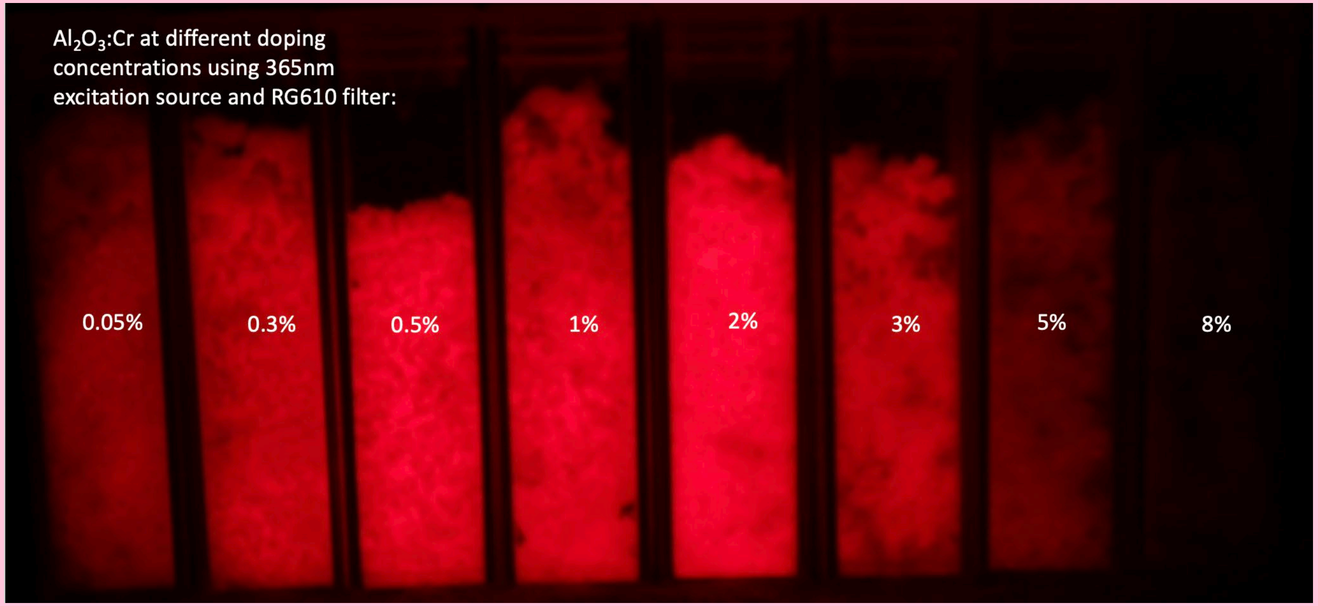
v-BFY July, 2021

Ruby, you thrill me so!

Dan Boye,
Physics Department, Davidson College
with help(!) from Ethan Cramer ’23



- Implemented in Modern Physics (PHY320) lab as “next experiment” beyond gaseous discharge tubes and line spectra.
- What happens to energy levels when atoms (ions) are exposed to an external electric field (Stark effect)?
- What happens to electron orbitals (probability clouds) when ion is placed among other, different regularly spaced charged ions?
- What happens when an excited ion with its probability cloud relaxes to a lower energy, differently-shaped probability cloud?

What's in a name?

Corundum (Al_2O_3) alumina, aluminum oxide

Dirty Corundum

Ruby (Cr^{3+}:Al_2O_3)

Sapphire (iron, titanium, vanadium, magnesium)

Pink Sapphire vs Ruby (same thing, Cr concentration, other impurities)

Ti-sapphire

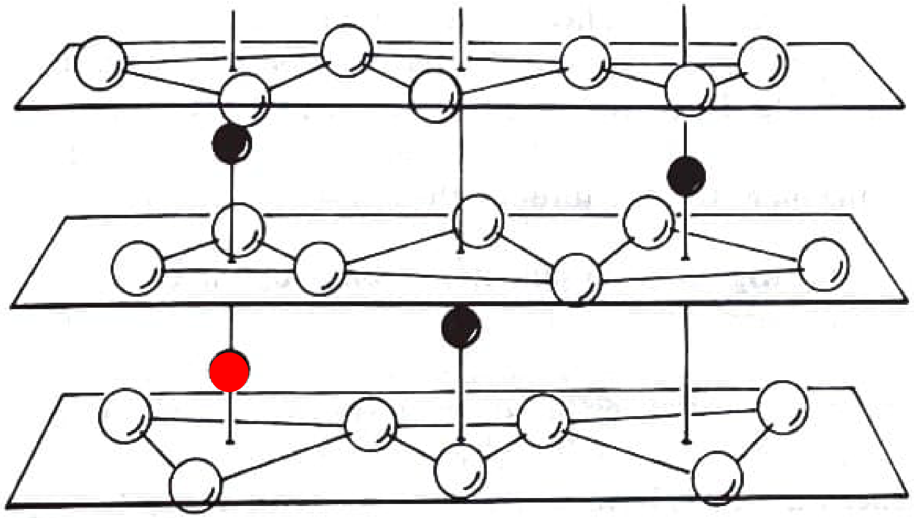


FIG. 9.4. A portion of the alumina lattice in which the Al^{3+} ions (dark circles) are shown between layers of O^{2-} ions (open circles). The optic axis of the crystal (trigonal axis at the site of the Al^{3+} ions) is perpendicular to the planes of oxygen ions. (After Geschwind and Remeika 1961.)

