Colorless and Green Grossularite From Tanzania

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Introduction

When the original East African finds of transparent green grossularite were made in the late sixties, the excitement created by this new gem overshadowed the simultaneous finds of colorless, yellow, and golden grossularite. All of these varieties were discovered in excellent gem quality. Dr. H. Bank, in 1968, was the first to describe colorless grossularite.(1) The green variety was promotionally introduced to the public by Tiffany & Co. in September, 1974, under the name "tsavorite."(2) But the other varieties received no special names. Tsavorite was named after the Tsavo National Park, a park in Kenya located near the discovery site in Tanzania. Even though tsavorite has received widespread recognition and acceptance, information in the literature on this green variety is limited.(1 thru 11) Literature references on the other varieties are frequent but very limited in content.(1,2,4 thru 12)

Discussions with a number of dealers who have bought and sold large quantities of Tanzania and Kenya grossulars, and who have subjectively estimated the relative quantities of the various varieties of grossularite, lead to these conclusions:

Yellow or golden grossularite is substantially more rare than green grossularite, and colorless grossularite is the rarest of all.

Furthermore, according to these dealers, all colorless grossularite is from finds in Tanzania. No more than ten cut colorless grossulars in excess of four carats are known to exist, none larger than eight carats. All or most of these stones are in the possession of private collectors. It is noteworthy that even the Smithsonian Institution by May 1978 did not have a colorless grossular on display. A reasonable estimate is that there are about forty stones ranging from two to four carats and a few hundred between one and two carats. The total weight of the stones below the size of one carat should be about six-hundred to eight-hundred carats.

We were fortunate to acquire a large number of cut East African gemstones for examination. All were reported to be grossulars and to have been found in 1968 and without a doubt from the early finds in Tanzania. They were machine cut and in a variety of colors. Some were pure colorless. All were transparent and of excellent gem quality. The examinations presented here were restricted to stones which were pure colorless or green. The green stones had various intensities ranging from near colorless with only a touch of green, through medium green, to deep green.

Our main objective was to determine the characteristics of the colorless stones, so that it could be verified that they were in fact colorless grossulars. Such information on the Tanzania colorless grossulars was not in the literature. Another objective was to better understand the cause of green color in grossularite.

Colorless Defined

The colorless and near-colorless gemstones were color graded against a GIA-Graded Diamond Master Set. Such grading presented no difficulties, even though the gemstones tended to have greenish tints and the diamonds of the diamond master set, yellowish tints. During the color grading of a great number of stones, consistent results were always obtained by different gemologists working independently.

The best GIA grade found among hundreds of small stones evaluated was G/H. And the best GIA grade found among the many stones over one carat was *I*. Typically, the GIA grade for a stone was K or L. We classify an N grade and grades of darker tones as near colorless. Even with a small brilliant cut, an N rated gem is noticeably colored to the naked eye.

Many dealers offer as colorless grossulars, stones that will grade between O and Z. In fact, all Kenya "colorless" stones we have seen and graded have been darker than O with clearly observable green or other tints. This may be why most prominent dealers claim that all colorless grossulars come from Tanzania despite the fact that in the literature there are references to colorless grossularite from Kenya, Canada, California, and Mexico.[2,5,9,11]

Chemical Analyses

Three colorless gemstones and one near-colorless gemstone were chemically analyzed by the nondestructive technique of X-ray energy spectrometry (XES). Their GIA grades were G/H, I, M, and O, respectively. Twelve tsavorites which had been selected to form a color suite with colors ranging from very light green to deep green, in small increments, were also chemically analyzed. All stones were brilliant cut and about 3 mm in diameter.

