Structure and thermoelectric properties of double-perovskite oxides: $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$

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The thermoelectric properties of the double perovskite-type oxides $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ were investigated in terms of K-doping at the A site of the oxides. The electrical conductivity, σ , of the oxides showed a metallic behavior, decreasing monotonically from ca. 10^3 S/cm at room temperature to ca. 10^2 S/cm at 1250 K. The Seebeck coefficient, S , showed that the oxides are of n-type over the measured temperature range. The absolute value of S increased with increasing temperature. The absolute value of S at 300 K increased up to $x = 0.2$ and then decreased dramatically for $x = 0.3$ – 0.4 . The Rietveld refinement of the XRD patterns of the oxides suggested that the increase in orbital degeneracy due to the eased distortion of FeO_6 and MoO_6 octahedra at $x = 0.2$ was responsible for the $|S|$ maximum at this composition. The power factor, $S^2\sigma$, of the oxides increased sharply with increasing K-doping level; the value for $\text{Sr}_{1.6}\text{K}_{0.4}\text{FeMoO}_6$ was ca. 4.2×10^{-4} W/mK², which is the highest among all the samples in this study. The thermal conductivity, κ , of the oxides generally decreased from ca. 3–5 W/mK at room temperature to ca. 2–4 W/mK at 1100 K. Because the power factor of the oxides increased above 900 K, the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, increased dramatically above 900 K. The largest ZT value of 0.24 was observed for $\text{Sr}_{1.6}\text{K}_{0.4}\text{FeMoO}_6$ at 1250 K.

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Key-words : Thermoelectric, Oxide, Double-perovskite, Rietveld analysis

[Received January 5, 2012; Accepted March 23, 2012]

1. Introduction

Efficient energy utilization is one of the most important requirements for the sustainable future of human society. It is said that more than 60% of the primary energy supply is wasted as heat during its conversion, transfer, storage, and usage. Recovery of this heat energy presents many difficulties because the energy is diluted spatially and degraded in quality (low exergie). Thermoelectric power generation is expected to become an energy harvesting technology that can convert the vastly dispersed thermal energy directly into electrical energy. Thermoelectric energy converters can transform heat into electrical energy, and vice versa, with high reliability without vibration or noise because they contain no moving mechanical parts, which are necessary for steam-powered electrical generators and compressor-driven refrigerators. Other advantages include a long lifetime and environmental friendliness of the conversion systems. Thus, much research has been focused on thermoelectric generators. A solid element consisting of a pair of p- and n-type semiconductors, operating over a temperature difference, generates a thermoelectromotive force, and thus, electricity via the Seebeck effect of the semiconductor materials. Materials that have been used in practice include heavy metal compounds such as Bi_2Te_3 ¹⁾, TAGS ((AgSbTe₂)_{0.15}(GeTe)_{0.85})²⁾ and PbTe .^{3),4)} However, these materials have several serious problems such as poor thermal durability, high toxicity, and high cost of constituent elements. As thermoelectric conversion attracts more and more attention, oxide materials that can replace conventional thermoelectric materials are becoming vitally important. We have

reported the successive development of several oxide materials, viz. (Zn, Al, Ga)O,^{5),6)} $\text{Ca}(\text{Mn}, \text{In})\text{O}_3$,⁷⁾ NaCo_2O_4 ,⁸⁾ CaCo_2O_6 ,⁹⁾ and $\text{Ca}_3\text{Co}_4\text{O}_9$.¹⁰⁾ The efficiency of thermoelectric materials increases with the dimensionless figure of merit, $ZT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. We have previously investigated the thermoelectric properties of a new class of thermoelectric oxide materials, the double-perovskite oxides $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6$ and $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$, from room temperature to 1100 K.¹¹⁾ These oxides show higher thermoelectric efficiency than the more conventional oxides. However, from the viewpoint of mechanical strength of sintering body and thermoelectric efficiency, these double-perovskite oxides from the previous study have never been used in any application. Moreover, n-type oxides are less efficient than their p-type counterparts.

