The Mechanism of (and Recipes for) **Dichroic Glazes**

Written by **Jenn Wicks** and **Ryan Coppage**

Figure 1: One mug glazed with holmium oxide colorant under fluorescent light (left) and LED light (right).

The science of glazes is an area not commonly explored or extremely palatable for most potters. And when you add dichroic properties to the mix, most artists would run for the hills (as many people do when my type start becoming technical). Specifically, when I start talking about characteristics of glazes, eyes start glazing over. It's far more enjoyable in text form, with some nice pictures and explanations for those interested enough give it a read.

Dichroism can be defined as a type of property in which different colors are seen across various types of light.[1] In objects with dichroic properties, certain wavelengths of light are absorbed under various qualities of light (i.e. LED, filament, halogen, or fluorescent) while others are not.[2] As a result, a different color is exhibited under a different type of light, visible in Figure 1.

Perception of light is not anywhere near as simple as seeing single colors, nor are single colors almost ever pure lines of color. Instead, light is reflected off an object in combinations of various frequencies and chunking of the visible spectrum that our brain rebuilds as a single color, when it is almost always many colors and highly complex.[3] These visible frequencies correspond to wavelengths and are known as the visible light spectrum. Light that can be detected by the human eye ranges from about 750 nanometers to 420 nanometers and runs from red (the longest wavelength), orange, yellow, green, blue, and violet (the shortest wavelength), as illustrated in Figure 2.[4]

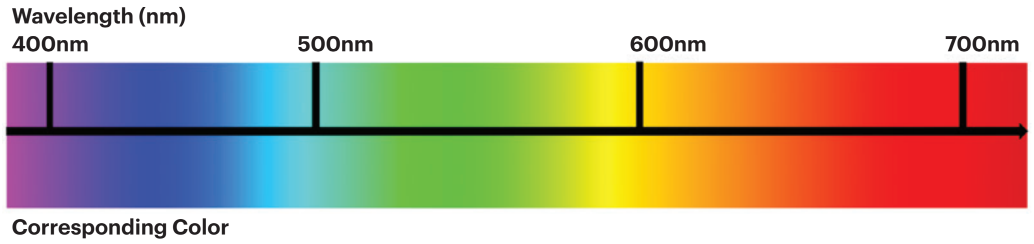


Figure 2: The visible light spectrum: wavelengths (nm) and their corresponding colors.

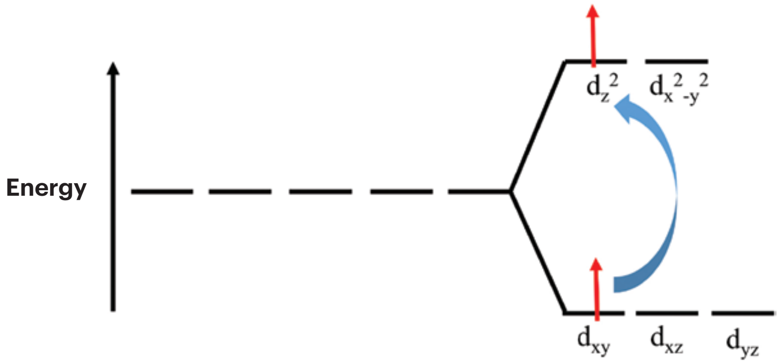
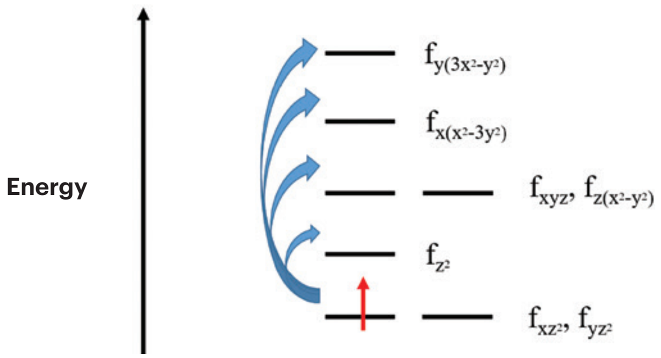


Figure 3: Energy diagram for splitting of transition metal d-orbitals in an octahedral coordination.

