CHEMIJA. 2015. Vol. 26. No. 1. P. 18–24

Chemical composition of rare garnets, their colours and gemmological characteristics

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The article describes the rare garnet chemical composition, the colour, the dependence on chemical elements and gemmological features. Chemical analysis of the garnet group minerals was performed with a Quanta 250/450/650 scanning electronic microscope, using an apparatus for coating the samples with metals Emitech SC7620 Mini Sputter Coater with a CA7625 attachment for carbon coating.

Key words: garnets, tsavorite, blue colour-change garnets, demantoid and rainbow garnets

INTRODUCTION

Garnets are a very broad group of minerals that is characterised by a variety of chemical elements and colours. According to their chemical composition, garnets are divided into the following main minerals: pyrope ($Mg_3Al_2(SiO_4)_3$), almandine ($Fe_3Al_2(SiO_4)_3$), spessartine ($Mn_3Al_2(SiO_4)_3$), grossularite ($Ca_3Al_2(SiO_4)_3$), andradite ($Ca_3Fe_2(SiO_4)_3$) and uvarovite ($Ca_3Cr_2(SiO_4)_3$). Typically, garnets are characterised by warm and deep red colour (pyrope, almandine and their mixture – rhodolite) (Figs. 1–3). However, there is a growing interest in garnets of other colours. The most valued are very shiny green garnets (demantoid – a variety of andradite, tsavorite, varieties of hydrogrossularite – grossularite, uvarovite) (Figs. 4–6) and colour-change garnets (a mixture of pyrope and spessartine) (Fig. 7). Among the attractive garnets there are yellowish, orange (spessartine, pinkish-orange grossularite – hessonite) (Figs. 8, 9), light orange (pink grossularite) (Fig. 10) and colourless (grossularite) (Fig. 11) ones. This variety of colours depends on the composition of the chemical elements present in the minerals.

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EXPERIMENTAL

The minerals used for the research are the following: blue colour-change garnet, rainbow garnet, colourless grossularite, dark green and medium green tsavorite, green demantoid. All the analysed garnets were the rare garnets. Chemical analysis of the garnet group minerals was performed with a scanning electronic microscope Quanta 250/450/650, using an apparatus for coating the samples with metals Emitech SC7620 Mini Sputter Coater with a CA7625 attachment for carbon coating. Each sample was measured from 3 to 5 points. The mean value was calculated.

RESULTS AND DISCUSSIONS

The blue colour-change garnet (Fig. 7) is the only one known example of blue garnet. This garnet is not of blue colour only, thus, it would not be entirely correct to refer to

