

COLOR IN MINERALS

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INTRODUCTION AND INSTRUCTOR'S NOTES

This lab exercise is adapted from one I've developed over the years to teach crystal field theory to students in my Geochemistry courses. I must confess that although my own research interests lie in this area (I had the good fortune to work with both Roger Burns and George Rossman), I have never included spectroscopy as part of my own Mineralogy courses. Why? ...because I did not think I could present it in a fashion that would make it interesting and relevant to my students without oversimplification. Now that George Rossman has a home page with easily accessible spectra and images, I've changed my mind. In preparing for this workshop, I've also reflected on the fact that the students I've had in Mineralogy are almost universally interested in gemstones, and by association, in their colors. I've tried to write this lab exercise to take advantage of that interest.

Unfortunately, most Geology departments do not have the equipment to make measurements of optical spectra in house. If you do, I encourage you to change this lab around so that the students actually take some spectra themselves. Sample preparation requires only that you have a slice of the mineral that is polished on both sides, a relatively easy undertaking with some elbow grease, a little diamond grit, and a polishing setup. If you lack the spectrometer, this "lab" becomes more of an exercise. To add a little "hands-on" work to it, you might consider pulling colored specimens from your own collections, and then ask the students to match spectra with samples. This reinforces the relationship between how the spectra look and how the colors actually appear. A visit to or from a local jeweler (look for someone with Gemological Institute of America certification) might also give you a chance to see some nice colored gems; most jewelers today also stock treated and untreated stones, which your students might want to see.

I also encourage you to take advantage of George Rossman's Mineral Spectroscopy Home Page (see information below), to which new spectra are constantly being added. Take a look at it from time to time; new updates will be added that will also stimulate good discussions of spectroscopy. Most of the entries for mineral spectra contain brief discussions of the causes of color that are applicable. You might want to ask your students to download and manipulate the spectra. The data files all contain information about the thickness of each sample when it was run; you could ask your students to download some spectra, normalize them all to the same thickness, and talk about the Beer-Lambert law and the relationship between absorption and concentration.

Finally, I encourage you to contact me (mddyar@amherst.edu) or George Rossman (see his home page for information on how to reach him) if you have questions about the subject matter presented here. I hope that some of my own enthusiasm for this subject matter and this lab will prove contagious, and inspire you to work with your students on this topic. Really, your imagination is the only limit to the interesting ways to present mineral spectra!

SHOW AND TELL

All of the spectra in this lab come from the Mineral Spectroscopy Home Page created by George Rossman at Caltech, which can be found at:

<http://minerals.gps.caltech.edu/>

We all owe George a huge debt of thanks for creating this facility, and I am particularly grateful that he allowed us to use the spectra in this exercise. Many of the spectra can be downloaded and printed out as images or saved as ASCII text files. This gives you an opportunity to go beyond the lab ideas presented here into territory of particular interest to you or your students.

BACKGROUND

I would insert this lab at the point in my course where I have completed the study of symmetry and want to begin basic mineral chemistry. I talk very briefly about atoms (what's a neutron, proton, electron; what are the symbols for them; charge neutrality) and then present the Schrödinger equation as a way of constructing the periodic chart. I stress that it also describes the positions of electrons in space around the nucleus, and I use some wood models to show them the shape of the orbitals. We then break into groups and run through the following exercise (it takes 30-45 minutes) to get them used to thinking about the periodic chart:

Periodic Chart Exercise

1. Use the periodic chart to decide what characterizes each of the following:

- A: Transition elements (e.g., Sc through Zn; also Y through Cd)
- B: Lanthanides (Ce through 72)
- C: Actinides (Th through Lr)
- D: Alkali Metals (e.g., Li, Na, K, Rb)
- E: Alkaline Earths (e.g., Be, Mg, Ca)
- F: Halogens (F, Cl, Br, I)
- G: Noble Gasses (He, Ne, Ar)
- H: Platinum Group Elements (e.g., Ru, Os, Rh)

2. Calculate the atomic weight of Mg_2SiO_4 .

Depending on the preparation of my students, sometimes I also have the class do an exercise predicting which valences each atom likes to take on, with emphasis on rock-forming elements. At this point it is also convenient to talk about ionic radius, emphasizing the fact that atoms have different radii in different coordinations with oxygen (John Brady has an excellent lab exercise on how ionic radii can be determined!) Pauling's Rules (with corollaries) and Hund's rules are also important background for this exercise.

