Title: SPACECRAFT SMART THERMAL RADIATOR BASED ON THERMOCHROMIC COATINGS DEPOSITED ON ALUMINUM PANEL

Abstract: A thermal radiator is provided for an aluminum surface comprising a coating of earth-doped manganese over a layer of oxidized aluminum. In a preferred embodiment, the thermal radiator has the formula La₆₋ₓSrₓMnO₃₋ₓ. In a more preferred embodiment, the thermal radiator has the formula La₆₋ₓSrₓMnO₃₋ₓ, La₉₋ₓSrₓMnO₃₋ₓ, or La₆₋ₓSrₓMnO₃. Further provided is a thermal radiator of the invention having a germanium overcoating. Methods of producing a thermal radiator for an aluminum surface are also provided.
SPACECRAFT SMART THERMAL RADIATOR BASED ON THERMOCHROMIC COATINGS DEPOSITED ON ALUMINUM PANEL

Cross-reference to Related Applications

[0001] This application claims the benefit of United States Provisional Patent Application USSN 61/736,827 filed December 13, 2012, the entire contents of which are herein incorporated by reference

Field of the Invention

[0002] The invention relates, in general, to materials science and engineering, and specifically to thermal and environmental control of space technologies.

Background of the Invention

[0003] The extreme temperature variations experienced by spacecraft in orbit during a space mission can considerably affect the functionality and even threaten the survivability of electronic equipment (payloads) onboard spacecraft. To maintain the critical operation of the spacecraft, and its payloads, during a mission, stringent thermal control of the spacecraft is required, the subsystem for which normally consists of heaters and thermal radiators. In the vacuum conditions of space, heat rejection into deep space can only be achieved by means of thermal radiation. Thus, the performance and technical parameters of the thermal radiator are an important part of thermal control design of a spacecraft. Furthermore, an optimal thermal control system does not overburden the spacecraft with excessive mass, volume or power consumption.

[0004] Several ways of designing a thermal radiator for a spacecraft have been described. In a conventional design, a thermal radiator cannot change its thermo-optical properties as a function of temperature. Therefore, the radiator is designed to release heat from the spacecraft. However, due to the additional heat loss caused by such radiators, supplementary heaters must be activated to compensate for heat loss in cold conditions. In cases where this functionality is required, it has been incorporated mechanically, i.e. through the use of a louver
(which can be opened or closed to vary the rate of heat rejection). This approach has several drawbacks. Firstly, the mechanical louvers are bulky, adding extra mass and volume to the spacecraft. Furthermore, the use of mechanical louvers may necessitate an active control system, thus increasing the cost of the spacecraft. In addition, the louvers are mechanical devices and therefore can be subject of failure. As a result, it may be necessary to use redundant louvers.

[0005] More recent design of spacecraft thermal radiators is based on use of a smart material. Smart Materials are materials which can change their mechanical, electrical and physical properties, as well as their structure, composition and function, in response to an environmental stimulus. A change can be triggered by stimuli such as temperature, voltage, pressure and light. Variable emittance thermal control coatings change the effective infrared-red emissivity of a thermal control surface to allow the radiative heat transfer rate to be modulated upon command or due to a change in the environment temperature.

[0006] Thermal radiators have been described which have a tunable thermal emissivity and therefore are able to regulate heat rejection by radiation. US Patent Application No. 2008/0057204 discloses a method for fabricating tunable variable emissivity materials, which can be used in the thermal control of spacecraft. These materials have the formula M1(1-(x+y))M2xM3yMnO3, wherein M1 comprises lanthanum, praseodymium, scandium, yttrium, neodymium or samarium, M2 comprises an alkali earth metal, M3 comprises an alkali earth metal that is not M2, and x, y, and (x+y) are less than 1.

[0007] In US patent No. 7267866, there is disclosure of thermal control of spacecraft based on composite perovskite oxides with formula A(x)BxMnO3, where A is at least one rare earth ion selected from the group consisting of La, Pr, Nd, and Sm, and B is at least one alkali earth metal ion selected from the group consisting of Ca, Sr, and Ba. The proposed structure, which can be fixed to the thermal radiator base plate using an appropriate adhesive, also consists of a top film to reflect the sunlight. These composite materials undergo a phase change from a metallic phase with low thermal emittance at low temperature to an
insulator state with high emittance at higher temperatures. For example, Figure 5 of US Patent No. 7267866 shows the temperature dependent emissivity of a \( \text{La}_{0.8}\text{Sr}_{0.075}\text{Ca}_{0.125}\text{MnO}_3 \) thick film obtained by means of a printing method onto an Yttria stabilized zirconia substrate having a rectangular configuration of 50 x 50 mm\(^2\) with a thickness of 50 \( \mu \text{m} \). The emissivity of this composite material changes from 0.46 at low temperature to 0.76 at high temperature, while the whole transition temperature range is about 220 K. (see Shimakawa et al (2002) App Phys Letter 80: 4864-4866 which describes the synthesis of smart coating on \( \text{ZrO}_2 \) substrate using sol-gel process, which involves high temperature firing at 900°C).