The objective of this study was to search for a new thermoelectric material, focusing particularly on n-type materials. We investigated the thermoelectric properties of the densely sintered double-perovskite type oxide $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$. Many researchers have reported the structural, magnetic, and electrical properties of the double-perovskite transition metal oxides $\text{Sr}_2\text{FeMoO}_6$ ^{12)–15)}. In the double-perovskite oxides $\text{A}_2\text{B}'\text{B}''\text{O}_6$ (A is an alkaline-earth or rare-earth element), two kinds of transition metals occupy the B' and B'' (perovskite B sites) site elements alternately^{16)–18)} (see Fig. 1). Moreover, some double-perovskite oxides are called half-metals, a new class of materials, which are neither metals nor insulators; they are not even semiconductors. They possess an unusual electronic structure in which electrons with one spin have semiconducting properties and electrons with the opposite spin have metallic properties.^{19),20)} An additional peculiarity of their electronic structure is

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Fig. 1. Crystal structure of $\text{A}_2\text{B}'\text{B}''\text{O}_6$.

that all the conduction electrons are completely spin-polarized in the vicinity of the Fermi level.^{21),22)}

We focused on the properties that could provide promising electrical characteristics, for instance, one spin has a wideband from a broad orbital, whereas the other spin has a sharp band (DOS) in the neighborhood of the Fermi level. Moreover, we took note of the new thermal properties of the 4-element systems, double-perovskite oxides, in which strong phonon scattering can be induced.¹¹⁾ Thus, the thermoelectric properties of the half-metal double-perovskite oxides $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ are investigated in this paper in an effort to obtain a combination of high electrical conductivity, large thermopower, and low thermal conductivity.

2. Experimental

The raw materials, SrCO_3 (99.99%), K_2CO_3 (99.9%), Fe_2O_3 (99.99%), and MoO_3 (99.5%) powders, were weighed to prescribed molar ratios, and were mixed by locking milling for 1 h and ball milling for 24 h. They were then pressed into disks under a cooling isostatic pressure (CIP) at 100 MPa for 1 h, and sintered at 1223 K for 10 h in an Ar + 5% H_2 atmosphere. The sintering bodies were triturated and mixed for mortaring, and then hot-pressed into disks at 1273 K for 2 h in Ar using alumina dies. Finally, the samples were annealed at 1543 K for 6 h in Ar + 3% H_2 . The micro-structure of all the samples was observed using scanning electron microscopy (SEM). A JEOL JSM-6340FSEM system was used. The following instrumental settings were used: 15 kV acceleration voltages, 1–5 nA beam current and a working distance of about 15 mm. A magnification setting of about $\times 20000$ was chosen corresponding to an area of about $7\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ for the bulk analysis. The powder X-ray diffraction (XRD) patterns were measured in the range of $2\theta = 10\text{--}90^\circ$ for each sample using a Rigaku Rint 2200 diffractometer with $\text{Cu-K}\alpha$ radiation at 40 kV and 40 mA. For Rietveld refinement of the powder X-ray data, a step size of 0.008° and a step time of 10 s were used. Data was collected on a PANalytical X'Pert PRO diffractometer in the range of $2\theta = 15\text{--}100^\circ$ for each sample with $\text{Cu-K}\alpha$ radiation at 45 kV and 40 mA. Structure refinement was performed using the multi-purpose pattern-fitting RIETAN-FP²³⁾ software for the Rietveld method. The standard procedure was followed for refinement with Sr or K ions statistically allocated to the 4d site ($I4/m$ symmetry), and Fe and Mo to the 2a and 2b sites ($I4/m$ symmetry), respectively. The final refinement cycle involved the unit cell, scaling factor, five terms for the background fitting, and

Fig. 2. SEM image of the present, hot-pressed $\text{Sr}_2\text{FeMoO}_6$ sample (a) which is much denser than that of previous, pressureless-sintered one (b) (ref. 11).

