CRYSTAL CHEMICAL STUDY OF GARNETS FROM METAMORPHIC ROCKS ALONG THE YAVUZ DERE RIVER IN THE SAKAR REGION, SE BULGARIA, WITH EMPHASIS ON USE IN THE ABRASIVE INDUSTRY

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INTRODUCTION

The garnets from the metamorphic rocks along the Yavuz Dere valley are the biggest ones in the Sakar region [1]. Their quantitative presence in the host rocks is significant. Data about their morphology and chemical composition could be found in the papers by Nikolov [2] and Kostov et al. [3].

Garnet is one of the most popular abrasives. It is capable of cutting an extremely wide range of materials in various hardness and thickness. Garnet sandpaper is the original application of this mineral. It is also used in a number of similar products, including sanding belts, discs and strips. Today, the vast majority of garnet is used as an abrasive blasting material, for water filtration, for abrasive powders and in a process called water jet cutting. Nearly all of the waterjets use garnet because it is the most effective product. Garnet is hard, tough and relatively inexpensive, however, in some cases aluminum oxide and other man-made materials are used. Aluminum oxide is harder than the garnet sand, but it is also more expensive and quickly wears out the
mixing tube.

Australia, China and India are the major exporters of industrial garnet worldwide. Producers of industrial garnet in Europe are: Czech Republic, Ireland, Italy, Norway, Poland and Russia. In SE Europe only Turkey is a producer, but the country does not yet export much of this material [4]. There is no active company in the moment in Bulgaria for research and extraction of the abrasive garnets.

Most important physical characteristics for garnet abrasive grains and powders

According to the ISO (the International Organization for Standardization) general requirements, almandine garnet abrasives are natural mineral grains that absorb no water but may be wetted on the surface only. Silica in almandine garnet abrasives shall be present as bound silicate. The content of free crystalline silica (such as quartz, tridimite or cristobalite) shall not exceed 1.0 % (m/m), as determined by X-ray diffraction. The material shall be free from corrosive constituents and adhesion-impairing contaminants. Almandine garnet abrasives as supplied have a predominantly angular shape. More spherical particle shapes are not excluded as their effect on the surface profile obtained corresponds generally to that produced by angular abrasives particles.

Particular requirements for almandine garnet abrasives are: apparent density (4.0 to 4.2 g/cm³); Mohs hardness (min. 6); moisture (max. 0.2 %); conductivity of aqueous extract (max. 25 mS/m); water-soluble chlorides (max. 0.0025 %) [5].

For making bonded abrasive products such as grinding wheels, additional important factors are stability under high heat and bonding characteristics of grain surfaces. The economic factors of cost and availability are always important.

Notes on the geological setting

The Sakar Mountain is situated in South-East Bulgaria. The Sakar unit is a part of the Strandza zone [6] in the Sredna Gora morphostructure zone [7]. The main magmatic body in the studied district is the Sakar granite pluton, surrounded by a frame of metamorphic rocks.

The studied garnet porphyroblasts are found in two-mica schists, which are outcropping northeast and east from the village of Hlyabovo along the Yavuz Dere River (Fig. 1). These rocks were related to the Zhult Chal Formation [8]. The rocks from the Zhult Chal Formation are of amphibolite facies [9] and in the eastern part of the Sakar unit (vicinity of the village of Lessovo) of epidote-amphibolite facies [10].

Experimental methods

The microscopic study was performed on microscope "Leitz Orthoplan". Analyses of the heavy concentrate from the garnet-bearing rocks (amount of 9 kg). The operation include: mechanical crushing, screening, magnetic and electromagnetic separation, separation with heavy solutions (CHBr₃ and CH₃I₂). Mineralogical analyses are made on the minimum of 500 grains under microscope in immersion eugenol with refractive index 1.541.

Powder X-ray diffraction (XRD) analyses of the samples, performed on DRON 3M diffractometer with a horizontal Bragg-Brentano goniometer, using Fe-filtered Co-Kα radiation (40 kV, 28 mA) in the Central Laboratory of Mineralogy and Crystallography "Acad. Ivan Kostov" of the Bulgarian Academy of Sciences, Sofia. The unit cell parameter was determined using Rietveld based software - the program Fullprof. The exact measured unit cell parameter of garnets was used for cell volume and density calculations.

The chemical compositions of the same samples were studied by Inductively coupled plasma with atom emission spectrometry (ICP-AES) in the laboratory of Geochemistry at the University of Mining and Geology "St. Ivan Rilski". The spatial variation of the chemical composition of the minerals was
studied with electron microprobe analyses (ARL-SEMQ S30, 4 spectrometers, EDS Link, 20 KV, 20 nA) in the University of Leoben, Austria.

The density (D) was calculated as a function of molecular weight, number of formula units and unit cell volume of garnets e.g. D=N/MV, where N is the Avogadro number (1/N=1,6502) and V=Vs.

The microhardness was examined as a function of the unit cell parameter and mol percentages of the end-members.

**Results and discussion**

**Microscopic study.** The garnet-bearing schists display lepidogradoblastic matrix, clearly porphyroblastic in garnet (Fig. 2a, b).

