



Article Negative Thermal Expansion Properties of Sm_{0.85}Sr_{0.15}MnO_{3-δ}

Yucheng Li *¹⁰, Yang Zhang, Yongtian Li and Yifeng Wu

Department of Avionics Engineering, Aviation Maintenance NCO Academy, Air Force Engineering University, Xinyang 464000, China; zy9804020@163.com (Y.Z.); 13937616646@139.com (Y.L.); 13937616450@139.com (Y.W.) * Correspondence: zzuleeyucheng@163.com; Tel./Fax: +86-376-6655-656

Abstract: A novel negative thermal expansion (NTE) material composed of Sm_{0.85}Sr_{0.15}MnO_{3-\delta} was synthesized using the solid-state method. By allowing Sr²⁺ to partially replace Sm³⁺ in SmMnO₃, the ceramic material Sm_{0.85}Sr_{0.15}MnO_{3-\delta} exhibits NTE properties between 360K and 873K, and its average negative thermal expansion coefficient was -10.08×10^{-6} /K. The structure of Sm_{0.85}Sr_{0.15}MnO_{3-\delta} is orthogonal, the space group is pbnm, the morphology is regular, and the grain size is uniform. The results of X-ray diffraction and XPS (X-ray photoelectron spectroscopy) suggest that the NTE phenomenon is related to the electron transfer of Mn ions. With the increase in temperature, Mn⁴⁺ is rapidly transformed into Mn³⁺, accompanied by Mn⁴⁺O₆ octahedron distortion and oxygen defects. It was found that the sample volume continually decreased at the same time.

Keywords: negative thermal expansion; $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$; lattice distortion; oxygen defects; Jahn–Teller effect

1. Introduction

We know that most instruments are composed of various materials, but with increases in temperature, different thermal expansion coefficients of various constituent materials may lead to thermal mismatches, and small cracks in the equipment can lead to performance failures and even instrument damage. NTE materials have attracted considerable research attention in the production of composites with accurately controllable positive, negative, or zero coefficients of thermal expansion [1–11].

A great number of NTE materials have been found, such as oxides ($Cu_{1.5}Mg_{0.5}V_2O_7$, $Cu_2V_2O_7$, and $HfMnMo_3O_{12}$, etc.) [12–16], antiperovskite Mn_3XN , and perovskite (BiNiO₃, $Gd_{1-x}Sr_xMnO_{3-\sigma}$, and $Er_{0.7}Sr_{0.3}NiO_{3-\delta}$, etc.) [17–21]. However, each material has limitations because of some defects. ZrW_2O_8 is a metastable phase at room temperature (RT), which is difficult to prepare due to it readily decomposing [1]. ZrV_2O_7 exists as a phase transformation at 375K [2]. $Y_2Mo_3O_{12}$ has a water-absorbing quality at RT. Although antiperovskite ($Mn_3Cu(Ge)N$, Mn_3NiN , and Mn_3ZnN , etc.) possesses the properties of superconductivity, giant magnetoresistance, magnetocaloric effects, and constant electrical resistivity [8], the NTE temperature range is usually under RT, and its preparation conditions are very strict. $Mn_3Cu(Ge)N$ needs to be grown on a silicon surface with high pressure and argon gas protection. The NTE perovskite ABO_3 (A = Gd, Er, and Bi, etc.; B = Mn, Er, Sr, Ni and Sr, etc.) not only shows NTE properties in a large temperature range above RT but also has simple preparation conditions.

Kurimamachiya-chouses conducted research on Sr^{2+} partly substituting Gd^{3+} in GdMnO_3 . They pointed out that $\mathrm{Gd}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_{3-\delta}$ had excellent NTE properties [18]. L. J. Fu reported the NTE material of $\mathrm{Er}_{0.7}\mathrm{Sr}_{0.3}\mathrm{NiO}_{3-\delta}$ with Sr^{2+} partly substituting Er^{3+} in ErNiO_3 [19]. These studies suggest that the substituting method is an effective way to prepare new kinds of NTE materials with excellent properties [16,18–20]. In the present study, we conducted research on Sr^{2+} partly substituting Sm^{3+} in SmMnO_3 . The thermal properties are discussed.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The sample was prepared according to the conventional solid-state method. Analyticgrade Sm_2O_3 (purity 99.5%), SrO (purity 99.5%), and MnO_2 powder were used as raw materials. Using MnO_2 as the raw material, Mn_2O_3 powder was prepared by burning in a 923 K furnace for 10 h.