The way in which we perceive the colors of transition metals has to do with how photons (light) are absorbed and what that process entails. The most common types of metal pigments or colorants in glazes have five electron d-orbitals that are all equal in energy, but change to various energy levels when surrounded by other elements. When electrons in the lower of these levels are struck with light, they can be promoted to higher energy levels, as seen in Figure 3.[5] As a result, different wavelengths are absorbed, and remaining wavelengths are reflected off of the surface and rebuilt by the brain as color. This "ligand field" color takes place when transition metals are encapsulated by other materials – compounds, a glaze matrix via silicates, etc. – creating an environment in which transition metal d-orbitals interact with their surroundings.[6] The presence of these metal-coordinate interactions in transition metal complexes cause the d-orbitals to split in energy (Figure 3). Furthermore, the stronger the interaction, the larger the split. As that difference in energy increases, so does the amount of energy (i.e., lower wavelength of light corresponds to higher energy) required for an electron to move from the lower level to the higher one. Based on this phenomenon, the surroundings can be changed to modify the split in energy between levels, which would allow for a change in color of the material.

Figure 4: One of a few possible theoretical f-orbital splitting patterns.



To that end, one can change the color properties of a metal colorant or pigment based on the splitting of energy between orbitals, which is known as the Crystal Field Theory.[7] Essentially, the surrounding glaze environment encapsulates a metal, and oxygen atoms (or other components in the recipe) coordinate themselves around the metal -- typically in an octahedral or tetrahedral geometry. Based on identity and arrangement of the surroundings, the electrons in the different d-orbitals can experience energy repulsions, which causes a split in energy between the existing orbitals.[8] Such a change in energy, due to electrons not filling every orbital, allows for the absorption of light of specific frequencies (photons); the rest is reflected off of the surface, transmitted back to our eye, and is rebuilt into the color we see![9]

In addition to transition metals, rare earth metals (Lanthanides), also exhibit a type of orbital splitting. Very different from d-orbitals, the f-orbitals are incredibly more complex and difficult to characterize. There are only a handful of models for these orbitals, but the theoretical math required to represent them dictates that their splitting patterns can vary and are only mildly representable like that of d-orbital splitting seen in Figure 3. While the mechanism of f-orbitals is similar to that of d-orbitals (interaction with orbitals, absorption of light, promotion of electrons, rebuilding of color, etc.), there are some significant differences. Both orbitals undergo splitting when surrounded by a silicate glaze matrix (or crystal field); however, when being split by the interactions with the crystal field, the d-orbitals split into (most often) only two different energies (just higher and lower), whereas the f orbitals can split into anywhere from five to seven, in Figure 4.[10] This difference in splitting can attribute to dichroic behavior in rare earth metals, as multiple possible absorbance events result in portions of the visible spectrum being absorbed from a light source, such that your eye builds back different colors, depending on the quality of and remaining wavelengths from that original source.

A ceramic glaze can act as a crystal field, and when mixed with small percentages of metal pigments, which allows for d-orbital splitting patterns in transition metals, color is born. Under the same mechanism – but significantly more complex – the presence of f-orbitals works identically. Instead of just one section of the visible spectrum of light absorbed via orbital splitting, multiple sections of the visible spectrum are absorbed and the remainders are transmitted back, which can allow for a range of colors to be observed across different qualities of light. Additionally, the recombination of sections of light contribute to the rare earth metals generating "highlighter" colors. This study explores initial characterization of the dichroic behavior of rare earth metals and how their role as a metal complex, as explained through CTF, can explain their unique color properties.

Materials/Methods

Glazes were formulated with four rare earth oxides in this work (Figure 5): neodymium oxide, erbium oxide, holmium oxide, and praseodymium oxide. Of the four lanthanides used, neodymium and holmium demonstrated the most dichroic responses across various light sources, while more subtle dichroics are observed for erbium and praseodymium. Three recipes were used from a previous Ceramics Monthly techno file[11], in addition to a holmium recipe adapted from the original non-crazing erbium pink glaze (Figure 5).

After the glaze was applied to bisqued cups, the glazed samples were fired in a kiln on a medium setting to cone 6.[12] Once fired and cooled, the glazed surfaces were used to generate reflectance profiles with a reflectance spectrometer, which simply measures and outputs a spectrum of the reflected light after absorbance events have taken place in the glaze profile and on the clay surface. More informatively, a reflectance spectrometer allows for the measurement of specific wavelengths and intensities of light reflected off an object and provides both qualitative and quantitative data on those wavelengths that all contribute to the net color profile of a surface.

