UNSTABLE RADIATION-INDUCED YELLOW-GREEN COLOR IN GROSSULAR GARNET

By Kurt Nassau, George R. Rossman, and Darwin L. Wood

Although conventional wisdom has been that irradiation will not alter the color of garnets, exposure of some colorless to pale-hued African grossulars to either ^{60}Co or ^{137}Cs gamma rays turns them light yellow-green. The resulting color is unstable and fades within hours to days in sunlight, and within weeks in the dark. The spectra of the radiation-enhanced garnets differ from those of similar-appearing naturally colored grossulars. In the dark, the irradiation-related absorption features undergo two stages of fading: an initial period of relatively rapid fading, followed by a longer period of slow fading. In daylight, a single rate of even faster fading is observed.

The colors of various gemstones can be changed by irradiation procedures. Some irradiation-enhanced materials, such as blue topaz and certain colored diamonds, are significant items of commerce. Other gems, including garnets, are considered to be unaffected by irradiation. We now report that some pre-

dominantly colorless to pale yellow-green grossular specimens from various sources in East Africa turn light yellow-green on exposure to gamma rays. The colors produced in these garnets by irradiation are unstable, fading after some hours to days in daylight, or after days to weeks in the dark.

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MATERIALS AND METHODS

In our initial survey, more than 100 colorless to pale-colored grossular specimens were exposed to 20 Mrads (million rads) of cobalt-60 (^{60}Co) gamma rays to determine if radiation would produce a significant change in color. The samples consisted of both (1) crystal fragments and rough pebbles 3-10 mm in longest dimension, and (2) faceted stones 3-10 ct in weight. Canadian, African, and unknown sources were represented in the samples, which ranged from colorless to pale shades of yellow, brown, green, and orange. Samples from only a few localities, all in Africa (reportedly Kenya, Tanzania, and Zimbabwe), were changed from predominantly colorless to pale yellow-green to a light yellow-green (as determined using ISCC-NBS color terminology; Kelly and Judd, 1976).

Subsequently, we chose an additional 33 radiation-sensitive grossular garnets that were reportedly from the Lelatema Hills, Tanzania, for detailed examination. These samples were originally colorless to pale yellow-green pebbles as large as 1 cm in diameter. They were selected from lots of rough provided by a number of dealers in 1986 and 1987. The same lots contained other pale yellow-green to light yellow-green, as well as pale orange-yellow to moderate orange, garnets that did not change color on irradiation. Twelve of the 33 samples were irradiated with gamma rays from cesium-137 (^{137}Cs , at 7 to 130 Mrads) and the rest with gamma rays from ^{60}Co (20 Mrads).

All radiation-sensitive samples changed to light yellow-green, and all showed essentially the same optical absorption spectrum, regardless of the type of radiation. However, all of these stones faded back to their original colors after some hours to days in daylight. In fact, fading occurred even in the dark, but required several days to weeks.

A search of the literature and inquiries with gemologists turned up no previous instances of radiation-induced change in the colors of any types of garnets, and only one report of heat-induced change in color in some rhodolite garnets (Nassau, 1984). Therefore, the radiation-induced change in color we observed in these grossulars appears to represent the first challenge to the generally accepted view that all members of the garnet group are color stable. To learn more about this new phenomenon in grossular, we proceeded to conduct additional experiments to establish the spectroscopic and fading properties of these stones.

COLOR, SPECTROSCOPY, AND IRRADIATION BEHAVIOR

Detailed spectroscopic examinations were performed on a 12-mm-long, 1.52-gram yellowish gray specimen from Kenya (M40868, Royal Ontario Museum [ROM], Toronto, Ontario, Canada; figure 1, left) that had one of the greatest changes in color on irradiation (as represented by figure 1, right). Additional spectra were obtained from four radiation-sensitive grossulars (two colorless, one greenish white, and one yellowish white) from the Lelatema Hills. We recorded the ultraviolet, visible, and near-infrared spectra of these samples before and after irradiation, as well as the spectra of four of the naturally colored pale yellow-green and light yellow-green grossulars that did not respond to irradiation.

Prior to irradiation, the spectra of the colorless gar-

Figure 1. The most extreme change in color produced by this irradiation experiment was observed in these grossular specimens from Africa. Left: a 12-mm-long, 1.52-gram crystal (ROM specimen M40868) in its naturally yellowish gray state. Right: a similar specimen after exposure to 20 Mrads of ^{60}Co radiation.

nets showed essentially no absorption in the visible region. The light-colored garnets that did not respond to irradiation showed a weak feature due to vanadium (V^{3+}) at 610 nm (figure 2). This feature is also found, at greater intensity, in the spectra of intense green vanadium grossulars (tsavorites) from the Tsavo region of Kenya and Tanzania (Schmetzer and Ottemann, 1979). In addition, three weak but sharp features at 409, 422, and 431 nm were superimposed on the poorly resolved 425-nm vanadium band of the unresponsive samples. These features are from manganese (Mn^{2+}) substituting for calcium, and they correspond to the main Mn^{2+} features observed in spessartine garnet (Moore and White, 1972). The vanadium and manganese features were also present (but at much lower intensity) in the spectra of the weakly colored radiation-sensitive garnets. The spectra of all these garnets also showed narrow bands near 1400 nm attributed to OH^- groups in the crystal structure, which are commonly found in grossulars (Rossman and Aines, 1991). This particular grouping of narrow bands has only been observed in grossular garnets from East Africa.