Ref 1 & 2

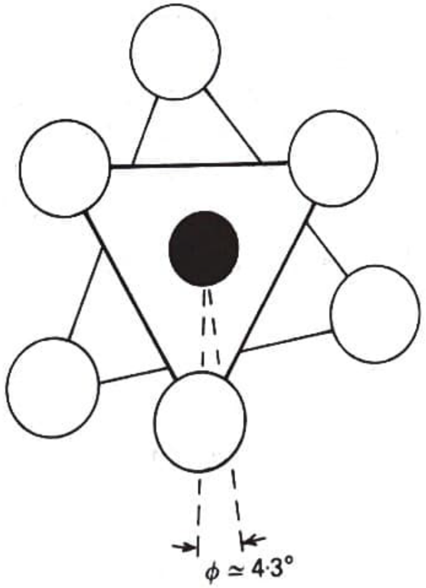


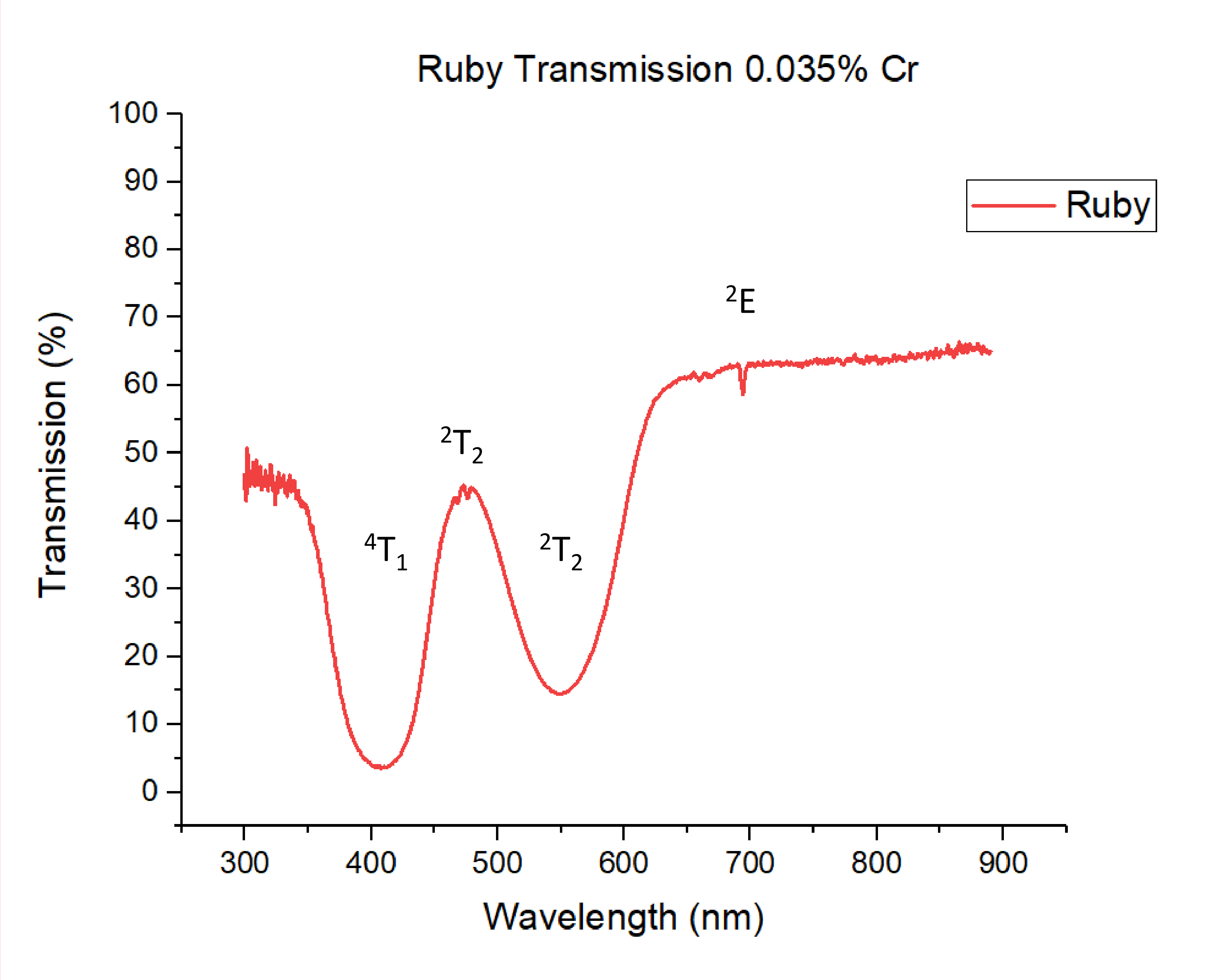
FIG. 9.5. The Cr^{3+} ion (dark circle) surrounded by its six neighbouring oxygen ions in ruby, as viewed along the trigonal crystal axis (optic axis of the sapphire or ruby crystal). (After Shinada *et al.* 1966.)

Ref 1 & 2

Interaction of light with matter - RATS (Reflection, Absorption, Transmission, Scattering)

Equipment:

- tungsten halogen lamp
- (flashlight)
- USB/fiber optic spectrometer
- 1cm cube ruby sample