Fig. 1. Pyrope (Russia). Photo by Dr. A. Kleišmantas

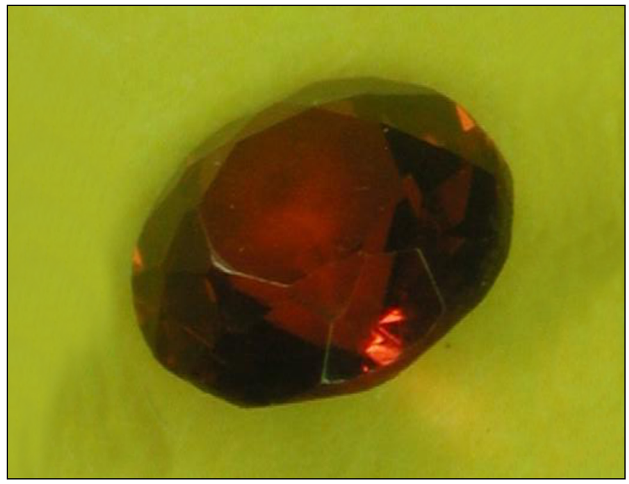

Fig. 2. Almandine (India). Photo by Dr. A. Kleišmantas

Fig. 3. Rhodolite (India). Photo by I. Balčiūnaitė

Fig. 4. Demantoid (Rusia). Photo by Dr. A. Kleišmantas

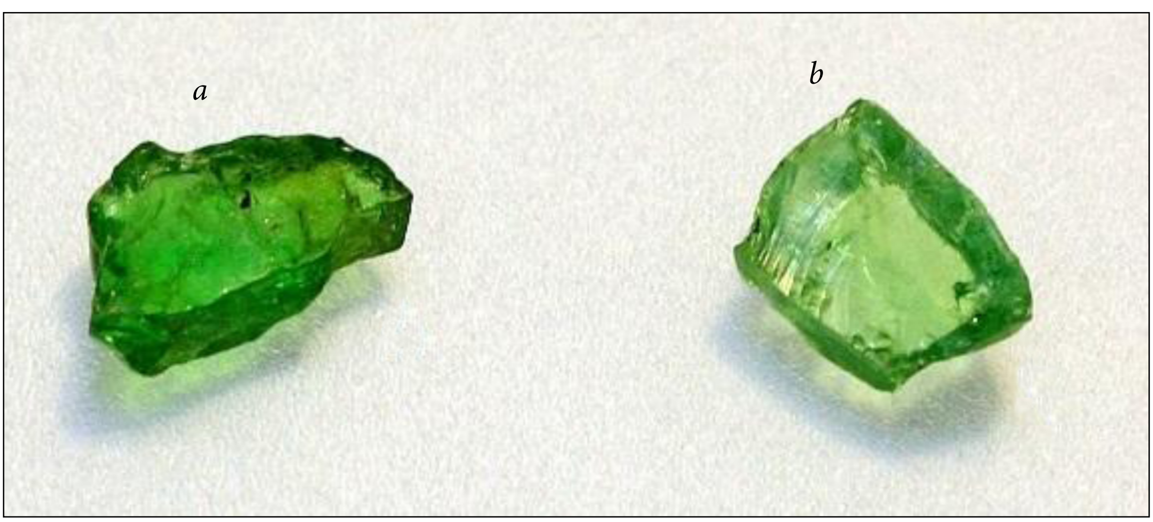

Fig. 5. *a* – dark green tsavorite and *b* – medium green tsavorite (Kenya and Tanzania). Photo by photographer Irzhi Korn

Fig. 6. Uvarovite (Russia). Photo by I. Balčiūnaitė

Fig. 7. Blue colour-change garnet (Sri Lanka). Photo by photographer Irzhi Korn

Fig. 8. Spesartine. Photo by I. Balčiūnaitė

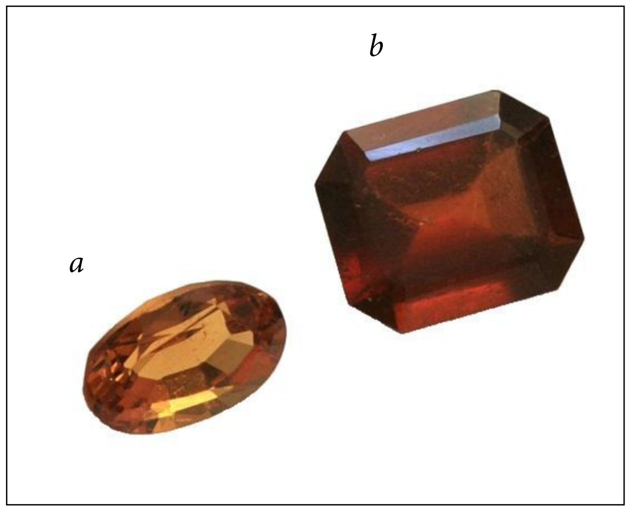

Fig. 9. *a* – orange hessonite *b* – pink hessonite (India and Sri Lanka). Photo by photographer Irzhi Korn