We used a Jeol Electron Microscope Model 100-C with a Kevex-Ray Model 5100 Energy Spectrometer for the analyses. This Kevex 5100 system identifies and provides a quantitative analysis of the chemical elements of a sample by measuring in the spectrum the dispersive X-ray energy that is a unique characteristic of each element. The X-ray spectrum is induced in the sample by placing it in the electron microscope and bombarding the sample with electrons. For accuracy of chemical composition, tsavorite, calcium carbonate, and some high-purity oxides were used as comparative standard. It is recognized that oxygen and lighter elements cannot be detected by this method. Therefore, it was assumed that oxygen was present

TABLE I
CHEMICAL COMPOSITION OF GROSSULARS
(X-Ray Energy Spectroscopic Analyses)

Sample No.	Weight Percent *									Color **
	CaO	Al_2O_3	SiO_2	MgO	TiO_2	MnO	FeO	Cr_2O_3	V_2O_3	
1	38.5	21.2	39.7	0.1	0.3	0.1	0.1	ND***	ND	Colorless, G/H
2	38.0	20.9	40.3	0.4	0.2	0.1	0.1	ND	ND	Colorless, I
3	39.7	19.9	39.5	0.1	0.4	0.2	0.1	ND	0.06	Colorless, M
4	32.3	22.8	43.3	1.0	0.3	0.1	0.1	ND	0.05	Near Colorless, 0
5	35.1	21.3	41.9	0.9	0.4	0.1	0.1	0.09	0.10	VL Green
6	33.9	22.4	42.1	0.9	0.4	0.1	0.1	ND	0.09	L Green
7	34.5	21.5	42.8	0.5	0.3	0.2	0.1	ND	0.11	L Green
8	34.5	20.5	43.0	0.3	0.2	0.6	0.1	0.09	0.7	M Green
9	34.8	21.7	41.6	0.1	0.3	0.4	0.03	0.06	1.0	MD Green
10	33.6	21.6	42.2	0.4	0.4	0.6	0.1	0.09	1.0	MD Green
11	33.7	21.1	42.5	0.7	0.2	0.5	0.04	0.10	1.1	MD Green
12	35.5	20.5	41.9	0.4	0.2	0.3	ND	0.02	1.2	MD Green
13	34.5	20.5	42.5	0.3	0.3	0.5	0.1	0.12	1.2	MD Green
14	34.6	21.0	42.0	0.3	0.2	0.4	0.03	0.14	1.4	D Green
15	34.9	20.5	41.9	0.4	0.3	0.4	0.1	0.15	1.4	D Green
16	36.3	20.6	40.3	0.2	0.2	0.2	ND	0.10	1.5	D Green

* Ideal grossular is: 37.36% CaO, 22.63% Al_2O_3, 40.01% SiO_2.

** Grossulars are ranked according to GIA diamond color grade and depth of green color; VL = Very Light; L = Light; M = Medium; MD = Medium to Deep; D = Deep.

*** Not Detectable

in such amounts as to form perfect metal oxides, and that elements of atomic number less than oxygen were not present.

The determined chemical compositions of all gemstones, ranked according to color grade or intensity of green color, are given in *Table I* in terms of oxide weight percentages. Their chemical compositions in terms of the number of metal atoms per twelve oxygen atoms are given in *Table II. Table II* is a convenient way to compare the measured chemical compositions of the stones with that of colorless, ideal grossularite. Colorless, ideal grossularite has a stoichiometric formula of $Ca_3 Al_2 (SiO_4)_3$, indicating that there are three calcium atoms, two aluminum atoms, and three silicon atoms for every twelve oxygen atoms. As is customary, it was accepted when constructing *Table II* that magnesium, manganese and iron replace calcium; that chromium and vanadium replace aluminum; and that titanium replaces silicon. There is doubt that this can be applied strictly.(13,14) However, considering the low concentrations of these impurity elements, the results would not be significantly different.

The chemical analyses showed that the chemical compositions of the colorless or near-colorless gemstones were similar to those of the tsavorites and very close to the calculated, theoretical composition of colorless, ideal grossularite. Sample No. 1 and Sample No. 2, the two most colorless stones, were found to be calcium-aluminum silicate of 99.6% and 99.5% purity, respectively. Colorless Sample No. 3 had a purity of 99.4%. These purities were all weight percentages calculated from the chemical compositions, assuming that there were twelve oxygen atoms to every eight metal atoms. We recognized that the oxygen atoms associated with the impurity metal atoms were not impurity oxygen atoms but oxygen atoms of the basic, ideal crystal.