Once the class seems comfortable with these fundamentals of chemistry, they are ready to tackle color in minerals. The materials included here may cover one or two lab periods depending on your student population. The only materials needed would be a periodic chart of

the elements and, perhaps, wood models of the shapes of the *d* orbitals to aid in understanding the crystal field theory. It's also nice to have examples of minerals of different color (only be sure you know why each one is colored the way it is -- the students are bound to ask!) If you can gather them together, it's particularly nice to have examples of something close to the six garnet end members (for obvious reasons).

I've included far more questions here than can be dealt with in a single lab period, but I am hopeful that you will choose the parts of this document that seem interesting and use them in any way you want. To help you do this, I've assembled the following table with a guide to some of the spectra that appear on the Mineral Spectroscopy Home Page, along with some references to get you started. Many other references are given in the list on the Home Page. I hope you find this useful...

Summary of Some of the Mineral Spectra Available on the Home Page

Mineral	Peak Position (nm)	Peak positions (cm ⁻¹)	Color	Assignment	Relevant references
ruby	556	18,000	red	Cr ³⁺ (oct)	Burns, 1983
	408	24,500			
beryl (Lone P.)	820	12,200	blue	Fe ²⁺ (oct)	Rossman's home page
	971	10,300			
	621	16,100			
beryl (WahWah)	556-500	18,000-20,000	red	Mn ³⁺ (oct)	Rossman's home page
beryl (syn. em.)	620	16,130	green	Cr ³⁺ (oct)	Rossman's home page
	425	23,530			
almandine	505	19,800	red	Fe ²⁺ (8-fold)	Burns, 1993
	574	17,430			
	694	14,400			
	1309	7,640			
	1718	5,820			
andradite	854	11,700	green	Fe ³⁺ in M3 (oct)	Moore and White, 1972
	588	17,000			
	441-437	22,670-22,900			
grossular	607	16,475	green	V ³⁺ (oct)	Rossman, 1988
	426	23,475			
pyrope	500	20,000	red/pink	Fe ²⁺ (8-fold)	Burns, 1993
	530	18,868			
	610	16,393			
	700	14,286			
spessartine	588	17,000	orange	Mn ²⁺ (oct)	Frendrup and Larger, 1981
	490	20,400			
uvarovite	600	16,667	green	Cr ³⁺ (oct)	Abu-Eid, 1976
	440	22,727			
sillimanite	462	21,645	yellow	Fe ³⁺ (tet)	Rossman's home page
	440	22,727			
	412	24,272			
fayalite	1076	9,290	green	Fe ²⁺ (oct)	Burns, 1970
	909	11,000			
	1250	8,000			
manganite	580	17,240	red	Mn ³⁺ (oct)	Rossman's home page
	500	20,000			

gahnite	450	22,222	???	Zn ²⁺ (tet)	Rossman's home page
	540	18,519			
	570	17,544			
	630	15,873			
	900	11,111			
spinel	400	25,000	red	Cr ³⁺ (oct)	Mao and Bell, 1975
	570	17,544			
chrysoberyl (Kenya)	565	17,700	green	Cr ³⁺ (oct)	Farrell and Newnham, 1965
	425	23,500			Schmetzer et al., 1980
chrysoberyl (M.G.)	375	26,600	yellow	Fe ³⁺ (oct)	Rossman's home page
	440	22,727			
grunerite	1000	10,000	blue	Fe ²⁺ in M4 (oct)	Mao and Seifert, 1974
	2336	4,200		" "	Hawthorne, 1981
	990	10,100		Fe ²⁺ in M1-M3 (oct)	
phlogopite (Ontario)	1176	8,500		" "	
	840	11,900	green	Fe ²⁺ (oct)	Rossman, 1984
phlogopite (Kimberley)	1124	8,900			
	521	19,200	red	Fe ³⁺ (tet)	Faye and Hogarth, 1969
	493	20,300			Hogarth et al., 1970
muscovite	441	22,700			
	400	25,000			
	673	14,850	red	Mn ³⁺ (dist. oct)	Burns, 1970
	525	19,050			
lepidolite	467	21,400			
	420	23,800			
	758	13,200	pink	Mn ³⁺ (dist. oct)	Annersten and Hålenius, 1976
epidote	548	18,250			
	458	21,850			
	1056-769	9,470-12,300	green	M3 (oct) Fe ³⁺	Burns and Strens, 1967
	607-559	16,480-17,900			
	472-455	21,200-22,000			