After irradiation, the four garnets that changed to a light yellow-green exhibited features not found in the naturally colored light yellow-green samples (again, see figure 2). The radiation-induced color derives from a steeply rising absorption in the blue region of the spectrum that produces a yellow color, and a trans-

Figure 2. Significant differences can be seen in these spectra of two yellow-green grossulars, one of stable color and one that changed color on irradiation (plotted for 0.433 cm thickness). Solid line: a naturally pale yellow-green garnet with stable color. Dashed line: sample M40868 (ROM) from Kenya immediately after 20 Mrads of ^{60}Co gamma ray irradiation. The spectra of ^{137}Cs gamma-ray irradiated grossulars from the Lelatema Hills, Tanzania, are essentially identical to that shown by sample M40868.

mission window near 560 nm that adds the green component. We do not know the detailed origins of the absorption features at 654 and 926 nm that define the transmission window in the spectra of the garnets that responded to irradiation, but we recognize that they are distinctly different from those of tsavorite. Although several manganese-containing minerals owe their radiation-induced colors to oxidation of Mn^{2+} to Mn^{3+} , the spectra of our irradiated grossulars differ from the spectra of synthetic garnets prepared with known amounts of Mn^{3+} in the Al site (Frentrup and Langer, 1981).

The Lelatema Hills garnets occur in the crystalline limestones and gneisses of the Mozambique Belt (Key and Hill, 1989). The electron microprobe analysis of a representative colorless radiation-sensitive Lelatema grossular (table 1) indicates that its composition is close to pure end-member grossular. X-ray fluorescence (XRF) analyses revealed only minor differences between a colorless sample that became light yellow-green on irradiation and a naturally light yellow-green sample that did not change on irradiation. Unlike the radiation-sensitive colorless sample, the naturally light yellow-green garnet had a trace of

chromium, as well as twice as much Mn and 1.5 times as much Ti and Fe.

Schmetzer and Bank (1982) described a pale yellow-green grossular from this same locality. The chemical composition and optical spectrum of their garnet were similar to those of our specimens, as represented by the naturally light yellow-green sample in figure 2.

FADING DYNAMICS

After irradiation, the spectrum of the initially yellowish gray ROM grossular from Kenya was measured at various times as the radiation-induced features (and related color) decayed in the dark. The same stone was then re-irradiated and its spectrum was again measured as it decayed in daylight while taped to an east-facing window in Murray Hill, New Jersey, in April. The dynamics of fading were then analyzed on the basis of the intensity of three features of the absorption spectra, specifically, changes in the absorption maxima at 926 nm and 654 nm and in the absorption edge at 454 nm.

When the results were plotted as a function of time, it was evident that, in darkness, the radiation-related absorption features first faded relatively quickly (short-term decay), but then graded into a longer period of slower fading (long-term decay; figure 3). Because the points lie fairly close to straight lines in these plots, it is possible to reduce the results to a mathematical formula from which can be determined the rates at which each of the radiation-induced

TABLE 1. Chemical composition of a representative nearly colorless grossular from the Lelatema Hills, Tanzania, that turns yellow-green on irradiation.^a

Oxide	Weight %	Formula proportion
NaO	0.00	0.00
MgO	0.36	0.04
Al ₂ O ₃	22.23	1.97
SiO ₂	39.76	2.99
CaO	36.75	2.96
TiO ₂	0.42	0.02
V ₂ O ₃	0.07	<0.01
Cr ₂ O ₃	0.08	<0.01
MnO	0.20	0.01
Fe ₂ O ₃	0.13	0.01
Total	100.00	

^aThe formula proportions are based on 12 oxygens. Electron microprobe analysis conditions: 15 keV, 50 nA. David R. Bell (California Institute of Technology, Pasadena, California) analyst.

Figure 3. Experimentation revealed the dynamics of fading of the irradiation-induced color for the ROM (M40868) grossular specimen in the dark. Part A: the slow component of fading in the dark, with a scale of hours along the horizontal axis. Part B: the fast initial decay in the dark (with a scale of minutes for the horizontal axis), an expansion of the first portion of curve A which lies above the slow component straight line. The vertical axis is the change in absorbance at 926 nm during fading. The three different symbols are for three cycles of irradiation and fading; the consistency of the results throughout these three cycles demonstrates the reproducibility of this experiment.

absorption features decayed as the color faded. The time in which each related absorption feature decayed to half its intensity as the color faded in darkness was 172 hours for the slow component, and 74 minutes for the fast component. For each of the radiation-induced absorption features measured, approx-

imately 58% disappeared with the fast component and 42% with the slow component. In daylight, the rate of fading was considerably faster and involved a single component with a half-intensity-loss time of 12.6 minutes.

The values for the fading constants were approximately the same for the three wavelengths measured, which suggests that only one color center is involved in the radiation-induced color. Although the nature of the color center has not been determined, it is likely that it is present only at very low concentrations. After fading, either in the dark or in daylight, the intensity of absorption was essentially the same as before irradiation, so the coloration due to irradiation was completely reversed. Visual inspection indicated that the same reversibility of the radiation-induced coloring applied for all samples, but with different saturation and decay times characteristic of each particular crystal.

CONCLUSION

It has been determined that some garnets, specifically some colorless to pale-hued garnets from various localities in East Africa, will turn light yellow-green when exposed to as little as 7 Mrads of gamma rays. Such stones, however, will fade to their original colors within hours to days in daylight and within two months in the dark.

Because they fade so rapidly, radiation-colored grossular garnets should not normally be encountered in commerce, since they would have to be offered for sale immediately after irradiation. Any confusion with similar naturally colored garnets could easily be eliminated by exposing the questionable material to strong light (e.g., sunlight or a 100-watt lamp placed about 25 cm from the sample) for a few hours, or merely by holding the stones in the dark for two to three weeks.

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