Fig. 10. Light orange grossularite (India). Photo by photographer Irzhi Korn

Fig. 11. Colourless grossularite. Photo by photographer Irzhi Korn

it as blue garnet. The most interesting thing is that this garnet can change its colour in the same manner as alexandrite, therefore the most correct name for this garnet would be the blue colour-change garnet [1]. The test of chemical elements showed that this garnet is a mixture of pyrope and spessartine. Magnesium oxide is characteristic of pyrope, whereas manganese oxide is characteristic of spessartine, these two, in addition to aluminium and silicon oxides, form the core of the chemical composition of these elements; this is confirmed by the tests of other authors [2]. In the garnet tested, the content of magnesium oxide varies from 11.18 to 13.43%, manganese (II) oxide from 8.63 to 17.37%, aluminium oxide from 22.03 to 25.29%, silicon (IV) oxide from 42.24 to 48.75%. In addition to these elements, the designated content of calcium oxide varies from 2.13 to 2.88%, iron (III) oxide from 1.78 to 3.32%, and colour determining chemical elements, i. e. vanadium (V) oxide content varies form 0.46 to 0.61%, chromium (III) oxide about 0.37%. The average content of these chemical elements is provided in Fig. 12.

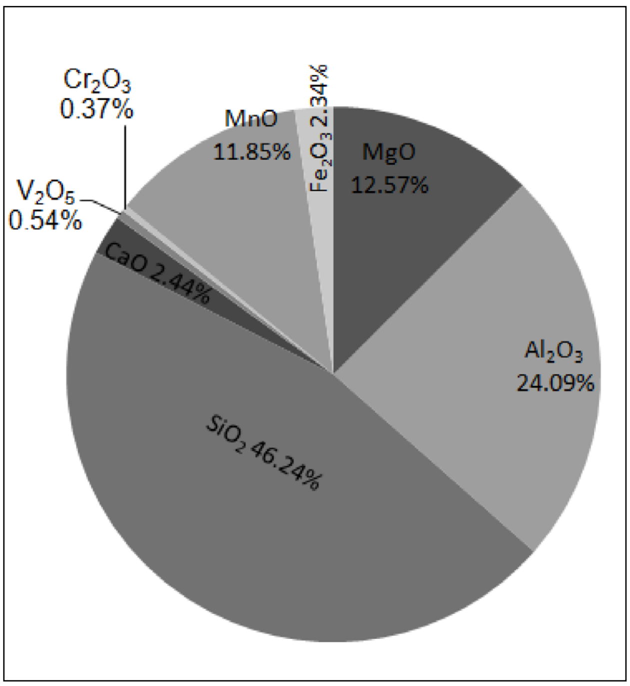

Fig. 12. Average content of chemical elements (in form of oxides) in the blue colour-change garnet

Demantoid (Fig. 4) is a variety of andradite. It is characterised by diamond luster, which gave it the name in the nineteenth century. The colour varies from cold, very pale green to mid or strong green, not as a rule a very livery colour and similar to certain shades of green in tourmaline, zircon, or olivine [3]. After the determination of chemical elements in demantoid it was found out that the content of calcium oxide varies from 28.23 to 28.75%, that of iron (III) oxide from 13.93 to 15.99%, which are characteristic of andradite and its varieties. In this mineral the aluminium oxide content varies from 0.99 to 1.38%, that of silicon (IV) oxide from 54.28 to 56.45%. The average content of chemical elements (in form oxides) in demantoid is provided in Fig. 13. The green colour of this variety is determined by chromium [4].

