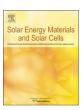
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## Solar energy materials for thermal applications: A primer

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#### ABSTRACT

Solar energy materials have properties that are tailored to the characteristics of the electromagnetic radiation in our natural surroundings, specifically its spectral distribution, angle of incidence and intensity. This tailoring can be made with regard to solar irradiation, thermal emission, atmospheric absorption, visible light, photosynthetic efficiency and more. Solar energy materials can be of many kinds, e.g., metallic, semiconducting, dielectric, glassy, polymeric, gaseous, etc. In particular, thin surface coatings of solar energy materials may exhibit the desired properties in their own right or may yield such properties when backed by an appropriate substrate. This article surveys a number of topics related to thermal applications such as solar thermal converters, transparent thermal insulators, devices for radiative cooling by exposure to the clear sky, and windows and glass facades with static or dynamic properties. The purpose of the present paper is to provide a bird's eye view over a wide class of materials of rising importance rather than giving detailed accounts of highly specialized topics.

## 1. Introduction

Solar energy materials for thermal applications have optical properties that make them well adapted for utilizing solar energy and for reaching energy efficiency, especially in the built environment [1,2]. This class of materials is of growing importance, which is connected with the fact that energy production today (2018)—and for decades to come—is dominated by the burning of fossil fuels with accompanying massive injection of carbon dioxide into the air. Specifically, the CO<sub>2</sub> concentration has risen from ~315 ppm at the end of the 1950s so that it now exceeds  $\sim 400$  ppm, with no change of this trend yet in sight [3]. It is widely understood that growing amounts of atmospheric CO2 lead to global climate change and rising sea levels [4] and that there are numerous secondary and often harmful side effects. Another important trend of significance for solar energy materials is the rapid growth of the global population [5] and its ongoing accumulation in mega-cities [6] whose local climate is altered and often considerably warmer than in surrounding rural regions [7].

Solar energy materials for thermal applications can be prepared and used in many ways, and here are some glimpses of the contents of this paper, with *italicized* key technologies and terms: *Solar thermal collectors* for hot fluid production make use of surfaces that are strong absorbers of solar energy, and energy efficiency is obtained via low thermal emittance, i.e., high reflectance for wavelengths where thermal radiation takes place [8,9]. These solar absorbers are often put behind *transparent convection shields* that let through solar irradiation. A key property of materials for thermal solar energy is frequently *spectral* 

selectivity, which means that the optical properties must differ qualitatively among different wavelength ranges. Spectral selectivity can also be employed for energy efficient glazing—a term referring to buildings and embracing both windows and glass facades-either for obtaining good thermal insulation together with high solar energy inlet or for having good transmittance of visible light together with minimum solar energy ingress [2,10]. Other kinds of spectral selectivity can be used to accomplish "radiative cooling" under a clear sky, and temperatures lying much below those of the ambient air can be obtained by exploiting surfaces that emit radiation at wavelengths for which the atmosphere is transparent while the same surfaces exhibit low absorptance at other wavelengths [2]. Materials with strongly angular-dependent optical properties [11] yield alternative options for optimizing solar energy utilization. For example, such materials can be employed in glazing-even non-vertical-to achieve high transmittance along nearhorizontal lines-of-sight and low transmittance at off-horizontal angles [12]. The materials mentioned so far are characterized by static properties, but there are also many solar-energy-related uses of "chromogenic" materials [13] whose properties can be varied and adjusted to changing properties of their surroundings. Electrochromic and thermochromic materials, and devices based on them, are especially significant and provide roads toward future architecture with "dynamic" buildings able to combine high energy efficiency with excellent indoor comfort and convenience [14-16]. The characteristic property of these materials is that the absorptance or reflectance can be altered by insertion and extraction of electrical charge or by temperature changes. Many of the solar energy materials for thermal applications make good use of

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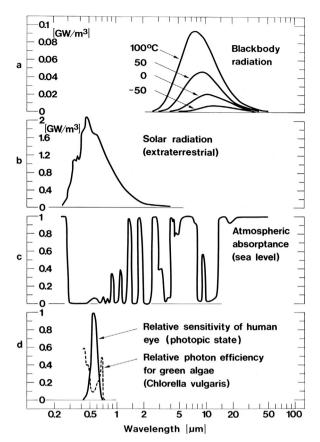


Fig. 1. Spectra for (a) black-body radiation at four temperatures, (b) solar radiation outside the earth's atmosphere, (c) typical absorptance vertically across the full atmosphere, and (d) relative sensitivity of the human eye and relative photosynthetic efficiency for green plants [20].

thin surface coatings (thin films) backed by transparent or reflecting substrates, and thin film deposition technology is important. A "primer" on the latter topic was published some years ago [17] and can be viewed as a companion to the present article.

