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Structural, Micro-Structural and Thermal Characterizations of Natural Garnet of Regions of Patharkhola from the State of Uttarakhand of India

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Abstract:
Garnet is an important group of nesosilicate minerals. These minerals are widespread in the earth's crust and the upper mantle as a major rock forming minerals. In petrology, they are frequently used as a geothermobarometers to understand the Pressure-Temperature (P-T) history of rock assemblage, which involve many equilibrium reactions occurring in the Earth's upper mantle. The garnets have been widely studied especially on electrical, magnetic and thermodynamic properties, as far as the properties are concerned. Natural Garnet grains obtained from Garnet-mica schist of Patharkhola area have been investigated using various techniques, such as SEM, XRD, DSC-TGA to study their structural and thermal properties. The crystal morphology obtained by SEM has been found in accordance with the XRD data crystallizing in cubic system refined in Ia3d space group making it pyrope to almandine rich garnet. DSC curve shows gentle endothermic peak of heat flow showing its decomposition at higher temperature while the gentle slope of TGA curve shows it to be more magnesium rich respectively.

Keywords: *Natural Garnet, Crystal Structure, Pressure-Temperature Phase transition, Microstructure, Thermal Behaviour, Lesser Kumaun Himalaya*

1. INTRODUCTION

The rocks of the Kumaun and Garhwal Lesser Himalaya have been subjected to repeated phases of tectonic movements (Auden 1937; Mehdi et. al. 1972; Gairola and Srivastava 1982; Thomas T and Thomas, H. 1992; Srivastava. H.B. and Thomas, T. 1999; Thomas, T and Thomas, H. 2003; Rana and Thomas 2018) which has resulted in a very complex geology. The rocks of the Dudhatoli Group are exposed in the Patharkhola area (Rana and Thomas, 2018).The Patharkhola area (Longitude 79°09'E to 79°17'56"E and latitude 29°47'42"N to 29°56'69"N) covering an area of about 125 square kms. is situated in District Almora, Uttarakhand forms a part of the Almora Nappe. The area around Patharkhola forms the southern limb of Dudhatoli Syncline where the Dudhatoli-Almora Crystallines and Phyllites are exposed. The rocks mainly include phyllites, schists and gneisses forming an anticlinal structure showing phyllites in the NW, S to SW and in the western part of the area, while the schists occur in the folded outcrop pattern in between both the limbs of the fold and the gneisses occur in the core of the fold. Although thin quartzitic bands has also been noticed

interbedded with phyllites and schists. The area under investigation is one such part of the Lesser Himalaya which is still lacking in the fundamental geological records and leaves behind many unsolved problems. This place can be approached by road from the nearest railway station, i.e. Kathgodam in India.

In the area under study, schists occur in a folded outcrop pattern and are characterized by their physical and mineralogical characters. Depending upon the biotite, muscovite and/or chlorite content, they exhibit a variation in colour from pinkish brown, dark brown, light grey to greyish green.

Schistosity is defined by the preferred orientation of the flaky minerals and are characterized by one or two sets of crenulations. The rock is friable in nature but at places increased percentage of quartz and feldspar imparts compaction. Thin bands of micaceous quartzites of 1cm to 20 cm in thickness are also present within the schist.

The schists of the area are characterized by the presence of garnet which ranges in size from 0.1 cm to 0.2 cm in hand specimen. Slightly bigger sized garnets (about 0.4 cm) are exposed in the NE of Udaipur and south of Wolmara and along river Bino (Fig. 1c). The quartz veins occur parallel to schistosity and at times shows folded structure. The author has collected samples of garnet-mica schist from North West of Patharkhola village (N 29°51'58.7" E79°12'53.8") shown in the lithological map (Fig. 1).

