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Illumination-Controlled Color Behavior in Doped Glasses

Clare, Alexis

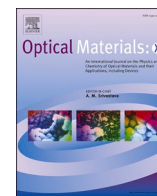
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Invited Review Article

(INVITED) Illumination-controlled color behavior in doped glasses

C.H. Bellows^{*}, A.G. Clare

Kazuo Inamori School of Engineering, Alfred University, USA

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ABSTRACT

Photochromism is the phenomenon of an object exhibiting a noticeable color change as a result of its interaction with the light illuminating it. However, this effect can be caused by a number of mechanisms. This paper examines some of these mechanisms, specifically as they pertain to glass systems. Specifically, we will investigate three general mechanisms: those resulting from direct light interactions with the glass matrix and dopants, those resulting from light interactions with inclusions within the glass, and those that do not depend on the glass matrix directly. Areas covered include rare-earth-doped silicates, smart windows, the Lycurgus cup, and commercial 'dichro' glass.

1. Introduction

Light and color are inextricably linked. Because color is the perceived phenomenon resulting from objects interacting with the visible range of the electromagnetic spectrum; the spectrum of the illuminating light sources can have a large impact on the color one observes. The intensity, position, incident angle, and even the energy distribution of 'white' light can alter how we view the world. These alterations can be minor or drastic. A simplistic example is that of a tomato; when purchasing, one would naturally select the brightest red tomato indicating an ideal ripeness and flavor. Unfortunately, that fruit that looked delicious at the grocery store now sits on the kitchen counter only minutes later a dingier shade of orange, possibly with a greenish cast. Chances are that the kitchen and grocery store are illuminated by different light sources and the tomato fell victim to lighting inequity. All 'white' lights have a varied proportion of the wavelengths that make up their emission spectra; meaning the light from the sun is different from an incandescent bulb, which is different from a room-illuminating 'white' light emitting diode (LED), which is different from fluorescent lighting used in commercial settings.

How an object is illuminated and what kind of light is shining can greatly affect the color. This can be as subtle as the grocery store tomato; but when the disparate colors have a high level of contrast with each other, it is known as photochromism. Photochromism, simply put, is the phenomenon of illumination-induced color change. Sometimes, colored objects are referred to as dichroic, meaning 'two color': a shift from one color to another. This is usually a result of light interactions; but need not be. Throughout this paper, we will discuss several photochromic

mechanisms as they pertain to glass.

2. Gaps in emission spectra

Observed color is a culmination of unabsorbed wavelengths seen as the complement to the color associated with regions of absorbed wavelengths. For example, if looking at an absorption spectrum as % transmission vs. wavelength; the closer to 100%, the more light of a given wavelength passes right through the object. Likewise, a dip in the graph indicates the path of light has been somehow interrupted by means of absorption, reflection, scattering, etc. Whatever wavelengths that aren't absorbed, reflected, etc. correspond to the color one perceives. In the case of a transmission dip, which can in most cases be also thought of as an absorption peak, located at a wavelength of e.g., 460 nm, that wavelength is transmitted only a bit if at all. Every color of the rainbow corresponds to a rough region of visible light. In the case of 460 nm, that corresponds to a blue-violet color. Because blue-violet light is not being transmitted while the other wavelengths are, assuming exposure to 'white' light the lack of blue-violet would lead to one observing that color's complement, in this case yellow. It should be noted that in this paper when stating a color in relation to a specified wavelength, we are referring to the observed color that is the complementary result of the wavelength being absorbed. Materials can exhibit a wide range of hues as a result of absorption spectra across the visible range of wavelengths. Likewise, light is rarely monochromatic, being composed of a range of wavelengths and not all 'white' lights have the same emission spectra. For example, incandescent bulbs and 'white' light LEDs possess a more continuous (overlapping) spectra, containing

^{*} Corresponding author.

E-mail address: chb1@alfred.edu (C.H. Bellows).

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the majority of visible wavelengths. On the contrary, a fluorescent light has a more discrete emission spectrum, having notable sharp delta function transitions across the visible range. Fig. 1 shows what is seen when different sources of white light are passed through a diffraction grating. The result is a showcase of the aforementioned continuous and discrete emission spectra. This is further illustrated in the emission spectra in Fig. 2. The dashed-outlined regions in Fig. 1a are used to highlight the wavelengths that are not produced by a fluorescent light, such as compact fluorescent light bulbs (CFL) or the buzzing tubes common in office spaces.