It should be emphasized that solar energy materials are of importance not only for thermal applications, which this tutorial paper is focused on, but also have numerous non-thermal applications related to photovoltaics [18], cleaning of water and air by solar-driven photocatalysis [19] and, in general, for solar-energy-effected chemical reactions. Furthermore it should be noted that this article does not list more than a tiny fraction of the references to work on solar energy materials for thermal applications, but an attempt has been made to include broad-coverage review papers, with the object of providing general overviews, as well as a selection of recent papers in order to give some flavor of ongoing endeavors. When appropriate, references are to books and book chapters which, arguably, are less ephemeral than journal publications.

## 2. The radiation around us: a look into Nature's rule-book for solar energy materials

Fig. 1 gives a unified presentation of the electromagnetic radiation of our ambience [20]. Most fundamental is *thermal radiation*, which is emitted by everything around us and by ourselves. This radiation is conveniently introduced via the ideal black-body whose spectrum—known as the Planck spectrum—is defined once the temperature is specified. Planck's law is a consequence of the quantum nature of radiation. Panel (a) in Fig. 1 illustrates such spectra pertaining to four temperatures. The vertical scale states power per unit area and wavelength increment (hence the unit GWm<sup>-3</sup>). The spectra appear bell-

shaped and lie in the  $2<\lambda<100~\mu m$  range of wavelengths. The peak in the spectrum moves toward shorter wavelength as the temperature rises; the peak is at  $\sim\!10~\mu m$  for room temperature. The actual thermal radiation from a material is obtained by multiplying the Planck spectrum by a numerical factor, known as the emittance, which is less than unity. The emittance is wavelength dependent for all real materials.

Panel (b) in Fig. 1 shows a spectrum for solar radiation outside the earth's atmosphere. This radiation displays a bell-shape defining the sun's surface temperature, which is  $\sim\!5500\,^\circ\text{C}$ . It should be noted that the solar spectrum is confined to  $0.25 < \lambda < 3\,\mu\text{m}$ , which implies that there is virtually zero overlap with thermal radiation. Therefore one can have surfaces with properties that are completely different for thermal and solar radiation. The integrated area under the solar spectrum gives the "solar constant" (1353  $\pm$  21 Wm $^{-2}$ ). This is the maximum power density on a surface perpendicular to the sun if there is no absorption or light scattering in the atmosphere.

Solar energy conversion systems are normally at ground level, and it is obviously interesting to contemplate how atmospheric absorption affects solar irradiation and net thermal emission. Panel (c) of Fig. 1 shows a characteristic absorption spectrum vertically across the full atmosphere under typical clear-sky conditions. This spectrum is complex and contains bands with high absorption—mainly due to water vapor, carbon dioxide and ozone—and bands with high transparency. Most of the impinging solar energy can reach the ground, and only some ultraviolet ( $\lambda < 0.4\,\mu\text{m}$ ) and infrared ( $\lambda > 0.7\,\mu\text{m}$ ) radiation is absorbed. Maximum power density at right angles to the sun is  $\sim\!1000\,\text{Wm}^{-2}$ . Thermal radiation from surfaces under a clear sky is strongly absorbed, except within the  $8 < \lambda < 13\,\mu\text{m}$  interval where the transmittance is large as long as the humidity is not too high.

Finally, panel (d) of Fig. 1 shows two highly relevant biological properties. The solid curve illustrates the relative sensitivity of the human eye under daylight conditions; the bell-shaped curve is in the  $0.4<\lambda<0.7\,\mu m$  range with a peak at  $0.55\,\mu m$ . It is evident that much of the solar energy is invisible infrared radiation. The dashed curve indicates photosynthetic efficiency and demonstrates that plants use light with about the same wavelengths as those perceived by the human eye.

Fig. 1 proves an important feature of ambient radiation, namely its *spectral selectivity*. In other words, the radiation around us is confined to specific and often well-defined wavelength intervals. There is also another type of selectivity—angular selectivity—since different angles may be characteristic for different types of radiation. For example, solar radiation mostly comes from angles that are far above the horizon, while visual contact between persons and their surroundings generally is of most concern at near-horizontal lines-of-sight. Finally and importantly, ambient radiation varies with time during the day and between seasons; it thus displays *temporal variability*. These three characteristic features of ambient radiation will be referred to frequently in the following text.

## 3. Transmitting and reflecting materials

## 3.1. Principles

Consider electromagnetic radiation incident on a material. One part of this radiation may be transmitted, a second part is reflected, and a third part is absorbed. Energy conservation dictates that, for each wavelength, one has

$$T(\lambda) + R(\lambda) + A(\lambda) = 1,$$
 (1)

where T, R and A denote transmittance, reflectance and absorptance, respectively. There is also another fundamental relationship that follows from energy conservation, namely

$$A(\lambda) = E(\lambda),\tag{2}$$

where E is emittance, i.e., the fraction of the black-body radiation (cf.

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