The garnet group includes all minerals isostructural with garnet regardless of what elements occupy the four atomic sites, i.e., the group includes several chemical classes (Takeuchi & Haga 1976; Grew et. al. 2013). The general formula for garnet group of minerals is $X_3Y_2Z_3O_{12}$, where X, Y, Z refers to dodecahedral, octahedral and tetrahedral sites respectively. Garnets are cubic, have high symmetry and contain SiO_4tetrahedra linked to AlO_6octrahedra and $M^{2+}O_8$ dodecahedra. Garnet has several unusual physical and thermodynamic properties such as its compressibility (Meagher 1975; Allen et. al. 1988; Mernagh 1990; Leger et. al.1990; Lager 1992; Iov 1996; Zhang et. al. 1999; Aparicio et. al. 2014) and large heat capacity at low temperatures (Haselton and Westrum 1980). Their physical properties, i.e. hardness and lack of cleavage, show that strong forces must exist which couple the motions of the individual units. Most garnets are formed at high pressures and temperatures and are particularly characteristic of metamorphic rocks but are also found in some igneous rocks and may also occur as detrital grains in sands and sandstones.

In an attempt to gain a better understanding of the physical properties of the garnets, the authors have tried to describe the characterization of natural garnets from the garnet-mica schist of Patharkhola area. In the present study, the samples have been characterized through XRD, SEM, and DSC-TGA to investigate the structural, micro-structural and thermal behavior of the discovered garnets.