Dissolved ions within the Lanthanide series possess exceptional spectral properties owing to their f-shell valence electrons. Because the 4f-shell is shielded by both the 5s- and 5p-shells, the spectra of the trivalent ions are highly resistant to influences from their host environment and have spectra that closely resemble rare-earth ions in any solution [1]. Interactions between f-f orbitals also generate narrower absorption bands than those of d-group interactions. Therefore, absorption peaks from rare-earth spectra are far more likely to overlap with gaps in emission spectra of the illuminating source. In some cases, this can cause high-contrast photochromic shifts.

2.1. Neodymium

The Nd^{3+} ion, whether in solution or doped into glasses, possesses two major absorption peaks, located at 521 nm and 575 nm. These peaks result in observed colors of violet-blue and red-purple, respectively. Under most light sources, the combination of the two peaks yields a lilac hued glass, seen in Fig. 3a. Yet, when observed under fluorescent lighting, the glass takes on a bluer coloration. All specimens of glass pictured were fabricated using System 96 soda-lime-silica art glass frit. Looking at the spectra in Fig. 4, it is evident that this color change is due to an overlap in the absorption spectra of neodymium and the emission spectra of fluorescent lighting. With no fluorescent emission wavelengths corresponding to the Nd^{3+} absorption peak at 575 nm, this leads to a lack of purple hue. It should be noted that the experimental Nd^{3+} absorption peak locations were found to be 524 nm, 574 nm, and 586 nm [2]. The splitting of the theoretical 575 nm peak into two experimental peaks at 574 nm and 586 nm is most likely due to the nephelauxetic effect. Via this effect, Nd^{3+} ions' presence affects the electron distribution within the structure of the glass matrix. According to Binemans and Görrler-Walrand, this would then translate to a shift in peak position from 575 nm to 589 nm at maximum; indicating the two peaks at 574 nm and 586 nm remain within an acceptable range to be considered accurate [1].

2.2. Holmium

The absorption spectrum of holmium is more complex than that of neodymium; but the same basis for its photochromism still holds true. The spectrum possesses two large absorption peaks associated with a yellow color by removing the blue-violet at 446 nm and 460 nm, and a weak peak at 488 nm. This is consistent with the observed yellow color displayed under incandescent lighting in Fig. 5a. Surprisingly, the spectrum also showcases small peaks at 520 nm and 536 nm, as well as one at 638 nm, associated with colors ranging from purple to blue-green. Under a continuous 'white' light source, the weaker peaks associated

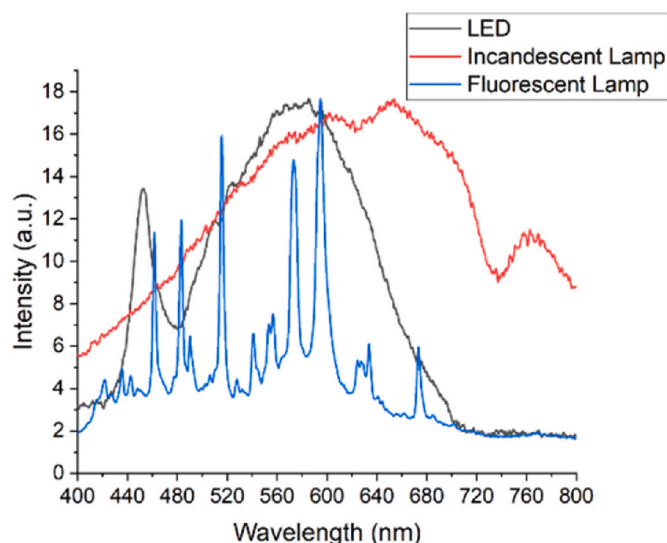


Fig. 2. The emission spectra of fluorescent, incandescent, and LED lamps.