The following parageneses have been defined in the studied rocks: Qtz+Ms+Ore (pre-kinematic); Grt+Bt+white mica+Qtz+Pl+Ore minerals (syn-kinematic)+Ky+St; Bt+white mica +Qtz (post-kinematic), as pre-kinematic one presents only as inclusions in the garnet which mark an earlier foliation [11]. The minerals Ky u St are observed only in the heavy mineral concentrates as a single grains. White mica (the most abundant mineral by comparison to the other rock-forming minerals in the studied rocks) and biotite are observed in fine flakes aggregates. White mica is represented by three morphological varieties, belonging respectively to three parageneses, whereas biotite is only syn- and post-kinematic. They show sub parallel orientation, defining the main foliation (syn-kinematic) in the schists and compose the main part of the third mineral paragenesis. The syn- and post-kinematic white mica and biotite show similar morphology and optical peculiarities.

The garnet porphyroblasts are with size up to 47.60 mm [1]. They show clear syn-kinematic growth - porphyroblasts contain S-type trails of inclusions. In some garnet porphyroblasts the ore inclusions show banded arrangement, fixing the primary banding of the rock (helicitic structure). The smaller porphyroblasts are almost free of inclusions. The cores of the bigger ones are intensively cracked with abundant of inclusions (quartz, white mica, ore mineral) (fig. 3a) in contrast to their rims.

These garnets show optical anisotropy close to the quartz inclusions. This anisotropy represents a relict deformation in the garnet crystals resulting from "stress" [12] and corresponds to their syn-kinematic fast growth (fig. 3b). The garnets are fresh. On rare occasions locally alteration of garnet substance in chlorite or ferric hydroxyls around the cracks or filling them may be observed.

Heavy concentrate analyses. As a result of analyses of the heavy concentrated probe the quantitative presence of garnet in the investigated rock samples from the upper parts of the host rocks is estimated on approximately 25 wt %. The mineral assemblage is: garnet, biotite, white mica, chlorite, apatite, zircon, rutile, staurolite, kyanite, monazite, tourmaline, titanite, anatase, quartz, plagioclase, ilmenite and
some pyrite, chalcopyrite and copper.

Garnets morphology. The garnets have a red-
brownish colour. They occur in grains with crystal-
lographic outlines. Three morphological types of
garnet are established: rhombododecahedral (110) -
habit type f (Fig. 2b), rhombododecahedral (110) -
crystals with small (211) faces - habit type e (Fig. 
4a) and crystals with equivalent development of 
{110} and {211} faces - habit type c (Fig. 4b) [1].
Deviations from the ideal rhombododecahedron are 
observed. They are presented in elongation of the 
crystals along one of the axes G4 or G3, around 
which the elongated in the same direction quadran-
gular rhombohedral or hexahedral faces are de-
veloped [13].

Chemical composition. The garnets are alman-
dine rich with a high content of the pyrope compo-
ponent - Alm 71.60 mol%, Grs 8.60 mol%, Prp 13.97 
mo% and Sps 5.83 mol%. The investigation of the 
spatial variations in the percent composition of the 
end-members shows normal chemical zonality in the 
garnets. It is expressed in a higher content of the 
almandine and pyrope components in the rims of 
porphyroblasts in contrast to their cores. An inverse 
correlation exists between the values of almandine 
and spessartine end-members (Fig. 5). The normal 
chemical zonality in garnet porphyroblasts is of pro-
grade genesis [14]. As seen from Fig. 5 two stages of 
the garnet forming process can be supposed: the first 
one is of formation of garnet core and the second -
of the other part of the porphyroblast. An abrupt 
transition between them is possible to be formed by 
increase in temperature or and pressure of meta-
morphism or by enhanced fluid activity.

On the basis of ICP-AES analysis the following 
trace elements (in ppm) are detected in the garnet 
samples: P₂O₅ - 1200, SO₃ - 300, Ba - 92, Co < 10, 

Physical properties
It is known that the microhardness of almandine 
garnets varies from 1000 to 1300 kg/mm² 
and depends on their chemical composition. 
The amount of the andradite component
has a major effect on 
its decreasing. The lack 
of the andradite end-
member and the pre-
dominant almandine 
composition of the 
studied garnets define 
higher microhardness 
than those of the 
quartz (1120 kg/mm²).
The value of the unit 
cell parameter (a) is 
11.558 (3) Å [15]. 
Using the relation-
ship between molecu-
lar weight, number of 
formula units and unit 
cell volume of garnets 
e.g. D = ZM/NV their density is calculated on 4.06 
(g/cm³).
The inverse correlation exists between unit cell 
parameter of the garnets and their density and 
refractive index i.e. decreasing in value of a as a rule 
is accompanied by increasing in their density and 
refractive index.
The refractive index n = 1.785 is estimated using 
diagram after Winchell [16] (Fig. 6). The relation-
ship between refractive index, cell parameter and 
density of the garnets is presented on this chart.
The use of such diagrams is based on the assump-
tion that the physical properties are additive func-
tions of the molecular proportions of the end-members, and that components other than the five common end-member garnet molecules are relatively insignificant.

Conclusions
The results at this stage of the research about utilization of the studied garnets in the abrasive industry enable to make the following conclusions:

1) The garnets are with significant presence in the metamorphic rocks, outcropping along the Yavuz Dere River in the region of the village of Hlyabovo, and further investigation of their quantity is necessary.

2) The garnets are fresh, with inessential alteration processes.

3) The physical and chemical characteristics (chemical composition, unit cell parameter, density and hardness) of the garnets are suitable for their use as a raw material in the abrasive industry.

4) The garnets possess chemical zonality, but in spite of this, all parts of the porphyroblasts (cores, medium parts and rims) are with predominant almandine composition.

5) Further investigations of quartz inclusions in the studied garnets are necessary to define harmful free silica content.

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