[0008] The thermal radiator designs based on the composite perovskite oxides either in the form of ceramic wafer (US Patent No. 7267866) or in form of coating deposited on silicone, \( \text{Al}_2\text{O}_3 \) (alumina) and partially stabilized-zirconia (\( \text{ZrO}_2 \)) (US Patent Application No. 2008/0057204), have two major drawbacks although they both offer some improvements over the mechanical louver. The first drawback is the low efficiency of heat transfer between the outer radiating surface and the radiator base plate, normally made of aluminum. The base plate serves as the end heat-sink of the spacecraft thermal control system before the heat is rejected into deep space. The low efficiency of heat transfer is due to two factors. First, the use of adhesive to bond an array of small radiating material pieces to the aluminum panel reduces efficiency because the adhesive layer has low thermal conductivity. Secondly, the low thermal conductivity of either the composite perovskite oxide ceramic wafer or silicone, \( \text{Al}_2\text{O}_3 \) (alumina) and partially stabilized-zirconia (\( \text{ZrO}_2 \)) substrates on which the perovskite oxide coating is deposited. Because of this low efficiency of heat transfer, the performance of such radiator designs is compromised.

[0009] The second drawback is the complexity of fabrication of the radiators. Because the poor thermal conductivity, composite radiator materials, either in form of ceramic wafers or in the form of a coating deposited on substrates (silicon, \( \text{Al}_2\text{O}_3, \text{ZrO}_2 \)), it is necessary for them to be made very thin, in a range of thickness of 0.1 mm or less. However, those materials are rigid and brittle in nature.
therefore it is extremely difficult to fabricate relatively large pieces and even more difficult to adapt them to surface curvature. As a result, an array of small pieces in a rectangle shape has to be carefully manufactured and assembled onto the aluminum base plate using an adhesive. Given this structure, there is a risk of cracking of the thin ceramic wafer or delamination of the adhesive bonding layer because of thermal cycling and associated thermal stress in orbit.

[0010] Accordingly, a need exists for a thermal radiator for spacecraft that overcomes the limitations of the prior art.

Summary of the Invention

[0011] A thermal radiator for spacecraft is provided comprising an earth-doped manganese oxides coating.

In accordance with a first aspect of the invention, there is provided a thermal radiator for an aluminum surface, said radiator comprising a coating of earth-doped manganese over a layer of oxidized aluminum.

In a preferred embodiment, the thermal radiator has the formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. In a more preferred embodiment, the thermal radiator has the formula $\text{La}_{0.7} \text{Sr}_{0.3} \text{MnO}_3$, $\text{La}_{0.825} \text{Sr}_{0.175} \text{MnO}_3$, or $\text{La}_{0.9} \text{Sr}_{0.1} \text{MnO}_3$.

In an even more preferred embodiment, the thermal radiator has the formula $\text{La}_{0.825} \text{Sr}_{0.175} \text{MnO}_3$.

Further provided is a thermal radiator of the invention having a germanium overcoating.

In accordance with a further aspect of the invention, method of producing a thermal radiator for an aluminum surface is provided, the method comprising forming an aluminum oxide buffer layer on the aluminum surface and, following oxidation, depositing an earth-doped manganese oxide coating on the aluminum surface.
Brief Description of the Drawings

[0012] In order that the invention may be more clearly understood, embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

[0014] Figure 1A is a graph of Reflectance versus Wavelength which illustrates solar reflectance of La_{1-x}Sr_x MnO_3 (x = 0.1, 0.175, and 0.3) coating on an aluminum substrate recorded at room temperature in spectral range of 350-2200 nm; Figure 1B is a graph of Reflectance versus Wavelength which illustrates solar reflectance of Ge/La_{0.825}Sr_{0.175}MnO_3/Al smart coating recorded at room temperature in spectral range of 350-2200 nm.

[0015] Figure 2 is a schematic of PSRD structure based on variable emittance characteristic of thermochromic smart coatings such as LSMO;

[0016] Figure 3A illustrates temperature dependence of infrared reflectance (FTIR) of La_{0.7}Sr_{0.3}MnO_3/Si; Figure 3B illustrates Reflectance switching of La_{0.7}Sr_{0.3}MnO_3/Si at \lambda = 2000 \text{ cm}^{-1};

[0017] Figure 4 is a graph illustrating temperature dependence of the total hemispherical emittance of LSMO coated silicon and metallic substrates;

[0018] Figure 5 is a graph illustrating a comparison of the temperature dependence of sheet electrical resistivity of La_{0.7}Sr_{0.3}MnO_3, La_{0.825}Sr_{0.175}MnO_3, and La_{0.9}Sr_{0.1}MnO_3-coated Al_2O_3.

