Orbital Translations Between Ground and Excited States of Atoms Responsible for Visual Spectra Experienced in Ceramics Glaze: A Statistical Analysis

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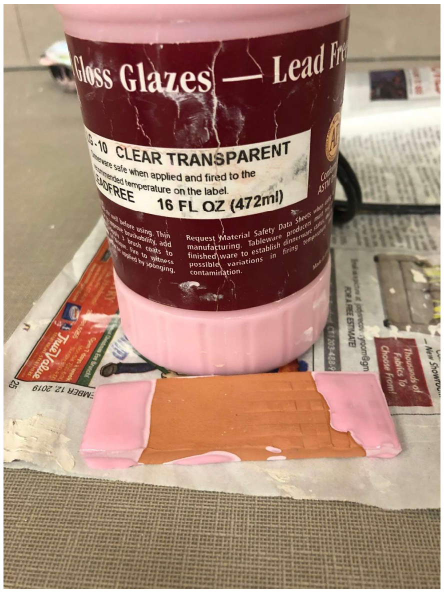
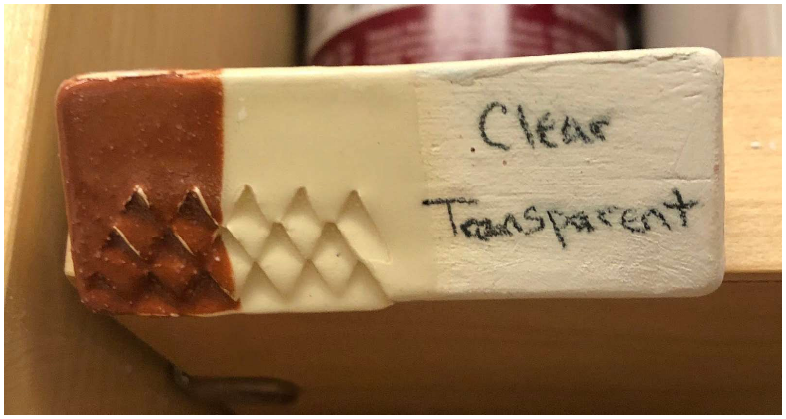
ABSTRACT

The use of glaze in ceramics has gone on for centuries. Yet potters and chemists alike have difficulty understanding exactly what is going on during the process, the goal of this research is to statistically analyse and summarize the findings of past research and experimentation to succinctly describe how the orbital translation of atoms results in visible spectra of glaze. Utilizing resonance technologies research showed that the translations between orbitals and release of energy from electrons in atoms allows for visible spectra to appear. It is also apparent from the data that each atom and therefore each substance will give off different spectra due to their independent and unique make ups.

TOPIC AND JUSTIFICATION

This paper in depth about molecular analysis of the ceramic glazing color developing process. I chose this topic because I have been doing ceramics for approximately four years and have always been interested in the science behind glazes and how they change color, form glass, the ways they mix and how the different types of substances in the glaze mixture affect the final finish of a piece. My curiosity was piqued when I noticed that the clear glaze was red and chalky when it came out of the bottle, and after it was fired the glaze came out glossy and clear (pictured below). This phenomenon is not unique to clear transparent glaze, at least four other glazes I have access to also have this color changing habit, so I wanted to dig into the science behind glazes to discover the causes of the color, shine, and stiffness changes of glaze after it has been fired.





RESEARCH QUESTION

To be more specific, this paper will dive into the question, “How does the chemical make up of a glaze impact the final color characteristics of a fired glaze?” looking into the chemical and physical causes of glaze characteristics.