READING LIST

The technical literature contains a wide variety of papers covering gems, color, and optical spectroscopy; projects on color in minerals make good term paper topics once students have gotten used to interpreting optical spectra of minerals. The majority of the recent work in this area has been done at Caltech, so searches of literature databases using George R. Rossman as author as a search criterion will yield a good starting point for such papers. I also recommend the *Reviews in Mineralogy* volume on *Spectroscopy* (F.W. Hawthorne, ed.), which has a good chapter in it (by Rossman) summarizing optical spectroscopy. The "bible" of this field is Roger Burns' book, *Mineralogical Applications of Crystal Field Theory* (1970 and 1993; Cambridge University Press). Despite the somewhat intimidating title, it contains clear explanations of all the material presented in this lab, along with data on just about every mineral group you could ever want to know about!

If you're not too familiar with this material yourself, you might want to begin with less specialized reading material. I highly recommend the following readings, which you might want to have available for eager-beaver students. Some of these papers are rather old now, but they are still (in my opinion) the best that have been written on this topic.

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and to George Rossman for perennial wisdom on this subject and for helping out with a few last minute spectra. I am also grateful for all that I learned from Roger Burns and from his book.

ANSWERS TO PROBLEMS

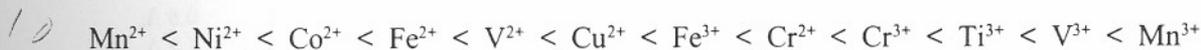
High-Spin Electronic Configurations for 3d Orbitals in Octahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		t_{2g}	e_g					
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	0						0	0
Ti ³⁺	1	↑					1	0.4 Δ _o
Ti ²⁺ , V ³⁺	2	↑ ↑					2	0.8 Δ _o
V ²⁺ , Cr ³⁺ , Mn ⁴⁺	3	↑ ↑ ↑					3	1.2 Δ _o
Cr ²⁺ , Mn ³⁺	4	↑ ↑ ↑ ↑					4	0.6 Δ _o
Mn ²⁺ , Fe ³⁺	5	↑ ↑ ↑ ↑ ↑					5	0
Fe ²⁺ , Co ³⁺ , Ni ⁴⁺	6	↑↑ ↑ ↑ ↑					4	0.4 Δ _o
Co ²⁺ , Ni ³⁺	7	↑↑ ↑↑ ↑ ↑					3	0.8 Δ _o
Ni ²⁺	8	↑↑ ↑↑ ↑↑ ↑					2	1.2 Δ _o
Cu ²⁺	9	↑↑ ↑↑ ↑↑ ↑↑ ↑					1	0.6 Δ _o
Cu ⁺ , Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	10	↑↑ ↑↑ ↑↑ ↑↑ ↑↑					0	0

Relationship Between Crystal Field Splittings and CFSE for Octahedral Coordination

Cation	Δ _o (cm ⁻¹)	CFSE (right column, above)	CFSE (cm ⁻¹) in hexahydrate
Ti ³⁺	18,950	0.4 Δ _o	7,580
V ³⁺	19,100	0.8 Δ _o	15,280
V ²⁺	12,600	1.2 Δ _o	15,120
Cr ³⁺	17,400	1.2 Δ _o	20,880
Cr ²⁺	13,900	0.6 Δ _o	8,340
Mn ³⁺	21,000	0.6 Δ _o	12,600
Mn ²⁺	7,800	0.0 Δ _o	0
Fe ³⁺	13,700	0.0 Δ _o	0
Fe ²⁺	9,400	0.4 Δ _o	3,760
Co ²⁺	9,300	0.8 Δ _o	7,440
Ni ²⁺	8,500	1.2 Δ _o	10,200
Cu ²⁺	13,000	0.6 Δ _o	7,800

It follows that:



From this list it is obvious that Δ³⁺ > Δ²⁺ is the general rule! For more information consult section 2.9 in Burns (1993).

2. Mystery minerals:

Before you do this section, remind the students of where the infrared portion of the spectrum is, and ask them if their eyes can see infrared light! This will avoid confusion over minima that occur in the IR that don't affect color. For more information on these spectra,

consult the summary table of mineral spectra for more information, or check out the Mineral Spectroscopy Home Page. There are lots of other good examples there that can be used for this type of question.

