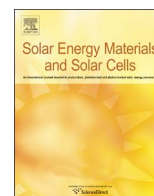




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Fluorescent cooling of objects exposed to sunlight – The ruby example

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ABSTRACT

Particularly in hot climates, various pigments are used to formulate desired non-white colors that stay cooler in the sun than alternatives. These cool pigments provide a high near-infrared (NIR) reflectance in the solar infrared range of 700–2500 nm, and also a color specified by a reflectance spectrum in the 400–700 nm visible range. Still cooler materials can be formulated by also utilizing the phenomenon of fluorescence (photoluminescence). Ruby, Al₂O₃:Cr, is a prime example, with efficient emission in the deep red (~694 nm) and near infrared (700–800 nm). A layer of synthetic ruby crystals on a white surface having an attractive red color can remain cooler in the sun than conventional red materials. Ruby particles can also be used as a red/pink pigment. Increasing the Cr:Al ratio produces a stronger (darker) pigment but doping above ~3 wt% Cr₂O₃ causes concentration quenching of the fluorescence. The system quantum efficiency for lightly doped ruby-pigmented coatings over white is high, 0.83 ± 0.10.

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1. Introduction

The purpose of this paper is to introduce a novel method for reducing the temperature of (non-white) colored materials exposed to sunlight, by utilizing the phenomenon of fluorescence. In order to illustrate the principle, we use the example of chromium-doped aluminum oxide, i.e., ruby. Of course, it is well known that fluorescent emission transports radiant energy, but its application to reduce the temperature of objects exposed to sunlight is novel.

There are a number of applications in which it is desirable to reject solar heat. These include building envelopes (roofs, walls, etc.) to reduce air conditioning energy use [1–4]. A similar need occurs if materials such as vinyl plastics can be damaged by excessive heat. Automobiles in hot climates likewise benefit from minimizing solar heating [5]. Further uses are cooling instrumentation enclosures and storage tanks, and cooling ships and military vehicles to reduce their thermal radiation signature [6]. Cool roofing is a key application and a focus of this paper.

In maintaining sunlit objects at low temperatures, high solar reflectance is of course quite beneficial. If some of the solar flux cannot be reflected, then high thermal-infrared emittance and efficient convective cooling are desired. White coatings have suitable solar reflectance and thermal emittance properties, and are appropriate for many applications. On the other hand for esthetic

reasons (or for camouflage) white or other light colors may not be suitable. Building energy codes may require cool roofing. However, manufacturers of roofing materials are then faced with a palette of mostly pastel colors not attractive for their customers. For this reason “cool” colors are needed.

Over the past several decades, cool colored roofing has increased in popularity. For the materials designers, the problem has been to match a desired color (spectral reflectance in the 400–700 nm visible range) while maximizing solar reflectance. This has been done mainly by minimizing absorption in the solar near-infrared range (NIR, ca. 700–2500 nm) [7,8]. Thus non-selective blacks such as carbon black and iron oxide magnetite black are omitted from recipes, and selective blacks such as mixed metal oxides of iron and chromium are used. In the NIR, the selective blacks have lower absorptance and also fairly high reflectance. Durable and cool pigments are available in a variety of colors, mainly based on inorganic mixed oxides containing transition metals. Some organic pigments are also useful and produce vivid colors. However the cost and durability of organics are limitations.

The modern strategy of color combined with high-NIR reflectance is effective but *passive*. Even higher performance is possible by utilizing the *active* phenomenon of fluorescence. Absorbed photons will not only produce heat but also cause fluorescence.

A prototypical fluorescent material is ruby, aluminum oxide doped with chromium. When lightly doped ruby is excited with ultraviolet (UV) or visible light, it fluoresces at 692.9 and 694.3 nm, a doublet called the R-lines [9]. The absorption strength is weak in

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the red part of the spectrum, and also weak in the blue. Thus the color of ruby varies from pink at low doping to a bluish red as more chromium is added. At high concentrations of chromium (ca. 1%), an additional emission spectrum extending from about 655 to beyond 800 nm is particularly apparent [10–13]. The 700–800 nm emission is thought to be due to neighboring pairs and possibly other clusters, of Cr^{3+} ions. At higher doping, first the R-lines are extinguished (concentration quenching), and then the additional spectrum also fades away.

Ruby certainly has remarkable optical properties. The first optical laser was fabricated from a lightly doped ruby crystal with silvered end faces, exposed to the light from a flash lamp [9]. Also, the spectral shift of the fluorescent R lines is used to measure pressure [14] and the brightness and decay time can be used to measure temperature [15].

As a first experiment to verify the cooling due to ruby fluorescence, inexpensive commercial synthetic ruby gems were employed. An array of square pyramidal crystals was attached to a bright white substrate (TiO_2 pigmented coating) using a transparent acrylic overcoat. An off-white sample with a calibrated solar reflectance of 0.65 was used for comparison. Both samples were mounted on an insulating substrate and exposed to full sunlight on a clear day. The reference sample's temperature was 21.3 °C above air temperature whereas the ruby-covered sample was only 14.8 °C above air temperature. Therefore the effective solar reflectance (ESR) (corrected for some exposed substrate) was larger than 0.65, and estimated to be about 0.71. (Effective solar reflectance is the fraction of incident solar energy that is rejected by reflectance and fluorescence. Additional, more complete, measurements on another ruby-crystal-covered substrate are reported below.) Thus the concept of utilizing chromium-doped alumina to provide reddish colors that are cool in the sun seemed worthy of further investigation.