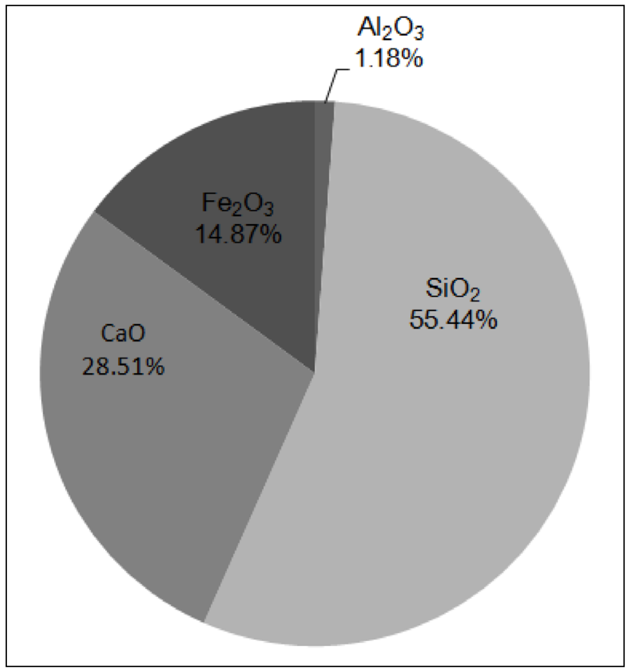

Fig. 13. Average content of chemical elements (in form of oxides) in the demantoide

Rainbow garnet is called in this way because its surface glows like a rainbow. After the chemical analysis it was indicated that the content of calcium oxide varies from 32.19 to 32.95%, iron (III) oxide from 23.49 to 24.91%, silicon (IV) oxide from 39.51 to 41.71%, aluminium oxide from 1.71 to 3.64%, and manganese (II) oxide from 0.24 to 0.32%. The average content of these chemical elements is provided in Fig. 14. Based on the results of the tests, it was found out that the chemical composition of the rainbow garnet is as that of andradite variety. By comparing the chemical composition of this rare variety with another tested variety of andradite, i. e. demantoid, it was found out that the content of manganese (II) oxide in the rainbow garnet varies from 0.24 to 0.32%, whereas in demantoid there is none. What is more, the content of iron (III) oxide (from 23.49 to 24.91%) in the rainbow garnet is higher than in demantoid (from 13.93 to 15.99%). These differences in the chemical composition determine difference in colour, and the multi-colourfulness of the rainbow garnet should depend on the surface reflectivity, i. e. irisation.

Grossularite has most varieties among the garnet group minerals. Its name is derived from the Latin word "grossularia" (Eng. *gooseberry*). Since the 1960s, it has been found in gem quality, mainly green [5]. However, this mineral can also be of other colours depending on impurities, even colourless.

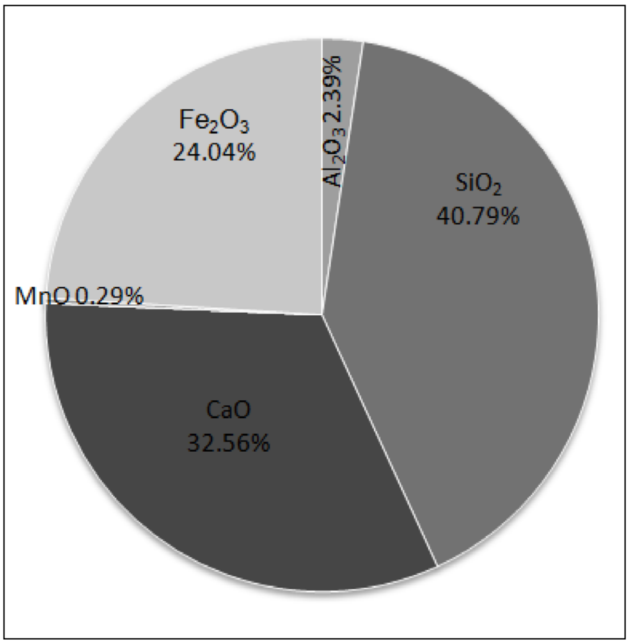

Fig. 14. Average content of chemical elements (in form of oxides) in the rainbow garnet

In the tested **colourless** grossularite (Fig. 11), the content of magnesium oxide found varies from 1.55 to 1.24%, aluminium oxide from 27.14 to 30.14%, silicon (IV) oxide from 52.95 to 55.75%, calcium oxide from 12.56 to 18.42%, iron (III) oxide about 0.25%. The average content of chemical elements of this mineral is provided in Fig. 15. Based on the results of the tests, it was found out that there were no colour-determining chromophores in the mineral, except for 0.25% of iron (III) oxide, which may not affect the colour at all.

