A Rare Nearly-Pure End-Member Grossular Garnet with Color-Change Effect

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Abstract

Most color-change garnets in gem market are intermediate in composition or solid-solution between pyrope and spessartine end-members with a trace of vanadium or vanadium-plus-chromium responsible for their color-change phenomenon. Some chromium-rich pyrope and grossular-andradite solid-solution with color-change effect have also been reported previously. In this study, two new color-change grossular garnets were examined at the GIT-GTL. Their UV-Vis spectra and chemical compositions revealed that the stones were a rare almost-pure end-member grossularite with chromium-plus/minus-iron as the significant color causing elements.

Introduction

Garnet is a vast family of valuable gemstones commonly used in jewelry since the ancient time. The garnet family can be found in a large variation of colors ranging from colorless to green, yellow, orange, red, pink, brown and black, including the valuable color-change varieties. Color-change garnets have been reported since the 1970's. The vanadium or vanadium-plus-chromium bearing varieties of pyrope-spessartine with color-change phenomenon were reportedly found in Tanzania (Crowningshield, 1970; Koivula and Kammerling, 1988; Manson and Stockton, 1984; Pardieu et al., 2011; Schmetzer and Ottemann, 1979; Stockton, 1982), in Sri Lanka (Johnson and Koivula, 1998; Johnson and Koivula, 1996) and in Madagascar (Johnson and Koivula, 1998; Krzemnicki et al., 2001; Schmetzer and Bernhardt, 1999). The chromium-rich pyropes with color-change effect were also reported (Carstens, 1973; Hysingjord, 1971; Schmetzer et al., 1980). In Recent past, color-change grossular-andradite was discovered in Mali, Africa (Wentzell, 2003).

Recently, the Gem and Jewelry Institute of Thailand's Gem Testing Laboratory (GIT-GTL) encountered two specimens of uncommon color-change garnet. The gemological properties and advanced analyses have revealed that the stones are a nearly-pure end-member grossularite which is an extremely rare variety of color-change garnet that is worthwhile to report hereafter.

Sample and Methods

Two facetted samples of the uncommon color-change garnet were examined by GIT-GTL. The first stone no. 170402 weighed 13.18 ct, and measured 15.1 × 12.2 × 9.1 mm in oval, brilliant-step cut, while the second sample no. 170401 weighed 6.73 ct, and measured 12.8 × 10.4 × 6.5 mm in oval, brilliant-step cut (Figure 1).

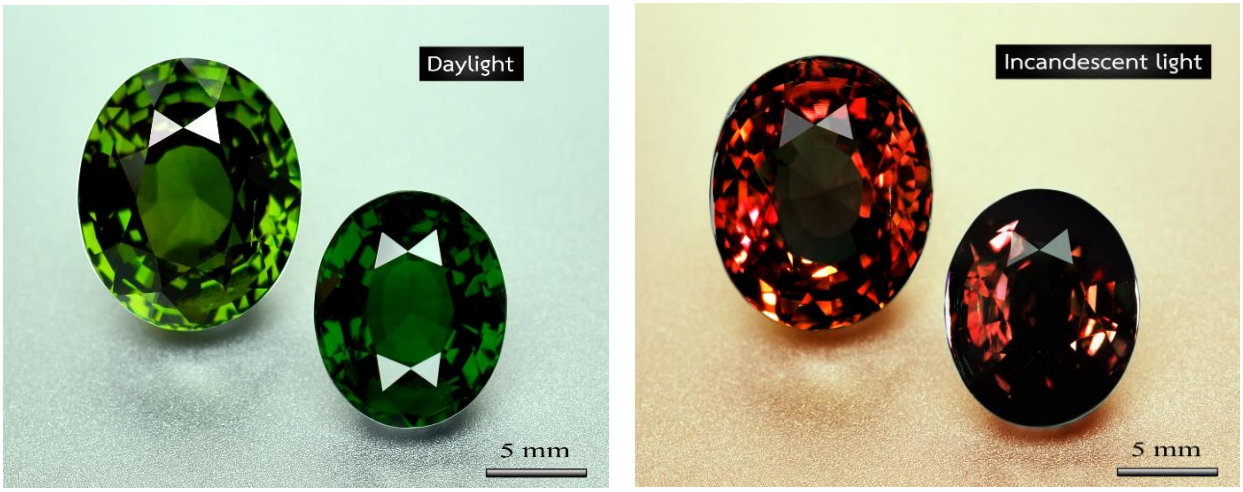

Figure 1. The distinct color-change effect of two grossular garnets. The 13.18 ct stone (left sample) appears yellowish green hue in a daylight source and brownish red hue in a warm incandescent light source. The 6.73 ct stone (right sample) give strong green hue in a daylight illumination and purplish brownish red hue in a warm incandescent light. Photos by S. Promwongnan

Basic gem instruments were used for the measurement of the stone's properties. Internal features were observed with high magnification gem microscope. All inclusions images were taken by using a gem microscope with Canon EOS 7D camera attached.