Glaze Color and Reflectance Profiles

Reflectance color profiles of four rare earth metals (neodymium, holmium, praseodymium, and erbium) suspended in cone 6 glaze bases, above, were used to obtain reflectance spectra in various light sources. In addition, two reflectance profiles were taken of chromium as non-dichroic examples. An Ocean View FX spectrometer under a xenon arc lamp was used to collect the reflectance profiles. Although the instrument can scan between 300 to 1000 nm, only 400-700 nm – the visible light wavelength region – are shown.

"WTF Purple"		"Sorority Pink"		"Nucular Green"		"WTF Pink"	
Neph Syenite	45.3%	Neph Syenite	26.2%	Neph Syenite	50.6%	Neph Syenite	26.2%
Borate Sub	15.5%	Borate Sub	15.7%	Borate Sub	14.2%	Borate Sub	15.7%
Whiting	14.5%	Whiting	11.3%	Whiting	11.7%	Whiting	11.3%
Flint	19.7%	Flint	23.3%	Flint	18.5%	Flint	23.3%
Grolleg	5.0%	Talc	6.1%	Grolleg	5.0%	Talc	6.1%
		EPK	17.4%			EPK	17.4%
Add: Neodymium Ox	7%	Add: Eribium Ox	8%	Add: Praseodym Ox	7.5%	Add: Holmium Ox	10%

Figure 5: Recipes for rare earth metal dichroic glazes.

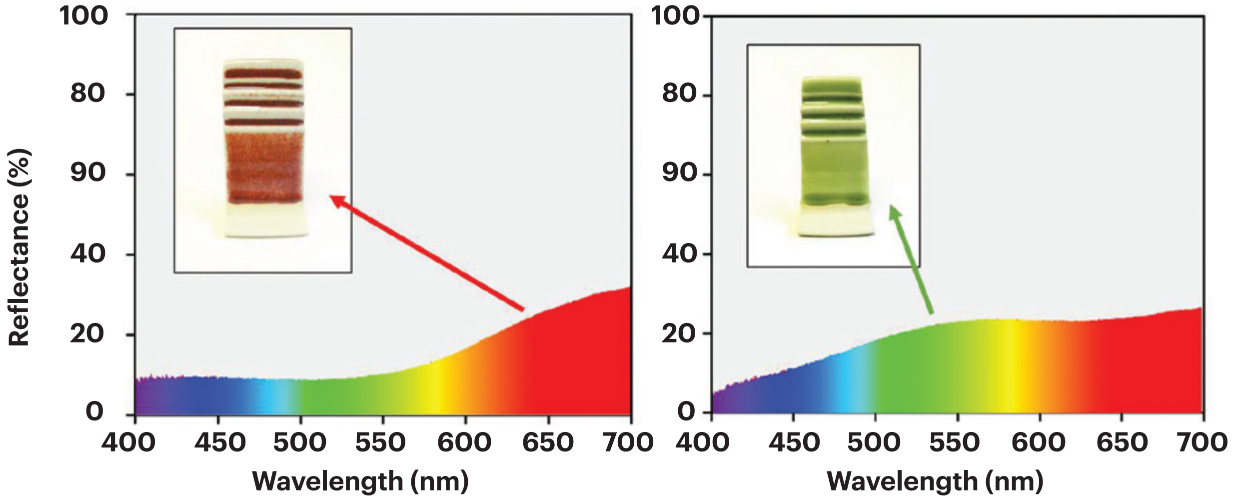
Figure 6 (left) and *Figure 7* (right): Reflectance examples of red and green chromium in a cone 6 raspberry red glaze, with (left) tin oxide and without (right) tin oxide, that changes the ligand field strength of the chromium splitting and thus color.

Chromium Red

The reflectance profile of chromium (in a cone 6, raspberry type of glaze) produces one peak (the reflected wavelength) within the red range of around 650-700 nm. As a result, this glaze looks red to the eye.

Chromium Green

In this reflectance profile of chromium (in a raspberry glaze without tin oxide), the majority peak of the reflected wavelength is within the green region of around 500-550 nm. To that end, the glaze looks green.