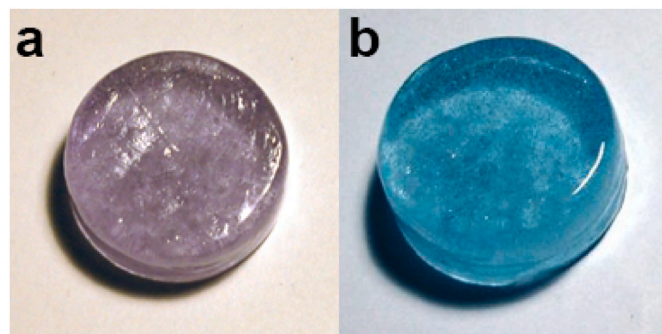


Fig. 3. Nd-doped silicate glass photographed under a) incandescent b) fluorescent lighting.

with the cooler hues are both neutralized by redder peaks and overpowered by the more intense yellows. However, similar to the case with neodymium, the large peaks at 446 nm and 460 nm correspond to a low intensity region in the fluorescent emission spectra. Without the intense yellows in the fluorescent emission compared to incandescent, the blue-green is still neutralized; but the remaining reds, oranges and violets dominate, resulting in the salmon color seen in Fig. 5b. Fig. 6 shows the overall absorption spectrum of holmium, with both major and minor peaks highlighted.

2.3. Praseodymium and erbium

Due to their similarly narrow absorption spectra compared to those of neodymium and erbium, both praseodymium and erbium exhibit only tonal variation under different lighting protocols. This minor color change can be seen in Fig. 7. However, these shifts are too minute to be classed as photochromic; but as showcased with the example of grocery

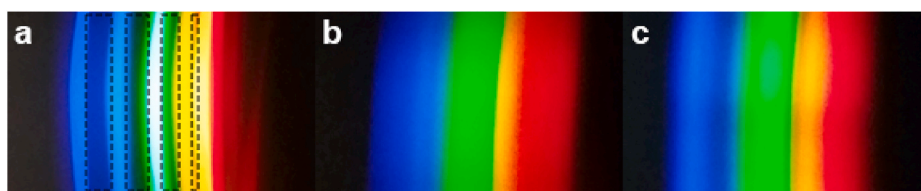


Fig. 1. Emitted light from a) fluorescent b) incandescent c) LED bulb through a diffraction grating.

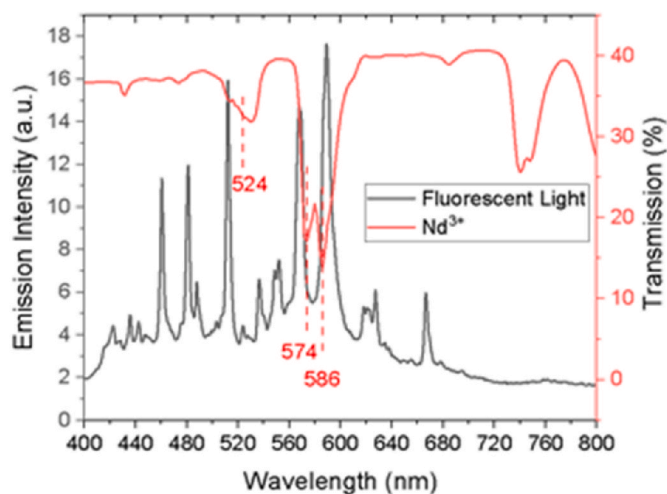


Fig. 4. The absorption spectrum of a Nd-doped silicate against the emission spectrum of fluorescent lighting.

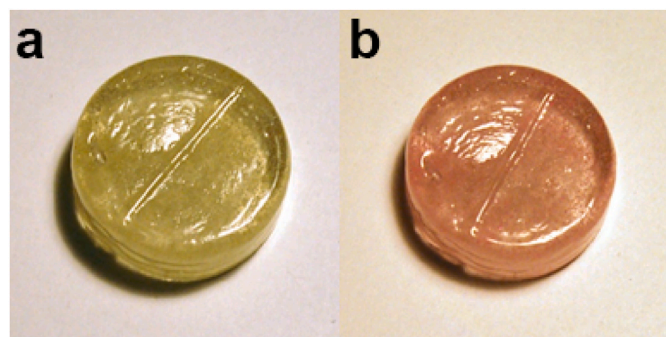


Fig. 5. Ho-doped silicate glass photographed under a) incandescent b) fluorescent lighting.