Description of Preferred Embodiments

[0019] Earth doped manganese oxides demonstrate a metal to insular phase transition in response to variations in temperature. However, this material has not previously been considered as a suitable coating for spacecraft surfaces because these surfaces are typically comprised of aluminum, which is not suitable for
deposition of such coatings because of the significant mismatch in lattice structures between the coating and substrate.

[0020] The present invention proposes to exploit the metal-to-insulator phase transition characteristic of earth-doped manganese oxide coatings for application as smart radiators in the thermal control of spacecraft. To overcome the drawbacks of existing technology, the coating is directly deposited on an aluminum substrate or panel and shows a variable total hemispheric infrared emittance with a low value at low temperatures and a high value at higher temperatures. The multilayer structure design also ensures a low solar absorptance for the radiator, which in turn ensures heat rejection even when the radiator is exposed to the sunlight.

[0021] The present invention utilizes a thermochromic coating comprising a smart thermal radiator. There are several known thermochromic materials. Among them is the Sr-doped lanthanium manganite oxide, La$_{1-x}$Sr$_x$MnO$_3$ (i.e., LSMO), compound which has a perovskite crystalline structure. It is derived from LaMnO$_3$ by substituting rare earth ions La$^{3+}$ with alkaline earth ions Sr$^{2+}$. To keep the balance of electrical charge, Mn$^{3+}$ has to change to Mn$^{4+}$ resulting in a mixed valency of Mn$^{3+}$ and Mn$^{4+}$. As a result, a rich and complex phase diagram with respect to the mole ratio of Sr$^{2+}$ doping ($x$) and temperature ($T$) is observed. Accordingly, LSMO coatings exhibit very interesting magnetic and electronic properties. Specifically, LMSO coatings exhibit colossal magnetoresistance and metal-to-insulator phase transition. For spacecraft thermal control, a preferred value for $x$ is 0.175.

[0022] The metal-to-insulator phase transition properties of LSMO make it a suitable candidate for use as a thermal radiator. Specifically, this property leads to a strong change of the infrared total hemispherical emittance with temperature. Earlier work by Shimakawa et al (App. Phys. Lett. (2002) 80: 4864-4866) has demonstrated the potential of LSMO ceramic elements to act as smart thermal radiators because the emittance of the LSMO materials increased as their temperature increased. However, the ceramic material has a rigid form which puts constraints on the design of the thermal radiator. A coating is more desirable
because it can provide more flexibility in the design of the thermal radiator. Furthermore, a coating can be used in other areas where proper thermal control is needed, for example by coating the surface of subsystems.

[0023] Although earth doped manganese oxides are known as smart materials, they have not been regarded as suitable coatings for spacecraft, which typically have an aluminium surface. Until the present invention, it has been generally believed that aluminum is an unsuitable surface for the deposition of doped manganese oxide coatings for it to achieve the desired crystalline structure and thus the required functionality. The reasons for this belief are twofold. First, a number of experiments on silicon substrates demonstrated that the temperature for successful deposition of earth-doped manganese oxide coatings is at least 800°C, whereas aluminum can only withstand temperatures up to a maximum of 550°C. Second, the metallic nature of aluminum does not provide a surface lattice structure which closely matches the lattice structure of the oxide coating to facilitate the deposition and growth of a thin coating of the required polycrystalline structure.

[0024] It is known that a very thin layer (below 5 nm) of amorphous aluminum oxide (in the form of Al₂O₃) will develop on any aluminum surface upon exposure to air. However, this oxide layer is very thin. Also it has an amorphous structure which may still not provide the required lattice structure for deposition and growth of a crystalline earth-doped manganese oxide coating.

[0025] In order to improve the suitability of the aluminum surface for the deposition of a doped manganese oxide coating, the surface of the aluminum substrate was modified by a controlled oxidation process. This oxidation process can be carried out in two different ways: it can be achieved by exposing the aluminum substrate in an oxygen atmosphere at an elevated temperature in the range of between 200°C and 550°C; or by plasma surface treatment in a controlled oxygen atmosphere at a temperature range between 200°C and 550°C. A preferred temperature range is 300°C to 500°C. An even more preferred temperature range is between 400°C and 500°C. Using both of the two oxidation processes, an aluminum oxide layer formed on the surface of the aluminum substrate which constitutes a
suitable buffer between the surface of the aluminum and the doped manganese oxide coating. This aluminum oxide layer has the required lattice surface structure to facilitate the deposition of a coating having a polycrystalline structure. The aluminum oxide layer had a thickness of 100 nm to 250 nm.