Tsavorite is a variety of grossularite, characterized by green colour. In the dark green tsavorite (Fig. 5a), the content of magnesium oxide was found to vary from 0.58 to 0.64%, aliuminium oxide from 21.89 to 21.92%, silicon (IV) oxide from 40.79 to 40.89%, calcium oxide from 35.06 to 35.30%, vanadium (V) oxide from 0.40 to 0.57%, manganese (II) oxide from 0.76 to 0.81%, and the content of titanium (IV) found is about 0.39%. In the medium green tsavorite (Fig. 5b), the content of magnesium oxide was found to vary from 0.40 to 0.73%, aluminium oxide from 20.12 to 21.52%, silicon (IV) oxide from 39.62 to 43.90%, calcium oxide from 31.91 to 37.59%, vanadium (V) oxide about 0.43%, chromium (III) oxide from 0.98 to 1.04%, manganese (II) oxide from 0.42 to 0.72%, titanium (IV) oxide from 0.35 to 0.37%. The average content of chemical elements in this mineral is provided in Figs. 16 and 17. According to the composition of the chemical elements identified, it might be observed that the green colour is determined by vanadium (V) and chromium (III) oxides (respectively 0.40–0.57%, 0.98–1.04%). It would be wrong to presume that the dark green colour density is determined only by slightly higher vanadium (V) oxide content (0.57%) in comparison with lighter tsavorite, in which the content of vanadium (V) oxide is 0.43%. Even though chromium (III) oxide (0.98–1.04%) was found in medium green tsavorites, they are still lighter than tsavorites in which no chromium

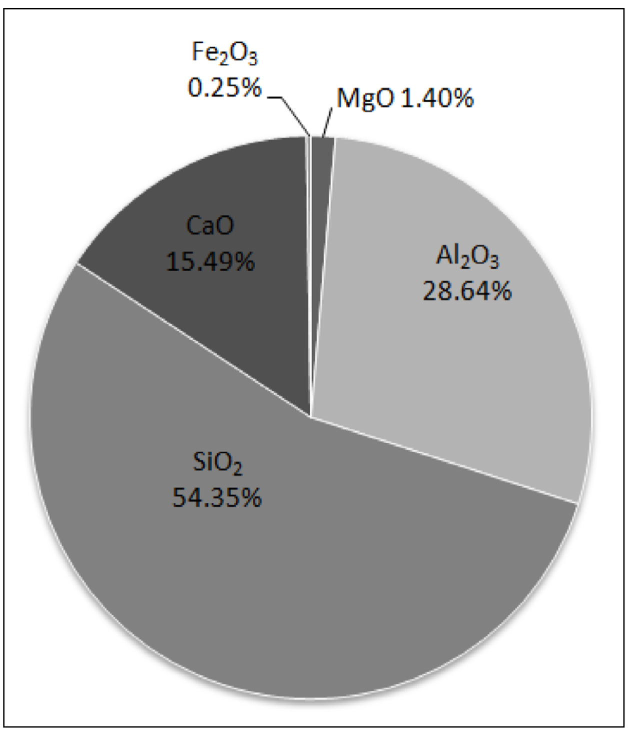

Fig. 15. Average content of chemical elements (in form of oxides) in the colourless grossularite