 Sm_2O_3 , SrO, and Mn_2O_3 powders were mixed according to the mole ratio of Sm:Sr:Mn = 0.85:0.15:1. The mixtures were ground using an agate mortar for 1 h and then ground with ethanol for 2 h. The obtained mixtures were then dried for 1 h at 353 K in a baking oven. Afterward, the mixtures were pressed into cylindrical-shape compacts (\emptyset 10 × 5 mm) using a powder pellet machine (769YP-15A, 200 MPa). The compacts were initially sintered in a pipe furnace (AY-BF-555-180) at 1273 K for 10 h in air and subsequently sintered at 1623 K for 10 h. The sample was allowed to cool in the furnace naturally.

The linear thermal expansion coefficient was measured using a dilatometer Linseis L76 (heating and cooling rates of 5 K/min). The XRD measurement was carried out using Bruker D8 Advance with CuK α radiation. The XRD pattern of the sample was analyzed using X'Pert HighScore Plus software. The lattice constants a, b, and c and the unit cell volume of the sample were calculated using powderX software and the least square method. The surface morphology of the sample was observed using the FEI Quanta 250 scanning electron microscopy (SEM), and the EDS energy spectrum was obtained using an Appllo XP. The TGA and DSC were tested using a LabsysTM thermal analyzer. The XPS (X-ray photoelectron spectroscopy) was performed using a Thermo Scientific K-Alpha instrument for the valence analysis of the Mn element. The BET tests were performed to determine the size and volume of the holes using an ASAP2460 device.

3. Results and Discussion

3.1. Phase Analysis

Figure 1a is the XRD pattern of the sample at RT. Comparing the XRD pattern with the JCPDS cards for SmMnO₃ (00-025-0747), $Eu_{0.9}Sr_{0.1}MnO_3$ (No. 00-051-0252), and $Eu_{0.8}Sr_{0.2}MnO_3$ (00-051-0251), we found that the diffraction peaks were similar to those of the JCPDS cards, except for some shifts, which suggests that the as-prepared sample had similar structure to that of SmMnO₃, $Eu_{0.9}Sr_{0.1}MnO_3$, and $Eu_{0.8}Sr_{0.2}MnO_3$. It can be confirmed that the ceramic Sm_{0.85}Sr_{0.15}MnO_{3- $\delta}$} crystallizes in an orthorhombic structure. As the ionic radius of Sr²⁺ (ionic radius 1.18 Å) is bigger than that of Sm³⁺ (ionic radius 0.958 Å), the difference in the ionic radius may cause lattice distortion. As Sr²⁺ partly substitutes for Sm³⁺, the diffraction peaks also shift.



Figure 1. The XRD patterns: (a) $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ and (b) $SmMnO_3$.

Figure 2a shows the SEM image of the sample. We found that the ceramic sample was composed of homogenous spherical or elliptic spherical particles with some obvious agglomerations. There were pores and microcracks in the sintered body. The size of the particles was uniform, with an average grain size of about $1~2 \mu m$. The EDS analysis of the sample revealed the primary elements of Sm, Sr, Mn, and O, and their atomic ratio (Sm:Sr:Mn:O) was about 0.85:0.15:1:3 (seeing Table 1). Combined with the XRD analysis, we identified the composition of the samples as being Sm_{0.85}Sr_{0.15}MnO₃.



Figure 2. (a) SEM image of the ceramic $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$; (b) EDS spectrum corresponding to the SEM image.