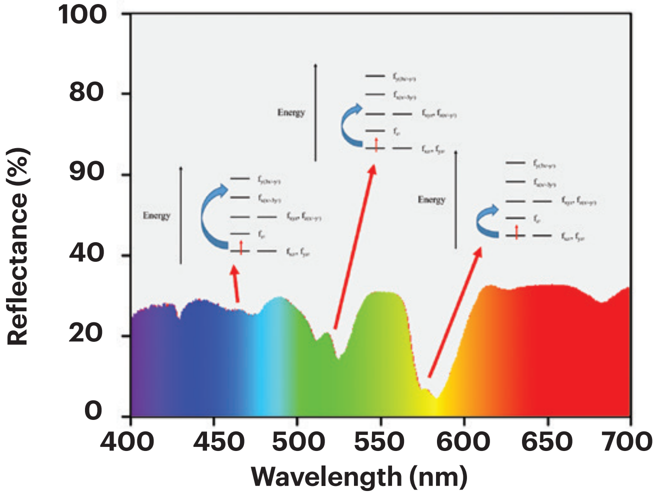


Figure 7: A possible splitting pattern mechanism for rare earth metals in glazes and how lanthanides contribute to more complex reflectance profiles and dichroism. The frequencies that are not absorbed reflect back to contribute to perceived color of the surface.

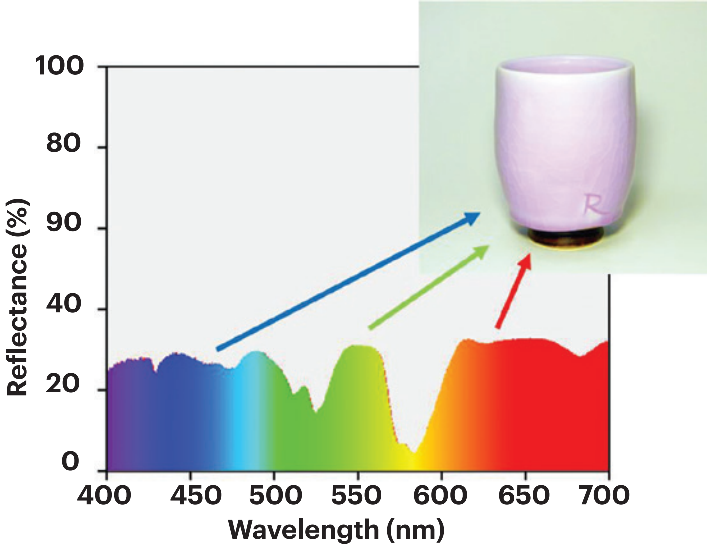
For general color promotion, the reflectance spectra for chromium are shown in Figures 6 and 7. Note that the majority peak contributes to the perceived color. These are relatively simple and straight-forward spectra with single majority peaks.

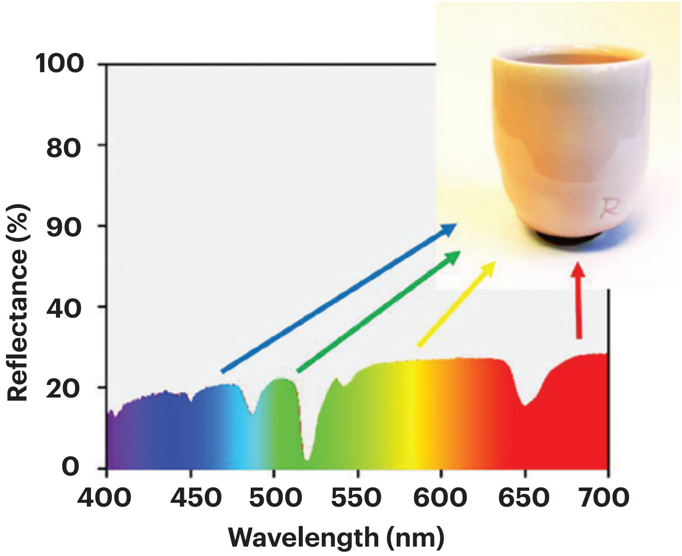
For neodymium oxide (and all Lanthanides, to my knowledge) in a glaze, however, multiple absorbance events take place. In each of the absorbance events, an electron is promoted to a higher orbital. Longer wavelengths of light (red, etc.) correspond to lower energies and correlate to lesser promotions of electrons, i.e., to lower levels. As the wavelength of light decreases, these photons correlate to higher energies and match the energy required for a larger promotion (more energy is absorbed and a bottom-lying electron is promoted to higher and higher levels) as seen in the blue and green regions.

The following page shows reflectance profiles of each of the rare earth metals, descriptions of them, and examples of how they appear in glazes.