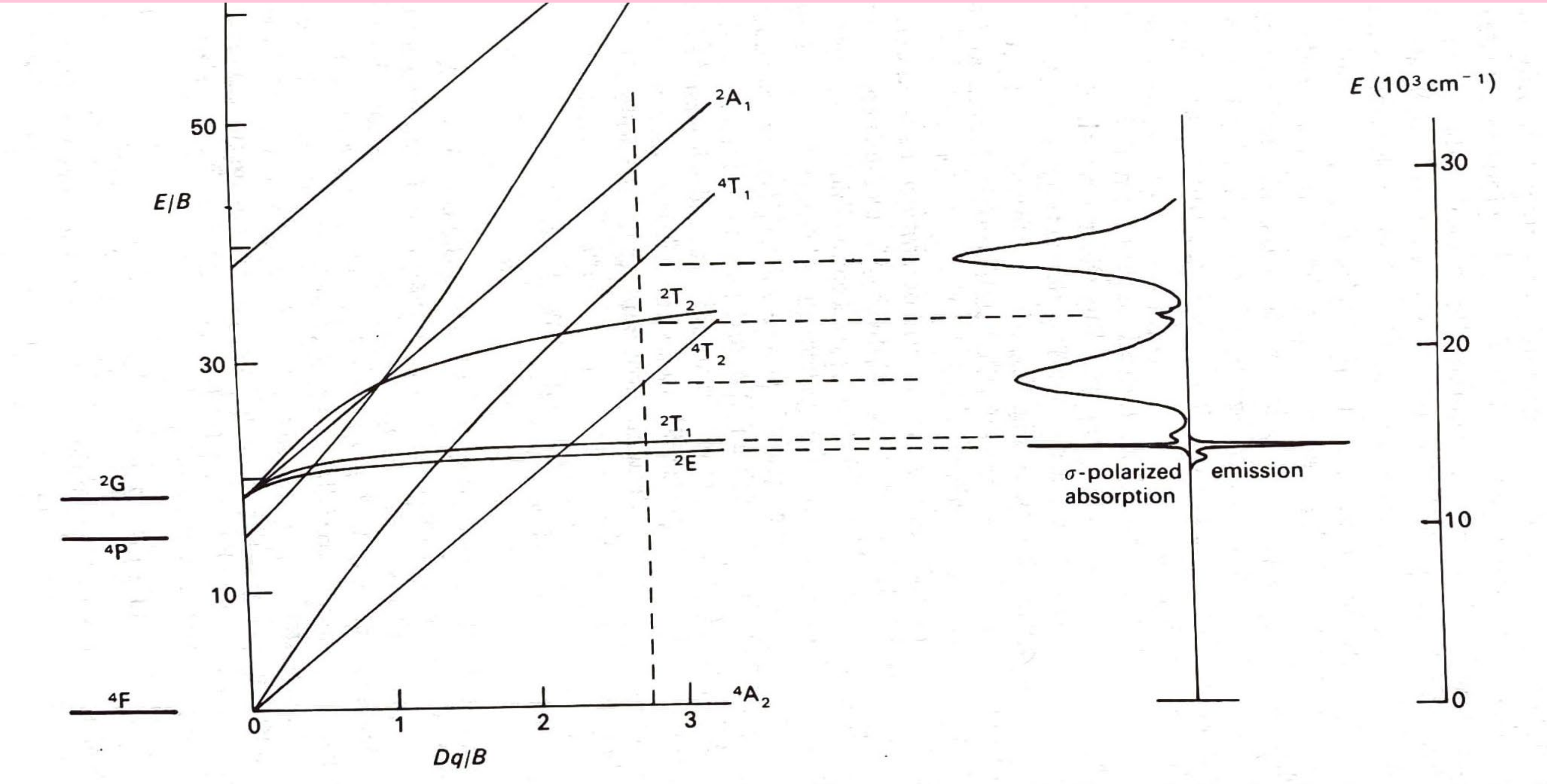
Cr^{3+} has an electronic $3d^3$ configuration

The free ion ground state of the electronic configuration is a ^4F state.

Under the influence of an octahedral electric field the ground state splits to three energy sublevels ($^4A_2$,$^4T_1$,$^4T_2$).

^2E level is the lowest energy excited state.

The $^4A_2$ -> $^4T_1$ and $^4A_2$ -> $^4T_2$ absorptions are broad band.



Transition Metal Ions in Solids

FIG. 9.1. Plot of E/B against Dq/B for $\gamma=4.8$, a value appropriate for Cr^{3+} in aluminium oxide. The vertical broken line is drawn for $Dq/B=2.8$, the ruby value. The observed levels of ruby (ignoring splittings due to trigonal crystal field) are shown on the right, and are seen to be in good agreement with the predictions of the crystal field analysis. At low temperatures luminescence is observed only from the ^2E level.

413

Ref 1 & 2

Cr^{3+} in different crystal fields

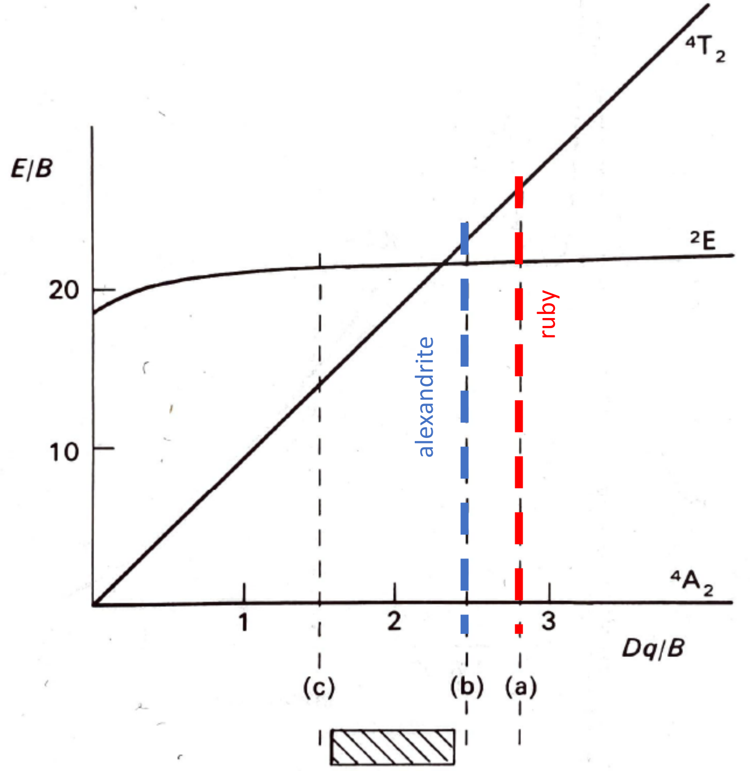
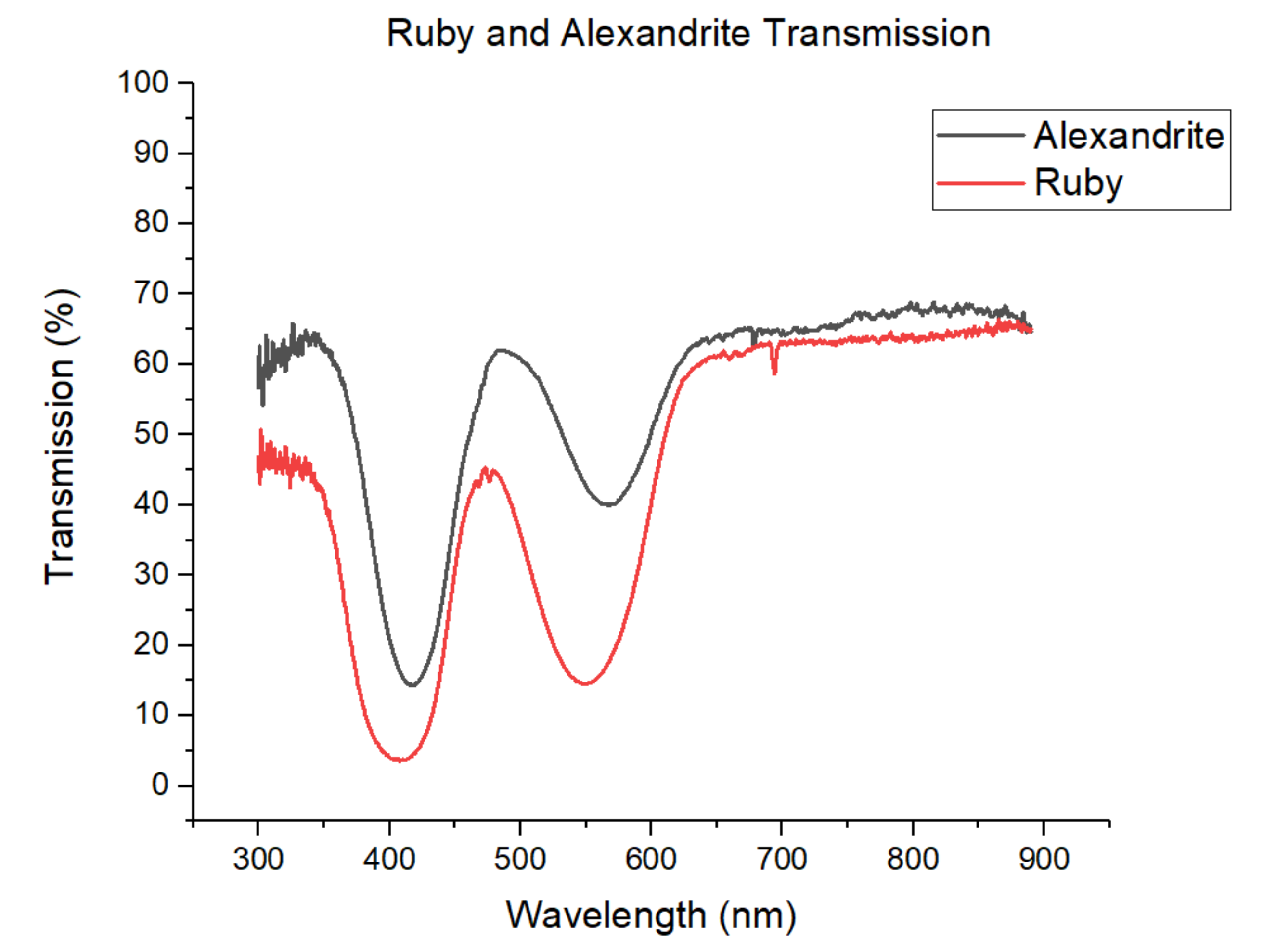