[0026] Following the production of an aluminum oxide buffer layer on the aluminum surface, an earth-doped manganese oxide coating was deposited using a pulse laser ablation deposition technique at 550°C.

[0027] The formation of an aluminum oxide buffer layer provides two advantages for a thermal radiator device using a doped manganese oxide thermochromic coating. Firstly, the buffer layer improves the adherence of the LSMO coating to the aluminum substrate because of better compatibility in crystalline lattice structures between aluminum oxide and LSMO coating than that between pure aluminum and LSMO coating.

[0028] Secondly, the buffer layer increases the emissivity of the LSMO coatings. It is well known that the emissivity of oxidized aluminum is much higher than that of non-oxidized aluminum. The value of the emissivity is dependent on the oxidation level of the aluminum substrate. This is demonstrated by the data in Table 1 which shows the influence of different levels of oxidation of an aluminum substrate on the emissivity of an La_{0.825}Sr_{0.175}MnO_3 smart coating.

This characteristic can be exploited to design a passive thermal radiator with high variable emissivities that can be used for higher temperature applications. Note that for a specific temperature range, other buffer layers with different emissivity such as anodized aluminum oxide, MgO, ZrO_2, CeO_2, and Yttria stabilized zirconia can be used to tailor the emissivities of the doped manganese oxide passive smart radiator devices.

[0031] Table 1: The Influence of Different Oxidation of Aluminum Substrate on the emissivity of La_{0.825}Sr_{0.175}MnO_3 smart coating

<table>
<thead>
<tr>
<th>Samples</th>
<th>Nominal thermal</th>
<th>Oxidation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Emittance</td>
<td>Description</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\text{La}<em>{0.825}\text{Sr}</em>{0.175}\text{MnO}_3$ /Oxidized Aluminum</td>
<td>0.179</td>
<td>Minimum oxidation in temperature between 500 and 550°C in partial oxygen pressure</td>
</tr>
<tr>
<td>$\text{La}<em>{0.825}\text{Sr}</em>{0.175}\text{MnO}_3$ /Oxidized Aluminum</td>
<td>0.245</td>
<td>Moderate oxidation in temperature between 500 and 550°C in partial oxygen pressure</td>
</tr>
<tr>
<td>$\text{La}<em>{0.825}\text{Sr}</em>{0.175}\text{MnO}_3$ /Oxidized Aluminum</td>
<td>0.356</td>
<td>Enhanced oxidation in temperature between 500 and 550°C in partial oxygen pressure</td>
</tr>
</tbody>
</table>

[0032] In a further aspect of the invention, a single layer of germanium over-coating can be used to reduce the amount of solar absorptance. Previously, multiple layer films comprising germanium were used on top of smart coatings (Soltani, M and Chaker, M. Thermochromic La1-Xsrxmno3 Smart Coatings as Passive Smart Radiator Device For Spacecraft Proceeding of CanSmart Workshop, Oct. 2007). A single layer has the advantage of simplicity in fabrication process and its control as well as fabrication cost. However, it has now been found that a single layer of germanium is effective to reduce solar absorptance. This is illustrated by the data shown in Figure 1. As can be seen in Figures 1A and 1B, and in Table 2, a single layer of germanium overcoating over an $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ coating on an aluminum substrate causes a reduction in solar absorptance by 15%, as compared to the same coating without the germanium overcoating. The thermochromic characteristics were not affected.
Table 2: Calculated Solar Absorptance of Ge/La_{0.825}Sr_{0.175}MnO_3/Al as compared to La_{0.825}Sr_{0.175}MnO_3/Al (without Ge over-coating)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Solar absorptance $\alpha_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La_{0.825}Sr_{0.175}MnO_3/Al</td>
<td>86.23</td>
</tr>
<tr>
<td>Ge/La_{0.825}Sr_{0.175}MnO_3/Al</td>
<td>71.66</td>
</tr>
</tbody>
</table>

For opaque samples such as La_{1-x}Sr_x MnO_3 smart coatings, the solar absorptance can be evaluated using the following equation

$$\alpha_s = \frac{\int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] I_s(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} I_s(\lambda) d\lambda}$$

Where:

- $R$ is the spectral reflectance
- $\lambda$ is the wavelength
- $I_s$ the intensity of solar radiation
- $\lambda_1 = 350$ nm
- $\lambda_2 = 2200$

A scheme of a thermal radiator comprising a doped manganese coating, with a germanium overcoating is shown in Figure 2. This device is termed a Passive Smart Radiator Device (PSRD). The PSRD can be fixed directly to the exterior of a spacecraft. Referring to Figure 2, the PSRD consists of a layer of germanium over-coating (identified in Figure 2 as a solar reflector). Immediately beneath the solar reflector is a layer of thermochromic coating. The infrared
transparent germanium over-coating reduces the solar absorptance by reflecting solar radiation. It also serves to protect the thermochromic coating from damage due to cosmic radiation such as proton, electron, atomic oxygen, UV, etc. As a further embodiment of the invention, the solar layer can consist of as SiO₂, MgF₂, Si or ZnSe. Each of the individual materials is selective for reflection in different spectra range of solar radiation. The use of one or combination of more than one of these materials as an over-coating (single layer or multilayer) may not be applicable to smart radiator design, but could enable a selective filtering function if an LSMO coating is used to design the sensor.