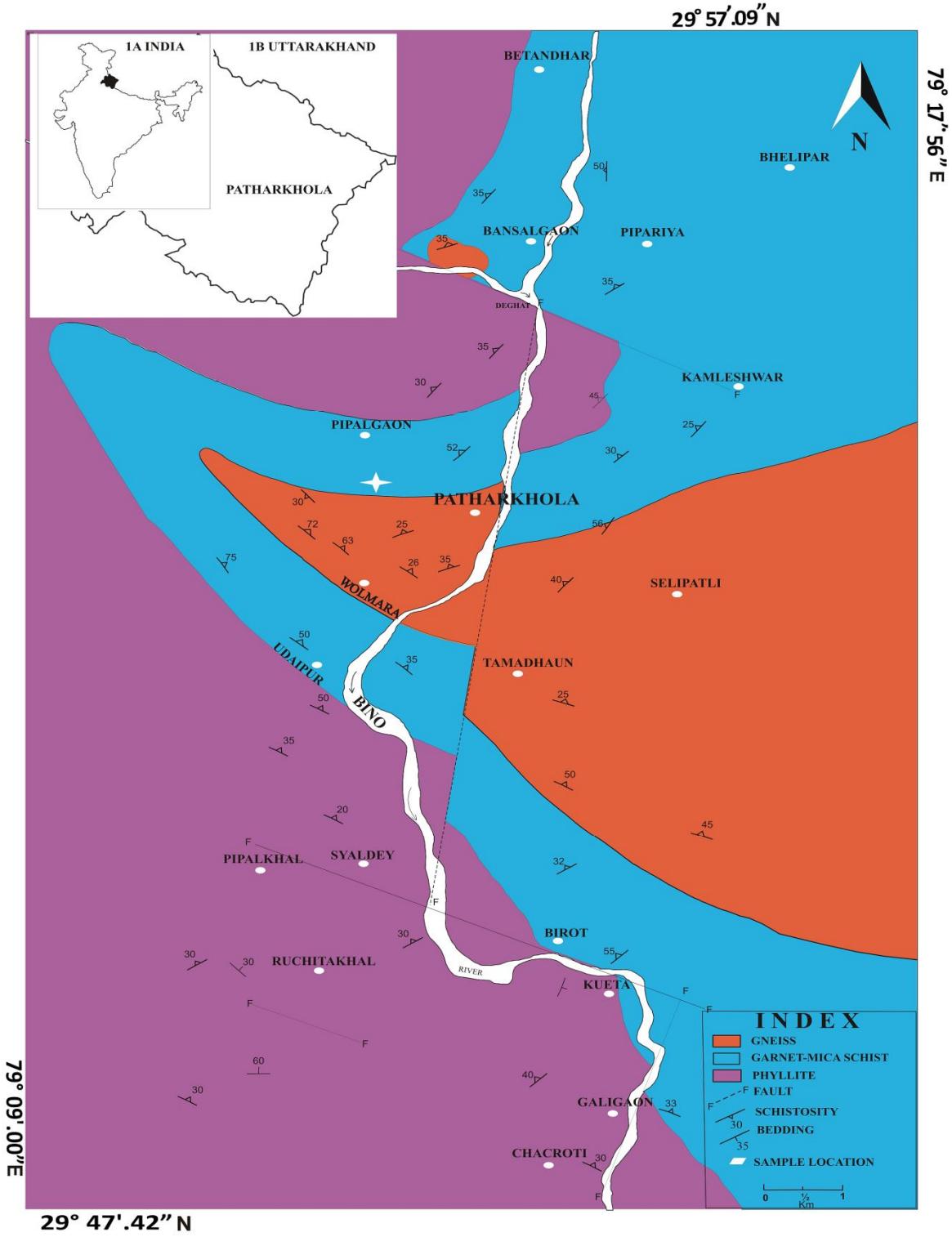

Figure 1: Location and Lithological map around Patharkhola, Lesser Kumaun Himalaya, Uttarakhand (by Thomas, T and Thomas, H., 1992); Modified by Rana, Haritabh and Thomas, H., 2018).

Sample Preparation and Experimental Details

The collected sample of garnet mica schist has been crushed finely in agate mortar where the mica sheets being fragile in nature break in to powder form and was removed leaving behind garnet grains. Under optical microscopy, small rounded pieces of garnet crystal of size 0.1 to 0.2 cm free of impurities were selected. The grains were then cleaned several times under isopropyl alcohol and distilled water and were air dried at room temperature. The obtained grains of garnet were then grounded into powder form using silica ball mill for several days to maintain homogeneity. The structural investigations on the garnets was done with the help of a Powder X-ray diffractometer [Huber G70 diffractometer, Rimsting, Germany] by using Cu-Kα radiation (λ=1.54 Å) at room temperature (RT= 293K). The morphological / microstructure investigations on the garnets were carried out using Thermo Fisher Nova NANOSEM-450, FEI at different scales ranging from 500 nm to 5µm. Both Thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried by Simultaneous Thermal Analyse r(STA 449F1 Jupiter NETZSCH)having heating temperature range from 27°C to 1000°C at a scan rate of 10K / min.

2. RESULTS AND DISCUSSION

Structural Studies

The sample of garnet is recognized by Intensity versus 2Theta (2θ) and from the 'd' spacing of diffractogram for various lattice planes, obtained by scanning the garnet samples in the range of 5° to 90°.The data obtained has been processed using chemical formula as $(Mg_{1.8}Fe_{1.2})_3Al_2(SiO_4)_3$ crystallizing in cubic system refined to be the space group as Ia3d with unit cell dimensions as a=b=c= 11.485 Å, making it a more magnesium rich mineral.XRD pattern of mineral shows parallel intensity peak at different 2θ values along with various (hkl) values, labelled as shown in the Table 1 and Fig. 2. This data corresponds to $(Mg_{1.8}Fe_{1.2})_3Al_2(SiO_4)_3$pyropeferroan crystalline mineral (Lager G.A 1992) as shown in Fig. 2.The crystallite size was calculated using a Scherer equation $D=k\lambda/\beta\cos\theta$, where K=0.9, D represents crystallite size(Å), λ is the wavelength of the Cu-Kα radiation, and β is the corrected half-width half maxima of the diffraction peak. The crystallite size has been calculated to be 68.533 Å.

Table 1: The details of the garnet crystal structure obtained from the xrd spectrum of the garnet, scanned through Cu Kα radiation.