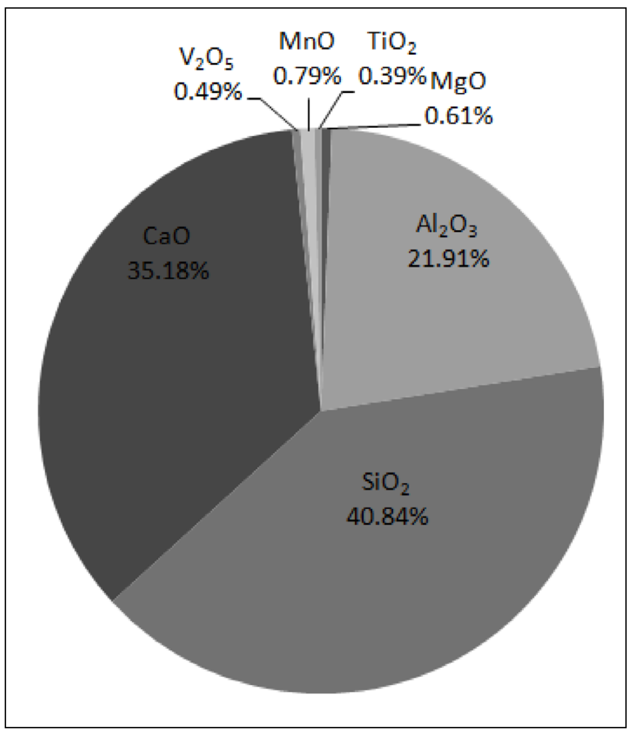

Fig. 16. Average content of chemical elements (in form of oxides) in the dark green tsavorite

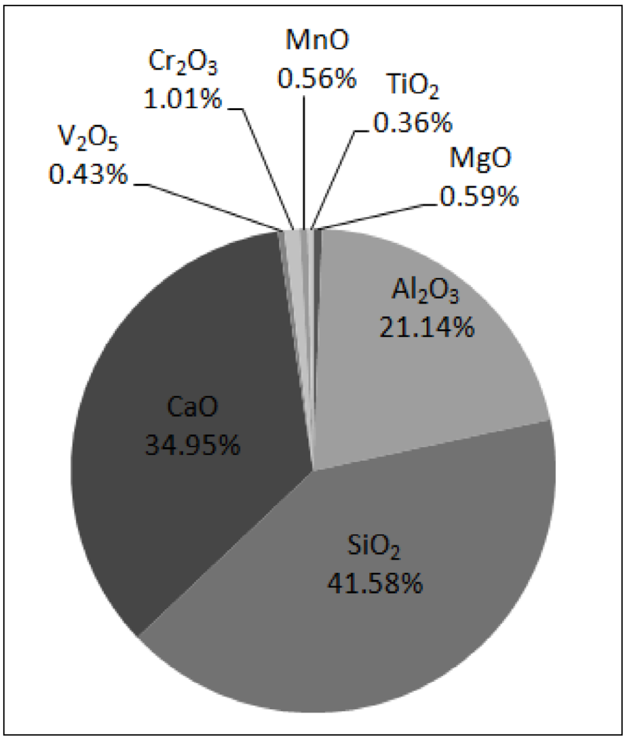

Fig. 17. Average content of chemical elements (in form of oxides) in the medium green tsavorite

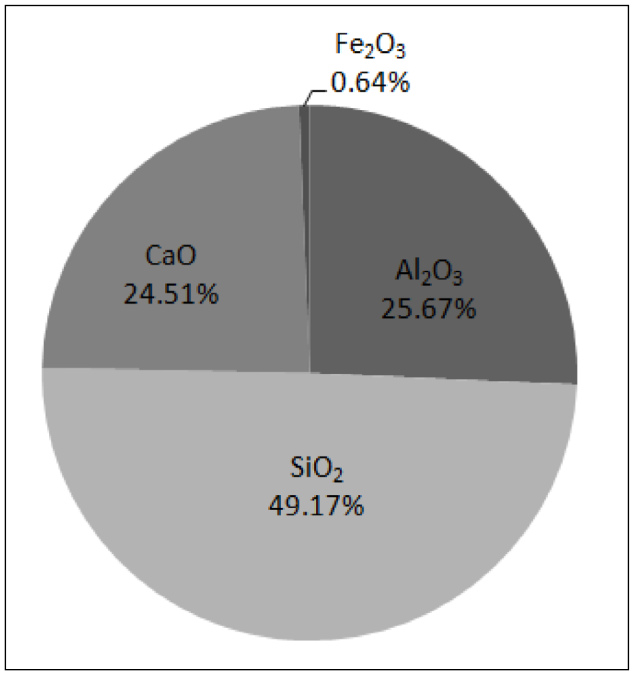

Fig. 18. Average content of chemical elements (in form of oxides) in the light orange grossularite