Table 1.	Atomic ratio	of Sm, Si	r, Mn, and	O in Sm	$_{0.85}$ Sr _{0.}	15MnO _{3-δ}	by	EDS
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Element	Sm	Sr	Mn	0
(at.%)	14.46	2.39	16.20	66.95

3.2. Thermal Expansion Property

Figure 3a–c show the relative length (*dL/L*) with the temperature increases of SmMnO₃, SrMnO₃, and Sm_{0.85}Sr_{0.15}MnO_{3- δ}, respectively. SmMnO₃ (Figure 3a) and SrMnO₃ (Figure 3b) showed positive thermal expansion. Calculating according to the curve, the expansion coefficients were 5.24×10^{-6} /K and 12.7×10^{-6} /K, respectively. When the temperature was below 360 K, the ceramic Sm_{0.85}Sr_{0.15}MnO_{3- δ} showed a positive thermal expansion of 0.46875×10^{-6} /K. As the temperature increased, the ceramic Sm_{0.85}Sr_{0.15}MnO_{3- δ} showed an NTE property in the range of 360 to 873 K. The average linear expansion coefficient was -10.08×10^{-6} /K.

Figure 4 shows the high-temperature XRD patterns of ceramic $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ from RT to 873 K. As the temperature increased, the diffraction peaks of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ moved slightly to small angles, except three diffraction peaks (31.54°, 33.79°, and 52.65°) that moved to a large angle.

Figure 5 shows the variation in the Sm_{0.85}Sr_{0.15}MnO_{3- δ} lattice parameters and volume with temperature increases, which was calculated using the powderX software. In a, c in Figure 5, the increase occurred gradually, while in b in Figure 5, it decreased as the temperature increased gradually. We believe that the thermal expansion of Sm_{0.85}Sr_{0.15}MnO_{3- δ} was due to anisotropy. We can see that from RT to 360 K, Sm_{0.85}Sr_{0.15}MnO_{3- δ} showed a positive expansion property. As the temperature increased to 360~873 K, Sm_{0.85}Sr_{0.15}MnO_{3- δ} showed an

NTE property with the average linear expansion coefficient of -3.33×10^{-6} /K. However, the original calculation of the negative thermal expansion coefficient of Sm_{0.85}Sr_{0.15}MnO_{3- δ} in this temperature range was -10.08×10^{-6} /K, according to Figure 3. As can be seen from Figure 2 above, there were pores and microcracks in the crystal. Therefore, we believe that when the temperature rises, the crystal squeezes the open space, namely, these pores and microcracks, which is another reason for the negative thermal expansion.



Figure 3. Relative length change (*dL/L*) with the temperature of the samples: (**a**) SmMnO₃, (**b**) SrMnO₃, and (**c**) Sm_{0.85}Sr_{0.15}MnO_{3- δ}.



Figure 4. XRD patterns of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ ceramics at high temperatures.



Figure 5. The variation in the $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ lattice parameters and volume with temperature increases.

Table 2 shows the pore size, pore volume, and BET surface area of the sample. The specific surface of the material itself is large, and the general level of adsorption is good. When the pore structure of carbon materials is more complex, it is easy to have a flexible hole, and the pore size becomes larger after gas adsorption. With the doping of Sr^{2+} , oxygen defects are caused, and the gas is adsorbed in the pores. With the further doping of Sr^{2+} , the adsorption oxygen saturation does not change. With the increase in temperature, the gas is sintered out, the b-axis shrinks at the same time, and the pore size becomes smaller, resulting in the negative expansion property.

Table 2. Pore size, pore volume, and BET surface area of the sample.

Sample	Pore Size (nm)	Pore Volume (cm ³ /g)	BET Surface Area (m ² /g)	
$Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$	15.7842	0.002563	0.6351	

Figure 6a is the XPS spectrum of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$; the characteristic peaks of Sm, Sr, Mn, and O are shown in the figure, respectively. The surface of the sample was free from any pollutants, and element C was used for the calibration of the XPS atlas. Figure 6b,c show the XPS spectra of Mn. In the XPS spectrum, the sample had a bimodal structure, which indicates that the Mn elements on the sample surface existed in two forms: Mn^{3+} and Mn^{4+} , which led to the oxygen vacancy. The presence of the oxygen vacancy facilitated the movement of electrons between Mn^{4+} and Mn^{3+} . The oxygen vacancy also led to the shortening of the bond length of the Mn-O bond, which led to lattice distortion and generated internal stress; this reduced the bond angle of Mn-O-Mn and increased the double-exchange effect.



Figure 6. Cont.



 $Figure \ 6. \ The \ XPS \ spectra \ of \ Sm_{0.85}Sr_{0.15}MnO_{3-\delta}: \ (a) \ elemental \ analysis, \ (b) \ Mn2p, \ (c) \ Mn3s, \ and \ (d) \ C1s.$

3.3. Discussion

 $SmMnO_3$ is a typical manganite perovskite structure. The structure of $SmMnO_3$ is shown in Figure 7. As for the MnO_6 octahedron in $SmMnO_3$, the distortion was caused by a change in the length of the Mn-O bond.



Figure 7. Structure diagram of SmMnO₃.

There are three kinds of common modes for this change [22–26] as follows. (1) The surface tension contract model Q_1 , as shown in Figure 8a. Six oxygen atoms of the unit cell move close to or far away from the manganese atom at the same time, making the Mn-O bond length decrease or increase significantly. This model can increase the energy of the system, which is not conducive to the system energy being able to decrease and makes the system extremely unstable in turn. (2) The plane distortion model Q_2 , as shown in Figure 8b. In a unit, two oxygen atoms in the horizontal plane leave a manganese atom, while the other two oxygen atoms become close to the manganese atom. The location of the two oxygen atoms in the vertical plane remains unchanged. (3) The expansion mode, or inspiratory mode Q_3 , which is shown in Figure 8c. In a MnO₆ octahedron, the two oxygen atoms in the vortical plane leave manganese atoms, while the four oxygen atoms in the horizontal plane become close to the manganese atom simultaneously. For a MnO₆ octahedron, the Q_1 and Q_2 models normally exist. Since the Q_1 model is unstable, the distortion of the MnO₆ octahedron is mainly the Q_2 model, also called the plane distortion model.



Figure 8. Three kinds of distortion models for the Mn-O bond (**a**) The surface tension contract model Q_1 ; (**b**) The plane distortion model Q_2 ; (**c**) The expansion mode, or inspiratory mode Q_3 .

We used MnO_2 , Sm_2O_3 , and SrO as the raw materials to prepare $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$. In the reaction process, there was a reciprocal transformation between Mn^{3+} and Mn^{4+} .

When Sr^{2+} substitutes the Sm^{3+} in $SmMnO_3$, Sr^{2+} will occupy the position of Sm^{3+} . To maintain the valence balance, electron transfer occurs in the Mn^{3+} converting into Mn^{4+} in $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$. Additionally, the p electron of O^{2-} will migrate to the orbit of the nearby Mn^{4+} , and the d electron of Mn^{3+} will migrate to the orbit of the nearby Mn^{3+} . Thus, this mechanism results in the electronic conduction and position exchanges of Mn^{4+} and Mn^{3+} ions. The system energy remains unchanged throughout. This process is known as the double exchange [27]. The structure of $Mn^{3+}-O^{2-}-Mn^{4+}$ forms in the process. However, according to the theory of Zener [28], the route of electron transfer between two Mn^{3+} , the magnetic moment between Mn^{3+} and Mn^{4+} ions should be parallel to each other. In this situation, it is favorable for there to be more electron transfer between Mn^{3+} and Mn^{4+} ions.

According to the analysis of the variable-temperature XRD data, we considered that the thermal property of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ might be related to the interaction of the lattice vibration and electron transfer between Mn^{3+} and Mn^{4+} . As the temperature rose, the lattice vibrated dramatically and Mn^{4+} converted into Mn^{3+} . Moreover, the electron transfer rate increased between the Mn^{3+} and Mn^{4+} ions. The number of Mn^{3+} ions that can cause the Jahn–Teller [29] effect increased. The oxygen ions in the $Mn^{3+}O_6$ octahedron became slant, or even produced oxygen defects, making the unit cell volumes decrease. From RT to 360 K, the unit cell volume increased. The reason is that the contribution of the lattice vibration to the thermal expansion exceeded that of the MnO_6 octahedral distortion and oxygen defects. As the temperature increased, $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ showed a low positive thermal expansion property, and above 360 K, the unit cell volume decreased. With more Mn^{4+} ions converting into Mn^{3+} , the $Mn^{3+}O_6$ octahedral distortion was enhanced and oxygen defects occurred. These contributed more to the thermal expansion than the lattice vibration. Therefore, $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ shows a negative thermal expansion property between 360 K and 873 K.

The DSC and TGA results of ceramic $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ also support the above statements. Figure 9a presents the DSC curve of ceramic $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$. In the curve, $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ has an endothermic peak at about 360 K. This shows that more Mn^{4+} ions were converted to Mn^{3+} with the increase in temperature. Thus, $Mn^{3+}O_6$ octahedral distortion was enhanced and oxygen defects occurred. The unit cell volume began to decrease, which is consistent with the results calculated by the high-temperature XRD (seeing b in Figure 5). As electron transfer occurred between the Mn^{3+} and Mn^{4+} ions, the amount of Mn^{4+} decreased, and oxygen ions in the $Mn^{3+}O_6$ octahedron became slant or even produced oxygen defects. The TGA results of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ confirm the existence of oxygen defects. In Figure 8b, the weight of the $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ sample decreased when the temperature increased from RT to 873 K. In addition, the variable-temperature XRD (seeing Figure 5) showed that there was no phase transition with the increase in temperature. As electron transfer occurred between the Mn^{3+} and Mn^{4+} ions, $Mn^{4+}O_6$ converted into $Mn^{3+}O_6$ and oxygen defects appeared. Therefore, we consider that the loss of the weight can be ascribed to the oxygen defects.



Figure 9. DSC (a) and TGA (b) curve of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$.

Moreover, the non-stoichiometric ratio of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ caused the mole ratio mismatch of the Sm, Mn, and O atoms. Some lattice vacancies and interstitials existed in the crystal lattice, making the lattice distortion continuous. In the structure analysis, the crystal distortion was found to have a direct impact on the bond length and angle of the MnO₆ octahedron. As for ABO₃, when we conducted the substitution in the A position with a different ionic radius, especially in the non-stoichiometric ratio manganese perovskite, the size mismatch effects of the A position ion together with lattice space and interstitial caused a difference in the crystal structure. These eventually led to a great change in the lattice parameters and unit cell size [30–32].

4. Conclusions

- (1) A novel negative thermal expansion material composed of $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ was synthesized using the solid-state method with an NTE coefficient of $-10.08 \times 10^{-6}/K$ from 360 to 873 K.
- (2) The particles were homogenous spherical or elliptic–spherical particles with a uniform particle size of about 1~2 μm.
- (3) The ceramic $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$ crystallized in an orthorhombic structure with the space group Pbnm. When Sr^{2+} substituted the Sm^{3+} in $SmMnO_3$, Sr^{2+} occupied the position of Sm^{3+} . To maintain the valence balance, electronic transfer occurred in the Mn^{3+} , converting into Mn^{4+} in $Sm_{0.85}Sr_{0.15}MnO_{3-\delta}$. The $Mn^{3+}-O^{2-}-Mn^{4+}$ structure formed in the process.
- (4) The thermal property of Sm_{0.85}Sr_{0.15}MnO_{3-δ} is considered to be related to the interaction of the lattice vibration and electron transfer between Mn ions. As the temperature rise, the lattice vibrated dramatically and more Mn³⁺ converted into

 Mn^{4+} . Additionally, the electron transfer rate increased between the Mn^{3+} and Mn^{4+} ions as the temperatures increased. The number of Mn^{3+} ions that can cause the Jahn–Teller effect increasesd. The oxygen ions in the $Mn^{3+}O_6$ octahedron became slant or even produced oxygen defects. The contributions of the lattice vibrations and electron transfer between Mn^{3+} and Mn^{4+} to the thermal expansion changed with the increasing temperature.

(5) The pore energy in the sintered body partially absorbed the expansion of the a-axis a and the c-axis; the negative expansion phenomenon can be explained from the perspective of the contraction of the b-axis. The abnormal thermal expansion behavior of the Sm_{0.85}Sr_{0.15}MnO_{3-δ} perovskite system is caused by the presence of pores in the sintered body combined with the negative expansion of the b-axis in the perovskite system.

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