PYROPE-SPESSARTEINE GARNETS WITH UNUSUAL COLOR BEHAVIOR

By D. Vincent Manson and Carol M. Stockton

The study of garnets by GIA's Department of Research continues with a collection of 32 garnets that display a variety of hues and yet share a common tendency to show different colors under different sources of light. Even when very slight, the change of color is invariably greater than that encountered in other types of garnets. These unusual garnets proved to be composed principally of a variable mixture of pyrope (25-60 wt.%) and spessartine (20-56 wt.%), with considerable almandine (2-17 wt.%) and grossular (3-23 wt.%) also present. Their primary chemical distinction lies in their V₂O₃+Cr₂O₃ content, which is always in excess of 0.2 wt.%. In conjunction with their distinctive color behavior, these garnets may also be characterized on the basis of specific gravity and absorption spectrum.

ABOUT THE AUTHORS
Dr. Manson is director of research and Ms. Stockton is senior research gemologist in the Department of Research, Gemological Institute of America, Santa Monica, California.

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PREVIOUS STUDIES
The only types of garnets reported in the past that resemble any of the specimens in this study have been those that display a distinct change of color. Among these, two types have been observed: pyropes with high Cr³⁺ content (Hysingjord, 1971; Carstens, 1973; Amthauer, 1976); and stones composed principally of pyrope and spessartine with Cr³⁺ and V³⁺ present (Crowningshield, 1970; Jobbins et al., 1975; Schmetzer and Ottemann, 1979). Since the former have not, as yet, been...
observed in sizes sufficiently large for cutting into gems (most specimens measure less than 5 mm in diameter), they will not be included in this discussion. It is the latter types, which do occur in gem sizes and qualities, that interest us here.

The color-change gem garnet reported by Crowningshield (1970) was described as blue-green in daylight and purple-red in incandescent light, with a refractive index of 1.765 and a specific gravity of 3.88. The semiquantitative spectrographic analysis reported gave a chemical composition that we calculate to be mostly pyrope and spessartine (see table 1). Cr$_2$O$_3$ and V$_2$O$_3$ were detected in small amounts. In 1975, Jobbins et al. reported a small piece of rough color-change garnet that appeared greenish blue in daylight and magenta by tungsten illumination. This stone gave somewhat lower refractive index and specific gravity results than Crowningshield’s, but it also proved to be primarily a blend of pyrope and spessartine. V$_2$O$_3$ but not Cr$_2$O$_3$ was detected. However, new figures for both V$_2$O$_3$ and Cr$_2$O$_3$ in the same garnet were obtained later by Schmetzer and Ottemann (1979) in a study of vanadium-bearing garnets (again, see table 1). In this same study, Schmetzer and Ottemann also reported six other change-of-color garnets that were all primarily mixtures of pyrope and spessartine (again, see table 1), and that all contained both V$_2$O$_3$ and Cr$_2$O$_3$.

Absorption spectra in the visible-light range were obtained on the first-reported specimens by use of the hand spectroscope. Crowningshield (1970) found total absorption from 400 to 438 nm, three narrow bands around 465, 485, and 505 nm, and a broad region of absorption between approximately 555 and 595 nm. Jobbins et al. (1975) reported similar findings: complete absorption to about 436 nm, narrow bands at 460, 486, and 506 nm, and a broad absorption between 550 and 590 nm. Using a spectrophotometer, Schmetzer and Ottemann (1979) found the broad region of absorption to be centered around 568 to 576 nm in all the color-change garnets in their study. They correlated this broad band with the presence of Cr$^{3+}$ and/or V$^{3+}$. The spectra of three of the stones they examined also indicate the presence of narrow bands at approximately 407–412, 417–425,
431–435, 461–463, 505–507, and 527 nm, with a faint band at 694 nm. The first three bands are present within a larger region of strong general absorption. These results correlate with the spectral data reported earlier by Crowingshield and lobbins et al., adding only those bands that are too weak to be visible with a hand spectroscope and those that are masked (e.g., the shorter wavelengths) by an overlapping strong absorption region.

DATA COLLECTION

The stones selected for this study are those that exhibit color change between incandescent and daylight-equivalent illumination. The result is a collection of 32 garnets of various hues, including purple, red, orange, and yellow.

Refractive index, specific gravity, visible-wavelength optical absorption spectrum, color coordinates, and chemical composition were determined for each stone. The methods and instruments used to collect these data are the same as those described in the first article on the GIA garnet project [Manson and Stockton, 1981] with two exceptions. The first was in response to the potential significance of minor elements (such as chromium and vanadium) in the compositions of these garnets, as well as to the difficulty of accurately measuring small quantities of these elements by means of the microprobe. This led us to perform separate analyses on each stone, we felt that the averages of these analyses would provide reasonably accurate figures for the minor elements despite relatively large individual margins for error.

The second departure from our original methods of data collection involved the measurement of color with the GEM ColorMaster. In addition to the key color normally used to characterize the color of a gemstone, these garnets may display two additional colors in any single type of illumination. One is seen in the light that is reflected from the stone's interior (the "reflected" color), while another is visible when light is absorbed by the stone.

### TABLE 1

<table>
<thead>
<tr>
<th>Data 1</th>
<th>2a</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tr>
<td>Oxide composition</td>
<td>SiO2</td>
<td>TiO2</td>
<td>Al2O3</td>
<td>V2O3</td>
<td>Cr2O3</td>
<td>MgO</td>
<td>CaO</td>
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<td>Garnets studied</td>
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<td></td>
<td></td>
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<td>Schorlomite</td>
<td>38.36</td>
<td>39.02</td>
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<td>38.23</td>
<td>40.91</td>
<td>40.77</td>
<td>37.17</td>
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<tr>
<td>Andradite</td>
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<td>0.06</td>
<td>0.24</td>
<td>0.71</td>
<td>0.39</td>
<td>0.19</td>
<td>0.27</td>
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<td>MnO</td>
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<td>3.54</td>
<td>2.29</td>
<td>1.7</td>
<td>0.95</td>
<td>0.37</td>
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<tr>
<td>Cr2O3</td>
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<td>0.54</td>
<td>0.17</td>
<td>0.51</td>
<td>0.16</td>
<td>0.13</td>
<td>0.11</td>
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<tr>
<td>MgO</td>
<td>13.7</td>
<td>7.06</td>
<td>12.9</td>
<td>19.8</td>
<td>12.95</td>
<td>14.1</td>
<td>15.27</td>
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<tr>
<td>CaO</td>
<td>2.38</td>
<td>3.46</td>
<td>5.31</td>
<td>6.42</td>
<td>4.82</td>
<td>5.5</td>
<td>1.9</td>
</tr>
<tr>
<td>MnO</td>
<td>16.73</td>
<td>25.31</td>
<td>18.22</td>
<td>22.24</td>
<td>15.57</td>
<td>15.5</td>
<td>14.8</td>
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<tr>
<td>FeO</td>
<td>1.45</td>
<td>1.77</td>
<td>1.2</td>
<td>1.79</td>
<td>2.36</td>
<td>1.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Total</td>
<td>99.46</td>
<td>99.44</td>
<td>100.63</td>
<td>100.12</td>
<td>100.96</td>
<td>100.87</td>
<td>99.67</td>
</tr>
</tbody>
</table>

**End-member components**

| Schorlomite | 0.50 | 0 | 0.18 | 0.14 | 0.11 | 0.67 | 0.25 | 0.28 | 0.06 |
| Andradite | 0 | 0 | 2.46 | 1.53 | 0 | 0 | 0 | 0 | 1.12 |
| Mno2O3 | 1.16 | 1.07 | 2.57 | 1.15 | 0.36 | 1.27 | 0.87 | 1.8 | 0.33 |
| Uvarovite | 1.78 | 1.78 | 0.56 | 1.68 | 0.53 | 0.43 | 0.36 | 0.89 | 0.12 |
| Pyrope | 43.68 | 23.50 | 43.01 | 36.14 | 42.84 | 47.01 | 50.91 | 48.01 | 25.27 |
| Spessartine | 37.86 | 58.48 | 39.99 | 50.79 | 35.89 | 34.90 | 33.53 | 37.78 | 21.56 |
| Grossular | 4.38 | 7.66 | 11.37 | 6.36 | 12.64 | 13.81 | 4.56 | 4.06 | 3.57 |
| Almandine | 2.91 | 4.06 | 0.24 | 0 | 5.22 | 2.74 | 4.74 | 10.37 | 2.64 |
| R.I. | 1.76 | 1.75 | 1.75 | 1.75 | 1.75 | 1.75 | 1.75 | 1.75 | 1.75 |

1. These data are from Crowningshield (1970).
2. Data for garnets as described by Schmetzer and Ottemann (1979), excluding stones from Jobbins (no. 3) and Jobbins (no. 8).
3. The ranges found for the 32 stones examined in this study.
4. n.d. = not detected; n.r. = not reported.
transmitted through the stone (the "body" color). Since the ColorMaster provides both daylight-approximation and incandescent lighting for the specimens, color-change stones can be described under each condition. We therefore determined coordinates for each observable color (a maximum of three for daylight-equivalent and three for incandescent illumination). The coordinates of the two key colors and the two reflected colors were determined with the stones in the normal face-up position, and those of the two transmitted-light body colors were determined by immersing the stones in glycerine to reduce reflections.

DISCUSSION OF DATA

Physical and Optical Properties. The refractive indices and specific gravities of our collection of unusual garnets cover quite broad ranges: 1.740–1.773 and 3.75–3.99, respectively. For what would at first appear to be a heterogeneous group of specimens, this variability is not surprising. However, these ranges lie within the parameters that we found previously for "pyrope-spessartine" garnets, most of which are more-or-less orange in color (Stockton and Manson, 1982). A comparison of our results with the others provided in table 1 shows agreement with the properties observed by previous researchers.

Chemical Composition. The compositions of the 32 stones that we analyzed are consistent with those reported in previous studies (see table 1). Moreover, with the exception of V2O3 and Cr2O3 content, the compositions of those 32 specimens are comparable to those of the pyrope-spessartines discussed in a prior article in our series on garnets. However, the present collection is in certain ways different from those pyrope-spessartines described earlier.

The most readily apparent chemical characteristic of these garnets is their high V2O3+Cr2O3 content. Although either of these components can be less than 0.1 wt.%, together they always exceed 0.2 wt.%. By comparison, other pyrope-spessartine garnets never exceed 0.2 wt.% and usually contain considerably less (commonly 0 to 0.1 wt.%). When V2O3+Cr2O3 content is expressed in relation to FeO content—a third chemical component that affects garnet color—this distinction becomes obvious (figure 2).

As a whole, these unusual garnets can be described by the ranges of their major end-member components as follows: pyrope, 25–60 wt.%; spessartine, 20–56 wt.%; grossular, 3–23 wt.%; and almandine, 2–17 wt.% (figure 3). Specimen GIA-96A, which is notable for its greenish yellow color, also has the highest grossular content of any of the stones examined.

Absorption Spectra. The spectrophotometer indicates the presence of nine to 11 absorption bands in the visible range of these 32 garnets. Eight of these bands lie between 400 and 600 nm at the following approximate locations: 407, 421, 429, 461, 485, 503, 523, and 569 nm. All eight are present in all 32 of the stones (figure 4), although one of the bands is notably displaced in one specimen: The single greenish yellow stone cited above (GIA-96A) revealed a band at 455 nm instead of about 461 nm.

Between 600 and 700 nm, one or more of three absorption features may be resolved with the spectrophotometer. A pair of narrow bands sometimes occurs at about 672 and 688 nm, with the former being considerably weaker than the latter so that at times the 688 nm band appears alone. A third band is centered around 685 nm.
Garnets from this study

Pyrope-Spessartines from prior study

Figure 3. The distribution of major chemical components in our collection of unusual garnets can be seen in the number of stones that contain various amounts of the four principal garnet end members. For comparison, the distribution of the orange "pyrope-spessartines" has been included. Note that our present assortment generally contains more grossular and less almandine than the overall distribution contains.

and is considerably broader than the other two in the same region. When all three occur together, the narrower bands can be discerned as distinct features inside the broad absorption of the third band (figure 4).

Some of these absorption features can be observed with the hand spectroscope (figure 5). There is generally an absorption edge around 430 nm, below which all features are obscured by the strong absorption. The 461 and 569 nm bands are invariably visible. The 489 and 523 nm bands are usually observable, but the 503 nm band is less readily apparent. The 672 and 688 nm bands, especially the former, are usually too weak to be visible or are obscured by the absorption of the broad 685 nm band. Generally, there appears to be increasing absorption beyond 670 nm toward 700 nm.

Various sources have attributed absorption features in pyropes, almandines, spessartines, and garnets of intermediate compositions to certain elements and cations (see, for example, Amthauer, 1976; Manning, 1967 and 1972; Moore and White, 1972; Schmetzer and Ottemann, 1979). A compendium of these sources and our data suggests that the following assignments can be made: The 407, 421, and 429 nm bands are due to Mn$^{2+}$; the 461, 503, 523, and broad 685 nm bands to Fe$^{2+}$; and the 672 and 688 nm pair to Cr$^{3+}$. Some absorption features appear to represent indistinguishably close, overlapping bands that are related to more than one cation: The 421 nm band may also include a contribution from Cr$^{3+}$; the broad, strong 569 nm band is undoubtedly a combined effect of Cr$^{3+}$, V$^{3+}$, and Fe$^{2+}$.