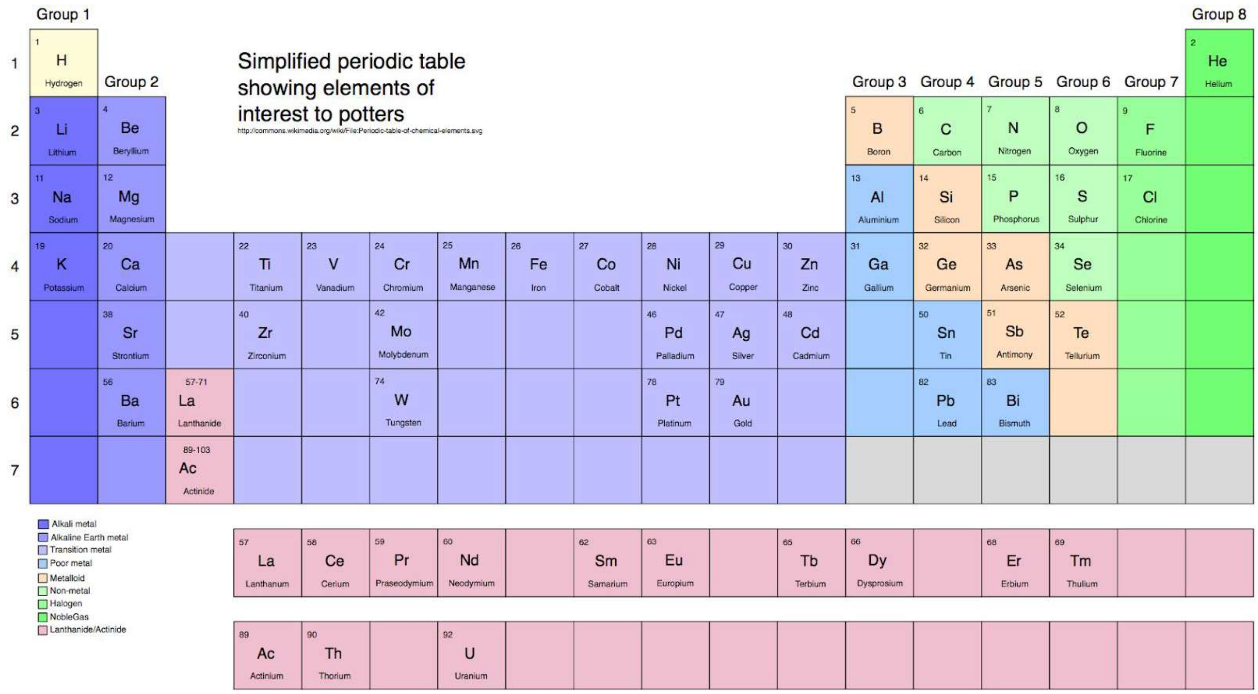
SAFETY

While ceramics is a relatively safe art form some problems can occur. The issues in safety for this research would be surrounding the heat from the kiln, should someone choose to open or touch the kiln they could be seriously burnt and injured. Glazes also contain toxic materials that if ingested could be potentially hazardous, especially if it is lead based. Lastly for safety, should the glaze be applied to a thin edge the glass could transform the edge into a razor sharp blade which could cut someone handling it. Environmentally, the biggest concern would be the overharvesting of elements and substances from the earth which are used in the glaze could harm the environment. There is also concern with dumping toxic chemical waste from ceramics and glaze mixing in areas where it cannot be properly disposed of which would cause toxicity in the environment.

BACKGROUND

Ceramic pottery has been around for tens of thousands of years BCE, however, the concept of glazing came around approximately during the 8th century BC.[1]

However, since that time glazing has become much more complicated and involved, combining specific types of substances in order to create colorful works of art. Ceramicists utilize the first layer of the transition metals most commonly in their glazes in order to obtain vibrant, varying colors.[2] There has been much research in choosing metals and oxides for colors, so much so, that potters have renovated the old periodic table in order to allow them to more easily determine the materials they want to work with (pictured below).[3] They eliminated all the unusable elements for glaze and kept the elements that can be used, typically in oxide form, to build glazes and colors.



Simplified periodic table showing elements of interest to potters

http://commons.wikimedia.org/wiki/File:Periodic-table-of-chemical-elements.svg

	Group 1	Group 2											Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
1	1 H Hydrogen																	2 He Helium
2	3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	
3	11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine	
4	19 K Potassium	20 Ca Calcium		22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium		
5		38 Sr Strontium		40 Zr Zirconium		42 Mo Molybdenum				46 Pd Palladium	47 Ag Silver	48 Cd Cadmium		50 Sn Tin	51 Sb Antimony	52 Te Tellurium		
6		56 Ba Barium	57-71 La Lanthanide			74 W Tungsten				78 Pt Platinum	79 Au Gold			82 Pb Lead	83 Bi Bismuth			
7			89-103 Ac Actinide															

57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium		62 Sm Samarium	63 Eu Europium		65 Tb Terbium	66 Dy Dysprosium		68 Er Erbium	69 Tm Thulium		
89 Ac Actinium	90 Th Thorium		92 U Uranium											

- Alkali metal
- Alkaline Earth metal
- Transition metal
- Poor metal
- Metalloid
- Non-metal
- Halogen
- NobleGas
- Lanthanide/Actinide

Hargis, Jessica Mariah, "Creating Color: Unearthing the Chemistry of Ceramic Glazes" (2016). Honors Thesis. 218.

