Nanometer thick thermochromic film based on K-doped manganite oxide prepared by magnetron sputtering

Teng Lu^a, Desong Fan^{a,*}, Qiang Li^a, Xiang Fan^b

^a*MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu, 210094, China*

^b*Shanghai Institute of Space Power-Sources (SISP), Shanghai, 200245, China*

Abstract

For seeking a lightweight thermochromic film acting as a smart radiation device in thermal control system for spacecraft, the (La,Ca,K)MnO_{3±δ} films with different thicknesses were deposited on Si(100) substrate by magnetron sputtering method with a target which was synthesized by a sol-gel method. The crystal structure and micro-morphology of these films are investigated. The results reveal that all films form an orthorhombic perovskite structure, and it undergoes a Volmer-Weber growth mode with the increased thickness. Temperature-dependent infrared reflectivity and emittance are investigated. Spectra data indicate that reflectivity of all films has a decreased trend with increasing temperature. In the temperature range of 173–373 K, the K-doped thermochromic films show a large emittance increment near 0.36 with film thickness only 321 nm. All of these results show that the thermochromic film has a great potential to be applied to a more lightweight and cost-effective thermal control device in spacecraft with an excellent radiation performance.

*Corresponding author. Tel. : + 86 025 84315837
Email address: dsfan@njjust.edu.cn (Desong Fan)

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1. Introduction

The satellites running in outer space will confront a huge temperature variation when they are exposed to the sunny side and the shadow side. To make the inner devices operating normally, thermal control systems must be employed. At present, some novel thermal control coatings are presented, such as thermochromic coating based on perovskite manganites. Investigations about the thermochromic coating have been performed since 1999s by Tachikawa et al[1], who reported for the first time that a large emissivity variation was observed in the Ca- or Sr-doped LaMnO_3 smart radiator device (SRD). Moreover, the emissivity of the sample shows a drastically increase upon heating to a critical temperature called MI transition temperature T_{MI} . Since their emissivity is small at temperature below the T_{MI} and large at higher temperature, emissivity adjustment can be achieved automatically by temperature control. If a radiator composed of thermochromic coating is fitted on a spacecraft surface, the emissive heat transfer from spacecraft can be automatically controlled without additional power consumption and moving parts. Thermochromic coating, therefore, attracted great attention in space thermal control application.

Over the past years, many efforts on improving the applicability of the material have been carried out[2, 3, 4]. Investigations from the from the Japan Aerospace Exploration Agency and Nippon Electric Company showed that the increment of emissivity for two bulk materials $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$

23 and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are reaching 0.4 in the temperature range of 173–373
 24 K[5, 6]. Their results revealed that the material can be fabricated to a
 25 thin tile with dimension $40 \times 40 \times 0.2 \text{ mm}^3$ and weight 1.2 kg/m^2 . We have
 26 also reported that the increment of normal emissivity can arrive 0.5 at 173–
 27 373 K for the sample of Ca and Sr doping $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ in our pervious
 28 work[7]. The size of sample is $40 \text{ mm} \times 40 \text{ mm}$ with $400 \mu\text{m}$ thick and weight
 29 is 1.23 kg/m^2 . In order to overcome the material drawback absorbing solar
 30 radiation, K. Shimazaki et al[8, 9] and D.Fan et al[10, 11] designed multi-
 31 layer optical structures on the material surface to reduce its solar absorp-
 32 tivity, and the reported solar absorptivity of the structured material can
 33 be reduced to 0.28. Moreover, the simulated experiment of space particles
 34 exposure revealed that the structured material possesses stabilized thermal
 35 radiative properties[12, 13]. M. Soltani et al[14] and D. Nikanpour et al[15]
 36 deposited $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.175$ and 0.3) film on Si(100) and metal sub-
 37 strate. The measured emittance variation is 0.25 in a temperature range of
 38 173–373 K. D.Fan et al[16] prepared the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ on YSZ substrate
 39 by magnetron sputtering. The result shows that the emittance increment
 40 at 173–373 K can approach 0.30 in properly condition. T. Shiota et al[17]
 41 fabricated $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ thin films on YSZ(100) substrate by pulsed laser
 42 deposition. The result found that $2.5 \mu\text{m}$ -thick film is the most proximate
 43 substitution for the ceramic tiles used in spacecraft. These thin films pre-
 44 pared in lab shown a favourable performance in the emittance variation. SRD
 45 based on the material $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) with a low transition tem-
 46 perature of 260 K is thought too low to fit application in space. It is desired
 47 that the transition temperature can be adjusted to near room temperature.

48 Recently, M. Bejar et al[18, 19] and S. Bhattacharya et al [20] reported that
49 the transition temperature of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ ($(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$) com-
50 pounds can be adjusted to higher temperature by an appropriate K-doping
51 concentration, inciting the investigation in SRD based on the monovalent
52 doped manganite.

53 In this work, the $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ thin film were deposited on Si(100)
54 substrates by magnetron sputtering technique using a target synthesized by a
55 sol-gel method. We discussed the crystal structure, the surface morphology,
56 the elementary composition and the surface roughness of films with different
57 thickness. The emittance at different temperature and solar absorptivity
58 were also studied to determine the film radiation performance.

59 2. Experiment procedures

60 The $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ thin film were deposited on Si(100) substrates by
61 the radio frequency (RF) magnetron sputtering system(JGP800, Shenyang
62 Scientific Instrument Co., China). The substrate sizes are 25 mm in di-
63 ameter and 0.5 mm in thickness. The $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ target was calcined
64 from nanoscale $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ powder, which was synthesized by a sol-gel
65 method using $\text{La}(\text{NO}_3)_3$, CaCO_3 , K_2CO_3 and $\text{Mn}(\text{NO}_3)_2$ solution(50%)[21].
66 Before the deposition, the air in deposition chamber was exhausted until
67 the pressure under vacuum at 6.0×10^{-4} pa. The $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ tar-
68 get is set a 50 mm distance from the substrate. The RF power, sputtering
69 pressure and deposition temperature were kept at 80 W, 0.8 pa and 298 K.
70 The $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film with different thickness is numbered from S1 to
71 S5 as listed in Table 1. We adopted a layer-by-layer deposition discontin-

72 ously to achieve the desired thickness in view of the overheat problem of
 73 equipment. After the deposition, these samples were annealed at 1073 K in
 74 flowing oxygen for 2 h. Crystalline phase of films was detected by grazing
 75 incidence X-ray diffraction (XRD, D8 ADVANCE, Bruker Co., Germany).
 76 The micro-morphology features of film was observed by scanning electron
 77 microscopy with an acceleration voltage of 15 kV (SEM, S-4800, Hitachi Co.,
 78 Japan). Composition analysis was detected by the energy dispersive X-ray
 79 spectroscopy (EDS, Thermo Electron Co., USA) accessory of S-4800 at an
 80 acceleration of 20 kV. The surface roughness of the film was measured by
 81 the atomic force microscope (AFM, Bruker Dimension icon, Bruker Co., Ger-
 82 many). Solar absorptivity α_s and emittance ϵ_{IR} are two important param-
 83 eters for the thermal control material of spacecrafts. The former determines
 84 the heat input of sun radiation, while the latter controls its heat rejection
 85 capacity[22]. In this work, the α_s and ϵ_{IR} are calculated using the experi-
 86 mental reflectivity data based on the expressions:

$$\alpha_s = \frac{\int_{0.25}^{2.5} [1 - \rho(\lambda)] I_s(\lambda) d\lambda}{\int_{0.25}^{2.5} I_s(\lambda) d\lambda} \quad (1)$$

87 and

$$\epsilon_{IR}(T) = \frac{\int_{2.5}^{25} [1 - \rho(\lambda, T)] I_b(\lambda, T) d\lambda}{\int_{2.5}^{25} I_b(\lambda, T) d\lambda}, \quad (2)$$

88 where $I_s(\lambda)$ denotes the solar radiation intensity, $I_b(\lambda, T)$ stands for Planck's
 89 spectral distribution of emissive power. $\rho(\lambda)$ and $\rho(\lambda, T)$ is the experimental
 90 reflectivity at room temperature and at various temperatures, respectively. It
 91 is measured in the solar radiation regions by an External Diffuse Reflectance
 92 accessory (Catalog No. DRA-2500, Agilent Technologies, Co., America) at-
 93 taching to the UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Tech-

94 nologies Co., America), in the thermal radiation regions by an accessory of
95 Transmission-Reflection Dewar (Catalog No. DER-300, Harrick Scientific
96 Products, Inc., America) mounting on the FT-IR spectrometer (VERTEX
97 80v, Bruker Co., Germany). The measured wavelength and temperature
98 ranges are 2.5-25 μm and 173-373 K, respectively.