The X-ray energy spectrum of colorless Sample No. 2 is shown in *Fig. 1.* For comparison, the X-ray spectrum of tsavorite with a deep green color is shown in *Fig. 2.* The similar nature of the silicon, aluminum, and calcium peaks of the colorless gemstone and tsavorite may be seen by comparing *Fig. 1A* with *Fig. 2A* between 0.5 and 3.5 KeV. In *Figs. 1B* and *2B* the 2.8 to 7.9 KeV range is magnified to show (a) the absence of vanadium and chromium in the colorless gemstones, (b) the vanadium and chromium peaks in the tsavorite, and (c) the lower manganese and iron peaks in the colorless gemstones.

The statement is often made that pure or nearly pure garnets do not exist in nature. However, the colorless grossulars we examined are very close to the pure end member grossularite. They are probably as pure a grossularite as can be found in a natural deposit. The purest grossular previously reported in the literature had a purity of 98.9%.(3) However, the color of this stone was pale yellowish green rather than colorless. This is in agreement with the lower purity observed. We calculated the purity of this grossular from the reported chemical composition and used the same assumptions as before. The reported

TABLE II
NUMBER OF ATOMS PER 12 OXYGEN ATOMS IN GROSSULARS *

Elem.	Sample No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Ca	3.10	3.06	3.20	2.60	2.82	2.73	2.78	2.79	2.80	2.72	2.72	2.87	2.79	2.80	2.83	2.93
Mg	0.01	0.04	0.01	0.12	0.10	0.10	0.05	0.04	0.02	0.04	0.08	0.04	0.03	0.03	0.05	0.03
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.03	0.04	0.04	0.02	0.03	0.03	0.02	0.02
Fe	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	ND	0.01	0.00	0.00	ND
	3.13	3.12	3.23	2.74	2.94	2.85	2.86	2.87	2.85	2.81	2.84	2.93	2.86	2.86	2.90	2.98
Al	1.88	1.86	1.78	2.02	1.89	1.98	1.90	1.82	1.92	1.92	1.87	1.82	1.83	1.87	1.82	1.84
V	ND	ND	0.00	0.00	0.01	0.01	0.01	0.05	0.07	0.06	0.07	0.07	0.07	0.08	0.09	0.09
Cr	ND	ND	ND	ND	0.01	ND	ND	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01
	1.88	1.86	1.78	2.02	1.90	1.99	1.91	1.88	2.00	1.99	1.95	1.89	1.91	1.96	1.92	1.94
Si	2.99	3.02	2.97	3.22	3.14	3.14	3.21	3.24	3.13	3.19	3.20	3.16	3.22	3.17	3.17	3.07
Ti	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01
	3.00	3.03	2.99	3.24	3.16	3.16	3.23	3.25	3.15	3.20	3.21	3.18	3.23	3.18	3.18	3.08

Ideal grossularite: Ca = 3 atoms; Al = 2 atoms; Si = 3 atoms; 0 = 12 atoms.