[0036] Example 1 – LMSO Coating on Al₂O₃

[0037] Three LMSO targets with different Sr doping concentrations (i.e. x = 0.1, 0.175 and 0.3) were used for deposition. Deposition was conducted as follows:

[0038] Coatings of two different stoichiometric compositions, La₀.₈₂₅Sr₀.₁₇₅MnO₃ and La₀.₇Sr₀.₃MnO₃, are selected in order to obtain the phase transitions from ferromagnetic metal (FM) to paramagnetic insulator or to paramagnetic metal over the temperature range between 200 K to 400 K. The coatings were grown by Reactive Pulsed Laser Deposition (RPLD) technique. A pulsed laser beam generated by a XeCl excimer laser at a wavelength of 308 nm and at pulse duration of 20 nano-seconds, was introduced in the deposition chamber through a quartz window and focused with a quartz lens onto the target. The laser fluence on the target was fixed at 5J/cm², while the repetition rate was fixed at 20 Hz. Two targets with different Sr doping concentration (x = 0.175 and 0.3), namely, the La₀.₇Sr₀.₃MnO₃, La₀.₈₂₅Sr₀.₁₇₅MnO₃, were used for fabrication of the coatings onto (100) silicon substrate and a metallic substrate. Note however, that the coatings were deposited directly on Si substrates without using any buffer layers such as yttria-stabilized-zirconia (YSZ) and Yba₂Cu₃O₇ (YBCO), which are often used to improve the adherence between the coating and substrate as well to improve crystallinity of the coatings.
[0039] To improve the homogeneity of the coating deposition, the focus of the lens was continuously translated, while both the substrate and the target were rotated. The deposition was performed under a background gas mixture of argon and oxygen with $O_2$-to-Ar ratio of 13% and the total pressure is constantly maintained at 100 mTorr. All coatings were deposited at substrate temperature of 500°C. After the deposition, the as-deposited films were cooled down to room temperature without post-annealing. The thickness of the coating is typically about 150 nm. Areas of up to 2 inches in diameter of LSMO coating were prepared with good uniformity.

[0040] The crystallinity of the LSMO coatings was examined at room temperature by x-ray diffraction (XRD) in the $(\theta - 2\theta)$ configuration between 20° and 80°. The chemical composition of the coatings was investigated at room temperature by x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDX) and Rutherford backscattering spectroscopy (RBS). The total hemispherical emittance of the LSMO coatings was onto Si and metal substrates was investigated using a calorimetric method. The solar absorptance of the coatings was evaluated from their reflectance diffuse measured at room temperature using a UV-Vis-Near IR spectrometer equipped with an integrated sphere.

[0041] The XRD characterization of the LSMO coating revealed that its crystallinity was not affected by the variation of the concentration of the Sr dopant. All LMSO coatings exhibited similar XRD patterns to that of the corresponding LSMO targets used. This showed that the stoichiometry of the LSMO target was transferred to the LSMO coating during the RPLD process. All LSMO coatings have polycrystalline structures with the preferred orientation.

[0042] The composition of the LSMO coatings was investigated by means of EDX spectroscopy analysis using a scanning electron microscope (JEOL JSM 6300F). The EDX measurements were conducted using an acceleration voltage of 20 kV, a working distance of 15 mm, and zoom of 500×. The EDX spectra of the LSMO coatings and the corresponding targets showed the various peaks due to the La,
Sr, Mn, and O elements. The detailed EDX analysis showed that the La/Sr ratios in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.1, 0.175$ and $0.3$) coatings were approximately comparable to that of the corresponding $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.1, 0.175$ and $0.3$) targets.

[0043] The surface chemistry of the fabricated LSMO coatings was analyzed at room temperature by XPS measurements using an ESCALAB 2201-XL spectrometer equipped with an Al $K\alpha$ source ($\lambda = 1486.6$ eV). In order to conserve the surface stoichiometry of the coatings, the high-resolved $\text{La}_{3d}$, $\text{Sr}_{3d'}$, $\text{Mn}_{2p'}$ and $\text{O}_{1s}$ core levels of XPS spectra were recorded without Ar $^+$ ions etching, which is currently used for cleaning the surface of the sample. From the intensities of the La, Sr, and Mn peaks and by taking account of the specific factors of these elements, it was possible to calculate the concentration of La, Sr, and Mn in the LSMO coatings. The concentration of Sr increased while that of La decreased with increasing the concentration of Sr dopant in the LSMO target. A much higher Sr-to-Mn ratio is obtained for all LSMO coatings. Sr segregation was observed at the surface of the LSMO coating.