Minas Gerais **muscovite** is red-purple (Mn^{3+}).

Grossular is green (V^{3+}).

Beryl is blue (Fe^{2+}).

Chrysoberyl is green, with flashes of red (this is called the "alexandrite effect"), because it has low absorption in both the green and the red regions of the spectrum. Chrysoberyl appears green in daylight and red in incandescent light. This occurs because in daylight, red and green are transmitted equally, but the eye is more sensitive to green, so it appears green. Incandescent light happens to be enriched in low energy red wavelengths, so alexandrite transmits more red than green and it appears red!

3. The Wah Wah beryl has maximum absorbance at 550-580 nm. In wavenumbers this is 18,182 - 17,241 cm^{-1} . The calcite, on the other hand, has maximum absorption at about 780 nm, or 12,821 cm^{-1} . Because the general rule from #1 is that $\Delta^{3+} > \Delta^{2+}$, the beryl must be the Mn^{3+} , while the calcite is Mn^{2+} .

4. Olivine has maximum absorption at about 1100 nm, or 9,091 cm^{-1} , while the pyrope has a maximum at around 1260 nm (7,937 cm^{-1}). Theory predicts that $\Delta_o : \Delta_c = 1 : 8/9$, so the garnet has the Fe in eight-fold coordination, while the olivine is six-fold. In staurolite and spinel, with maximum absorbances around 1400-2200 nm (7143-4545 cm^{-1}) and 2070 nm (4831 cm^{-1}), the energies are roughly 4/9 of the value for octahedral Fe^{2+} (as in olivine), so the Fe^{2+} in those minerals is in tetrahedral coordination.

5.

High Spin Electronic Configurations for 3d Orbitals in Tetrahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		e		t_2				
$Ca^{2+}, Sc^{3+}, Ti^{4+}$	0						0	0
Ti^{3+}	1	↑					1	$0.6 \Delta_t$
Ti^{2+}, V^{3+}	2	↑	↑				2	$1.2 \Delta_t$
V^{2+}, Cr^{3+}, Mn^{4+}	3	↑	↑	↑			3	$0.8 \Delta_t$
Cr^{2+}, Mn^{3+}	4	↑	↑	↑	↑		4	$0.4 \Delta_t$
Mn^{2+}, Fe^{3+}	5	↑	↑	↑	↑	↑	5	0
$Fe^{2+}, Co^{3+}, Ni^{4+}$	6	↓↑	↑	↑	↑	↑	4	$0.6 \Delta_t$
Co^{2+}, Ni^{3+}	7	↑↓	↑↓	↑	↑	↑	3	$1.2 \Delta_t$
Ni^{2+}	8	↑↓	↑↓	↑↓	↑	↑	2	$0.8 \Delta_t$
Cu^{2+}	9	↑↓	↑↓	↑↓	↑↓	↑	1	$0.4 \Delta_t$
$Cu^+, Zn^{2+}, Ga^{3+}, Ge^{4+}$	10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

In case you're wondering, most cations in the first transition series have high spin configurations at ambient pressure and temperature. The exceptions to this are Co^{3+} and Ni^{3+} , but for simplicity, only high spin configurations are used in this lab exercise. For more

information on high spin vs. low spin, see Burns (1993) or a chemistry text.

Octahedral Site Preference Energies of Transition Metals

Cation	CFSE _o (Kj/mole)	CFSE _t (Kj/mole)	OSPE (Kj/mole)
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	0	0	0
Ti ³⁺	-87.4	-58.6	-28.8
V ³⁺	-160.2	-106.7	-53.5
Cr ³⁺	-224.7	-66.9	-157.8
Cr ²⁺	-100.4	-29.3	-71.1
Mn ³⁺	-135.6	-40.2	-95.4
Mn ²⁺ , Fe ³⁺	0	0	0
Fe ²⁺	-49.8	-33.1	-16.7
Co ³⁺	-188.3	-108.8	-79.5
Co ²⁺	-92.9	-61.9	-31.0
Ni ²⁺	-122.2	-36.0	-86.2
Cu ²⁺	-90.4	-26.8	-63.7
Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	0	0	0

These would predict the following uptake systematics:

