Colour and photoluminescence of Fluorite


http://www.mindat.org/min-1576.html
Some important terms:

Photoluminescence:

When a substance absorbs, then reemits photons.
This term is generally restricted to UV, visible and IR radiations.

Photoluminescence can be expressed as fluorescence and/or phosphorescence

Very similar phenomenon, but a phosphorescent mineral continues to emit radiations even after it stopped being exposed to the exciting source

Thermoluminescence: absorption of electromagnetic radiation et re-emission as light upon heating of the material
Fluorite - General mineralogical information

- Formula: CaF₂
- Space group: 4/m-32/m (isometric system)
- Unit cell measurements: a = 5.4631 Å, all angles = 90°
- Z = 4
- Density: 3.18 g/cm³
- Cleavage: perfect on {111}
- Hardness: 4
- Ca in cubic coordination
- Most common habit: cubic
- Common in hydrothermal mineral deposits
- Type of bonding: ionic
- Not very resistant to weathering

From Xtal Draw
Colour?

Fluorite is found in a wide variety of colour, going from colourless to blue, purple, green, yellow, brown, pink...

Rare-earth elements, thermal history, and the colour of natural fluorites (Naldrett et al. 1987)

What causes the different colours seen in different fluorite samples?

- Relationship between REE content and colour
- Effects of ionizing radiations from incorporated radioactive elements
- Thermoluminescence and thermal history
- Other factors
**Relationship between REE content and colour**

REE elements are quite large, they can replace some of the Ca in the crystal lattice.

Analysis of the amount of REE in Fluorite of different colours (but similar habit):

- The amount of Y was measured by atomic absorption spectroscopy.
- The amount of La and other REE elements were measured using neutron activation analysis methods.

There doesn’t seem to be any correlation between the amount of different REE present and colour of the sample!!

Table 1. Rare-earth element and yttrium content (ppm)

<table>
<thead>
<tr>
<th>Chondrites (Herrmann 1970)</th>
<th>F1 Colorless</th>
<th>F2 Brown</th>
<th>F3 Purple</th>
<th>F4 Yellow</th>
<th>F5 Blue</th>
<th>F6 Iridescent</th>
<th>F7 Green</th>
<th>F8 Purple</th>
<th>F9 Green</th>
<th>F10 Purple</th>
<th>F31 Green</th>
<th>F32 Yellow</th>
<th>F33 Green</th>
<th>Average</th>
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<tbody>
<tr>
<td>La</td>
<td>0.32</td>
<td>1.77</td>
<td>6.03</td>
<td>4.62</td>
<td>1.08</td>
<td>1.11</td>
<td>2.33</td>
<td>2.83</td>
<td>7.52</td>
<td>1.20</td>
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<td>2.70</td>
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<td>3.02</td>
<td>6.30</td>
<td>8.69</td>
<td>14.8</td>
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<td>0.47</td>
<td>0.81</td>
<td>1.10</td>
<td>3.38</td>
<td>0.48</td>
<td>4.28</td>
<td>0.86</td>
<td>0.72</td>
<td>1.78</td>
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<td>4.40</td>
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<td>Eu</td>
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<td>0.29</td>
<td>0.60</td>
<td>0.79</td>
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<td>4.00</td>
<td>1.04</td>
<td>0.92</td>
<td>1.40</td>
<td>1.95</td>
<td>6.23</td>
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<td>6.61</td>
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<td>3.72</td>
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<td>Tb</td>
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<td>0.18</td>
<td>0.72</td>
<td>0.72</td>
<td>0.12</td>
<td>0.13</td>
<td>0.30</td>
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<td>1.86</td>
<td>1.22</td>
<td>0.42</td>
<td>0.44</td>
<td>0.79</td>
<td>1.05</td>
<td>4.58</td>
<td>0.53</td>
<td>6.07</td>
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<td>0.070</td>
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<td>0.21</td>
<td>0.067</td>
<td>0.055</td>
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<td>0.21</td>
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<tr>
<td>Total</td>
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<td>52.6</td>
<td>38.3</td>
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<td>20</td>
<td>10</td>
<td>20</td>
<td></td>
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</tr>
</tbody>
</table>

Other test: Does a relative enrichment of a certain REE affect the colour of the sample?

Measurement of the ratio of a particular REE to the total REE content of sample compared with ratio of that same element to the total REE in chondrite.

Conclusion:

- Similar curve for all colour, general enrichment in light REE and depletion in heavier REE

- There doesn’t seem to be any correlation between colour and enrichment/depletion of REE, although colour tend to be more intense with higher REE content

**Ionizing radiation and colour**

Electromagnetic waves with high energy can take out electrons from atoms (ionization)

➢ Thought to give purple-blue colour to Fluorite

➢ The amount of radiation required (between 10kR and 250kR) naturally occurs in fluorite due to radioactive elements (K, Sm, Nb, Lu, Gd and but U) contributing to ionizing radiation.

➢ More intense radiation (above 250kR) can bleach the sample and cause structural damage.

➢ Ionizing radiation is most likely what gives rise to different colours in fluorites since the radiation due to radioactive decay is always present. If the colour was produced by a single radiation event, it would disappear quite rapidly.
When Ca$^{2+}$ is replaced by a trivalent REE in the crystal, the charge as to be balanced, this can be done by:

- adding a F$^{-}$ ion in a interstitial position
- substitute F$^{-}$ by O$^{2-}$
- Na$^{+}$ replacing Ca$^{2+}$ ...
“The colour of fluorite is initially produced by ionizing radiation that has removed an electron from a fluorine ion, or from an oxygen ion, the released electrons then having reduced trivalent REE ions to divalent REE ions, most of which absorb visible light” (Naldrett et al. 1987)

Therefore $F^-$ becomes $F^0$, which can then attract electrons, creating “traps”

Those “traps” are emptied as $T$ increase, leaving a hole
This hole can then take an electron from a divalent REE which becomes a trivalent REE in an excited state. When this trivalent REE reverts to a stable state, there is emission of light

According to studies made, lower temperatures give rise to red colour and higher temperature to purple colours, in other words the wavelength decreases with increasing $T$. At even higher temperatures, fluorite becomes colourless.

http://www.mindat.org/gallery.php?cform_is_valid=1&min=1576&cf_pager_page=2
Other causes of colour variability

- Change in condition as fluorite was crystallizing (temperature, composition of mother solution) can affect the growth pattern of the crystal, which can affect the colour.
- Pressure could also affect the colour
- Presence of colloidal size particles (typically 1 nanometre to 10 micrometres)

Blue John type fluorite: different absorption spectrum

http://www.mindat.org/min-698.html

The iridescence of some fluorites is thought to be due to the presence of colloidal size particles, which scatter visible light

Photoluminescence

Photoluminescence properties of a natural fluorite (Sidike et al. 2000)

- Study based on one fluorite sample from China, green with bluish-violet fluorescence under UV (fluorescence monitored at $\lambda=440\text{nm}$)
- Temperatures of 10, 80 and 300K

Photoluminescence is thought to be caused by the presence of trivalent REE or some divalent REE ($\text{Eu}^{2+}$, $\text{Yb}^{2+}$, $\text{Sm}^{2+}$, $\text{Tm}^{2+}$)

Photoluminescence spectra at 300K

Peak at 423nm,
Corresponds to emission band of $\text{Eu}^{2+}$ in synthetic fluorite crystal

Figure 4. The PL emission spectra of the natural fluorite at 300 K. Curves 1, 2 and 3 show the emission spectra under excitation on the C band at 339 nm, the B band at 308 nm and the A band at 228 nm, respectively. For the A, B and C excitation bands, refer to Figure 2.
Three bands observed:
- A-band at 228nm
- B-band at 308nm
- Wide C-band between 320-420nm

Results very similar to results for synthetic crystal containing Ce$^{3+}$ and smaller amount of Eu$^{2+}$
**Energy levels of Ce$^{3+}$ and Eu$^{2+}$ (in a cubic crystal)**

For both: Orbital splitting into two levels (in the excited state) $T_{2g}$ and $E_g$, separated by crystal field parameter $10Dq$.

For Ce$^{3+}$: splitting of energy level also at ground state. Two levels, $^2F_{7/2}$ and $^2F_{5/2}$. 

Sidike et al. 2000
The A-band (228nm) must come from the electronic transition from ground state $4f^7(8S_{7/2})$ to the excited state $4f^65d(T_{2g})$ of Eu$^{2+}$.

The B-band must be due to the transition from $4f(^2S_{5/2})$ to $5d(E_g)$ of the Ce$^{3+}$ ion.

The C-Band is thought to come from the transition between $4f^7(8S_{7/2})$ and $4f^65d(E_g)$ of Eu$^{2+}$.

Other band observed (other study) (Ce$^{3+}$)

At 185 nm: $4f(^2S_{5/2})$ to $5d(T_{2g})$.
For most divalent REE (except Eu$^{2+}$ and Yb$^{2+}$) the absorption spectra is located in the visible region. That implies that for most of them, fluorescence might be observed in the IR region.

Since visible fluorescence is observed, most of it must comes from then presence of trivalent REE or Eu divalent ions (emits fluorescence in visible spectrum)

Bluish-violet fluorescence of fluorite is due to the presence of Eu$^{2+}$ in the crystal structure (Ce$^{3+}$ transfer its energy to Eu$^{2+}$)