[0044] In order to evaluate the bulk composition of the LSMO coatings, XPS depth profiling of the LSMO-coated metal at room temperature was performed by sputtering the surface of the coating with an Ar $^+$ ion beam. It was observed that the Ar $^+$ ions etching affect the O1s region: the shoulder peak below the well-known O1s peak is removed. The concentration of La, Sr, Mn, and O as a function of the Ar $^+$ ions sputtering time (from 0 up to 115 min) was calculated. Since the sputtering yields vary substantially for different elements, the real composition of the analyzed LSMO coating changed. This preferential sputtering is clearly observed when the etching of the coating was started (during the first 34 min). After that, equilibrium of sputtering was reached and then the concentration of different elements remained relatively constant. These results showed that the XPS profiling is not an adequate technique to evaluate the bulk composition of complex materials such as LSMO coatings.
[0045] Therefore, to evaluate the stoichiometry of the LSMO coatings, the RBS process was used, which is an ion scattering technique used currently to analyze quantitatively the composition of thin films without using any reference standard. The RBS measurements were performed in random geometry with a He$^{++}$ beam at energy of 3.062 MeV. The measured RBS spectra were compared to those simulated with SIMNRA code and then the compositions of the coatings were determined, e.g. La$_{1-x}$Sr$_x$MnO$_3$/Al (or Si) (x = 0.1, 0.175, and 0.3). Since the RBS technique is less sensitive to detect the low elements such as oxygen, the concentration of O in the coating is lightly different to that of the corresponding target. However, the concentrations of the higher elements (La, Sr, and Mn) of the coating match that of the corresponding LSMO target.

[0046] The thermochromic properties of the La$_{1-x}$Sr$_x$MnO$_3$/Si (x = 0.1, 0.175, and 0.3) were investigated by measuring the temperature dependence (from room temperature up to 160 °C) of their IR reflectance using an FTIR spectrometer. The reflected signals from the LSMO coatings were recorded, relative to an aluminum mirror, in the IR spectral range between 400 and 6000 cm$^{-1}$. The variation of the reflectivity with temperature was observed only for La$_{0.7}$Sr$_{0.3}$MnO$_3$ for which the transition temperature is relatively close to room temperature.

[0047] Figure 3B shows the temperature dependence of the IR reflectance for La$_{0.7}$Sr$_{0.3}$MnO$_3$/Si. It is observed that the reflectance decreases as the temperature increases. This clearly shows the signature of the metallic-to-insulator phase transition of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films. Figure 3B shows the reflectance switching (about 25 %) at a wavelength of 5 µm (i.e., 2000 cm$^{-1}$), which was deduced from the variation of the IR reflectance with temperature (see Figure 3.1). At room temperature, the La$_{0.7}$Sr$_{0.3}$MnO$_3$ coating is in its quasi-insulating state for which the reflectance is about 47%. The coating become less reflective and more insulating when the temperature increases. At high temperature, the coating switches to its insulating state and the reflectance drops
to about 22%. This thermochromic characteristic of LSMO coating can be exploited in fabrication of IR optical switching devices.

[0048] The temperature dependence (from 200 up to 400 K) of infrared $\varepsilon_T$ of the fabricated LSMO coatings on Si and metallic substrates was measured by means of the calorimetric method. These measurements were performed in a liquid nitrogen cooled vacuum chamber in accordance with the ASTM-C835-01 standard. A testing fixture was designed, which can test simultaneously up to 8 samples. In order to minimise the heat loss of the samples during the emittance test, thin wire (0.1 mm diameter) K-type thermo-couple, which have lower thermal conductivity than the commonly used T-type thermo-couple, were used for the temperature measurements. Also, lead wire for flexible heaters banded on the backside of the samples was used. The tested samples had an effective radiating surface area of about 3.8 cm$^2$. A reference sample of the same radiating surface area, covered by VDA (vapor deposited aluminum) Kapton film (which has emissivity less than 0.02), was used to calculate the heat loss of the tested LSMO sample through the lead wires at different temperatures. During the test, the pressure within the vacuum chamber was maintained to about $10^{-9}$ Torr. The $\varepsilon_T$ was calculated using the following equation:

$$\varepsilon_T = \frac{Q - Q_l}{A_s \times \sigma \times (T_s^4 - T_w^4)}$$

where $Q$ is the heating power (watt), $Q_l$ is the heat loss through the lead wires (watt), $A_s$ is the area of radiating surface (m$^2$), $\sigma$ is Stefan-Boltzmann constant, $T_s$ is the temperature of sample, and $T_w$ is the temperature of wall of the thermal vacuum chamber.