81-0540 — Wavelength= 1.54060 — C

(Mg1.8Fe1.2)Al2(SiO4)3

Magnesium Iron Aluminum Silicate

Pyrope ferroan, syn

Rad.: CuKa1 λ: 1.54060 Filter: d-sp: Calculated

Cut off: 17.7 Int.: Calculated I/Icor.: 1.88

Ref: Calculated from ICSD using POWD-12++, (1997)

Ref: Armbruster, T., Geiger, C.A., Lager, G.A., Am. Mineral., 77, 512 (1992)

Sys.: Cubic S.G.: Ia$\bar{3}$d (230)

a: 11.485(2) b: c: A: C:

α: β: γ: Z: 8 mp:

Ref: Ibid.

Dx: 3.867 Dm:

Peak height intensity. R-factor: 0.011. PSC: cI160. Mwt: 440.98. Volume[CD]: 1514.93.

2θ	Int	h	k	l	2θ	Int	h	k	l
18.912	3	2	1	1	68.271	9	6	5	3
21.871	2	2	2	0	69.376	1	8	2	2
29.068	3	3	2	1	70.474	4	7	4	3
31.124	426	4	0	0	72.648	4	7	5	2
34.909	999*	4	2	0	73.725	84	8	4	0
36.672	143	3	3	2	75.861	136	8	4	2
38.365	214	4	2	2	76.922	13	6	5	5
39.997	158	4	3	1	77.978	60	6	6	4
43.106	127	5	2	1	79.030	23	7	5	4
44.594	30	4	4	0	81.124	2	9	3	2
48.843	178	6	1	1	82.166	1	8	4	4
50.199	24	6	2	0	83.205	33	8	5	3
51.528	2	5	4	1	84.242	1	8	6	0
54.116	3	6	3	1	85.278	4	10	1	1
55.378	135	4	4	4	86.311	16	10	2	0
56.622	4	5	4	3	87.344	4	9	4	3
57.848	314	6	4	0	89.407	4	7	6	5
59.058	13	5	5	2					
60.252	430	6	4	2					
63.756	8	7	3	2					
64.900	92	8	0	0					
66.033	14	7	4	1					
67.156	4	8	2	0					