It has been widely concluded that the color change in glazes is due to the interaction between metal ions in d-block metals and the fullness of their f and d orbitals.[3] Because these orbitals are not filled from bottom to top but actually from orbital 4s, 4p, then back down to orbital 3d, electrons are forced to expend energy to fill the third shell d orbital and absorb energy in order to do so. When this occurs the energy absorbed can fall into the range of the visible light spectrum, causing the substance to be perceived as a color. However there are many rules to the ways in which electrons can translate orbitals.[4]

Rules

Laporte selection rule

- Translations moving between two or more shells may not occur, translations may only be ± 1 shell away from the point of origin.[5]

Spin selection rule (Spin refers to singlet, doublet, triplet, etc. orbitals)

- Electrons may not translate between different spin state multiplicities. This can be stated in an equation $\Delta S = 0$, therefore this translation is permissible ^2p -> ^2s but ^2p -> ^4d is not.
- Absolute spin is governed by similar rules where $\Delta J = 0; \pm 1$.[6]

There are no rules prohibiting certain translations to orbitals with varying n values

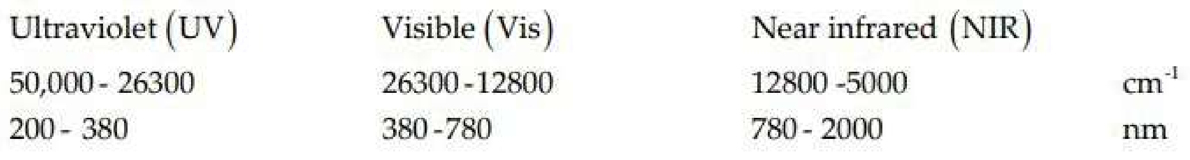
- N value dictates the level of which the orbital shell is on, for example, the S orbital has two levels so the n value on the second S orbital level would be 2 and it would be annotated as 2s.[7]

METHODOLOGY

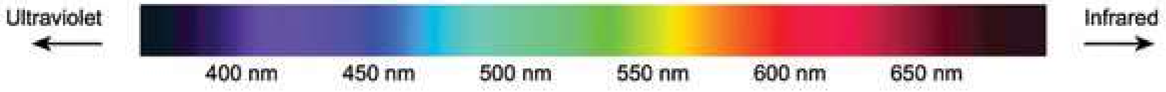
Past experiments have been conducted to calculate the electronic absorption spectra of transition metals of the 3d variety specifically. These are the types of metals explicitly stated to be most commonly utilized in ceramics glaze recipes so this research is extremely relevant.

Experiments were conducted through a fairly simple procedure; substances were placed between a light source and a spectrometer. The substance then absorbed certain light wavelengths and those were cataloged as the substance's absorption spectrum (the spectrum may span from the ultraviolet all the way to the near infrared). Researchers also utilized EMR which uses microwave radiation to discover molecules with unpaired spin electrons.[8]

The data from these experiments are catalogued by the emission and absorption spectra which can be measured in two ways, wavenumbers, cm^{-1} or, wavelength, nm.