Of the features that can be resolved with a hand spectroscope, only one absorption band appears to distinguish the spectra of these garnets from those of the pyrope-almandine series (see Manson and Stockton, 1981, and the sources cited.
Figure 4. These two representative spectra illustrate the variability of absorption features in our collection of 32 garnets. Both have major transmission regions between 430 and 550 nm and above 580 nm. Both also display all eight absorption bands below 600 nm, although in differing strengths. Above 600 nm, both spectra show two weak bands, at about 672 and 688 nm, while one has an additional broad region of absorption beyond 700 nm.

in the paragraph above). The band at about 485 nm, which can usually be observed in our present collection of specimens as well as in orange pyrope-spessartines and spessartines (unpublished data), is absent in stones of the pyrope-almandine series (usually red-orange to red-purple in color), which instead display a band around 473 nm.

Figure 5. These spectra demonstrate the range of absorption features that can be observed with a hand spectroscope for unusual garnets such as the stones discussed in this article. Spectrum A is that of a high pyrope-content specimen with weak color change, while spectrum B is from a high-spessartine and very high-vanadium-and-chromium stone with a strong change of color.

also display a different color when light is passed through the stone, as compared to internally reflected light from the same source. We refer to this latter phenomenon as “color shift.” Both of these phenomena contribute to the overall color appearance of our specimens.

Although change of color has been well studied (e.g., White et al., 1967; Schmetzer et al., 1980) and is generally well understood, we would like to briefly summarize the concept of color change. This phenomenon occurs when a material has an absorption spectrum in which two regions of the visible spectrum are transmitted while the rest is absorbed (see figure 4). Moreover, the wavelengths and intensities transmitted must be in proportion such that the spectral differences between day (or fluorescent) light and incandescent light cause one hue to be perceived in the former case and the other hue in the latter. Let us say, for a very simplified example, that fluorescent light contains more intensity in the green wavelengths than in the red, while incandescent light has exactly the reverse relationship. If a stone that transmits only green and red is exposed to fluorescent light, the greater intensity of green in this light source in conjunction with the stone’s own absorption characteristics results in a green color appearance. Conversely, the greater measure of red in incandescent light provides for perception of a red coloration.

Color shift, however, does not occur with a change in illumination but rather with the relative amounts of light [from a single source of illumination] that a viewer observes either [1] passed through or [2] internally reflected by a
Figure 6. A garnet pebble that exhibits four different colors, one each in (A) reflected fluorescent, (B) transmitted fluorescent, (C) reflected incandescent, and (D) transmitted incandescent light. Photos by Tino Hammid.

gemstone. The former condition reveals the stone's body color; the latter requires the viewer and illuminant to be on the same side of the gem so that the internal reflections (which represent the reflected color) may be observed. As yet, we have not been able to determine the optical or physical mechanism whereby this phenomenon occurs, but it apparently requires an absorption spectrum similar, although not necessarily identical, to that which produces a change of color.

The key color for these stones, as defined by the GIA colored-stone grading system, is the representative or characteristic color that can be seen through the crown facets. For any single light source, it is influenced by the reflected color, the body color, and the cut of the stone. If a stone changes color, then it has two such key colors (one each for incandescent and day or fluorescent light), two body colors, and one or more reflected colors. The magnitude of color change is usually greatest for body color, less for key color, and least for reflected color. In fact, a strong change in body color combined with a weak or nonexistent change in reflected color will result in only moderate change in the key color. Thus, the change-of-color phenomenon in garnets is not exactly the same as the "alexandrite effect," which has been described as the "color change of a solid from green or bluish green in daylight to red or reddish violet in artificial (incandescent) light" (Schmetzer et al., 1980). In the case of alexandrite itself, this involves a change of color due to selective absorption enhanced by pleochroism alone (White et al., 1967). For the unusual garnets in this study, however, it is due to selective absorption modified by color shift. Nonetheless, the
phenomenon in garnets fits the traditional definition for change of color, that is, "any stone that shows a difference in color from daylight to artificial (incandescent) light, caused by selective absorption" (Shipley, 1974).

The color description of our present collection was therefore more difficult than usual. Figure 6 illustrates the foregoing phenomena with an uncut stone that exhibits different reflected colors and body colors in incandescent and daylight-equivalent illumination. It should be noted that different sets of illuminants may either enhance or reduce the degrees to which these phenomena are observed in various stones. Color shift, for instance, is strongest in fluorescent light as compared to daylight and incandescent light.

CONCLUSIONS
In a previous paper (Stockton and Manson, 1982), we used the term pyrope-spessartine to describe uncut stones that exhibit different reflected colors and body colors in incandescent and daylight-equivalent illumination. It should be noted that different sets of illuminants may either enhance or reduce the degrees to which these phenomena are observed in various stones. Color shift, for instance, is strongest in fluorescent light as compared to daylight and incandescent light.

REFERENCES