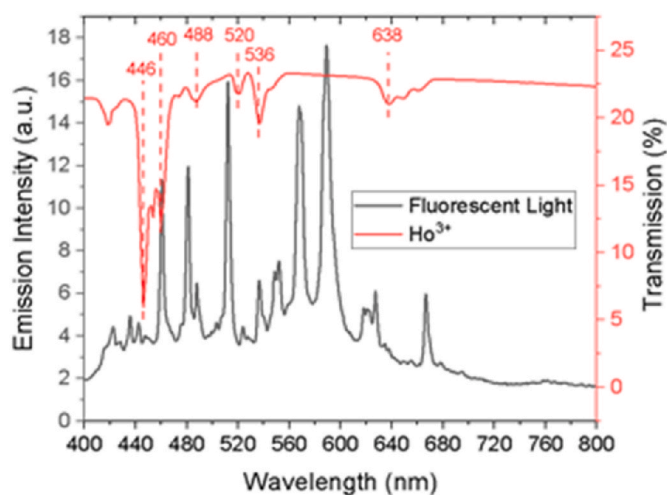


Fig. 6. The absorption spectrum of a Ho-doped silicate against the emission spectrum of fluorescent lighting.

store produce, even subtle variation can be important given the right context.

3. Colloidal interference

Another mechanism of photochromic behavior is through the



Fig. 7. Silicate glass a) doped with Pr under fluorescent b) doped with Pr under LED c) doped with Er under fluorescent d) doped with Er under LED lighting.

incorporation of metallic nanoparticles within the matrix. Within these nanoparticles, the conduction electrons interact with wavelengths of entering light, oscillating in resonance. This is known as localized surface plasmon resonance (LSPR) and is the cause of the exhibited photochromic behavior of such a glass. The resonant frequency of the electrons is highly dependent on the shape and size of the nanoparticles; therefore, they also control the wavelengths of light that are scattered and/or absorbed [3]. More specifically, the shape of the nanoparticles has been found to determine coloration, owing to the sensitivity to aspect ratio of the longitudinal oscillation [4]. Alternatively, particle size has been noted to influence the proportion of light scattering to absorption [3]. The concentration of nanoparticles in a given area as well as the index of refraction of the host material also impact this phenomenon [4].

While many metals experience LSPR, only those with free electrons resonate with wavelengths within the visible spectrum. These metals include elements within the alkali group and more notably gold, silver, and copper. For example, gold nanoparticles suspended in glass are capable of producing a wide range of colorations from blues and purples to reds, oranges, and yellows; all dependent on the size of the metal particles [4]. The much-sought-after gold ruby color is produced through LSPR of nanoparticles smaller than 100 nm in diameter [5]. It was also found that the ratio of scattering to absorption increases as the particle size of gold increases. In the case of spherical gold particles, absorption was the dominant interaction with nanoparticles of diameters around 20 nm. When increased to diameters around 40 nm, interactions were still predominantly absorbing; however, scattering was observed. At around 80 nm in diameter the proportion of scattering to absorption was nearly 1:1 [3]. However, in order to achieve this kind of precision many factors must be taken into account while fabricating the desired glass system. In addition to the required composition and dopants needed; the melting atmosphere, time and temperature must be closely controlled. Extended annealing profiles or successive heat treatments are also crucial to the successful production [6].

3.1. *Lycurgus cup*

The most famous example of photochromic behavior due to

nanoparticles is that of the Lyncurgus cup. Presently housed at the British Museum; the Lyncurgus cup dates back to 4th century CE Rome. One aspect which makes this piece remarkable is its stunning and drastic display of photochromism, which is illumination angle dependent [5]. When illuminated reflectively, the light is scattered, resulting in an opaque green reminiscent of jade. However, if viewed with light being transmitted through the piece, the cup appears a brilliant gold ruby. Few other surviving pieces have been found exhibiting this effect; all Roman in origin and none to the extent as the Lyncurgus cup [6]. Owing to the cup's fame and spectacular example, this phenomenon is commonly referred to as the "Lyncurgus effect". Fig. 8 showcases a similar effect in a decorative glass marble.