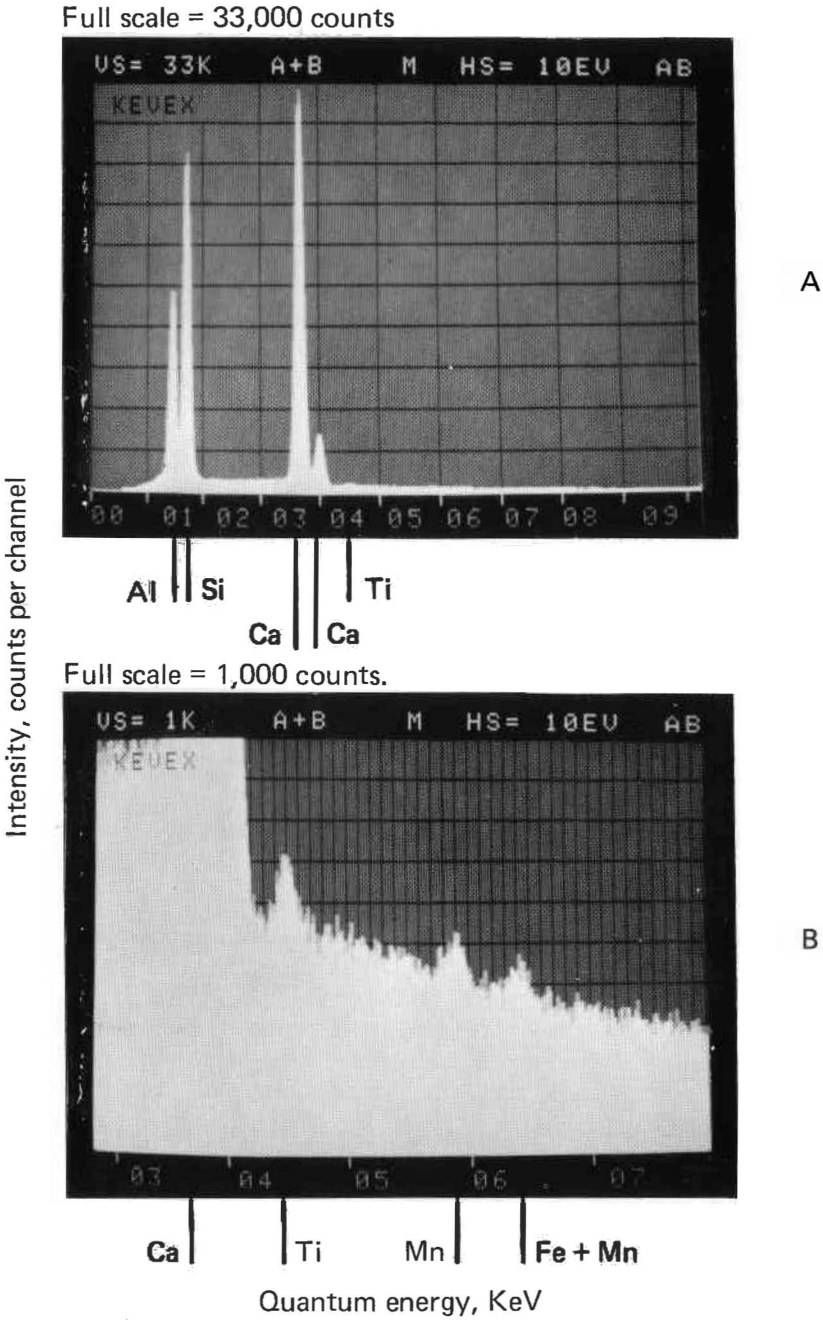

Figure 1. X-ray energy spectrum of colorless grossular (Sample No. 2).