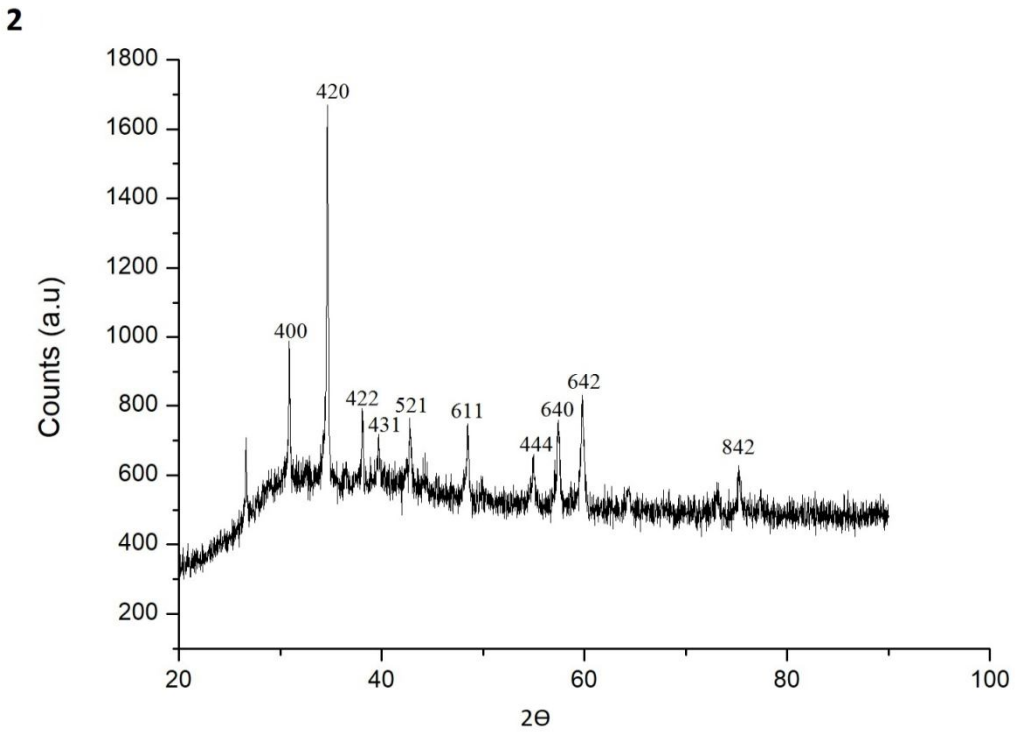

Figure 2: X-ray diffraction pattern of the garnet with all its peaks labeled with (hkl) planes.

Micro-Structural Studies

To understand the morphology, microstructure and crystalline behaviour of the garnet crystals, the SEM images are analyzed as shown in Fig. 3(a-h). Garnet usually crystallizes in isometric/cubic form having common form as dodecahedron and trapezohedron or often in combination. The cubic form has been obtained in the SEM images observed at various scales of 1µm, 2µm, 5µm and 500nm.

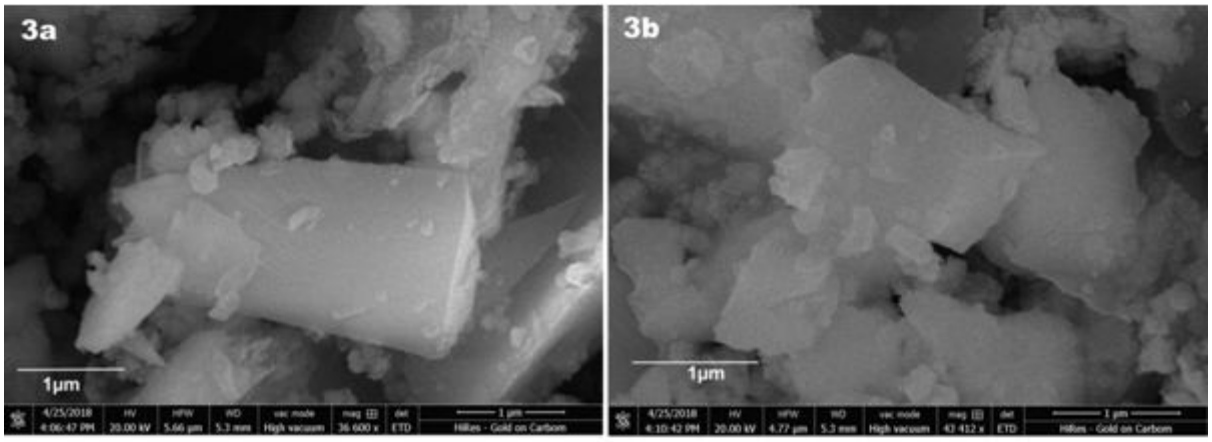

Fig.3a: SEM image of garnet (Scale= 1µm) Fig.3b: SEM image of garnet (Scale= 1µm)

