



A new crystal $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ for daytime radiative cooling

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ABSTRACT

Structures or materials with both high reflectivity in ultraviolet-visible-near infrared region (UV-Vis-NIR) and high emissivity in middle infrared region (MIR) can achieve radiative cooling. In this paper, a new crystal $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ was synthesized by hydrothermal method. Measurement results show that this crystal presents a reflectivity of 88.04% in 0.2–2.5 μm region and an emissivity of 87.57% in 2.5–25 μm region, suggesting that this material could reflect most of the solar light radiation, and in addition dissipate heat to the surroundings and outer space. The cell parameters and structure simulation diagram were obtained from the result of the Rietveld refinement. The properties and mechanisms were discussed based on X-ray diffraction, FTIR spectroscopy and electron microscopy results. The cooling test under strong sunshine showed that the temperatures in space below $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ coating were 2–4 °C lower than those below the coatings based on commercial solar heat reflection materials as TiO_2 and CaCO_3 , and 6–8 °C lower than that below Al-foil, suggesting the potential application of the new crystal in radiative cooling.

1. Introduction

Global warming is a tough environmental problem which should not be underestimated. Survival and development of humankind will face serious environmental challenges if we take no action. Undoubtedly, the ever-increasing energy consumption which brings vast greenhouse gases into the atmosphere assumes the main responsibility. Energy usage in China has increased steadily from 0.59 billion tons of standard coal equivalents in 1980 to 3.23 billion tons in 2016. Building energy consumption accounted for 27.5% of the total final energy consumption in 2011 and this ratio will increase to 35% in 2020 [1,2]. Air conditioning accounts for most of the primary energy consumption by buildings. Therefore a radiative cooling strategy that cools without any electricity input could have a significant impact on global energy consumption [3].

Most radiative cooling materials or devices only work at nighttime when the air temperature can be significantly lower than the ambient temperature without the solar radiation, sometimes by 20 °C [4]. Objects on the earth surface offload heat to the air and to the cold outer space through infrared radiation and the atmospheric transparency window respectively. However, at daytime, the cooling effect will be weakened (even disappeared) as the thermal absorption added to objects from solar radiation. Actually, daytime radiative cooling is more needed. To achieve daytime radiative cooling, we need one more

property, high reflectivity at UV-Vis-NIR region, compared to nighttime radiative cooling material or device. Recently, researches show that daytime radiative cooling material or device, however, usually requires a definite fabrication process. Raman et al. [3] introduced an integrated photonic solar reflector and thermal emitter consisting of seven layers of HfO_2 and SiO_2 that reflect 97% of incident sunlight while emitting strongly and selectively in the atmospheric transparency window. Rephaeli et al. [5] designed their radiative cooling device by five layers of α -Quartz, SiC, MgF_2 , TiO_2 and Ag with unique microtopography. The device had low absorptivity in solar spectrum and high emissivity in atmospheric window. Zhai et al. [6] embedded resonant polar dielectric microspheres randomly in a polymeric matrix, resulting in a metamaterial that is fully transparent to the solar spectrum while having an infrared emissivity greater than 0.93 across the atmospheric window. When backed with a silver coating, the metamaterial shows a noontime radiative cooling power of 93 W/m^2 under direct sunshine. Most of the studies on daytime radiative cooling have focused on the design of devices, such as materials with photonic structures [5], multilayer systems [3], metalodielectric systems, and metamaterials [7–9]. Their common characteristic is a combination of reflective layer and emissive layer and most of them have complicated structure and rely on expensive preparation technology.

Daytime radiative cooling occurs also in nature. An insect called silver ant, living in the Sahara Desert, can keep a comparatively low

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body temperature even at the midday temperature of $\sim 47^\circ\text{C}$ through radiative cooling by its special hair [10]. Shi et al. [11] measured the reflectivity of the sliver ant's body surface and obtained a hemispherical reflectivity of 0.69 in the Visible-Near Infrared region (0.43–1.68 μm) and a MIR emissivity of 0.89. As a result, the steady-state temperature maintains at 34°C for these unique properties. Inspired by the sliver ant, we have suggested that a new crystal, if having similar morphology to the sliver ant's hair, would also possess high reflectivity and high radiation due to composition and structure.

In this paper, we synthesized a new crystal $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ and found it has both high reflectivity in UV–Vis–NIR and high emissivity in MIR. We put forward reasonable explanations about the corresponding mechanism. In addition, radiative cooling coating was also prepared, the test result showed an obviously cooling effect.

2. Experiment

2.1. Preparation of $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ powders

All chemicals were of analytical grade purity and were used as received without further purification. 4.29 g of magnesium acetate (0.02 mol) and 1.64 g of phosphorous acid (0.02 mol) were added to 60 mL of deionized water. The mixture was stirred on magnetic stirrer for 10 min (200 r/min). After the solution settled, 10 mL cyclohexylamine was added into the mixture. The beaker was covered with plastic wrap, and the solution was stirred for one more hour and gradually turned into a uniform white emulsion. The solution was then poured into a Teflon-lined stainless-steel autoclave (100 mL) and was heated in a thermostatic oven at 180°C for 3 h. Lastly, we took out the turbid solution from the Teflon-lined steel-stainless autoclave after the complex reaction proceeded completely. Uniform and well-dispersed powders were obtained after filtrating, washing and oven dry at 105°C for 3 h.