Neodymium Oxide

Unlike the examples of chromium, which only show one peak and in turn one color corresponding to that peak, the reflectance profile of neodymium (from a xenon lamp source) produces several ranges of reflectance peaks. Specifically, there are three main portions of reflected light. These include a large section in the orange-red region (600-700 nm), a narrow section in the green-yellow region (480-560 nm), and another large section of light in the indigo-violet-blue region (400-470 nm). In simpler terms, the light reflected off this glaze is a combination of red, green, blue, and indigo/violet. The mixture of indigo-violet-blue peak and the red peak combine to create a purple color. As multiple wavelengths are present, this approaches white light, contributing to a pastel lavender purple.



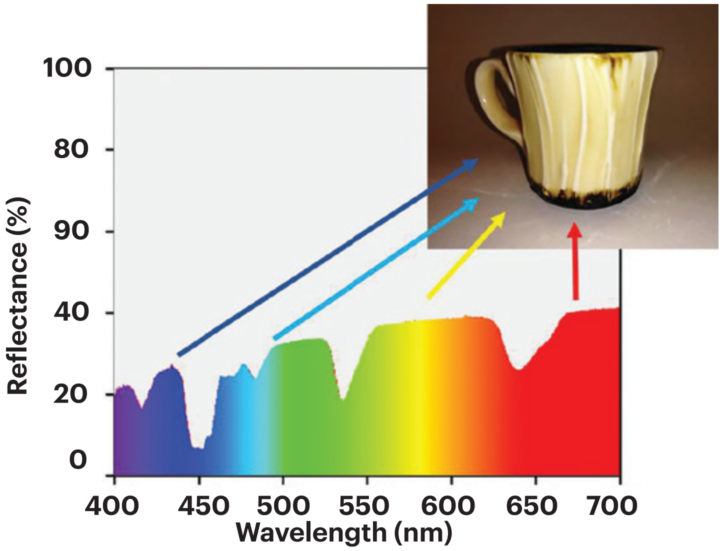


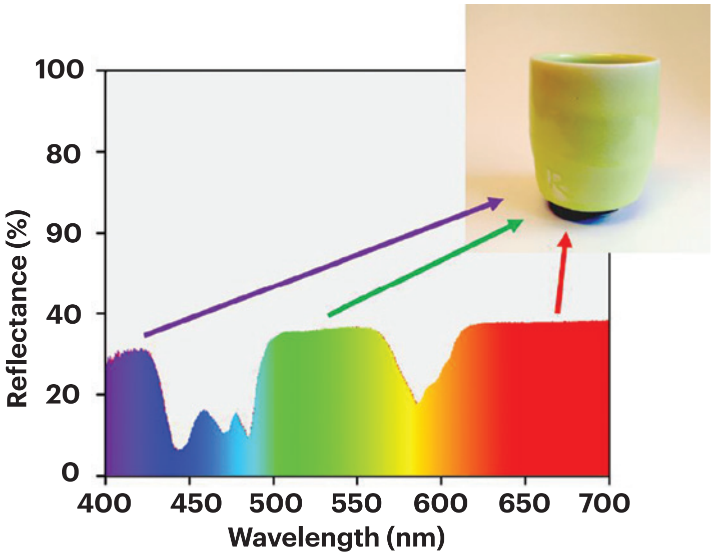
Erbium Oxide

The glaze color of erbium oxide is similar to that of holmium: a light, pastel pink. However, because of the different location and width of sections of light, erbium's pink has more of a purple/blue tint rather than holmium's orange/yellow tint. This possesses a narrow red section (670 – 700 nm), a broad region from green through yellow to orange/red (550 – 640 nm), a narrow cyan section (490-510 nm), and a somewhat broad blue-indigo section (400-475 nm).

Holmium Oxide

Holmium, which to the eye looks like a golden yellow in full sunlight, also combines multiple reflected sections of the visible spectrum to produce the color perceived from its profile. Four distinct sections of reflected light contribute to a holmium oxide glaze reflectance profile. There is a section of light in the red region (650-700 nm), another in the yellow-orange-red region (560-630 nm), one in the blue-green (480-540 nm), and a small one in the violet-indigo-blue region (400-440 nm). The final product of this mixture of reflected wavelengths is a pastel pink with hints of orange and yellow.