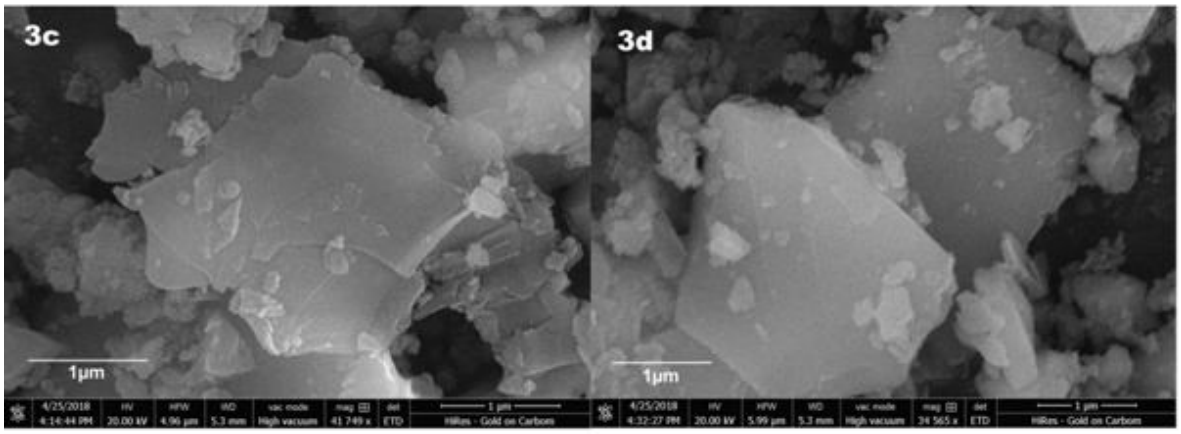

Fig.3c: SEM image of garnet (Scale= 1µm)

Fig.3d: SEM image of garnet (Scale= 1µm)

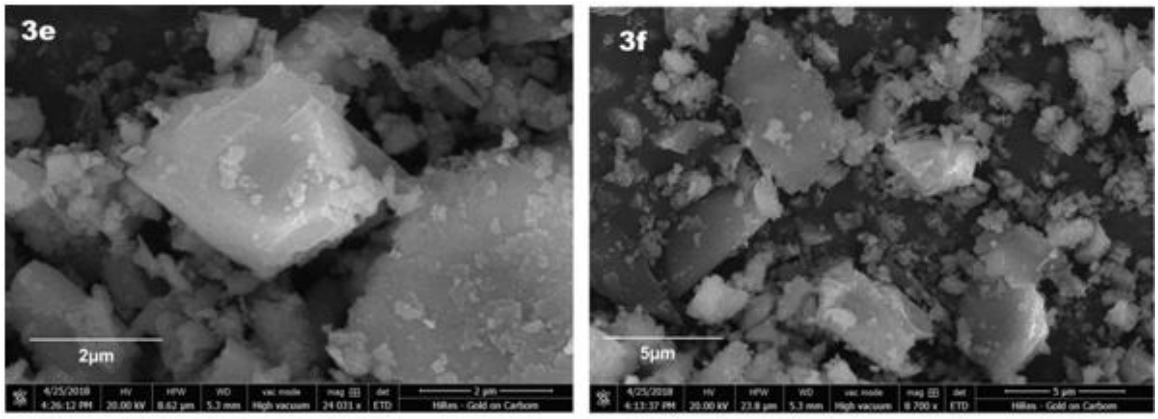

Fig.3e: SEM image of garnet (Scale= 2µm)

Fig.3f: SEM image of garnet (Scale= 5µm)

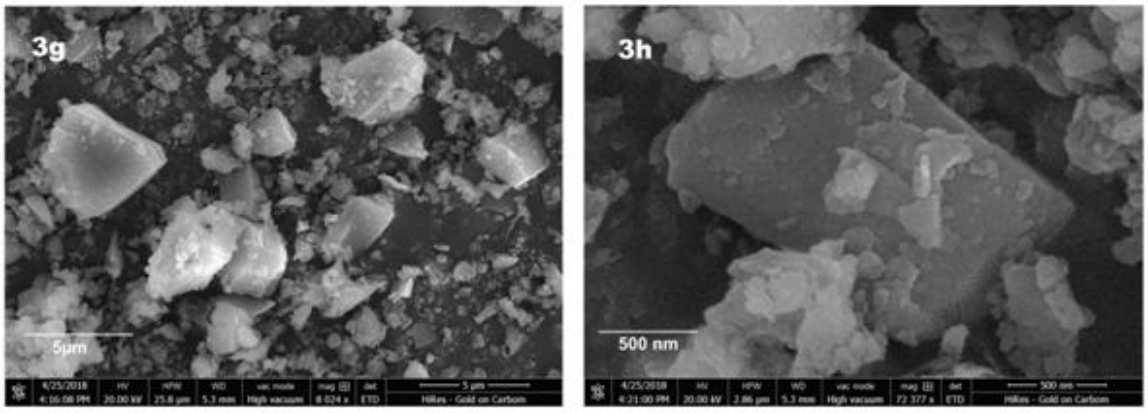

Fig.3g: SEM image of garnet (Scale= 5µm)

Fig.3h: SEM image of garnet (Scale= 500 nm)

Figure 3: The SEM micrographs of the garnet sample at different scales.