was found. Therefore, it might be asserted that the darker colour of a mineral, i. e. its colour tone, is determined by manganese and titanium oxides. Darker tsavorites had higher content of manganese (II) oxide (0.76–0.81%) and titanium (IV) oxide (0.39%) compared to lighter tsavorites (respectively MnO 0.42–0.72% and TiO_2 0.35–0.37%) that might determine the darkness of the mineral.

In **light orange** grossularite (Fig. 10) there are predominantly aluminium and calcium oxides. Having performed the tests, it was found out that the aluminium oxide content varies from 23.91% to 27.84% and the calcium oxide content varies from 18.13 to 28.59%. At different points of the sample testing, it was found out that if the aluminium oxide content increases, the content of calcium and iron oxides become lower. The silicon (IV) oxide content was found to vary from 46.62 to 54.09% (Fig. 18). Based on the results of the tests, it is presumed that the content of iron (III) oxide, which determines the colour of this variety, varies from 0.38 to 0.88%.

Hessonite is a variety of grossularite, which can vary from yellow to brown colour; sometimes this variety is referred to as essonite. Those are honey-yellow, yellow-brown garnets, tending to a reddish orange colour similar to that of spessartine. Its name comes from a Greek word "esson", which means "inferior". Minerals of this colour are regarded as less valuable. Brown colour hessonite is of the lowest value. Hessonites have good luster and seemingly good transparency, but when viewed with a lens, they seem to be undulated, in places of inclusions the view becomes contorted and they become non-transparent. In the tested hessonites the aluminium oxide content varies from 21.89 to 22.43%, calcium oxide from 27.52 to 29.51%, silicon (IV) oxide from 45.34 to 47.51%, manganese (II) oxide from 0.26 to 0.41%, iron (III) oxide from 2.35 to 2.84% (Figs. 19, 20).

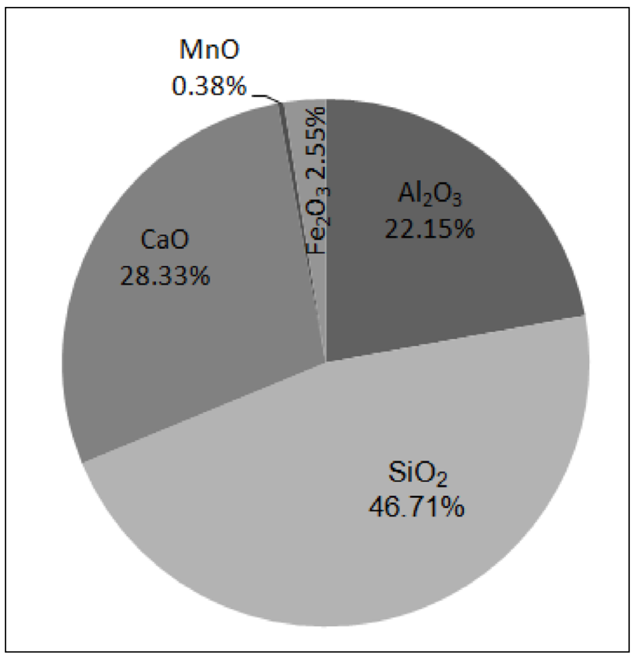

Fig. 19. Average content of chemical elements (in form of oxides) in the pink hessonite