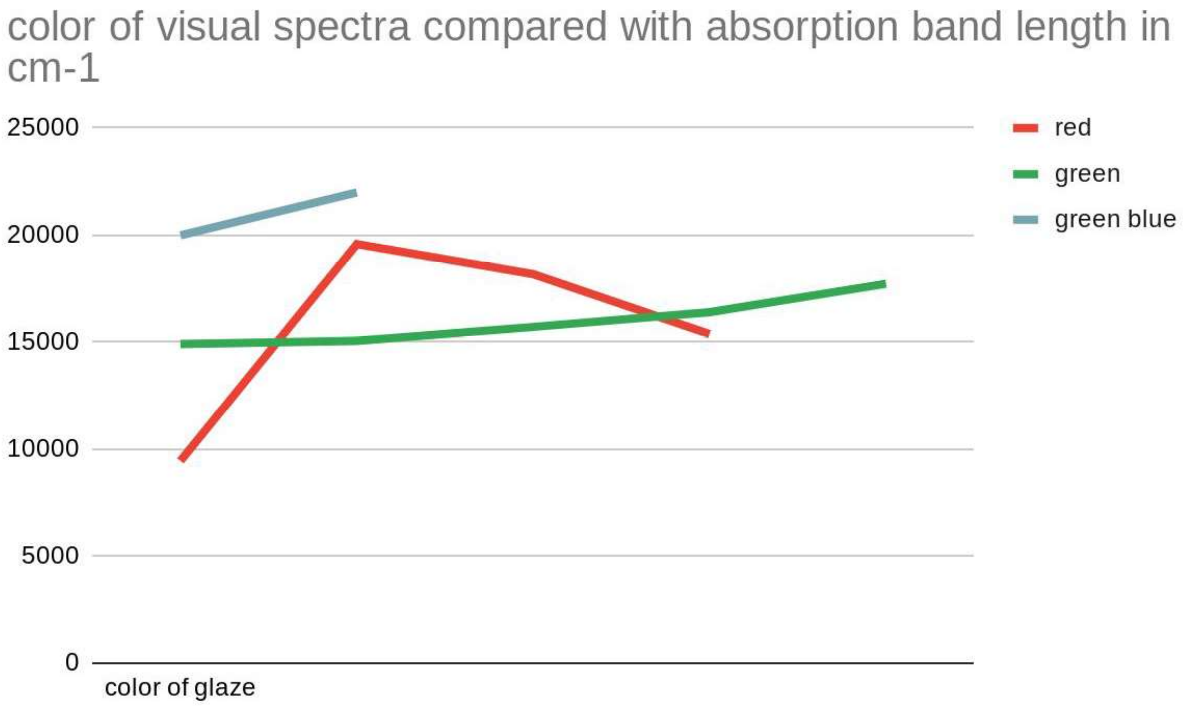


Ultraviolet (UV)	Visible (Vis)	Near infrared (NIR)	
50,000 - 26300	26300 - 12800	12800 -5000	cm^{-1}
200 - 380	380 - 780	780 - 2000	nm

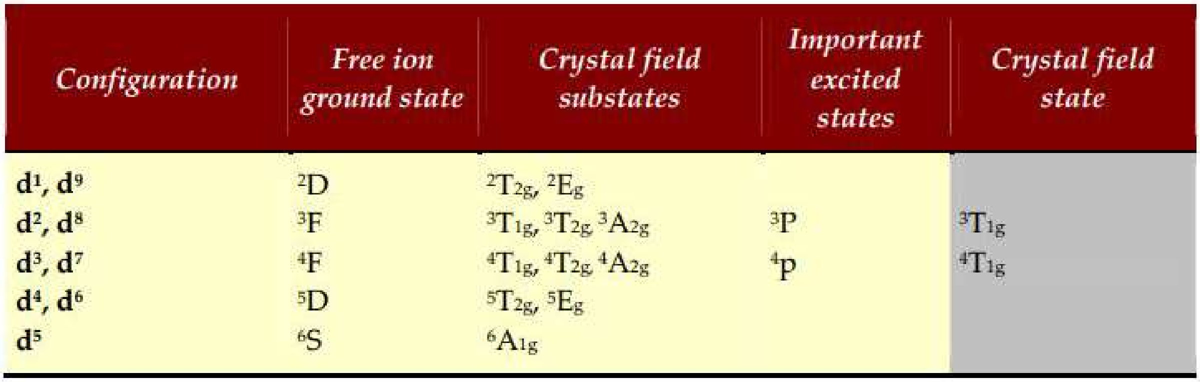


The data collected through experiments showed many changes in electronic absorption spectra after heating in various mineral examples shown in the table below.