As for the advanced equipment, UV-Vis-NIR absorption spectrum of the sample was taken with a PerkinElmer Lambda 950 spectrophotometer in the range 250–800 nm with a sampling interval of 3.0 nm and scan speed of 441 nm per minute. Raman spectroscopy was performed on the samples using a Renishaw inVia Raman micro-spectrometer with the Nd:YAG laser (532 nm). The chemical analysis was carried out by an Energy-dispersive X-ray Fluorescence (EDXRF) spectroscopy of Eagle III.

Results

General Properties

Both samples revealed a yellowish green to strong green color in daylight, with a distinct change to brownish red or purplish brownish red in incandescent light (Figure 1). Their refractive indices varied slightly from 1.745 (no. 170401) to 1.741 (no. 170402) and the SG values of both stones were 3.63. The samples were singly refractive and showed no pleochroism. The R.I. and S.G. values of these samples were consistent with the grossular garnet properties. Furthermore, these samples were inert to both long-wave and short-wave UV radiation and appeared brownish orange to brownish red when observed through the Chelsea filter.

Microscopic Features

Examination of the sample (no. 170402) with dark field illuminator showed pronounced parallel growth lines (Figure 2a), needles (Figure 2b) and tube-like inclusions (Figure 2c). Careful examination at higher magnification with fiber optic light illumination revealed minute particles and needles (Figure 2d). With bright field illuminator, the several high relief colorless crystals were also observed (Figure 2e-f). A colorless rounded inclusion near surface (Figure 2f) was identified as diopside by Raman spectroscopy.

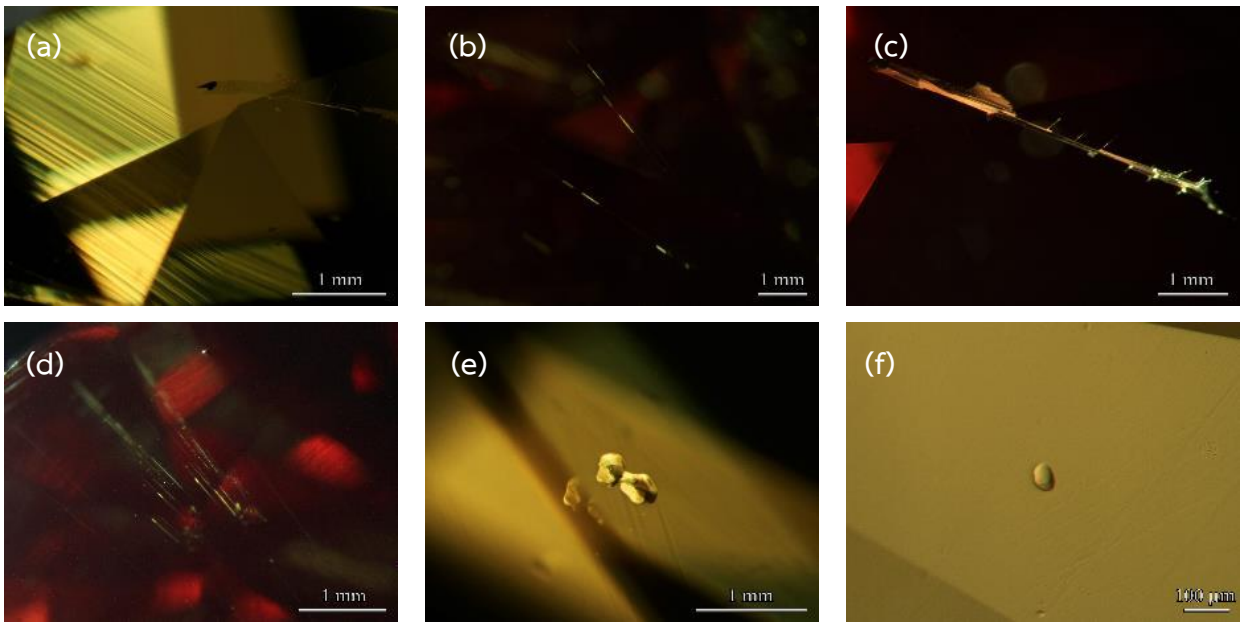

Figure 2. Microscopic examination of sample no. 170402 with dark field illuminator showed the strong parallel growth lines (a, magnified 4x), needles (b, magnified 2x) and tube (c, magnified 3x). At high magnification with fiber optic light illumination, minute particles and needles were noticed (d, magnified 4x). With bright field illuminator, the colorless crystals were also observed (e, magnified 5x. A colorless rounded inclusion near culet (f, magnified 20x) was identified as diopside by Raman spectroscopy. Photomicrographs by S. Promwongnan