Praseodymium Oxide

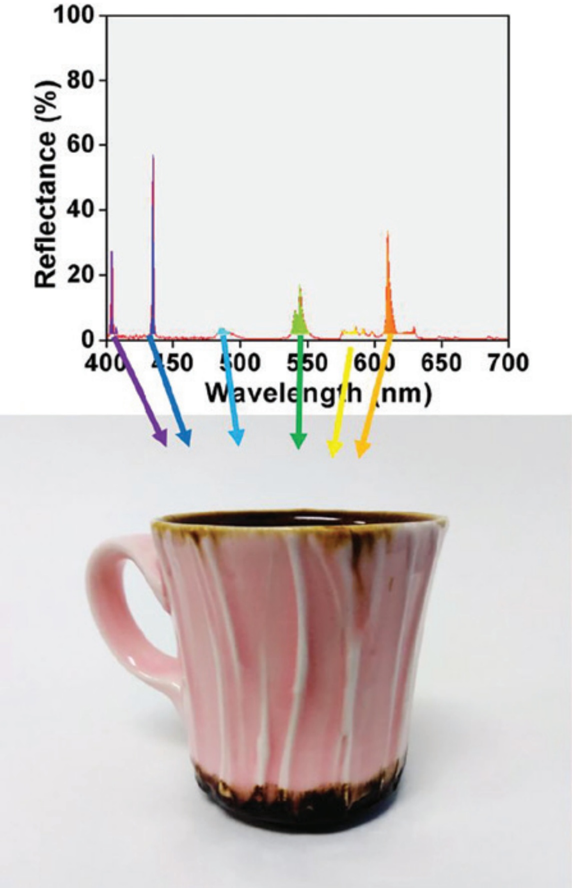
There are three main sections of the visible spectrum in a glaze reflectance profile for praseodymium oxide. One is an orange-red peak (600-700 nm), another is in the green-yellow region (500-560 nm), and the final one is in the violet-indigo-blue section (400-440 nm). Together, a pastel, vibrant green is observed, which is consistent with the majority center peak reflecting most light and highlighter contributions coming from red and blue – contributing to a fluorescent color nature.

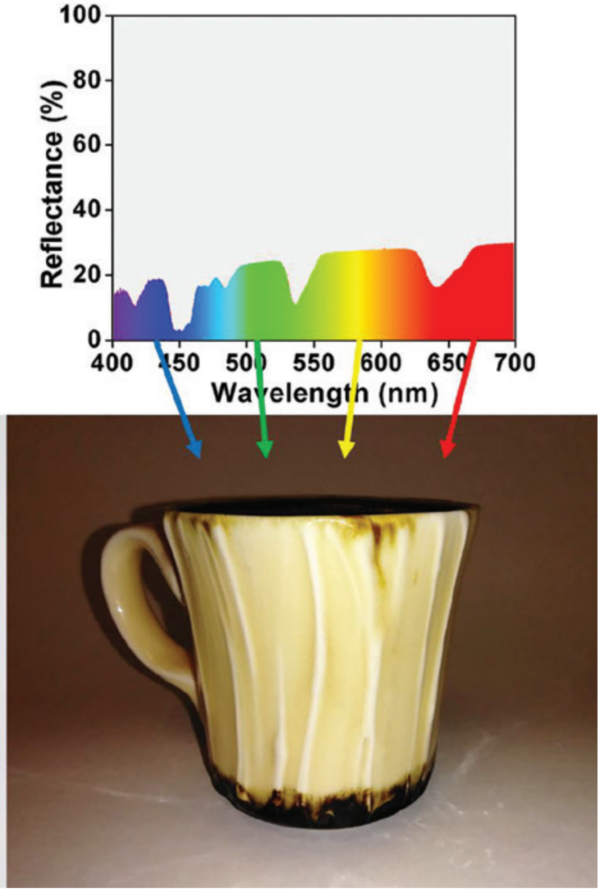
Additional reflectance profiles of neodymium and holmium were obtained using the same spectrometer, but this time under fluorescent light. Their profiles are evident of the dichroic effect: a shift in perceived color is observed across various types of light, due to absorbances and the recombination of those different qualities of light.

Holmium under fluorescent light

The reflectance profile of a holmium oxide glaze under fluorescent light is similar to that of neodymium oxide; however, there is an additional yellow peak around 570-600 nm. These combine to be visible as a pastel pink – in which the yellow addition to the reflectance profile shifts the combined lights to be more magenta.