substance	Absorption band (cm^{-1})	Color corresponding to wavenumber	Substates translated
Tetravalent chromium (within garnet and forsterite)	9460, 19590	Red	3A2g 3T2g, 3A2g 3T1g
Trivalent chromium	14925, 15070, 15715, 16400, 17730	Green	4A2g(F) → 4T2g(F) and 4T1g(F)
Manganese III	20000	Green blue	5Eg→ 5T2g c
Iron	10525, 15380-18180, 22000		6A1g(S) → 4T1g(G) (v1), 6A1g(S) → 4T2g(G)(v2), 6A1g(S) → 4A1g(G), 4Eg(G)
Divalent nickel (falcondoite)	9255, 15380, 27390, and a weak band at 24385	NIR	T1g(P), 3T1g(F), 3T2g(F), 1T2g(D)



Below is a table showing the alternate notation for the d orbital configurations, the experiment utilized in this paper denoted the configurations in the crystal field states and substates notation.



Configuration	*Free ion ground state*	*Crystal field substates*	*Important excited states*	*Crystal field state*
d^1, d^9	^2D	$^2T_{2g}$, ^2E_g		
d^2, d^8	^3F	$^3T_{1g}$, $^3T_{2g}$ $^3A_{2g}$	^3P	$^3T_{1g}$
d^3, d^7	^4F	$^4T_{1g}$, $^4T_{2g}$ $^4A_{2g}$	^4P	$^4T_{1g}$
d^4, d^6	^5D	$^5T_{2g}$, ^5E_g		
d^5	^6S	$^6A_{1g}$		

Table 7. Crystal field components of the ground and some excited states of d^n (n=1 to 9) configuration

S. Lakshmi Reddy, Tamio Endo and G. Siva Reddy (August 29th 2012). Electronic (Absorption) Spectra of 3d Transition Metal Complexes, Advanced Aspects of Spectroscopy, Muhammad Akhyar Farrukh, IntechOpen, DOI: 10.5772/50128. Available from: https://www.intechopen.com/books/advanced-aspects-of-spectroscopy/electronic-absorption-spectra-of-3d-transition-metal-complexes

CONCLUSION

By the data uncovered in these experiments it is valid to conclude that the orbital translations between ground and excited states of atoms are responsible for the visual spectra experienced in ceramics glaze. Further, it can be concluded that because every atom has a slightly different spectra, different substances will give off different colors when going through orbital translation, for example Iron has spectra at 10525 whereas divalent nickel has spectra lines at 9255. This means that different elements utilized in glaze or other crystalline substances will give off different visual spectrum light, and that the colors may change between the ground and excited state. This is an extrapolation however as all measurements have been of the substances at room temperature so atoms are not as excited as they may be in differing conditions; this leads me to a limitation in this research. The information taken in through this experiment only gives spectra for one state of the atom and should give examples of the substances at relatively high (100°c) and relatively low (0°c) as well.

Notes

1. Priddy, Brenda. “The History of Glazing.” *Our Pastimes*, 10 Jan. 2019, ourpastimes.com/the-history-of-glazing-12311173.html.
2. Hansen, Tony. “Glaze Chemistry.” *Glaze Chemistry*, 2003, digitalfire.com/4sight/glossary/glossary_glaze_chemistry.html.
3. Hargis, Jessica Mariah, "Creating Color: Unearthing the Chemistry of Ceramic Glazes" (2016). Honors Thesis. 218.
4. Bloomfield, Linda. “Techno File: The Chemistry of Color.” *Ceramic Arts Network*, The American Ceramic Society, 8 Aug. 2017,

ceramicartsnetwork.org/ceramics-monthly/ceramic-glaze-recipes/glaze-chemistry/techno-file-chemistry-color/#.

5. S. Lakshmi Reddy, Tamio Endo and G. Siva Reddy (August 29th 2012). Electronic (Absorption) Spectra of 3d Transition Metal Complexes, Advanced Aspects of Spectroscopy, Muhammad Akhyar Farrukh, IntechOpen, DOI: 10.5772/50128. Available from: https://www.intechopen.com/books/advanced-aspects-of-spectroscopy/electronic-absorption-spectra-of-3d-transition-metal-complexes
6. Ibid.
7. Ibid.
8. Ibid.
9. Fitsch, Emmanuel. “AN UPDATE ON COLOR IN GEMS. PART 1: INTRODUCTION AND COLORS CAUSED BY DISPERSED METAL IONS .” Gemological Institute of America, 1987.