UV-Visible Spectroscopic Analysis

The UV-Vis spectrum of the color-change grossular garnets (Figure 3; blue and black lines) displayed a strong absorption band centered at around 432 nm (due to Cr^{3+} with possible combination of Fe^{3+}; Schmetzer and Bernhardt, 1999; Pardieu et al. ,2011) and 600 nm (due to Cr^{3+}), see also chemical analyses in Table 1. As a consequence, two transmission windows in the green and red regions of the visible spectrum were responsible for its coloration or the green-to-red color-change effect. In comparison with a tsavorite sample----the green variety of grossular garnet (Figure 3; green line), its spectrum usually showed broader absorption bands centered around 430 and 620 nm toward the red region (due to V^{3+} , see Table 1). As such, a strong trnsmission window in green region was responsible for its green hue. Moreover by comparing with a color change pyrope-spessartite garnet sample (Figure 3 red line), its spectrum displayed broader absorption bands centered around 573 and, possibly, 415 nm (due to V^{3+} and/or Cr^{3+}), including small hump around 408 and 422 nm in the violet region (due to Mn^{2+}; Schmetzer and Bernhardt, 1999; Krzemnicki et al., 2001, see also Table 1). Thus, two transmission windows in the blue-green and orange-red regions of the visible spectrum were responsible for its yellowish-bluish-green-to-purplish-orangy-red color-change phenomenon.