FIG. 9.9. Simplified energy level diagram of some of the low-lying energy levels of $3d^3$ ions in octahedral crystal fields. At $Dq/B \simeq 2.3$ the ^2E and $^4T_2$ levels cross. Above and below this value ions are said to be in high-field and low-field sites, respectively. The vertical lines correspond approximately to the cases of (a) ruby, (b) alexandrite ($BeAl_2O_4:Cr^{3+}$), (c) $KZnF_3:Cr^{3+}$ and $MgF_2:V^{2+}$. The shaded area represents the range of values of Dq/B found for Cr^{3+} ions in a typical borate glass; the ions can occupy both high-field and low-field sites in this glass.

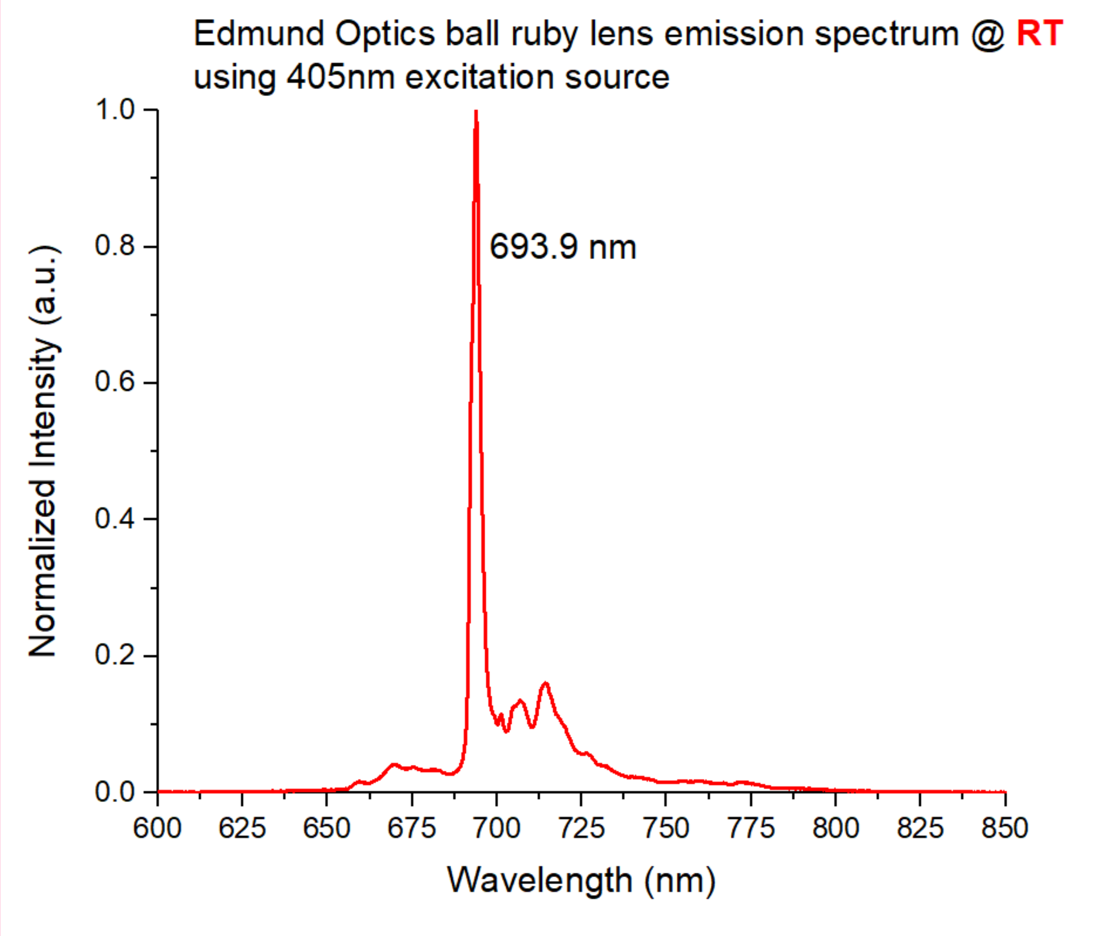
Ref 1 & 2



Scattering (fluorescence)