[0049] Figure 4 compares the measured temperature dependence (from 200 up to 400 K) of $\varepsilon_T$ of the $\text{La}_{1-x} \text{Sr}_x \text{MnO}_3$ ($x = 0.175$ and 0.3)-coated silicon, and metallic substrates to that of copper substrate. The Cu exhibits constant emittance (about
0.02) in the temperature range investigated. However, the emittance of the LSMO coating increases with increasing temperature. The detailed analysis of these results shows that both the substrate type (either Si or metal) and the concentration of Sr dopant influence the emittance of the LSMO coating.

[0050] Independent of the temperature, all LSMO coated Si exhibit much higher emittance than the coatings onto the metallic substrate. This dependence of the emittance on the substrate type is due probably to the influence of the intrinsic emittance of the substrate itself (either Si or metal). Since the emittance of the IR transparent Si (with its native silicon oxide) is much higher than that of the metallic substrate, the emittance of LSMO/Si is higher than that of LSMO/M (see Figure 4). Also, the difference in the microstructures of the LSMO coatings formed onto these different substrates can influence the emittance of the coatings.

[0051] As shown in Figure 4, Sr doping levels influence the emittance of the LSMO/Si. The $\varepsilon_r$ of $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ /Si is higher than that of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ /Si. Shimazaki et al. Int. J. Thermophys., 22(5), 2001, pp.1549-1561. obtained similar results for their $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15, 0.175, 0.2, 0.3,$ and $0.4$) ceramics fabricated by the standard ceramic process. However, the opposite behaviour (i.e., $\varepsilon_r$ increases with increasing Sr doping level) is observed in the case of the LSMO-coated metallic substrates (see Figure 4). The $\varepsilon_r$ of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ /M is much higher than that of $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ /M.

[0051] The solar absorptance ($\alpha_s$) of LSMO coated opaque metallic substrates was evaluated from their reflectance diffuse $R(\lambda)$ at room temperature in the spectral range between $\lambda_1 = 250$ nm and $\lambda_2 = 2200$ nm as follows:

$$\alpha_s = \frac{\int_{\lambda_1}^{\lambda_2}[1 - R(\lambda)]I_s(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2}I_s(\lambda)d\lambda}$$

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where $I_s$ is the intensity of the solar radiation.

Measurements were taken using a UV-Vis-Near IR spectrometer equipped with an integrated sphere. Independent of the Sr dopant level, a high $\alpha_s$ (about 80%) was obtained for all LSMO coatings. The concentration of dopant had no effect on the reflectance of the LSMO coatings. A similar value for $\alpha_s$ has been obtained for LSMO ceramic tiles (Shimazaki et al.).

[0052] The temperature dependence of sheet electrical resistivity of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.1, 0.175,$ and $0.3$) coatings onto sapphire substrates was investigated by using a four-point probe setup equipped with a controllable cooler-heater element allowing temperature variation of the sample from $-40$ up to $200\, ^\circ C$. In order to prevent water condensation on the coatings, the measurements were taken by purging the system continuously with nitrogen gas. Figure 5 compares the temperature dependence of the sheet electrical resistivity of La$_{0.7}$Sr$_{0.3}$MnO$_3$, La$_{0.825}$Sr$_{0.175}$MnO$_3,$ and La$_{0.9}$Sr$_{0.1}$MnO$_3$-coated sapphire. It is shown that the resistivity decreases as the temperature increases and no metallic-to-insulator phase transition is observed for the three LSMO coatings in the temperature range from $-40$ to $140\, ^\circ C$.

[0053] This resistivity change as a function of temperature is exploited in the IR uncooled bolometer sensors. This type of sensor exploits the change of the electrical resistance of the coating due to heating by IR radiation. The main parameter to achieve high sensitivity of the IR bolometer is the thermal coefficient of resistance ($TCR$), which is defined as the slope of the log of the electrical resistivity ($R$):

$$ TCR = (1/R) \times (dR/dT) $$
where \( T \) is the temperature of the coating.

[0054] From the recorded sheet electrical resistivity as a function of temperature and using the equation shown above, TCR was calculated at room temperature for LSMO-coated Al\(_2\)O\(_3\). The calculated TCR is very sensitive to the composition of LSMO coatings as shown in Table 3.