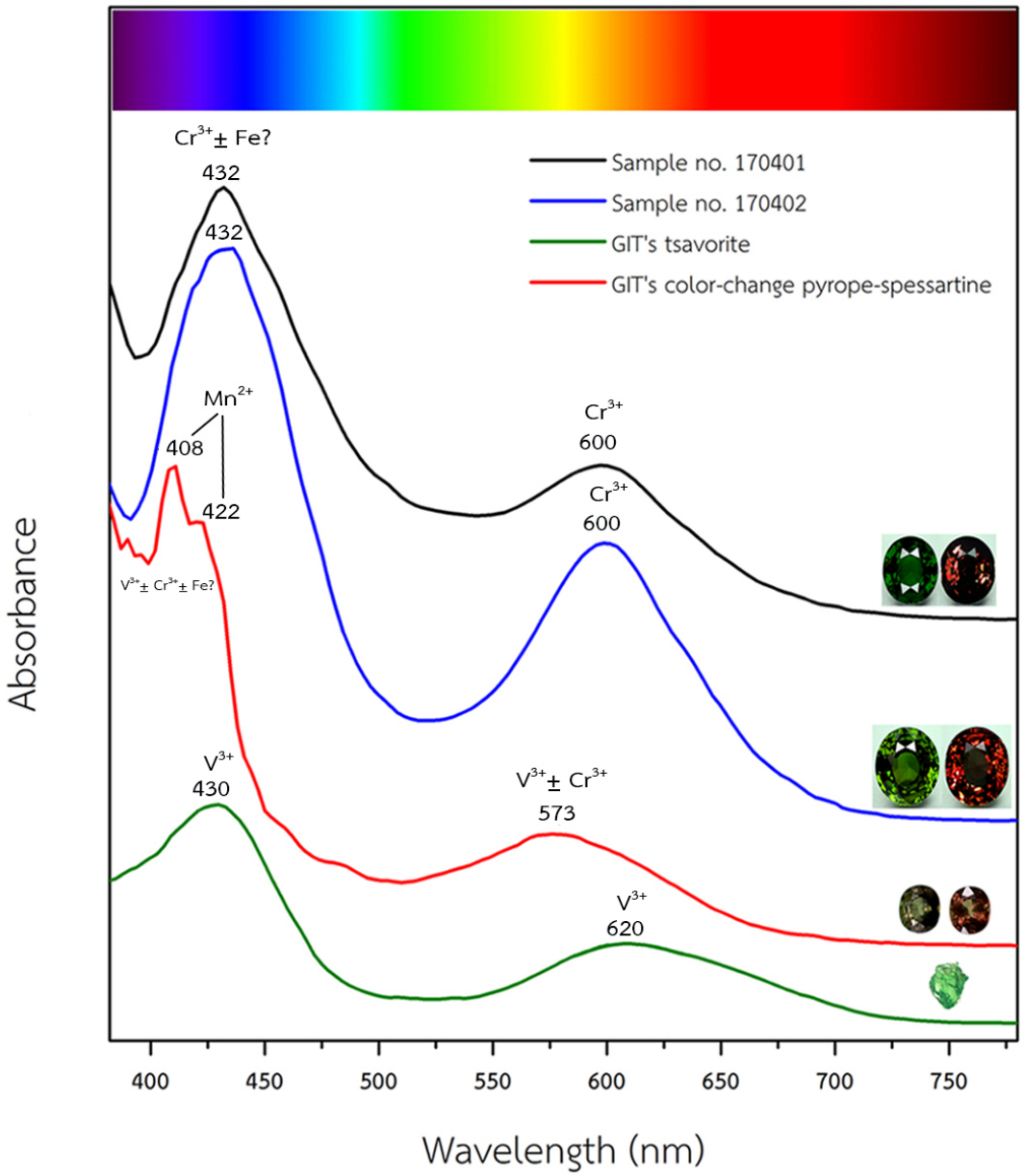

Figure 3. Visible absorption spectra of the color-change grossular garnets (blue and black lines) showing typical absorption bands centered at around 432 nm (due to Cr^{3+} plus/minus Fe^{3+}) and 600 nm (Cr^{3+}), as compared to the absorption bands of the GIT's tsavorite spectrum (green line) and color-change pyrope-spessartite spectrum (red line). The absorption bands of the GIT's tsavorite are centered around 430 and 620 nm toward the red region (due to V^{3+}). Those of the GIT's color-change pyrope-spessartite are centered around 573 nm (due to V^{3+} and/or Cr^{3+}), including small humps around 408 and 422 nm in the violet region (due to Mn^{2+}).

Raman Spectroscopic Analysis

The Raman spectra of both samples were perfectly match with the RRUFF reference spectrum of grossular garnet in our database (Figure 4).