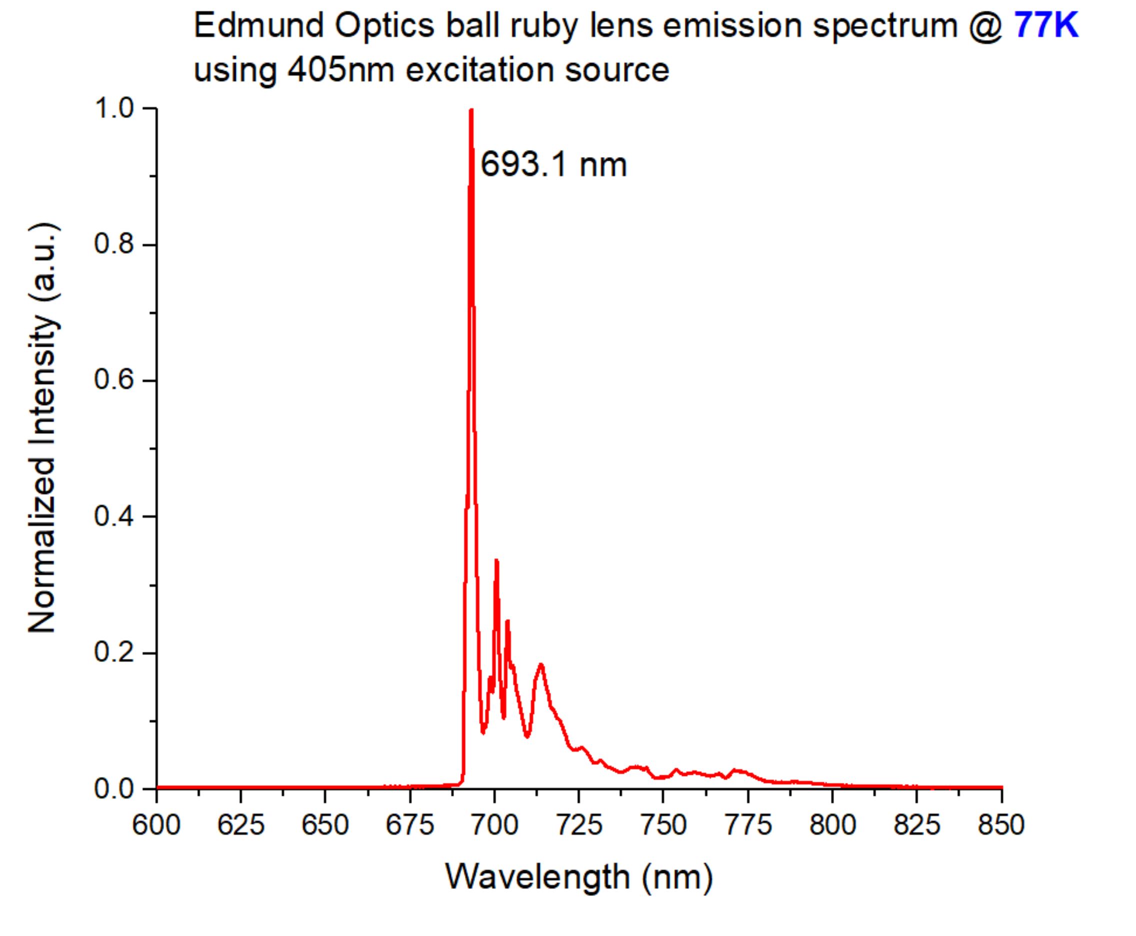
- Elastic or inelastic?
- Why isn't an ion in a crystal a sharp single line?

- sample – Edmund Optics ruby ball lens (~1-2% Cr^{3+})
- excite with 405nm laser pointer or diode laser