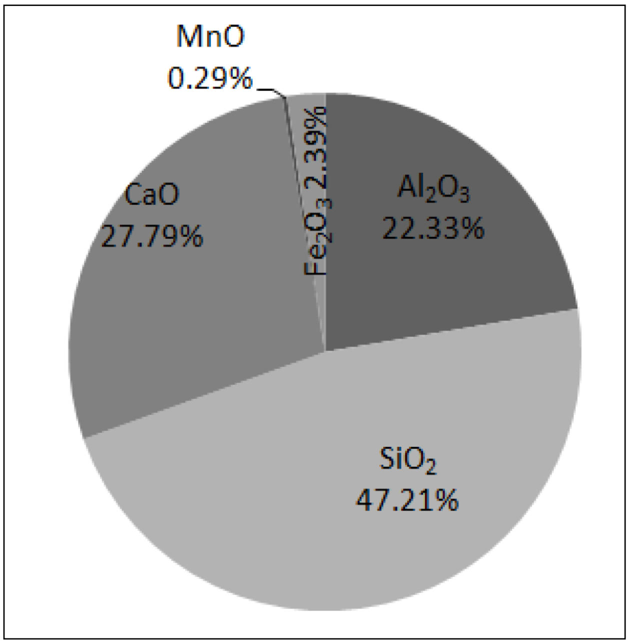

Fig. 20. Average content of chemical elements (in form of oxides) in the orange hessonite

CONCLUSIONS

After the performed chemical analysis of garnet group minerals, the following might be stated:

– the chemical composition of the blue colour-change garnet is the same as that of the pyrope and spessartine mixture, and its colour is determined by the content of vanadium and chromium oxides;

– the rainbow garnet is a variety of andradite, as its chemical composition is predominantly of iron, calcium and silicon oxides, its multi-colourfulness depends on the surface reflectivity, i. e. irisation;

– the demantoid colour is determined by the chromium oxide content;

– in the colourless grossularite only small content of colour-determining chemical substances (MgO, Fe_2O_3) was found, thus, they may not affect the colour at all;

– the colour of tsavorites is determined by the content of manganese and titanium oxides;

– the light orange colour of grossularite is determined by the iron oxide content;

– the colour of hessonite is determined by the content of manganese and iron oxides.

Received 28 November 2014
Accepted 9 December 2014

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RETŲJŲ GRANATŲ CHEMINĖ SUDĖTIS, JŲ SPALVOS IR GEMOLOGINIAI YPATUMAI

Santrauka

Straipsnyje aprašoma retųjų granatų cheminė sudėtis, jų spalvos priklausomybė nuo cheminių elementų ir gemologiniai ypatumai. Cheminė granatų grupės mineralų analizė atlikta skenuojančiu elektroniniu mikroskopu „Quanta 250/450/650" naudojant mėginių dengimo metalais aparatą „Emitech SC7620 Mini Sputter Coater" su CA7625 dengimo anglimi priedu.

Mėlynasis spalvą keičiantis granatas yra vienintelis žinomas mėlynojo granato pavyzdys. Šis granatas yra piropo ir spesartino mišinys. Spalva priklauso nuo chromo ir vanadžio oksidų. Demantoidas yra andradito atmaina. Šiai atmainai žalią spalvą suteikia chromo oksidas. Vaivorykštinio granato įvairiaspalviškumas priklauso nuo paviršiaus atspindžio, t. y. irizacijos. Šis mineralas – andradito atmaina. Grosuliaras yra daugiausia atmainų turintis granatų grupės mineralas. Tsavoritas – grosuliaro atmaina, kuriai žalią spalvą suteikia chromo ir vanadžio oksidai. Spalvos tonas (sodrumas) priklauso nuo mangano ir titano oksidų. Šviesiai oranžinę grosuliaro spalvą lemia geležies oksido kiekis. Hesonitas yra grosuliaro atmaina, kurio spalva priklauso nuo mangano ir geležies oksidų kiekių.