Extensive research has been conducted to ascertain the origins of the Lyncurgus effect. Since the piece's discovery, many theories as to what caused this phenomenon were formulated. Eventually the prevailing theory was that it was likely the result of pigmentation from multiple metals, with colloidal metal giving rise to additional physical coloration. In 1962, Dr. Robert Brill of the Corning Museum of Glass, in collaboration with the General Electric Company Ltd sought to determine precisely what constituents were responsible for which effects. Through experimentation on samples of the cup and similar artifacts, and fabricated replica melts they were able to determine that two colloidal metals were responsible for the Lyncurgus effect. The glass composition contained trace amounts of metal dopants: approximately 40 ppm of gold and 300 ppm of silver. They were able to surmise that the Romans reheated the glass under a reducing atmosphere for the purpose of growing the metallic nanoparticles. The formation of this tandem nanoparticle system resulted in the observed shift from transmitted red to reflected green due to the presence of gold and silver, respectively [6]. As technology advanced, so too did the understanding of the Lyncurgus effect. In the 1980s the scale of the nanoparticles, with a distribution of 50–100 nm, was discovered through the use of transmission electron microscopy (TEM). Further studies using X-ray analyses found that the gold and silver were not wholly present as disparate particles; but also existed as alloys within the glass matrix. The alloy consists of a silver to gold ratio of approximately 7:3, while the overall ratio is closer to 7:1; suggesting a nontrivial amount of silver present independent from the alloy. The presence of polyvalent antimony found at a concentration of about 0.3%, commonly used during the Roman period, was likely a key factor in the reduction of silver and gold. Fine particulates of sodium chloride were also found within the glass. While the salt has no direct bearing on the phenomenon, halides are utilized to encourage gold ruby development; as well as its presence indicating that the glass was heat treated resulting in the exsolving of the sodium chloride [7].

3.2. Dichroic copper ruby

Though commonly seen incorporated into silicate glasses as Cu^{2+} to produce a characteristic cerulean blue; copper nanoparticles can also be grown to varying sizes to exhibit other effects. Notably is copper ruby: a

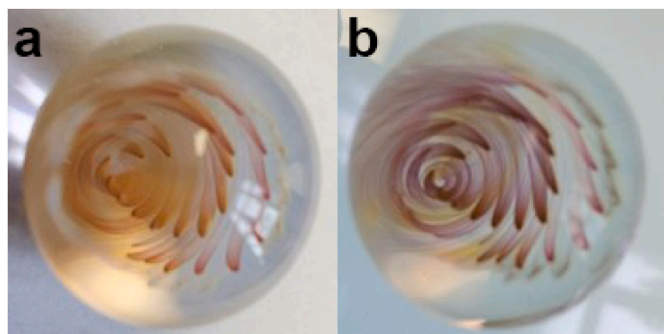


Fig. 8. A glass marble displaying the Lyncurgus effect; under a) reflected b) transmitted light.

cheaper, though not necessarily simpler to produce, alternative to gold ruby. It has also been found that when in liquid solution, Cu^+ possesses a dichroic effect; shifted from yellow in reflected light to pale blue in transmitted light [3]. However, monovalent copper in silicates does not impart a visible color to the glass.

In terms of copper displaying photochromic effects within glass, Schreiber, Stone and Swink conducted a study using a borosilicate basal system [8]. They found that, through the addition of europium, a dichroic copper ruby glass was produced. In reflected light, the glass appears red, as is expected from a ruby glass; when observed using transmitted light, the glass is blue. It was verified that europium was essential to the dichroic effect. Several other components within the composition, such as titanium, zinc and zirconium, were tested in isolation from the europium and did not yield the aforementioned phenomenon. In order to achieve the copper ruby, a temperature of 1150°C was utilized. They found that at this point, most of the Cu^+ was reduced to elemental copper; however, above this temperature they noted a decline in copper nucleation until no evidence was seen above 1250°C . Furthermore, a 1:1 wt ratio of europium to copper was ideal; needing to increase the europium content if melting at 1200°C [8]. The heating process had to be closely controlled, in order to not grow the nanocrystals too large. If the size nanocrystals responsible for the copper ruby glass are allowed to increase, an opaque red, sometimes known as purpurin glass, develops. Continued growth will eventually result in the crystals growing to the microscopic scale, assuming sufficient density of the host, resulting in glittering aventurine glass.

4. Glass independent mechanisms

4.1. Commercial 'Dichro'

While many types of dichroic glass, sometimes marketed as 'dichro', are commercially available, by far the most common example utilizes thin film optics. For this category of glasses, this phenomenon is usually caused by optical interference: the shift in color is dependent on the direction at which the observer views the glass. This can easily be achieved through diffraction mechanics of incident light refracting through the different layers, as seen in Fig. 9. To produce such an effect, metal oxides are layered onto quartz and/or silicate glass through vapor deposition. Though the term 'dichro' implies a shift between just two discrete colors; sometimes over 30 layers of metals can be present, leading to a wide display of colors in a singular piece [9].