Temperature dependence

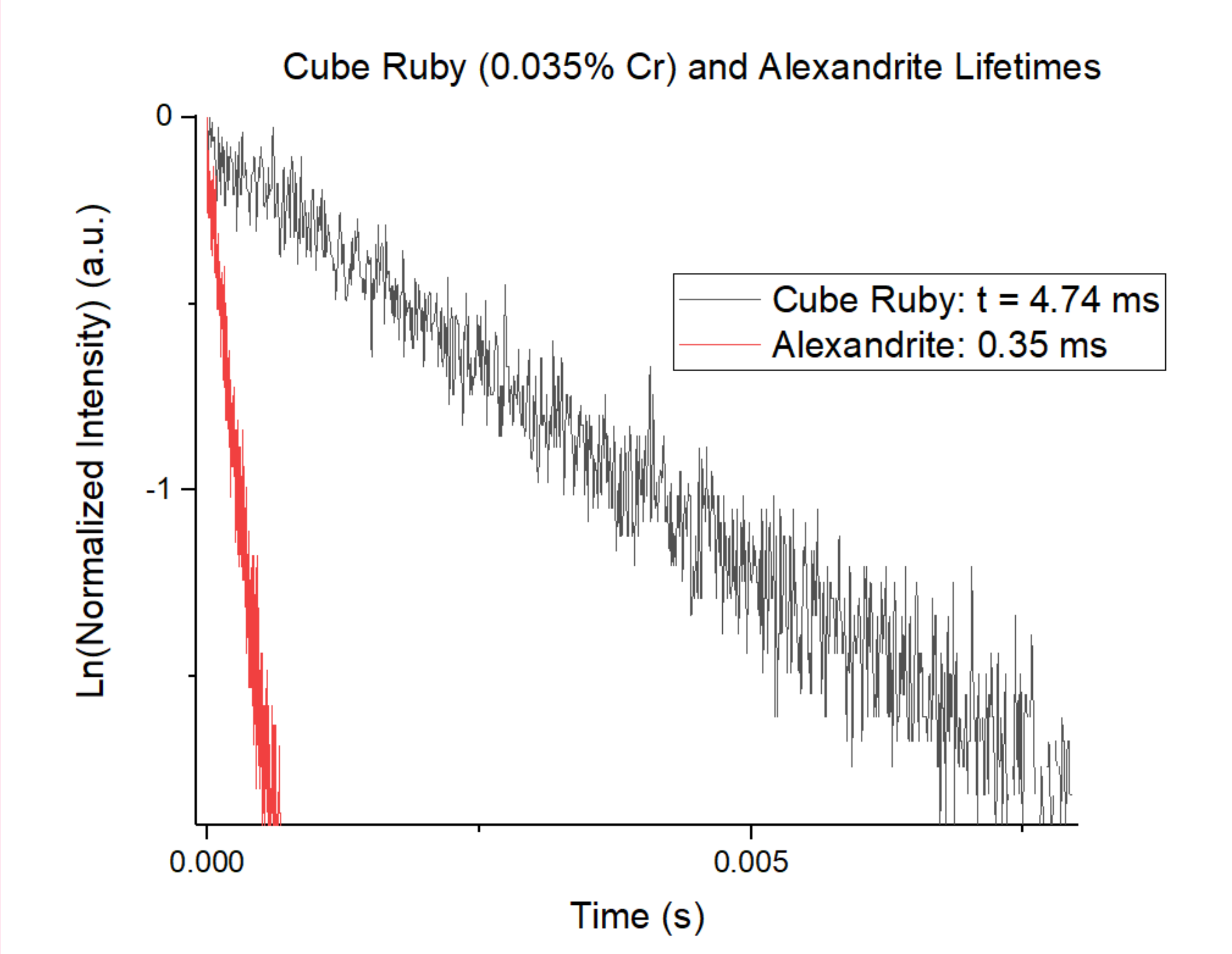
- line shift
- electron and lattice vibration coupling
- phonons
- phonon "sidebands"
- vibronics



Lifetimes of Ruby and Alexandrite

Equipment:

- pulsed diode laser
- digital oscilloscope
- photodiode or PMT



Making nanorubies: recipe

Combustion Synthesis for Al2O3:

Dopant 1 molar mass:	400.15
% Dopant 1 by mole:	0.30%
Dop. 1 sol'n molarity:	

Dopant 2 molar mass:	NA
% Dopant 2 by mole:	0.00%
Dop. 2 sol'n molarity:	0

Amount of Urea(g)	0.4

Moles of Urea:	0.00666
Moles of Al(NO3)3*9H2O:	0.002664

	Compound Amount:	Measured:
Urea	0.4000 g	0.4001 g
Al nitrate	0.9994 g	0.9998 g
Dopant 1	0.0032 g	0.0030 g
Distilled H20	1.7263 mL	1.7000 mL

Ingredients:

Sigma-Aldrich Compounds	Product:	Amount:	Price:	MW:
Urea	U5128-100G	100 g	$35.70	60.06 g/mol
Al-nitrate	229415-10G	10 g	$61.90	375.13 g/mol
Cr-nitrate	379972-5G	5 g	$65.20	400.15 g/mol
Distilled H2O	NA	NA	$0.00	18.02 g/mol

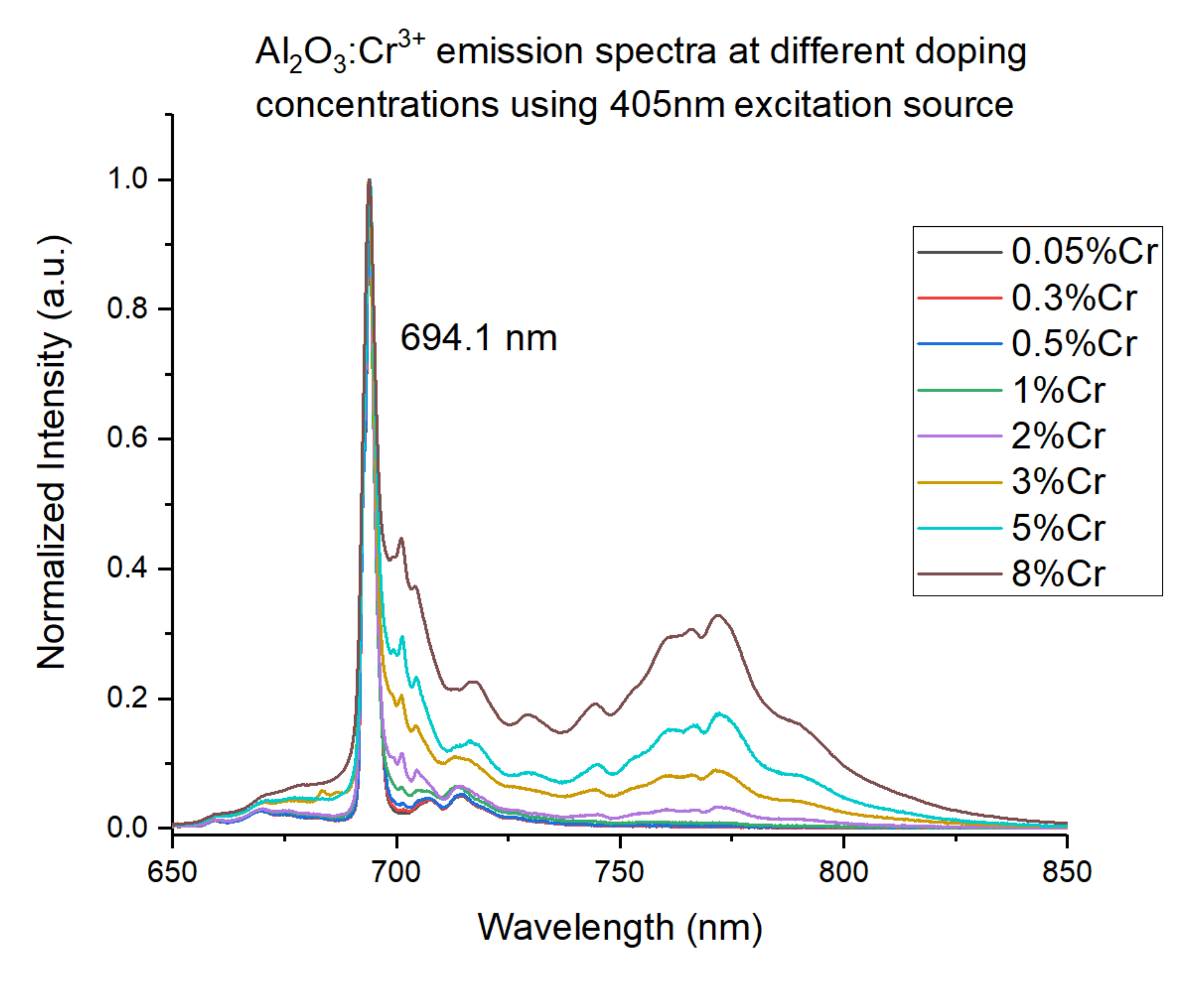
1) Furnace to 550°C.
2) Make mixture, stir for <30 min in ultrsonic stirrer or until all salts are disolved.
3) Mixture into ceramic crucible, into (already 550°C) oven for 1.5-2.5 min. (till combustion).
4) Remove and allow to cool.
5) Anything that is pinkish-white has completed combustion, and anything that is more of a yellowish green is a product of incomplete combustion, and will not glow.