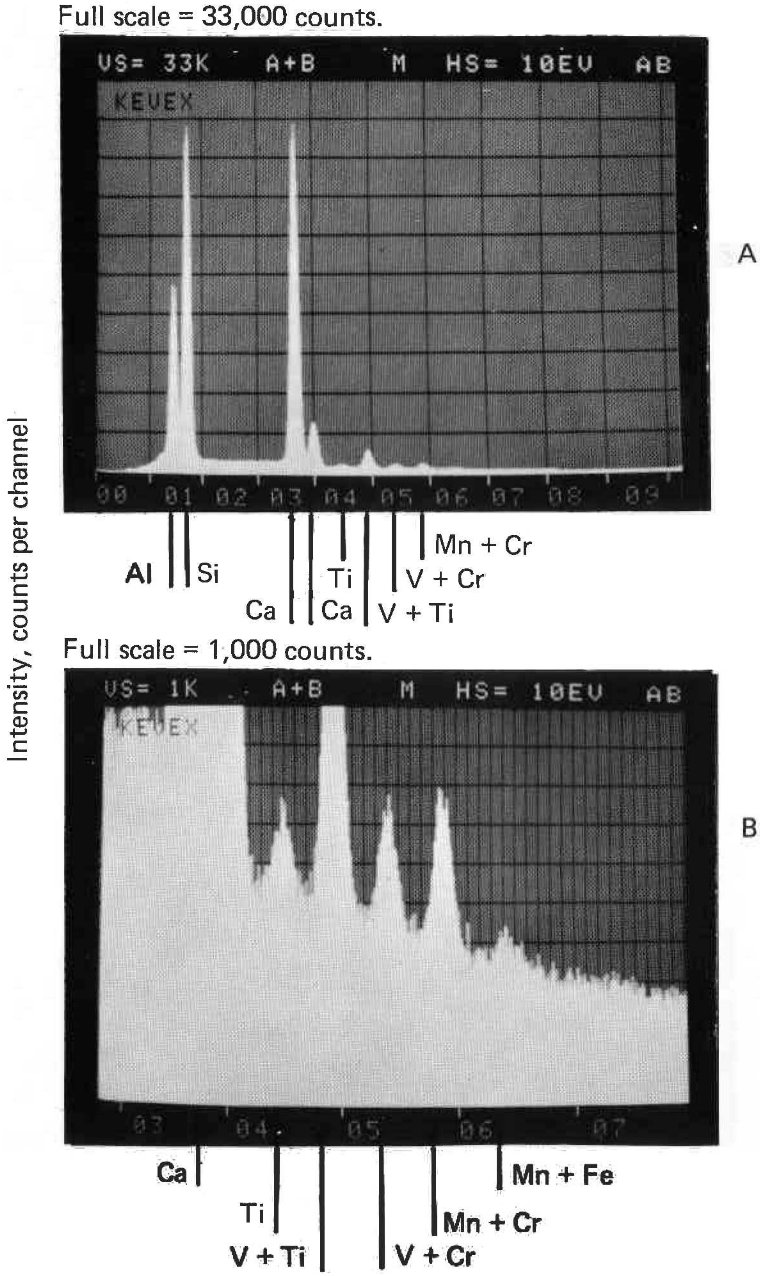

Figure 2. X-ray energy spectrum of tsavorite.

chemical composition had been determined by a technique of X-ray spectrometry comparable to our own.

The results of the chemical analyses, augmented by our physical and optical property determinations, further showed that the colorless and near-colorless stones formed an expanded color suite with the tsavorites. This expanded suite consisted of the sixteen grossulars listed in *Tables I and II*, with tones and intensities of green ranging all the way from G/H colorless to deep green. This greatly facilitated the evaluation of the effect of chemical composition on color.

A direct relationship was found between the vanadium content and the intensity of the green color of the grossulars, as may be seen in *Table I.* No vanadium or chromium was detected in the two most colorless stones. And as the vanadium-oxide content gradually increased to 1.5%, the intensity of the green color gradually increased to deep green. In the colorless grossular that graded an M color, the vanadium-oxide content was 0.06%, but no chromium was detected in this stone, either. In fact, no chromium was detected in the first seven grossulars of the color suite except for Sample No. 5, and the color of Sample No. 6 was already rated as light green. Therefore, chromium could not account for, nor contribute to, the green colors of these grossulars.

Unfortunately, there was no stone in our color suite that contained chromium without vanadium. Therefore, we were not able to determine the effect of chromium without vanadium. However, Sample No. 5, which contained 0.09% chromium-oxide and 0.10% vanadium-oxide, was lighter green than Samples No. 6 and No. 7, which contained no chromium and about the same amount of vanadium. Except for the chromium-oxide content, the chemical compositions of these three grossulars were very similar. Therefore, it appeared that chromium did not increase the intensity of the green color, but rather, had a slightly negative, or lightening, effect. The chromium-oxide content was mostly not greater than about 0.1%. It was 0.15% as a maximum. Therefore, the effect of chromium on the green color of the grossulars of this investigation seemed to be insignificant.

Except for influencing the tones of the colorless and near-colorless stones, no remaining element at the levels present seemed to influence color significantly.

The magnesium-oxide content varied erratically between 0.1% and 1.0% in the color suite, with no significant effect on the green color.

