of $\text{Ca}_{0.9}\text{Y}_{0.1}\text{Mn}_{1-x}$
 289 Fe_xO_3 ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) was investigated in
 290 details. Structural analysis shows that lattice parameters
 291 slightly increase with increasing amount of Fe substituent,
 292 which originates from the difference in the ionic radii
 293 between Fe and Mn ions. The thermoelectric properties
 294 were found to be improved for the Fe-doped samples with

$x < 0.1$, particularly for the SPS samples with further
 annealing mainly due to the increase in the Seebeck
 coefficient that could overcome the simultaneous decrease
 of the electrical conductivity. The thermal conductivity
 was suppressed by the substitution of Fe for Mn. The
 maximum PF attained was $2.1 \times 10^{-4} \text{ W/mK}^2$ for the
 $x = 0.05$ sample at 1150 K giving a maximum $ZT = 0.11$,
 which is about 20 % higher than the $x = 0$ sample. Further
 study should be performed with finer Fe substituent tuning
 with $x < 0.1$ in order to optimize these compounds high-
 temperature thermoelectric properties.

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