2. Performance of array of synthetic ruby crystals

Polished ruby crystals intended for the jewelry industry were purchased from a commercial supplier. The cost was about 60 USD per lot of 200 crystals. The footprint of each crystal is a 5 mm × 5 mm square with a chamfered pyramidal shape about 2.6 mm high. A 75 mm square aluminum substrate was coated with 3 layers of an acrylic white paint. The crystals were arranged in a square array to cover the substrate and coated with two coats of clear acrylic. The white underlay enhances absorption of excitation light that may pass through the ruby and also reflects fluorescent emission that strikes the substrate. The clear acrylic coating holds the crystals in place and also raises the thermal emittance to 0.89 from 0.71. Fig. 1(A) shows the appearance of the crystal array in full sun; the red color is dark, having reflectance in the center of the visual range at 550 nm of only 0.044. The fluorescence is not visible in Fig. 1(A) because the camera (and eye) is not very sensitive at 694 nm and is completely insensitive in the 700–800 NIR range. Fig. 1(B) shows the glow of the array at 694 (and 655–700) nm when excited by UV in the dark. The fluorescence tends to emerge from the edges of the crystals.

Temperature measurements in full sun were used to estimate the effective solar absorptance of the crystal array and, by subtracting from unity, its effective solar reflectance. Temperature rise in the sun is roughly proportional to solar absorptance. Calibrated non-fluorescent gray and white samples were used for comparison, as was a reference ruby array over-coated with an opaque white paint. The white array was used to check that convective cooling was not unduly enhanced by surface roughness. A first estimate, made by interpolating between calibrated gray and white samples, yielded an effective absorptance of 0.262. A second

estimate used the white-coated ruby crystal array as a reference, and employed estimates of the solar flux (1050 W m^{-2}) and of the longwave radiative cooling of a blackbody emitter, referred to ambient air temperature (70 W m^{-2}), to infer the sum of the radiative and convective heat transfer coefficients of $h_r + h_c = 14.7 \text{ W m}^{-2} \text{ K}^{-1}$. These coefficients were then used to compute the effective solar absorptance of the ruby crystal array as 0.264. Averaging the two estimates of absorptance and subtracting from unity yields $\text{ESR} = 0.737 \pm 0.010$. Spectrometer measurement, excluding the fluorescence, yields solar reflectance $\text{SR} = 0.434$. Thus the fluorescence contribution (“boost”), the difference $\text{ESR} - \text{SR}$, is about 0.30; the fluorescent energy flux is over 300 W m^{-2} . The ruby array is as cool in the sun as typical white commercial materials with SR in the range of [0.65, 0.85], but is quite visually dark.

3. Combustion synthesis of ruby powder

The combustion synthesis method of Kingsley and Patil [16] was chosen as a convenient method for synthesizing small quantities of ruby powder with various chromium concentrations. Briefly, hydrated nitrates of aluminum and chromium are dissolved in water, as is sufficient urea (fuel) for a combustion reaction. A glass beaker containing the solution is placed in a 500 °C furnace. After boiling for several minutes, the dehydrated solution ignites for several seconds. What remains in the beaker is a fluffy pink product consisting of $\text{Al}_2\text{O}_3:\text{Cr}$. The yield is ~95% crystalline α -phase alumina with γ -phase alumina as a second phase. The Cr doped γ phase is easily identified as its color is not pink. Depending on the Cr concentration, this phase is green, yellow or white [17]. The unwanted γ phase was physically removed, although we also verified that annealing it at 1200 °C for two hours in air can convert it to the α phase.

In preparing various ruby powders, we found that some excess fuel improved preparation of larger lots. Further, higher furnace temperatures were beneficial for higher Cr doping. The combustion process is more rapid at higher furnace temperatures, though if it is too fast the product is dispersed inside the furnace.

X-ray fluorescence (XRF) verified the expected chromium concentration for two of the samples (1%, 3%). (In this paper, we express the doping by means of w , the weight fraction of Cr_2O_3 in Al_2O_3 . A common alternative is to use x , the ratio of numbers of Cr to Al atoms; $x = 0.67w$.) BET-measured surface area varied considerably from run to run, with typical values of $1 \text{ m}^2 \text{ g}^{-1}$, ranging up to $11 \text{ m}^2 \text{ g}^{-1}$ with higher furnace temperatures. Electron micrographs (Fig. 2) show slab-like particles with typical thickness of 2–5 μm . The morphology is likely a replica of the walls of foam just prior to combustion. After each synthesis a small UV lamp was used to visually check for the expected red fluorescence. X-ray diffraction also was used to verify that the observed peaks are those of the α phase of alumina.

To measure optical properties, the powders were mixed with a transparent acrylic paint using a spatula on a smooth glass surface, and spread as a ~500 μm coating onto a white substrate (75 mm square of aluminum with three coats of an artists' titanium dioxide white). This process is crude but simple. About 3 g of pigment was used in each coating. In what follows, the coatings are identified by the weight fraction of chromium oxide in the alumina pigment: 0.0% 0.2%, 1%, 2%, 3%, and 4%.

4. Spectral fluorescence and effective solar reflectance (ESR)

The optical setup included a 6 V lamp (tungsten filament, xenon gas fill), a filter to block excitation light in the spectral range of

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