In the colorless stones, the manganese-oxide content was only 0.1% or 0.2%. The manganese-oxide contents of the remaining stones varied erratically between 0.1% and 0.6%. Within this range, the manganese did not noticeably modify the green color of the tsavorites. However, the green color was always of high intensity at the high levels of manganese. This may have obscured any effect of manganese on color.

The titanium-oxide content was always in the range of 0.2% to 0.4%, and the iron-oxide content was never more than 0.1%. Under these conditions, no noticeable influence of these elements on the green color of the tsavorites was observed.

None of the gemstones examined had a measurable nickel content.

Optical and Physical Properties

The optical and physical property determinations were restricted to the colorless gemstones. We evaluated birefringence, refractive index, ultraviolet fluorescence, and specific gravity. In addition, some gemstones were microscopically examined for inclusions.

Birefringence: None of the colorless gemstones examined exhibited birefringence under the GEM Illuminator Polariscope. All were found to be singly refractive but with medium strain.

Refractive Index: The small colorless gemstones, Sample No. 1, Sample No. 2, and Sample No. 3, all showed a refractive index of 1.731 to 1.732. Their GIA color grades were G/H, I, and M, respectively. Ten colorless gemstones which were one to two carats in size showed an average refractive index of 1.732. Five of these measured 1.731, and five measured 1.732. Their GIA color grades ranged from I to M. All refractive indices were determined with the GEM Duplex II Refractometer.

Ultraviolet Fluorescence: Under both short and long wave length ultraviolet radiation, the colorless grossularite fluoresced a weak to moderate golden-yellow visible light. The color of this light could also be called yellow with a touch of orange. The ultraviolet fluorescence was determined with the UVSL-25 Combination Mineralight Lamp using an ultraviolet viewing cabinet.

Specific Gravity: The specific gravity of the colorless grossularite was 3.62 as determined by the direct-weighing method. The small colorless stones of our color suite were too small for accurate, reliable measurement of specific gravity. Therefore, we made three different batches of large grossulars, each consisting of three stones, and determined the joint specific gravity in each case. The weight of each batch was between four and five carats. And the measured specific gravities were 3.61, 3.62, and 3.62.

Characteristic Inclusions: We examined many of the colorless grossulars under the microscope at magnifications up to 60x for inclusions. To date we have not been able to catagorize any of the inclusions we observed as "characteristic." One stone exhibited short stubby inclusions *(Fig. 3)*. Another showed two long parallel needles *(Fig. 4)*. A third had short needles and angular inclusions *(Fig. 5)*. And a fourth displayed a plane of small "fingerprint-like" inclusions *(Fig. 6)*.

Further Discussion

Bank reports the refractive index of colorless grossularite to be in the range of 1.732 to 1.736.[1] Eppler reports pure synthetic grossularite as having a refractive index of 1.734.[5] And Mackowsky gives 1.735 for the refractive index of pure grossularite.[1] Webster reports 1.738 to 1.744 for transparent green grossularite (tsavorite).[1] The GIA shows 1.736 to 1.742

Figure 3. Colorless grossular with short stubby inclusions (60x). Arrow points to cluster of inclusions.

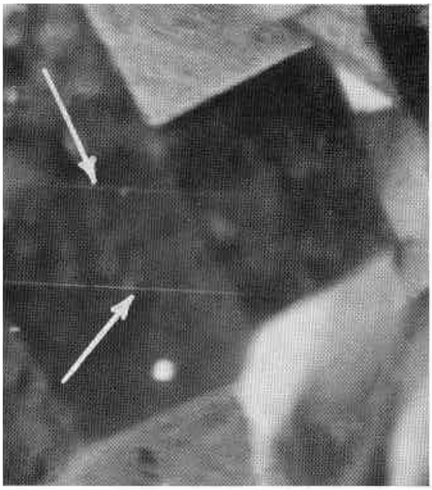

Figure 4. Colorless grossular with long parallel needles (60x). Each arrow points to a long needle-shaped inclusion.