**Table 3.** Thermal coefficient of resistance (TCR) at room temperature for LSMO/Al\(_2\)O\(_3\).

<table>
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<tr>
<th>Sample</th>
<th>TCR (%/°C)</th>
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<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})MnO/Al(_2)O(_3)</td>
<td>-1.64</td>
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<tr>
<td>La(<em>{0.825})Sr(</em>{0.175})MnO/Al(_2)O(_3)</td>
<td>-2.26</td>
</tr>
<tr>
<td>La(<em>{0.9})Sr(</em>{0.1})MnO/Al(_2)O(_3)</td>
<td>-2.30</td>
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[0054] The TCR decreases with increasing concentration of Sr dopant in the LSMO coatings. A much higher TCR of -2.3%/°C is achieved in La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\). The calculated TCR values are in good agreement with that obtained recently by Choudhary et al (Appl. Phys Lett 84, 3846, 2004) (about -2% at room temperature) in their La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) films grown on silicon substrates by PLD.

Recently, Yang et al (J. Appl. Phys. 99, 024903, 2006) obtained a TCR of about -1.7%/°C and low-frequency noise in their epitaxial La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) thin films deposited by PLD on SrTiO\(_3\) and (LaAlO\(_3\))\(_{0.3}\)(Sr2AlTaO\(_6\))\(_{0.7}\) single crystals. They found that the noise equivalent temperature (NET) was about 6x10\(^{-7}\) KHz\(^{-1/2}\) at 10 Hz and it was constant in the temperature range from room temperature up to 40 °C. This very low NET value is comparable to the measured values for LSMO thin films reported by other researchers and much lower than that measured for other materials such as amorphous semiconductors, vanadium oxides, and semiconducting Yb\(_2\)Cu\(_3\)O\(_7\), which are currently used in IR uncooled bolometers. This characteristic (i.e. low electrical noise in LSMO films) coupled to the high
TCR value of -2.3%/°C achieved in La$_{0.9}$Sr$_{0.1}$MnO$_3$/Al$_2$O$_3$ make this smart coating an excellent material for development of advanced IR uncooled bolometers.

The embodiments and examples described herein are illustrative and are not meant to limit the scope of the invention as claimed. Variations of the foregoing embodiments, including alternatives, modifications and equivalents, are intended by the inventors to be encompassed by the claims.
Claims

1. A thermal radiator for an aluminum surface, said radiator comprising an external coating of earth-doped manganese over a layer of oxidized aluminum.

2. The thermal radiator of claim 1 wherein the external coating has the formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.

3. The thermal radiator of claim 2 wherein the external coating has the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$, or $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$.

4. The thermal radiator of claim 3 wherein the external coating has the formula $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$.

5. The thermal radiator of any one of claims 1 to 4 further comprising a germanium overcoating.

6. The thermal radiator of any one of claims 1 to 6 wherein the aluminum surface is a spacecraft surface.

7. A method of producing a thermal radiator for an aluminum surface, said method comprising:

   i) forming an aluminum oxide buffer layer on the aluminum surface; and

   ii) depositing an earth-doped manganese oxide coating on the aluminum oxide buffer layer.

8. The method of claim 7 wherein the aluminum oxide buffer layer is formed by exposure to a temperature in the range of 200°C and 550°C in an oxygen atmosphere.

9. The method of claim 7 wherein the aluminum oxide buffer layer is formed by plasma surface treatment at a temperature in the range of 200°C and 550°C in an oxygen atmosphere.
10. The method of claim 8 or 9 wherein the temperature is in the range of 300°C to 500°C.

11. The method of claim 10 wherein the temperature is in the range of 400°C to 500°C.

12. The method of any one of claims 7 to 11 wherein the earth-doped manganese coating has the formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.

13. The method of claim 12 wherein the earth-doped manganese coating has the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$, or $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$.

14. The method of any one of claims 7 to 13 further comprising the step of adding a germanium coating over the earth-doped manganese oxide coating.

15. The method of any one of claims 7 to 14 wherein the aluminum surface is a spacecraft surface.
Fig. 1A
Fig. 1B
Solar reflector

Thermochromic coating $\varepsilon = \varepsilon(T)$

Spacecraft structure

Interior of spacecraft

Fig. 2
Fig. 3A

Fig. 3B
Fig. 4
Fig. 5
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/001042

A. CLASSIFICATION OF SUBJECT MATTER
   IPC: C09K 9/00 (2006.01) , B64G 1/58 (2006.01)
   According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
   Minimum documentation searched (classification system followed by classification symbols)
   IPC: C09K 9/00 (2006.01) , B64G 1/58 (2006.01)
   Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
   Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
   Epocpe-Internal. Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X</td>
<td>US7267866B2, Mase et al., 11 September, 2007 (11-09-2007) <em>see the abstract, column 1, lines 11-12, column 3, lines 40-45, column 4, lines 50-60, column 7, lines 2-15, column 8, lines 1-15, Figure 5</em></td>
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

Date of the actual completion of the international search 06 February 2014 (06-02-2014)

Date of mailing of the international search report 27 February 2014 (27-02-2014)

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Facsimile No.: 001-819-953-2476

Authorized officer
Toby Maurice (819) 997-2963
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