*Entire process takes ~45 minutes

Concentration dependence

Lower energy components due to Cr^{3+} pairs and complexes coupled through spin-spin type exchange interactions

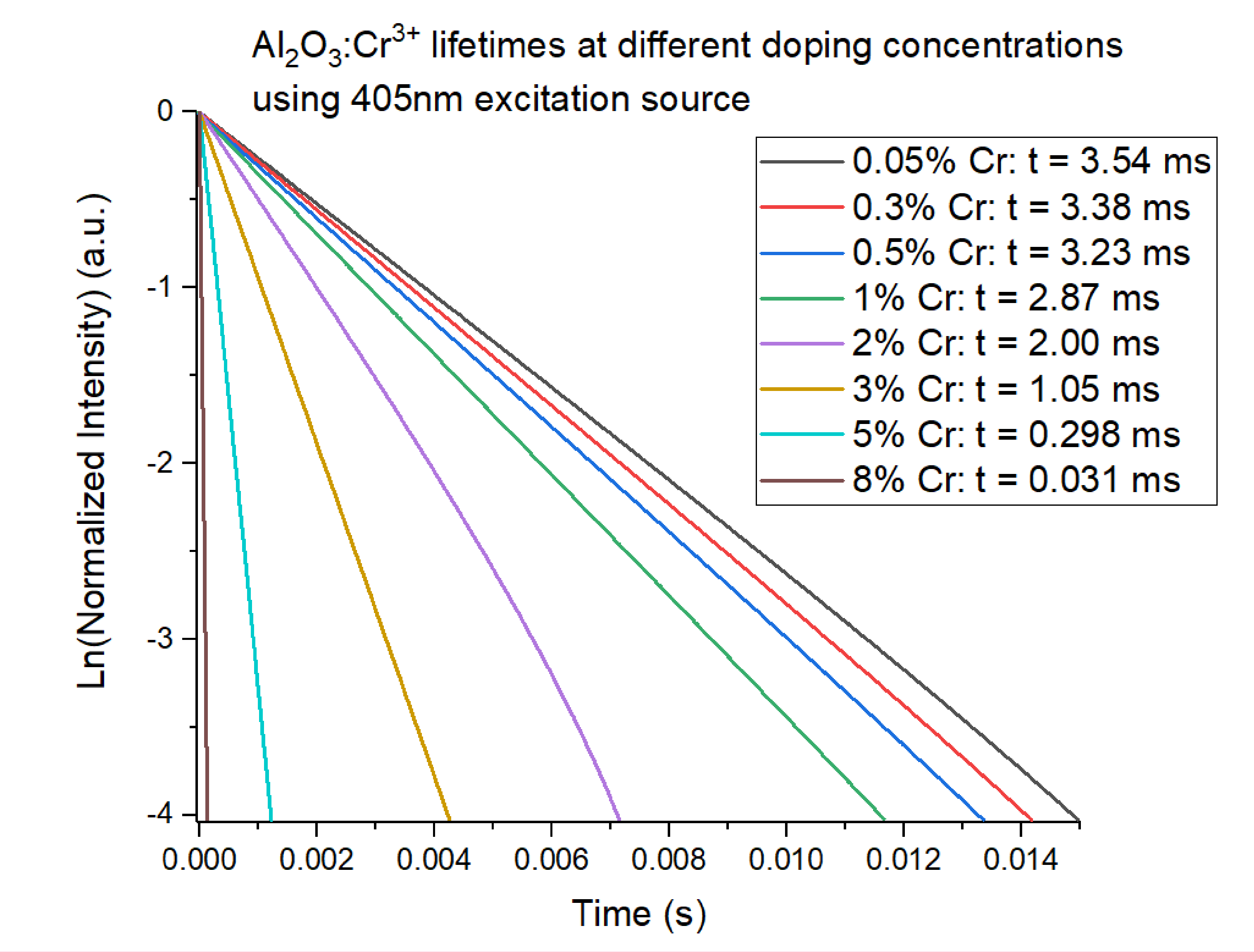
See Ref 3.