the site occupancy factors. The isotropic thermal parameters for all the atoms were fixed at 0.5. Samples for electrical measurements were prepared by cutting the pellets into rectangular bars of approximately $3\text{ mm} \times 3\text{ mm} \times 10\text{ mm}$. Electrical conductivity and Seebeck coefficient were measured from room temperature to 1250 K in Ar on an Ozawa Science RZ2001i thermoelectric property measurement system using the 4-wire method and the steady-state method, respectively. A temperature step of 50 K was selected and the total measurement time was adjusted to approximately 10 h for each measurement. The Seebeck coefficients were determined from slopes of values of ΔT at about 1, 3, 5, 10 K. The van der Pauw technique was used to measure the Hall coefficient at room temperature in 5 T magnetic fields. An electrical current, which could choose values from 0.05 to 75 mA, was used to measure the voltage across the samples and the current flowing through them. The carrier concentration, n_{H} , and Hall mobility, μ_{H} , were calculated from the Hall coefficient, R_{H} , and resistivity, ρ , using the equation $1/\rho (= \sigma) = en_{\text{H}}\mu_{\text{H}}$. Thermal conductivity, κ , was determined from the thermal diffusivity, and the specific heat capacity was obtained by laser flash measurement on a Kyoto Electronics Manufacturing (KEM) LFA-502 instrument, from room temperature to 1250 K. The total measurement time was 6–7 h. The square-shaped samples for the measurements were $5\text{ mm} \times 5\text{ mm}$ and 0.8 to 1 mm in thickness.

3. Results and discussion

Figure 2 shows SEM images of hot-pressed $\text{Sr}_2\text{FeMoO}_6$ sample (a) and pressureless-sintered one (b) in a previous study.¹¹⁾ As can be seen in Fig. 2(b), the microstructure of the previous $\text{Sr}_2\text{FeMoO}_6$ sample has a porous structure. In the

Table 1. Density, d , and relative density, R. D. of the $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ both before and after hot-press treatment

Sample	$\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$				
x	0.0	0.1	0.2	0.3	0.4
Before hot-press treatment					
$d/\text{g cm}^{-3}$	3.55	3.45	3.47	3.32	3.24
R. D./%	63.1	61.5	62.2	60.4	59.8
After hot-press treatment					
$d/\text{g cm}^{-3}$	5.19	5.14	5.06	5.04	5.03
R. D./%	91.3	91.1	90.9	91.7	92.9

Fig. 3. XRD patterns of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ measurement from $\text{Cu-K}\alpha$ radiation. From bottom to top, $x = 0, 0.1, 0.2, 0.3, 0.4$. The square and diamond symbols represent the $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ and unknown peak position, respectively. The vertical solid lines show the Bragg reflection peak position of $\text{Sr}_2\text{FeMoO}_6$.

previous study, the relative density of the sintering body of pressureless-sintered the $\text{Sr}_2\text{FeMoO}_6$ sample was described at ca. 60%. However, as can clearly be seen in Fig. 2(a), the microstructure of the sample prepared by hot-press treatment appears dense. Moreover, the grain sizes of the hot-pressed sample are much larger than those before hot-press treatment. The bulk density and relative density of this $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ synthesized by both before and after hot-press treatment are summarized in Table 1. As can be seen in Table 1, the density of sintered body improved drastically from approximately 60% T. D. to 90% T. D. using the hot-press technique. The powder XRD results for $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ are shown in Fig. 3. Although a few of the $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ samples contained a small amount of unknown phase, almost single-phase samples were obtained. The XRD patterns were refined by the Rietveld Method using the multi-purpose pattern-fitting system RIETAN-FP.²³⁾ In our search for possible tetragonal and cubic space groups, we first used the pattern matching model to restrict the possibilities. The remaining space groups were checked one by one, e.g., $P4/mmm$, $Fm-3m$ and $I4/mmm$, and finally, $I4/m$. Detailed structural data for the samples, a tetragonal structure with the space group of $I4/m$, were presented by Sher²⁴⁾ and reinvestigated by Zhang et al.^{13),25)–27)} Table 2 shows the lattice parameters, the R factors of the fits, and the bond lengths and bond angles between the transition metal and oxygen for $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ obtained from this analysis. As can be seen in Table 2, the R factor for all $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ samples indicated a good fit. Hence, the

Table 2. Crystallographic data for $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ ($0.0 \leq x \leq 0.4$) from Rietveld refinement of X-ray powder diffraction data. For all the samples, the tetragonal space group $I4/m$, with the following atomic positions, was assumed: Sr(K) at $4d$ ($0, 0, 1/4$), O_{8h} at $8h$ ($x, y, 0$), O_{4e} at $4e$ ($0, 0, z$), Fe (anti-site defect (ASD):Mo) at $(0, 0, 0)$, and Mo(ASD:Fe) at $(0, 0, 1/2)$. Numbers in parentheses are standard deviations of the last significant digit. The weighed (R_{wp}) and expected (R_e) agreement factors are also given. Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) are shown

x	$\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$				
	0.0	0.1	0.2	0.3	0.4
$a/\text{\AA}$	5.582(3)	5.585(5)	5.589(8)	5.592(2)	5.594(2)
$c/\text{\AA}$	7.901(0)	7.893(0)	7.886(5)	7.896(3)	7.901(0)
$V/\text{\AA}^3$	246.76(6)	246.24(7)	246.42(7)	246.94(5)	247.26(6)
Fe– $\text{O}_{8h}/\text{\AA}$	2.09(2)	2.01(6)	1.96(0)	1.94(0)	1.91(3)
Mo– $\text{O}_{8h}/\text{\AA}$	1.89(7)	1.95(4)	1.99(2)	2.01(4)	2.04(3)
Fe– $\text{O}_{4e}/\text{\AA}$	2.0(2)	2.2(2)	1.90(1)	1.85(5)	1.7(7)
Mo– $\text{O}_{4e}/\text{\AA}$	1.9(4)	1.8(8)	2.04(2)	2.09(3)	2.2(0)
$\angle\text{Fe–O}_{8h}\text{–Mo}/^\circ$	163.3(0)	168.4(8)	180.0(0)	180.0(0)	180.0(0)
ASD:Fe/%	38.9	22.4	5.5	5.3	5.2
$R_{wp}/\%$	4.52	4.12	3.82	3.17	4.35
$R_e/\%$	3.22	2.80	2.76	2.76	2.37
$\chi = R_{wp}/R_e$	1.4024	1.4733	1.4019	1.3842	1.5938

χ values, one of the most important R factor numbers, ranged between 1.3 and 1.6. The a - and c -axis lengths, and thus, the unit cell volume, V , tended to increase with increasing K-concentration, x (see Table 2). The reason for this was understood through the effective ionic radii of Shannon,²⁸⁾ which show that the K^+ ($= 1.64 \text{\AA}$) ion is bigger than the Sr^{2+} ($= 1.44 \text{\AA}$) ion. Furthermore, because the Goldschmidt ionic tolerance factor²⁹⁾ crossed to 1 with a small amount of K-substitution, the Fe– O_{8h} –Mo bond angle increased with increasing K substitution level, that is, the rotation angle of the BO_6 octahedra decreased with increasing substitution level, x (see Table 2). As a result, the bond angle reached ca. 180° , almost leveling off at $x = 0.2$. Figure 4 shows the bond lengths between the transition metal and oxygen as a function of K-concentration, x , obtained by the Rietveld refinement for K-substitution. In the ab -plane, the Fe– O_{8h} bond length decreased and the Mo– O_{8h} bond length increased with increasing substitution level, x . Furthermore, also in the c -axis, the Fe– O_{4e} bond length tended to decrease and the Mo– O_{4e} bond length tended to increase. Both the M –O length ($M = \text{Fe, Mo}$) of the ab -plane and the c -axis crossed at around $x = 0.2$. These Rietveld refinement results reveal that the FeO_6 and MoO_6 octahedra of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ appear almost like regular octahedra and have figures similar to each other at $x = 0.2$.

Figures 5 and 6 show the Arrhenius plots of the electrical conductivities, σ , and the Seebeck coefficient, S , as a function of temperature. The electrical conductivity values are of the order of 10^3 S/cm at room temperature. The electrical conductivity decreases with increasing temperature. This behavior is typical of metals. The Seebeck coefficient of the samples is negative over the whole temperature range, which indicates that they are n-type materials. The Seebeck coefficient increases with temperature. The absolute value of the Seebeck coefficient remains below $10 \mu\text{V/K}$ at room temperature. The electrical properties of a few samples show subtractive aberration at around 1000 K. The absolute values of S for all the samples changed the behavior of T -dependence at around 1000 K. We have reported that the electrical properties of slightly Ba- or Ca-substituted $\text{Sr}_2\text{FeMoO}_6$ samples showed similar behavior.^{30),31)} In the previous reports, we investigated the high-temperature X-ray diffraction of the slightly Ba-substituted $\text{Sr}_2\text{FeMoO}_6$ sample and the heavily Ba-

Fig. 4. Bond length between the transition metal and oxygen in the ab-plane and along the c -axis of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ as a function of the doping level.

Fig. 5. Arrhenius plots of the electrical conductivity of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$.

substituted $\text{Sr}_2\text{FeMoO}_6$ sample.^{30,31)} The data revealed that the heavily Ba- and Ca-substituted $\text{Sr}_2\text{FeMoO}_6$ samples undergo a phase transition at approximately 1000 K, presumably making a modulation in the electronic density of state (DOS). The absolute value of S for $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6$ that increased drastically at around 1000 K may be due to a change in DOS with a similar phase transition. For this reason, the negative peak was observed in the electrical properties at around 1000 K.

Fig. 6. Seebeck coefficient of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ as a function of temperature.

Fig. 7. (a) Electrical conductivity and (b) Seebeck coefficient of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ at room temperature as a function of the doping level.

Figure 7 shows the electrical conductivity and Seebeck coefficient as a function of K-concentration, x , at room temperature. The electrical conductivity increased with increasing

Table 3. Electrical resistivity (using van der Pauw method), ρ_H , Carrier concentration, n , Hall mobility, μ_H , of the $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$

Sample x	$\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$				
	0.0	0.1	0.2	0.3	0.4
$\rho_H/10^{-4} \Omega\text{cm}$	13.62	6.04	3.87	3.21	3.46
$n/10^{21} \text{cm}^{-3}$	3.9	5.7	ca. 10	ca. 10	ca. 10
$\mu_H/\text{cm}^2(\text{Vs})^{-1}$	1.7	1.8	—	—	—

Fig. 8. Thermoelectric power factor of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ as a function of temperature.

K-substitution level. The reason for this becomes clear through Hall effects measurements, which show that the carrier concentration tended to increase with increasing K-doping level, x (see **Table 3**). $\text{Sr}_2\text{FeMoO}_6$ exhibits n-type conduction. Thus, when the A-site cations substitute Sr^{2+} with K^+ , the electrical conductivity may decrease with increasing K^+ -concentration because the carrier concentration decreases. However, this result is in conflict with the assumption. This discrepancy may be explained by the presence of oxygen vacancies induced by charge compensation with K^+ -doping. Moreover, the bond angle of $\text{Fe-O}_{8h}\text{-Mo}$ increased up to 180° at $x = 0.2$, then remained unchanged at $x = 0.3$ and 0.4 . This may mean that the transfer integral improved with x . This indicates that the carrier mobility can be increased with x . The absolute value of the Seebeck coefficient increased with x up to $x = 0.2$ and then decreased in the range $x = 0.3$ – 0.4 . The Rietveld refinement of the XRD patterns of the oxides revealed that the distortion of the FeO_6 and MoO_6 octahedra was eased by crossing to a substitution level of 0.2. Thus, the showing maximum $|S|$ values at $x = 0.2$ would be accounted for by the improvements of crystal-field symmetry. Ohta et al. proposed that $|S|$ values increase with increasing in the orbital degeneracy on crystal-field between transition metal and oxygen, however the conduction band width decrease.^{32),33)} That is, from the Rietveld refinement in this study, Fe-O_{4e} , Fe-O_{8h} , Mo-O_{4e} and Mo-O_{8h} bond lengths show almost the same values at $x = 0.2$, and also in case of consequent, the $|S|$ values increase and the conduction band width may decrease.