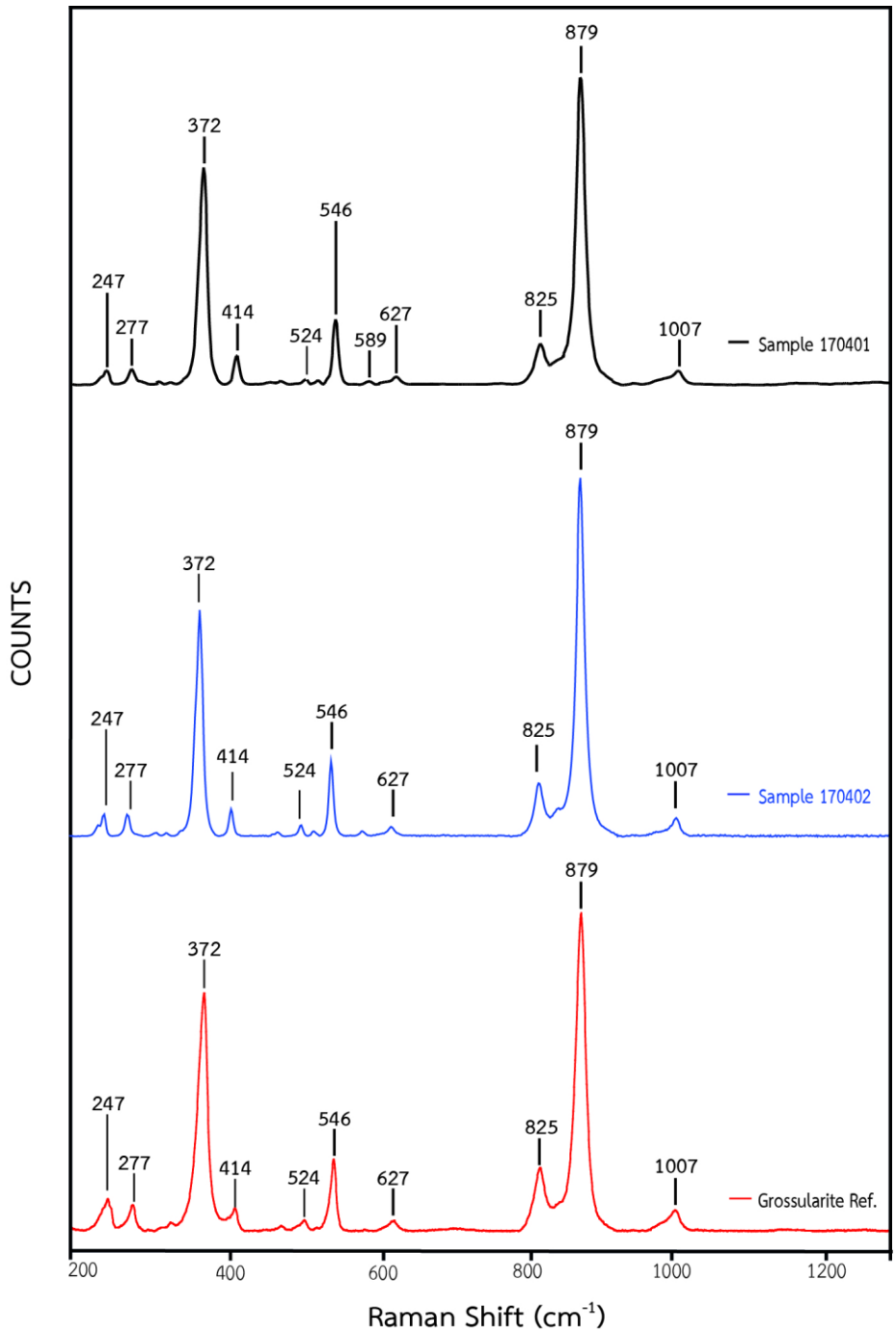

Figure 4. Raman spectra of the sample no170401 (black) and sample no170402 (blue) as compared to reference spectrum from RRUFF database (red)

Chemical analysis

The qualitative energy-dispersive X-ray fluorescence (EDXRF) analysis on both samples revealed mainly Si, Al and Ca and trace amounts of Fe, Cr, Ti, Mn Mg and V (Table 1). The extensive substitution of calcium and aluminum in its lattice (86.4-88.4% grossular end-member) suggested that this stone was a rather pure end-member grossularite ($Ca_3Al_2(SiO_4)_3$) with significant traces of iron and chromium. In comparison, the GIT's tsavorite garnet sample was also a nearly-pure end-member grossularite (91.3% grossular end-member) with a significant trace of vanadium instead. The GIT's color-change pyrope-spessartine sample showed significant pyrope (45.9%) and spessartine (42.9%) end-member components with significant traces of vanadium and some chromium.

Table 1. Trace element contents of the color-change grossular garnet, measured by EDXRF

Element Oxides (wt.%)	Sample no. 170401	Sample no. 170402	GIT's tsavorite	GIT's color-change pyrope-spessartine
SiO_2	43.75	46.47	44.88	43.46
TiO_2	0.04	0.03	0.26	0.23
Al_2O_3	22.27	19.73	23.84	18.76
Cr_2O_3	0.86	0.44	0.15	0.39
Fe_2O_3	2.47	1.94	0.12	3.10
MnO	0.71	0.40	0.49	22.55
MgO	0.85	1.12	1.33	6.44
CaO	29.01	29.84	28.09	3.90
V_2O_5	0.04	0.03	0.83	1.18
Sum	100.00	100.00	99.99	100.01
Mole% garnet end-members				
Amandine	5.90	4.56	0.32	7.31
Pyrope	3.62	4.69	6.10	27.07
Grossular	86.43	88.37	91.28	11.53
Spessartine	1.72	0.96	1.28	53.85
Uvarovite	2.24	1.34	0.40	0.16
Andradite	0.00	0.00	0.00	0.00
Ca-Ti Gt	0.10	0.09	0.62	0.09
Total	100.00	100.00	100.00	100.00

Conclusions

Garnets with color-change effect have been circulated in the gem market for several decades and they commonly belong to an intermediate type of pyrope- spessartite solid-solution or a chromium-rich pyrope or a grossular-andradite solid-solution rather than true end-member grossularite. In this study, we encountered two rare nearly-pure end-member grossularite samples with color-change property. The UV-Vis spectrum and chemical data revealed that chromium plus/minus iron were the significant color causing trace elements responsible for their body color and color-change phenomenon. The source of these exceptionally rare color-change grossular garnets could be from Africa (pers. comm.) which may originate from the same source as the color-change chrome grossular garnets from Ethiopia recently reported by Sun et al. (2018) based on their spectral and chemical similarities, though color-change phenomemon was fairly different.

Acknowledgements

The authors would like to pass on our thanks to Dr. Visut Pisutha-Anond, Wilawan Atichat and Thanong Leelawattanasuk for their valuable suggestions and their extensive reviews of this article.

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