Nanoruby lifetimes

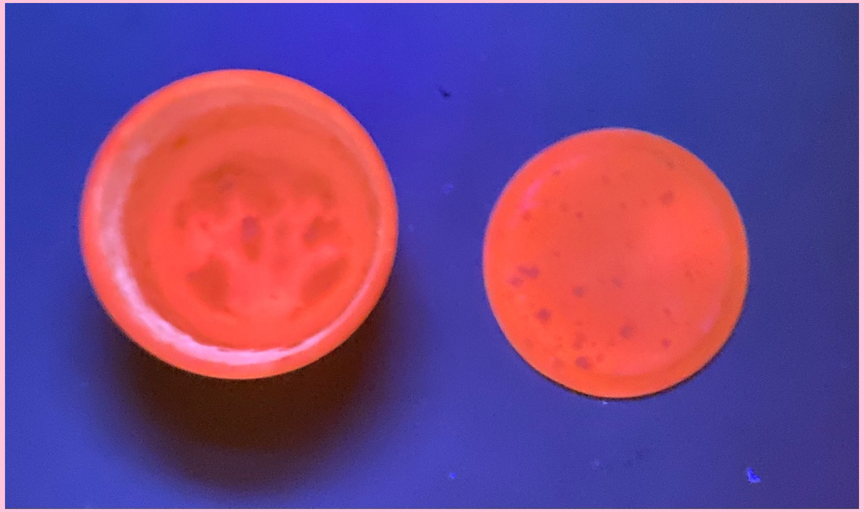
Probability of energy transfer between Cr^{3+} ions depends upon dipole-dipole interaction ($1/r^3$).

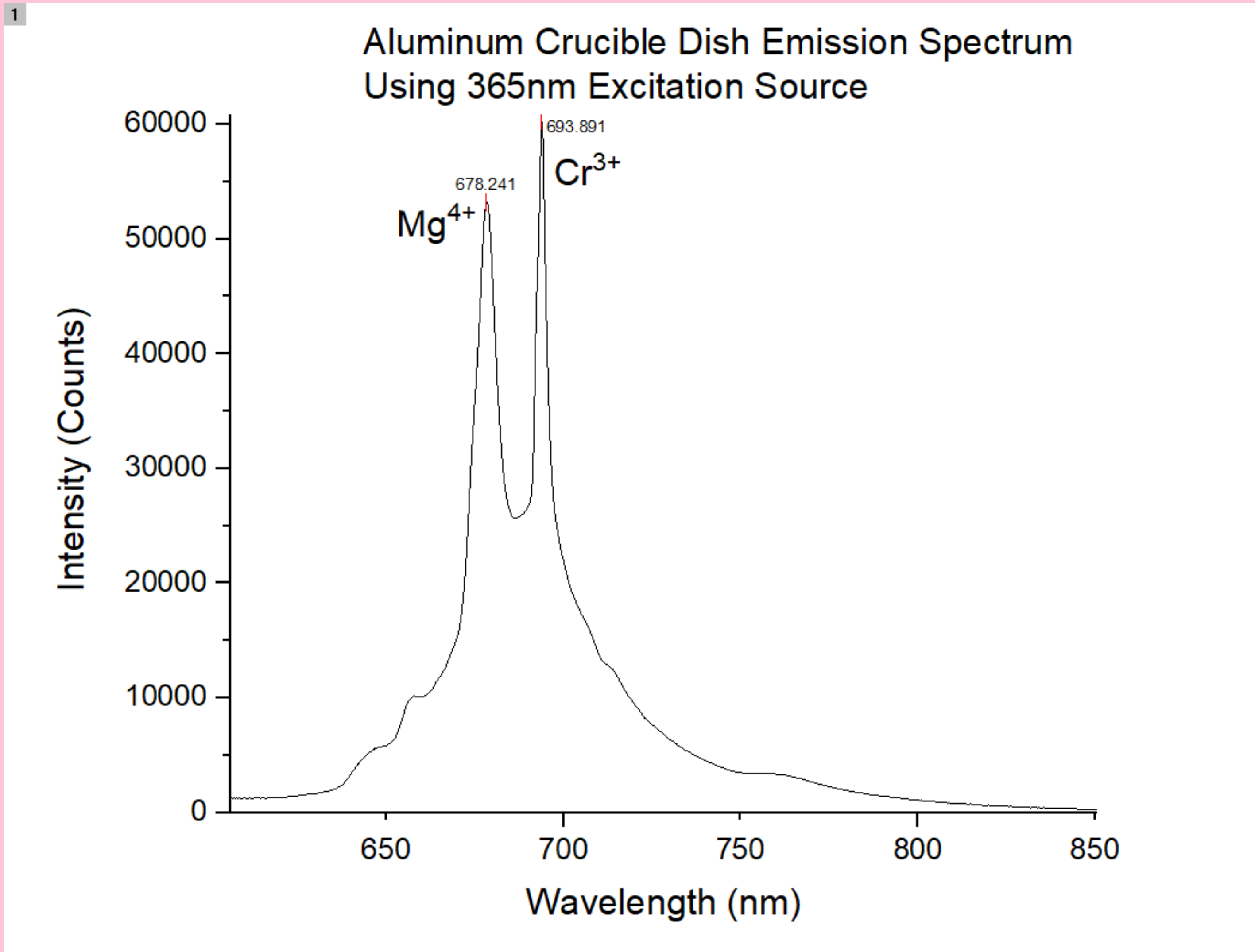
See Ref 3.



Y-axis data taken as the natural log of the exponential decay fits of the decay data

Alumina crucible fluorescence





References:

1. "Optical spectroscopy of transition metal ions in solids." *Optical Spectroscopy of Inorganic Solids*, by Brian Henderson and G. F. Imbusch, Clarendon Press, 1989, pp. 413-429.
2. "Luminescence centers of transition metal ions." *Phosphor Handbook, 2nd ed.*, edited by Shigeo Shionoya and William Yen, CRC Press, 2007, Chapter 3 Section 2, pp. 167-190.
3. "Spectroscopy at high dopant concentrations." *Optical Spectroscopy of Inorganic Solids*, by Brian Henderson and G. F. Imbusch, Clarendon Press, 1989, pp. 445-504.

Webpages with applicable material

Optical spectroscopy in ruby and hydrogen AAPT advlab Alpha Immersions wiki

A Low-Cost Time-Resolved Spectrometer for the Study of Ruby Emission, G.C. McBane, C. Cannella, and S. Schaertel, *J. Chem. Educ.* 2018, 95, 1, 173–177.

Spectroscopy of Ruby, D. Heiman, Northeastern U.