99 3. Results and discussions

100 Numerous factors will affect film characteristic during the preparation
101 process. Sputtering thickness is taken into analysis in this study as one of
102 the most important factors. The grazing incidence X-ray diffraction(GIXRD)
103 test was performed to find out whether the correct crystalline structure was
104 obtained. Fig. 1 shows the XRD patterns of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films with
105 different thickness. Seven single peaks are showed in these five samples,
106 which agree with that of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ bulk[23]. These films are single
107 perovskite phase with an orthorhombic structure except the thinnest sample,
108 containing an impurity of Ti_2O_3 . Any reflection peaks of a single-crystal
109 Si(100) substrate are not observed in GIXRD patterns, since the incident
110 angle value was set as 1° . The Ti_2O_3 content is from the contamination of
111 sputtering system for the other TiO_2 deposition.

112 The EDS patterns of six samples including LCMO film are shown in
113 Fig. 2. According to the EDS pattern and the atom percent of each related
114 elements, the actual stoichiometric ratio of these films are labeled on the
115 pictures. The contents of La, Ca, and K are less than the ideal ratio of
116 0.7:0.2:0.1. Especially the K content experiences a worst loss, with 80% of
117 its ideal content. As such, the contents of La and Ca in LCMO film are

also less than the ideal ratio of 0.7:0.3. The fact shows that it is difficult to realize an ideal stoichiometric ratio in $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films. Firstly, the sol-gel method which was used to synthesize the bulk target will affect elementary composition of films[21]. In addition, the layer-by-layer deposition discontinuously may influence the detecting result. The Si content comes from the substrate, and the element of Au is caused by the sputtered Au film to enhance the image quality.

Fig. 3 displays the SEM micrographs of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films surface and cross-section. The thickness of films are labeled in Fig. 3(f)–(i). It can be found from the surface micrographs that the more thicker film is, the more denser surface is. Obviously, the granules at film surface is still discrete when the film thickness increases to 321 nm. Until thickness up to 389 nm, the film begins to become dense. This causes a huge discrepancy in film surface with different thickness, and it conforms to a Volmer-Weber film growth mode[24]. From Fig. 3(a), some single granules are distributed discretely over the whole film, the other starting to gather. That is an initial nucleation. With the thickness increased, the granules are getting bigger and more concentrated, just like each island. An island-like structure is formed over the film surface with the increased thickness. This structure can also be detected from the cross-section micrographs in Fig. 3(g)–(h). Every single island is concatenated when thickness rises to 456 nm, and ultimately forms a flat and dense film.

The AFM micrographs with five different thickness of films are showed in Fig. 4. The scanned area was $1\ \mu\text{m}\times 1\ \mu\text{m}$. Corresponding to the SEM images described above, these AFM images indicate a same grow mode that films

143 experience an initial nucleation, an island-like structure and then coalesces
 144 with each other with increasing film thickness[24]. The surface roughness
 145 (Ra) is also calculated from the analysis of AFM image with $10\ \mu\text{m} \times 10\ \mu\text{m}$
 146 areas showed in Fig. 4(f). The results indicate that the Ra decreased from
 147 9.47 nm for the 179 nm thick film to 0.858 nm for the 456 nm thick film. The
 148 tenfold decline of Ra originates from the growth mode of film on unheated
 149 Si substrate. The nucleation and the formation of island-like structure will
 150 both increase surface roughness until the ‘islands’ are concatenated. A lower
 151 roughness is beneficial to obtain a more dynamic variable emittance surfaces.
 152 Fig. 5 shows the reflectivity of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film in the temperature
 153 range of 173–373 K. The result illustrated that the reflectivity of film de-
 154 creases with increasing temperature below 293 K and keeps almost unchange
 155 with the increase of temperature above 293 K. This is due to the phase transi-
 156 tion which film undergoes from the ferromagnetic metal to the paramagnetic
 157 insulator with increasing temperature as reported in bulk manganites[7]. At
 158 the wavelength of $17\ \mu\text{m}$, a sharp peak can be detected in all samples, re-
 159 sulting from the transverse optical phonon existing in perovskite structure
 160 compounds[25, 26]. There are other two peaks appear at $30\ \mu\text{m}$ and $59\ \mu\text{m}$
 161 actually. While we can not observe them because of the limited test region
 162 of spectrometer. In general, the three peaks occur at $17\ \mu\text{m}$, $30\ \mu\text{m}$ and 59
 163 μm , are corresponding to Mn-O stretching mode, Mn-O-Mn bending mode,
 164 and La-site external mode, respectively. The phonon peak of the low tem-
 165 perature is flatter than the high temperature. That has been explained by
 166 a dielectric screening effect. Specifically, the active free electron may screen
 167 of phonon model at a low temperature[27]. There is another abnormal peak

168 occurring at the wavelength of 10 μm . And the lower temperature is, the
 169 thicker film is, however the flatter peak becomes. This phenomenon mostly
 170 caused by the substrate. Namely, the reflectivity of film is heightened under
 171 a lower temperature when the film exhibits a metal phase. Therefore, sub-
 172 strate influence will not show up at low temperature. The thicker film can
 173 also eliminate the substrate impact, and exhibiting the $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$
 174 film reflectivity characteristic.

175 The emittance with different temperature and thickness of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$
 176 film are showed in Fig. 5(f). It can be seen that thermal emittance of all the
 177 samples rises rapidly with increasing temperature, and the rising trend ceased
 178 at the temperature near 290 K. This change is due to the phase transition
 179 from metal phase to insulator phase of the film. It noted that the transition
 180 point in $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film is higher than that of LCMO film. The in-
 181 crease of transition temperature arises from the effect of K doping. When
 182 increasing the K concentration, a strong disorder of structure properties ap-
 183 pears in film, in turn the transition temperature rises[18]. From the Table 1,
 184 it can be found that the emittance increment can be achieved around 0.36
 185 when the thickness is over 321 nm. When the thickness increases to 456
 186 nm, we get a dense and uniform thermochromic film with emittance incre-
 187 ment $\Delta\epsilon=0.34$. Compared with the previous reports by[17, 28, 29], which
 188 says that the deposition thickness should reach 1.5 μm at least to realize
 189 $\Delta\epsilon=0.35$. However, we suggest that the $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film can accom-
 190 plish comparable property with a low thickness less than 500 nm. In fact,
 191 thermal radiation of materials are emitted from a thin layer of the surface.
 192 The thickness of the layer is called penetration depth. The characteristic of

193 thermal radiation of a film is similar to bulk materials when the thickness of
 194 film is higher than penetration depth. Contrary, it is affected by the substrate
 195 underneath the film. The penetration depth of IR spectrum in material can
 196 be educed from the expression $\delta_{pd} = \lambda/2\pi k$. We measured the reflectance of
 197 (La,Ca,K)MnO_{3±δ} film in the wavelength of 0.2–25 μm at room temperature.
 198 The extinction coefficient k can be obtained by the spectral reflectance[30].
 199 We obtained the $\delta_{pd}=0.1\text{--}1.5\ \mu\text{m}$ for the whole wavelength, which is four
 200 times thinner than that of La_{1-x}A_xMnO₃ reported in Reference[13]. It is
 201 considered that the doping of monovalent K may lead to a reduction in pen-
 202 etration depth. Compared with the 230 nm thick sample, the $\Delta\epsilon$ of 179 nm
 203 thick sample is smaller than the thicker one. It illustrates that film thickness
 204 will influence thermal radiation characteristic fiercely at the initial stage.
 205 After the island-structure formed, the $\Delta\epsilon$ is almost unchanged. Since our
 206 detecting mode is aimed to several single point, we classify these five sam-
 207 ples into two type, i.e., before forming the island-structure (the first type)
 208 and after forming the island-structure (the second type). For the first type,
 209 the deposition particles are gathered together which can not form a contin-
 210 uous film covering the substrate. Some of the incident lights may penetrate
 211 the thin film, and are absorbed by the substrate as shown in Fig. 3, that
 212 makes the emittance of first type rise. With the increase of thickness, the
 213 emittance tends to be higher. This tendency is identical to the first type,
 214 but just the reverse with the conclusion reported by Shiota et al[17], whose
 215 thickness is set as 1.2 μm to 4.3 μm . We guess this discrepancy derived from
 216 the different thickness magnitude and measurement error. While just as the
 217 result mentioned above, when the magnitude changes to two type, it is ac-

cord with the document. In addition, we prepared another repetitive samples with identical sputtering parameters to verify the conjecture. The result is showed in Fig. 6. There is always a small deviation existing between the two batch film samples at different thickness and temperature. The deviation can be evaluated as $\delta\epsilon = |\epsilon_{1st} - \epsilon_{2nd}|$, where ϵ_{1st} and ϵ_{2nd} is the emittance of the first and second batch film sample, respectively. The deviation probably comes from the different temperature control process, the detecting points and even the surroundings including room temperature and humidity. In Fig. 7, the emittance deviation $\delta\epsilon$ with different temperature and thickness of these films are listed. It is found that the $\delta\epsilon$ of all samples is less than 0.1, and the higher thickness is, the lower deviation is when the temperature ranges from 173 K to 213 K and 273 K to 373 K. While during the rest range, these deviation become irregular. The result clarified that the thicker sample will reduce the deviation to a certain extent.

Solar absorptivity of these films is measured in Fig. 8. Obviously, reflectivity of these films is under 40% in the wavelength range of 200–2500 nm, and it is higher in near-infrared region than the visible region. The solar absorption of (La,Ca,K)MnO_{3±δ} film rises as the thickness increases. It is demonstrated that the thicker film is easily to absorb solar radiation due to the strong absorption of K-doped manganites in this regions. The transmissivity of Si(100) substrate and S4 film are measured by integrating sphere over the wavelength region of 200–2500 nm as shown in Fig. 8. Compared with Si substrate, the transmissivity of (La,Ca,K)MnO_{3±δ} film decreases significantly above the wavelength of 1 μm, the average transmissivity of film is lowered to 0.05. This means that the sample can be seen as opaque in this

243 region. A larger solar absorptance is not expected for thermochromic film in
244 thermal control application. We are going to design a multilayer structure
245 to overcome this shortage in follow-on work.

246 4. Conclusions

247 (La,Ca,K)MnO_{3±δ} film with 179 nm, 230 nm, 321 nm, 389 nm, and
248 456 nm were deposited on Si(100) substrate by a RF magnetron sputter-
249 ing method and annealed at 1073 K in flowing oxygen for 2 h. XRD patterns
250 show that the films form an orthorhombic perovskite structure because the K
251 content is insufficient. The film tends to be dense from the micro-morphology,
252 and as the thickness increased, it undergoes a Volmer-Weber growth mode.
253 Reflectivity spectra indicates that the films have a phase transition from a
254 metallic state to a non-metallic state with increasing temperature. Compared
255 with the LCMO film, the (La,Ca,K)MnO_{3±δ} film exhibits a higher transition
256 temperature and a smaller penetration depth. The emittance change with
257 different temperature can be arrived at 0.36 for the 321 nm thick film. An
258 acceptable deviation of thermal emittance exists between two batch samples,
259 and a higher thickness will eliminate the deviation to a certain extent. Con-
260 sidering the acceptable reflectivity and physical characteristic, We suggest
261 that the K-doped thermochromic film can apply to a more lightweight and
262 cost-effective thermal control device in spacecraft.

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Fig. 1: The grazing incidence X-ray diffraction patterns of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films.

Table 1: Deposition condition and characteristic of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films.

Sample	DR(nm/min)	FT(nm)	ϵ_l	ϵ_h	$\Delta\epsilon$	α_s
S1	1.70	179	0.29	0.53	0.24	0.78
S2	1.28	230	0.34	0.64	0.3	0.79
S3	1.43	321	0.17	0.53	0.36	0.80
S4	1.44	389	0.23	0.58	0.35	0.80
S5	1.26	456	0.27	0.61	0.34	0.84

Fig. 2: The EDS patterns of LCMO film (a) and of (La,Ca,K)MnO_{3±δ} films with different thickness for (b) 179nm, (c) 230nm, (d) 321nm, (e) 389nm, (f) 456nm.

Fig. 3: The SEM micrographs of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ films surface and cross-section with different thickness for (a), (f) 179 nm, (b) 230 nm, (c), (g) 321 nm, (d), (h) 389 nm, and (e), (i) 456 nm. The cross-section of SEM (b) is not showed.

Fig. 4: AFM images of (La,Ca,K)MnO_{3±δ} films with thickness of 179 nm (a), 230 nm (b), 321 nm (c), 389 nm (d), 456 nm (e), and surface roughness(Ra) of films (f).

Fig. 5: Variation of the infrared reflectivity spectra of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film with temperature, (a) 179 nm, (b) 230 nm, (c) 321 nm, (d) 389 nm, (e) 456 nm, and (f) emittance of the $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film at different thickness and of the LCMO film.

Fig. 6: Repetitive experiment on the Emittance of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film at different thickness of (a) 230 nm, (b) 321 nm, (c) 389 nm, and (d) 456 nm.

Fig. 7: The deviation of emittance $\delta\epsilon$ between the two batch sample with identical sputtering parameters.

Fig. 8: Reflectivity in solar regions and solar absorptivity of $(\text{La,Ca,K})\text{MnO}_{3\pm\delta}$ film at different thickness, and the transmissivity of S4 film and Si(100) substrate.