The optical interference effect observed with these dichroic glasses is referred to by a multitude of different terms both scientifically and colloquially. Iridescence, goniochromism, holography, multi-chromism, and pearlescence are all complete or partial synonyms for the angle-dependent phenomenon, depending on how pedantic one chooses to be. The prevalence of varied terms most likely arises from the plethora of

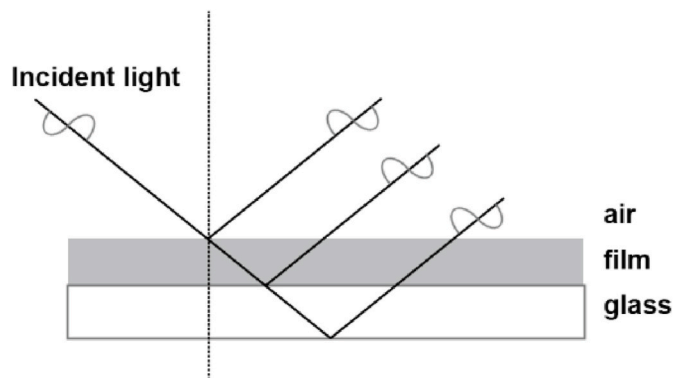


Fig. 9. A schematic showing the diffraction of light through a multi-layer material.

natural and artificial examples present in the world. All of which have in common the dominant mechanism for this spectral interference: an asymmetry within their microstructure [10]. This microstructure can be formed naturally, such as in select bird feathers and insect parts; or they can be inorganically deposited, such as oblate particles of metals, metallic halides or oxides [11,12]. Columnar geometries that facilitate a dichroic effect are even able to be engineered by strategic application using the aforementioned deposition process. By altering the flux direction and the tilt of the deposited columns, material is able to be physically oriented to specific angles of incident light [13].

An alternative to vapor deposition is the friction transfer method developed by Wittman and Smith. A block of poly(tetrafluoroethylene) (PTFE) is transferred across the glass, depositing highly oriented polymeric chains. Thereby, a variety of polymers, liquid crystals, or smaller molecules can be added to the glass surface with a high degree of orientation. Gold nanoparticles have even been incorporated to exploit their LSPR photochromism. To be applied to the glass substrate, the particles of gold were coated in alkanethiol and suspended in an organic solvent. After application, heat treatment was necessary to remove both the PTFE host and the alkanethiol coating. This allowed for interactions between particles and greatly strengthened the dichroic effect. The resultant glass possessed a red hue when observed with light parallel to the frictional path of application; shifting away from the red end of the spectrum when viewed perpendicular to the path [14].

4.2. Photochromic smart windows

While not as widely utilized as electrochromic systems, smart windows that rely on a photochromic darkening mechanism are favorable for the non-necessity of external energy input beyond a source of light. For this reason, photochromic windows are customarily employed in solar-blocking applications; where electrochromics are seen more in use as privacy windows. Desirable attributes for a sufficient smart window are the capability to produce a high-contrast shift in color coupled with a short reversibility lifetime. Typically, a photochromic polymer is applied to the glass as a coating or embedded layer. The organic photochromic material found in smart windows undergoes structural changes when exposed to electromagnetic radiation [15]. Commonly, a molecular transition from one isomer to another occurs as a result of UV irradiation, subsequently resulting in a shift in the absorption spectra. Conversely to the other examples discussed, this slow transition is not instantaneously reversible upon removal of the radiation source; it is of a relaxation process with the exception of certain materials, such as naphthopyran or spiropyran. For these molecules, the resulting colored state is thermally unstable owing to the fact that the initial transition is an uphill reaction. As a result, the compound will naturally return to a colorless state after UV wavelengths are no longer present. Other photochromic molecules, namely diarylethene and the like, are thermally stable while in a colored state. These molecules require additional energy, either from visible radiation or elevated temperatures, to be bleached [16].

5. Conclusion

As described above, a wide array of mechanisms are responsible for the general photochromic effect. These mechanisms may involve direct spectral interactions with dissolved ions in the glass or disparate metallic or crystalline nanoparticles suspended in the matrix. They may also be indirect interactions independent of the glass; as seen in the metallic coatings of some 'dichro' glasses and polymeric coatings common in smart windows. The phenomenon of photochromism seems to be a widely known, yet poorly documented subject; especially in terms of glass compositions. It is therefore the authors' hope that this paper be utilized to garner a better generalized understanding of these effects and able to reach an interdisciplinary audience.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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