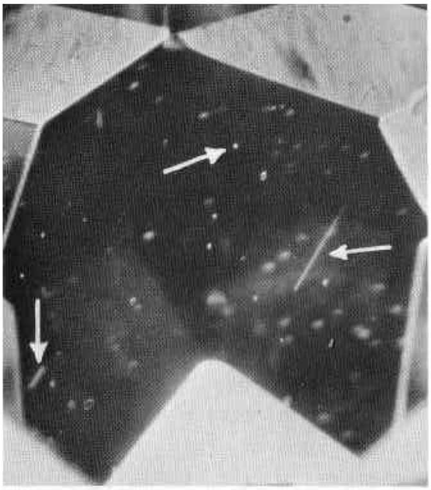

Figure 5. Colorless grossular with short needles and angular inclusions (60x). Two arrows point to short needles, and one arrow points to one of numerous angular inclusions.

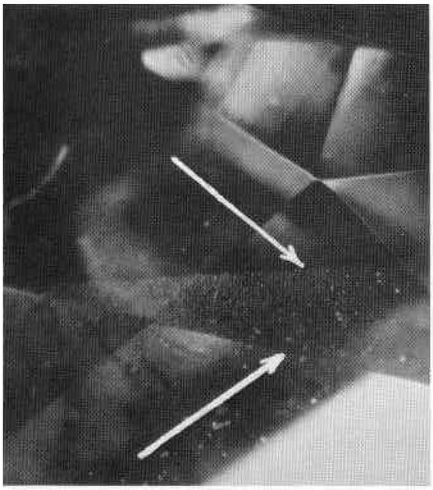

Figure 6. Colorless grossular with small fingerprint-like inclusions (60x). Arrows point to plane with small inclusions in "fingerprint" pattern.

for green transparent grossularite (tsavorite).

The colorless gemstones we examined showed an average refractive index of 1.732. Therefore, our experimental results are in agreement with the data reported by Bank for colorless grossularite, even though some of our colorless stones measured 1.731, the lowest refractive index ever reported for colorless grossularite. It should be noted that the measured refractive indices of our colorless grossulars were at the lower end of the 1.732 to 1.736 range reported by Bank. And they were lower than the 1.734 reported for pure synthetic grossularite by Eppler and lower than the 1.735 reported for pure grossularite by Mackowsky. Since we define colorless rather tightly, it appears that many of the stones examined by the other investigators were near colorless rather than colorless. This seems especially true since the GIA shows a refractive index of 1.736 to 1.742 for green transparent grossularite (tsavorite).

Previous work by Switzer suggested that the green color in tsavorite was related to the vanadium content and probably in part to the chromium content.[3] However, both vanadium and chromium were always present in the four green grossulars Switzer examined, so that the effectiveness of each of these elements alone to impart green color could not be determined. Also, an interaction of vanadium and chromium could not be ruled out.

The present work clearly showed that vanadium is the effective element that gives tsavorite its intense, beautiful green color. The presence of chromium is not essential. Furthermore, it appears that chromium at the low levels found in tsavorite during both investigations – 0.3% chromium oxide or less – does not have any significant effect on green color, neither in a positive nor negative sense.

Conclusions

The chemical compositions and the optical and physical properties, determined during this investigation, verify the reports that the colorless gemstones discovered in Tanzania in the late sixties are colorless grossulars. Such grossulars are exceedingly rare and have characteristics that qualify them as desirable gemstones. It appears that most, if not all, "colorless" grossulars from Kenya are not colorless, but "near colorless" with clearly observable green or other tints.

Similar to diamonds, colorless grossulars can be color graded accurately and with consistent results. A GIA-Graded Diamond Master Set is suitable for such grading.

The beautiful green color in tsavorite is caused by vanadium alone. Chromium is not essential. In the absence of chromium, a vanadium-oxide content of 0.1% already causes a light green color. And a vanadium-oxide content of 1.5% causes a deep green color. Presumably, the tsavorites that black out have higher vanadium-oxide content. It appears that chromium at the levels found in tsavorite during this investigation has no significant effect on green color. The chromium-oxide contents were about 0.2%, or less.

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