The full spectrum reflectance profile, however, shows very strong peaks from across the spectrum. As a combination of all light results in white, this color is approaching white light and is a soft yellow/gold under LED/sunlight.





About the Author

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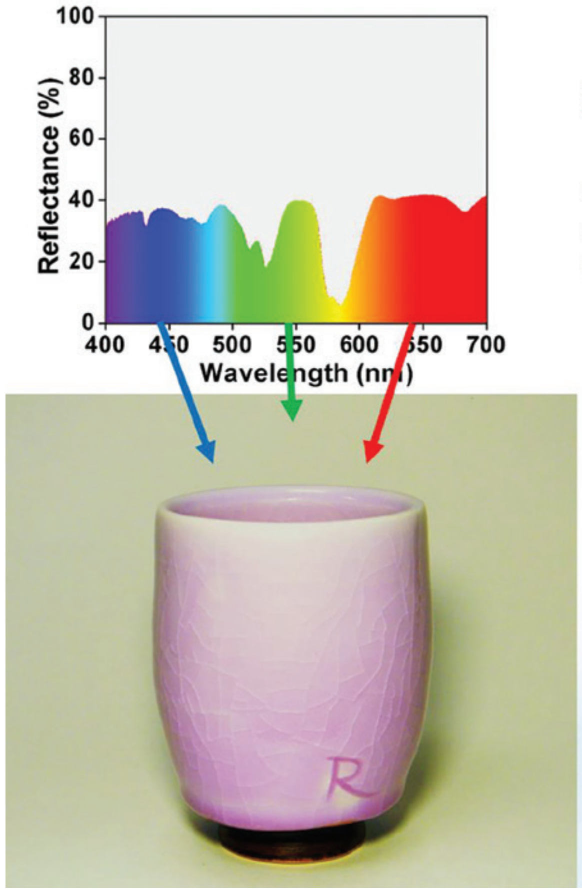
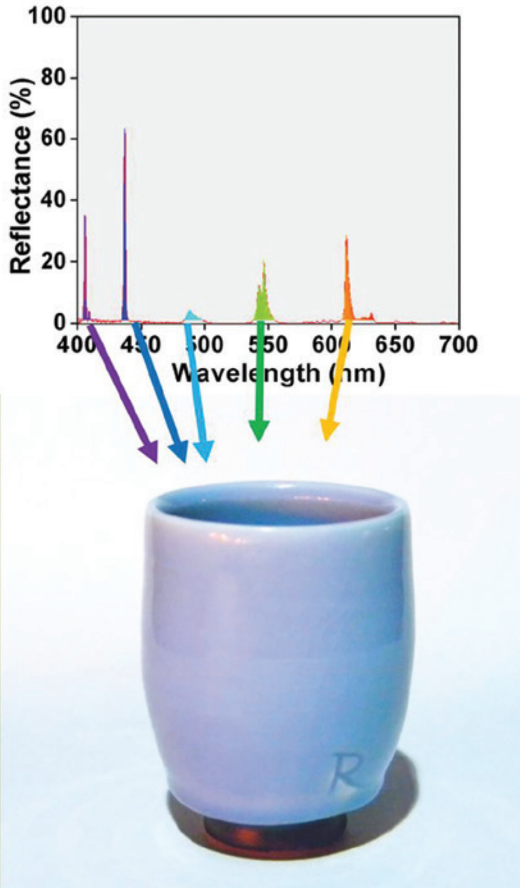
Neodymium under fluorescent light

The most classic/well-known of dichroic colorants, neodymium can be red, purple, or blue, depending on the quality of light striking it. On the left, below, the reflectance spectrum shows that a large portion of blue and red are present – made pastel by a lesser amount of yellow-green. This combines for a pastel purple, as seen beneath the spectrum. Similarly, the fluorescent reflectance profile for light from a neodymium oxide glaze surface combines to make a pale grey-blue, as most of the light from fluorescent sources are reflected back as color – except yellow. There is a strong yellow absorbance peak at 580, which color-shifts the reflected fluorescent light to light blue.

Summary

Ultimately, rare earth metals behave with a degree of complexity greater than that of d-orbital transition metals, but can still be explained under additive color theory and the Crystal Field Theory. Informatively, this study provides visible evidence of dichroism, additive color theory (light and colored light), and provides some fun glaze recipes for you to try out at home. Although not commonly intertwined, art and science are woven together more than most artists or scientists are often comfortable admitting. ■





Endnotes

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