The power factor, $S^2\sigma$, which represents the electrical contribution to the overall thermoelectric performance, is shown in **Fig. 8**. The power factor of the present samples increased with increasing temperature. The maximum value of the power factor was $4.2 \times 10^{-4} \text{ W/mK}^2$ at 1250 K for the $\text{Sr}_{1.6}\text{K}_{0.4}\text{FeMoO}_6$ sample.

The thermal conductivity, κ , another fundamental parameter used for assessing thermoelectric performance, may cancel out

Fig. 9. Thermal conductivity of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ as a function of temperature. The circle symbols represent the $\kappa - L_0\sigma T$ of each sample.

the advantage of having a large σ as in the case of metals. The thermal conductivities of the present samples are shown in **Fig. 9** as a function of temperature. All these values were lower than what is generally observed for thermoelectric single perovskite-oxides.^{7),32),34)} The thermal conductivities of the samples were about 3–5 W/mK at room temperature, and decreased monotonically with increasing temperature. The samples with $x = 0.0$ – 0.2 showed a systematic decrease in thermal conductivity with increasing temperature, indicating that phonon–phonon scattering was dominant in the temperature range studied. The thermal conductivities of the samples with $x = 0.3$ and 0.4 were less dependent on temperature. This may be due to the relative increase in temperature-independent phonon–impurity scattering. The phonon thermal conductivity, κ_{ph} , is obtained by subtracting electronic thermal conductivity, κ_{el} , from the total thermal conductivity, κ_{total} . The $\kappa - L_0\sigma T$ ($\sim \kappa_{\text{ph}}$ values of these compounds show on the white color symbols of each sample symbol in **Fig. 8**). Here, the L_0 ($\sim 2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^2$) is the Lorenz number. The $\kappa - L_0\sigma T$ values of these samples show about 2 W/mK, and decrease slightly with increasing temperature. The systematic decrease in the $\kappa - L_0\sigma T$ values of all the samples with increasing temperature indicates that the phonon–phonon scattering is dominant in the temperature range measured.

The dimensionless figures of merit of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ were calculated by the equation $ZT = (S^2\sigma/\kappa)T$, which evaluates the performance of thermoelectric materials. The dimensionless figures of merit of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ samples are shown in **Fig. 10** as a function of temperature from room temperature to 1250 K. Because the power factor of the oxides increased above 900 K, and thermal conductivity decreased monotonically over the whole measurement temperature range, the dimensionless figure of merit increased dramatically above 900 K. $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ shows the highest ZT value, as high as 0.24 at 1250 K.

4. Conclusion

The physical properties of densely sintered double-perovskite oxides $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ were investigated from room temperature to 1300 K in terms of the A-site doping effect. The relative density of hot-pressed $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ samples showed ca. 90%. XRD results revealed that although the samples contained a small amount of unknown phase material, almost single-phase samples were obtained. At room temperature, the σ value increased with increasing K-concentration. In contrast, the absolute value of the

Fig. 10. Dimensionless figure of merits of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ as a function of temperature.

Seebeck coefficient increased for x values between 0.1 and 0.2, but then decreased between $x = 0.3$ and 0.4. Furthermore, the electrical properties, and thus, both electrical conductivity and Seebeck coefficient of these compounds, exhibited local minima at 1000 K. This was caused by a crystal structure phase transition at high temperature. As a result, the power factor increased with temperature, with the $\text{Sr}_{1.6}\text{K}_{0.4}\text{FeMoO}_6$ sample showing a power factor as high as $4.5 \times 10^{-4} \text{ W/mK}^2$ at 1250 K. The thermal conductivities ranged from 3–5 W/mK at room temperature, and decreased monotonically with increasing temperature. The dimensionless figures of merit, $ZT = (S^2\sigma/k)T$, of $\text{Sr}_{2-x}\text{K}_x\text{FeMoO}_6$ were calculated. $\text{Sr}_{1.6}\text{K}_{0.4}\text{FeMoO}_6$ was found to have the highest ZT value: 0.24 at 1250 K. The crystal structure of the double-perovskite oxide $A_2B'B''\text{O}_6$ showed high potential as a thermoelectric conversion material in which low thermal conductivity can occur simultaneously with high electrical conductivity.

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