Thermal studies

In the measurement of DSC/TGA on the samples, the samples were individually heated from room temperature to 1000°C, with a heating range of 10°C /min in an open alumina crucible in N_2 atmosphere at a flow rate of 60/40m per minute. Once the selected temperature was reached, the sample was cooled down to room temperature with a cooling rate of 40°C /min. The DSC curve shows exothermic peak indicating the decomposition process of garnet. Before the onset of thermal decomposition, a small amount of water has been observed at 69.5°C and 101°C with -2.39 and -1.865 mW/mg heat flow respectively as shown in Fig. 4a.The TGA curve shows decrease in mass after the beginning of the thermal decomposition. The gentle slope of curve shows a very small amount of mass loss as shown in Fig. 4b. 19 % of mass loss (Δm) has been observed till 1000 °C. This loss of mass may be due to presence of H_2O and other volatile gases embedded in minerals resulting in 80% of mineral present.

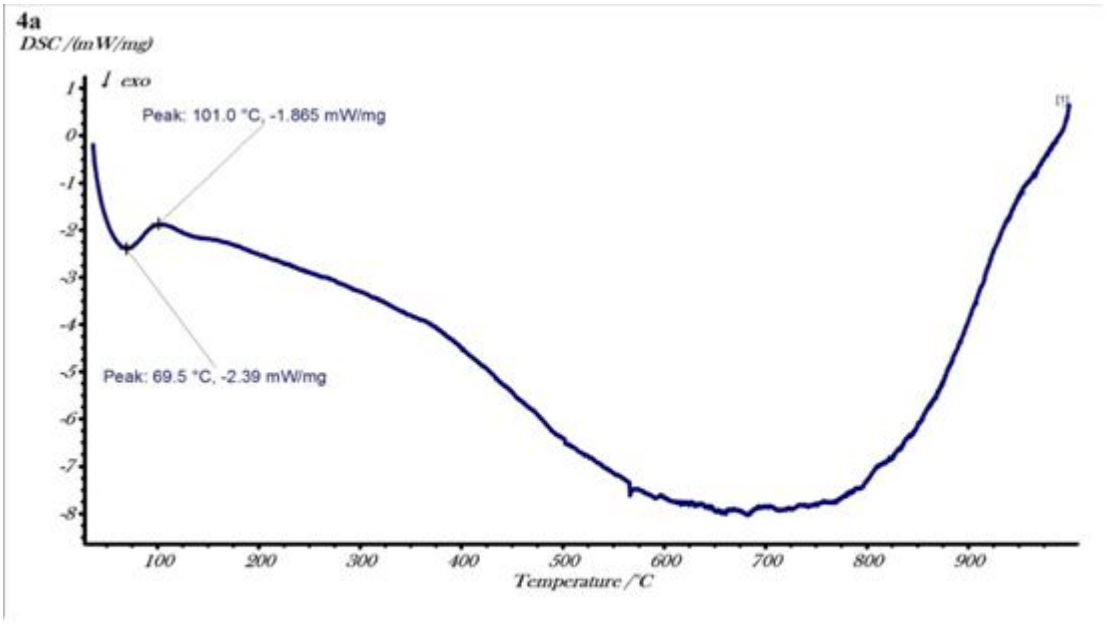

Fig4a: DSC curve of Garnet

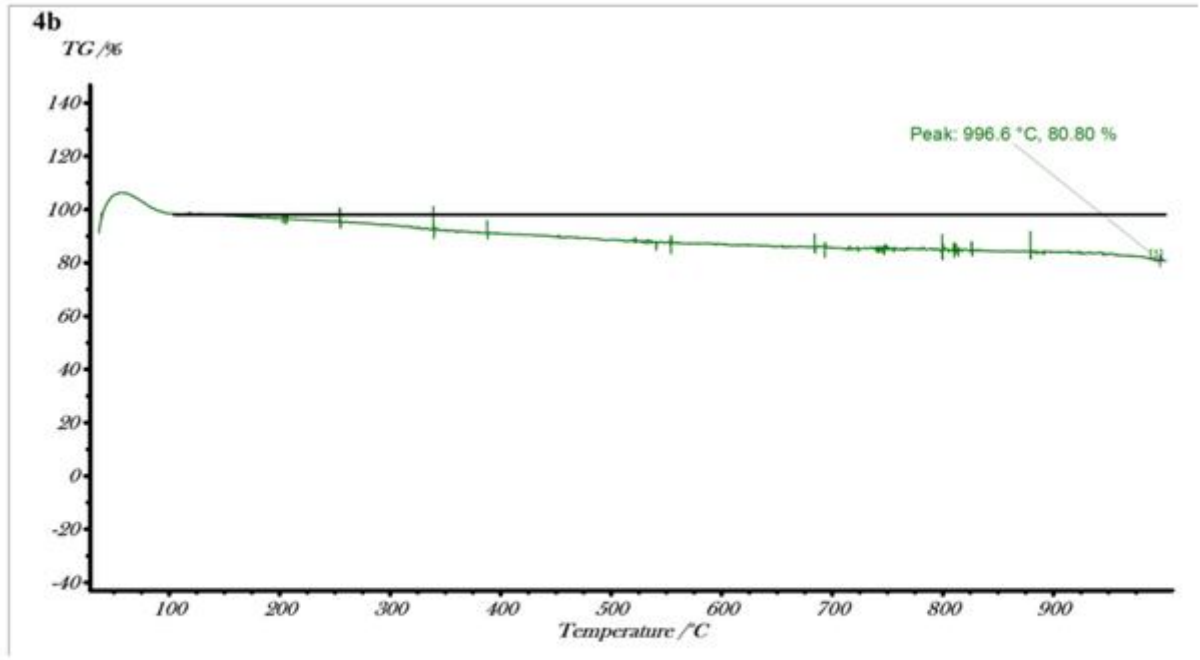

Fig4b: TG Curve of garnet

Figure 4(a): The DSC curve of the natural garnet sample showing the various transition behaviors at different temperatures **(b)** The TGA curve of the natural garnet sample showing the various mass loss behaviors at different temperatures.

3. CONCLUSIONS

Interestingly the natural Garnet obtained from the garnet-mica schist of Patharkhola area has been confirmed through structural / microstructural / thermal characterizations. The crystal system of garnet confirmed by the SEM study at different resolution has been found in accordance with the XRD data depicting its crystallization in cubic system. The garnet has been found to be pyrope to almandine rich $(Mg_{1.8}Fe_{1.2})_3Al_2(SiO_4)_3$ refined in (Ia3d) space group with unit cell dimension as a =b=c= 11.485 Å having highest intensity at 2θ=34.909°, and having crystallite size of 68.533Å.The DSC curve shows endothermic peaks around 100 °C, while the TGA shows a gentle slope of mass loss of 19 % till 1000 °C showing major peak at 996.6 °C.

The thermal stability of the garnets decreases with the increase of iron content, but when the iron content is very low, i.e., for a garnet composition close to pyrope, the thermal stability decreases as depicted in the curve. Therefore, with all the analysis used has confirmed the presence of pyrope to almandine rich garnet.

4. DECLARATIONS

Conflict of interest: The authors declare that they have no conflict of interest

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