2.2. Preparation of coatings and design of device

To test the cooling effect, we prepared several coatings including $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$, TiO_2 , CaCO_3 and aluminum foil for comparison. The coating consists of 85 wt% of the powder and 15 wt% of Polyvinylidene Fluoride (PVDF) as the binder. The mixture was dispersed in Nitrogen-methyl pyrrolidone (NMP, organic solvent) and disposed by ball-milling for 10 h. The mixture was painted on aluminum foil. Smooth coating was obtained after drying for 3 h to evaporate NMP. The thermal performance of the radiative coolers partly depends on the ambient conditions including ambient temperature, wind speed, humidity, solar radiation and thermal radiation from the sky and the surrounding environment. In order to reduce the influence of those uncontrollable factors, the coatings (15 cm \times 5 cm \times 1 mm) were placed on top of a cuboid space (3 cm \times 3 cm \times 3 cm) which is thermally insulated from the surrounding by cotton. The coatings and cottons were settled in glass dishes which were covered by polyethylene film to avoid heat convection. Temperature data in the cooling spaces were measured and recorded by real-time temperature recorder (Fig. 1).

2.3. Characterization

The crystal structures of the $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ powders were examined by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, $5^\circ < 2\theta < 90^\circ$, WV/WC = 40 kV/40 mA) and Fourier transform infrared spectrometer (FT-IR, VERTEX 70, Bruker). The microstructures of the powders were observed by scanning electron microscopy (SEM, ZEISS EVO 18). The diffuse reflectivity of the samples was measured with a UV–Vis–NIR spectrophotometer (lambda-950 with an integrating sphere attachment) using Poly-tetrafluoroethylene (PTFE) as a reference. Samples were

tested from 200 nm to 2500 nm with 2 nm intervals. The reflectivity in UV–Vis–NIR was defined using the following formula:

$$R_{\text{UV-vis-NIR}} = \frac{\int_{200}^{2500} R(\lambda)M(\lambda)d\lambda}{\int_{200}^{2500} M(\lambda)d\lambda} \quad (1)$$

where $R(\lambda)$ is the reflectivity of samples and the $M(\lambda)$ is the solar spectral irradiance profile as a function of wavelength [12],

$$M(\lambda) = \frac{c_1}{\lambda^5} \frac{1}{e^{c_2/(\lambda T)} - 1} \quad (2)$$

$$c_1 = 2\pi hc^2 = (3.7415 \pm 0.0003) \times 10^8 \left(\text{W} \frac{\mu\text{m}^4}{\text{m}^2} \right) \quad (3)$$

$$c_2 = \frac{hc}{k} = (1.43879 \pm 0.00019) \times 10^4 (\mu\text{m K}) \quad (4)$$

The emissivity in MIR was measured with Spectral Emissivity Measurement System (BHU-VII200), equipped with a Fourier transform infrared spectrometer (Nicolet iS50) and MIR integrating sphere. The spectral emissivity of the powders at 298 K was defined using the following formula

$$\varepsilon(\lambda_1 - \lambda_2) = \frac{\int_{\lambda_1}^{\lambda_2} M_s(\lambda)M(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} M(\lambda)d\lambda} \quad (5)$$

where $M_s(\lambda)$ was the radiance of powders sample, $M(\lambda)$ was the radiance of blackbody, $T = 298 \text{ K}$. The band gap energy (E_g) is obtained by the Kubelka–Munk (K–M) reemission function $F(R)$ as [13]

$$F(R) = \frac{(1 - R)^2}{2R} = K/S \quad (6)$$

where R is the reflectivity, K is the absorption coefficient, S is the scattering coefficient. According to the relationship of band gap energy and absorption coefficient, we can get:

$$[F(R)h\nu]^2 = B(h\nu - E_g) \quad (7)$$

Plotting $[F(R)h\nu]^2$ to $h\nu$ and linear extrapolating to $F(R) = 0$, the intercept on the $h\nu$ corresponds to the band gap E_g .

3. Result and discussion

3.1. Structure analysis

Fig. 2 shows the XRD spectrum of $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ powder sample, and the insert shows a comparison between $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ and $\text{Co}_{11}(\text{HPO}_3)_8(\text{OH})_6$ from ICSD database (ICSD#72431) [14]. For $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$, the Rietveld refinement resulted in a reliability factor R_{wp} of 8.98%, and the cell parameters, $a = 12.730875 \text{ \AA}$, $b = 12.730875 \text{ \AA}$, $c = 4.986062 \text{ \AA}$ and $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, agree well with the values reported previously [15,16]. The reasonably small R_{wp} factor suggests that single-phase $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ were obtained in our preparation process. Fig. 3 shows the structure of $\text{Mg}_{11}(\text{HPO}_3)_8(\text{OH})_6$ based on the crystal structure parameters obtained from Rietveld refinement. The structure is a close resemble to $\text{Co}_{11}(\text{HPO}_3)_8(\text{OH})_6$ which had been synthesized and described by M. Dolores Marcos [17]. The complicated crystal possesses four kinds of O, three kinds of P and four kinds of H. The occupancy of Mg is 0.917. The $[\text{MgO}_6]$ octahedrons (marked in yellow) assemble to the $[\text{Mg}_4\text{O}_{12}]$ unit by sharing edges and faces, and then the $[\text{Mg}_4\text{O}_{12}]$ units assemble to a double chain structure by sharing peaks on the hexatomic ring (Fig. 3b). One type of the $[\text{HPO}_3]$ tetrahedrons locate within the hexatomic ring through sharing peaks, and the other two types of the $[\text{HPO}_3]$ tetrahedrons (P2 and P3 in Fig. 3b) sit in triangular domain through sharing their faces (Fig. 3a).

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