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X-Ray Diffraction Studies of Gemstones from Shigar Valley, Skardu, Gilgit-Baltistan Region, Northern Areas of Pakistan

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Abstract: Variety of world class gemstones are found in the Shigar Valley of Gilgit Baltistan. Granitic pegmatites are mainly hosting these gemstones, however, some of the gemstones are also found in the metamorphic rocks. These gemstones have been identified as garnet (almandine-spessartine), beryl, tourmaline (foitite-schorl), fluorite, apatite, topaz, epidote (zoisite and clinozoisite) and axinite through X-Ray Diffraction technique.

Keywords: Shigar Valley, Gilgit Baltistan, pegmatites.

INTRODUCTION

Shigar Valley is one of the most famous valleys of the Gilgit-Baltistan region of Pakistan which is located north of Skardu in the northern areas of Pakistan **(Fig. 1)**. A variety of gemstones have been reported mainly in the pegmatites and also in the metamorphic rocks of Shigar valley. The pegmatites of the Shigar valley are usually complex or zoned but unzoned pegmatites are also not uncommon. Majority of the gemstones are generally found in the zoned pegmatites, where these are

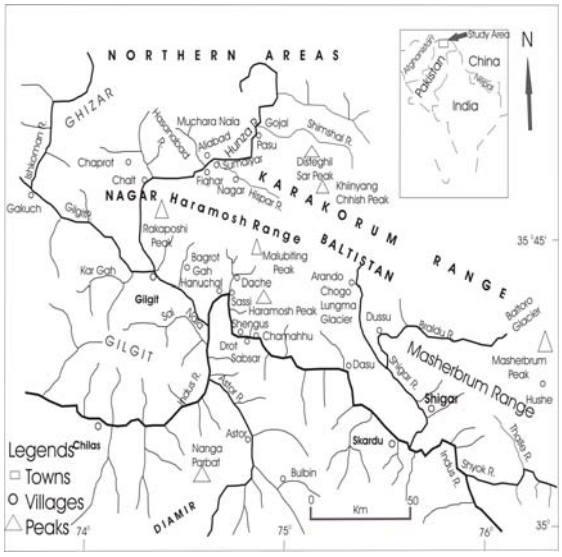


Fig. 1. Map of the Shigar valley, northern

are tightly packed, usually surrounded by light-pink or white clay material, within the cavities or primary pockets. These gemstones were collected confined to the central parts of the intermediate zone and also at the core-margin zone. These gemstones during field and were subjected to further identification and categorization by various techniques.

The gemstones are normally identified by their physical properties such as color, specific gravity, refractive index and response to ultraviolet light. The identification of gemstones on the basis of physical properties is needed to be confirmed through other sophisticated instrumental techniques.

The important among these are the Electron Probe Microanalyser (EPMA), Scanning Electron Microscope having Energy Dispersive Spectrometer (SEM-EDS) and X-Ray Diffractometer (XRD). During this study the Shigar valley gemstones have been analyzed by the through X-Ray Diffraction technique. The data, obtained through this technique, have been used in combination with physical properties and field features for the proper nomenclature of the gemstones of the Shigar Valley.

MATERIAL AND METHODS

Most of the gemstones studied during this study have been either collected from the local miner at the mining site but at places some of the gemstones have been collected from the cavities and vugs within the host rock.

Qualitative analysis of 22 crystals of different gemstones, collected during the field work, was carried out on X-Ray Diffractometer at the National Centre of Excellence in Geology, University of Peshawar. All the analyses were performed on the Rigaku X-Ray Diffractometer under the following operating conditions: the target material was Cu Kα, the operating voltage and current were 35 Kv and 20 Ma respectively. Both step scanning and continuous scanning were performed at step size of 0.05 and 0.01 respectively.

A small portion of each collected gemstone was cut with a very fine diamond blade in the Gems and Gemological Institute of Pakistan (GGIP), Peshawar. These cut pieces were pulverized and mounted on the glass slide. The slide was then fixed in the sample chamber of the XRD for qualitative analysis under the above mentioned operating conditions. A computer program was used to calculate the d-values and intensities of each sample. For the qualitative analysis, the obtained powdered diffraction patterns of each gemstone sample were compared with the data files of International Centre for Diffraction Data (ICDD) through a computer software program and all the samples were identified properly.

RESULTS AND DISCUSSION

The gemstones identified during this study are discussed individually as under.

Garnet ($3RO.R_2.O_3SiO_2$)

It was noticed during the field work that the large and gem-quality crystals of garnet are rare in the pegmatites of the Shigar valley but tiny crystals (~ 2 cm) along with massive habbit are present in the same pegmatites. Though, the small gem-quality crystals of garnet are found in all the exposures of pegmatites, especially in the gem-bearing class of pegmatites but the pegmatites at Dassu and Yuno are the main host rocks. These pegmatites have been extensively mined for the occurrences of euhedral garnet crystals along with other associated gemstones. The collected garnet crystals are translucent, reddish-brown and generally <1 cm in diameter.

The pattern of the X-Ray Diffractogram and the calculated d-values **(Fig. 2)** of the studied garnet from the Shigar valley indicate that it is very near to the almandine-garnet but some of the peaks that are common in spessartine and almandine are also present, which confirm that these are almandine-spessartine garnets with the major input of almandine. Following the classification scheme of Sobolov (1965), the analyzed garnets of the Shigar Valley pegmatites are not pure but contain significant quantities of different end-members especially.

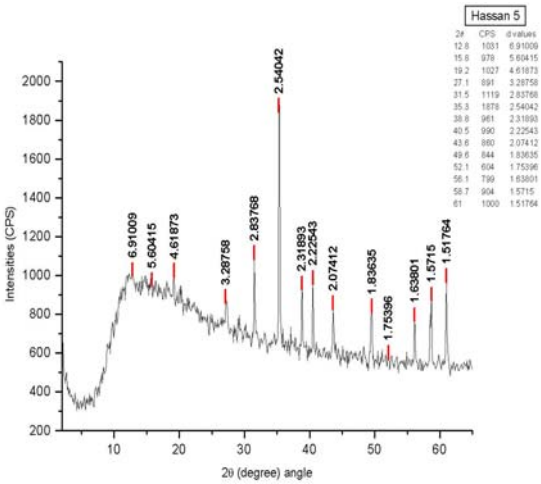


Fig. 2. X-Ray powder diffractionpattern of garnet from a pegmatite at Yuno, Shigar Valley.

However, pure spessartine or almandine may occur and have then reported from various pegmatites elsewhere in the world (Strock, 1930; Hall, 1965; Gresens, 1966). According to Hall (1965) almandine-spessarine garnets most commonly occur in those granitic pegmatites, where the % of MnO of muscovite is in the range of 0.06-0.08wt. %. In this context, Hassan (2007) has reported MnO contents of muscovites in the pegmatites of the Shigar valley are ranging from 0.03 to 0.09 wt. %. It is, therefore, feasible that the manganese has been retained in the residual magma until the formation of garnets occurs near the core-margin zone of pegmatites.

Beryl ($Be_3Al_2Si_6O_{18}$)

Two gem varieties of beryl such as light to dark blue colored aquamarines and a colorless variety known as goshenite are found during the field work from the Shigar Valley pegmatites. The transparent and pale blue aquamarine crystals have been reported earlier by Middlemiss and Parshad (1918) from Dassu pegmatites. These aquamarines are world famous and are found in the famous museums of the world as reported by Kazmi *et al.*, (1985). Both of the above two varieties ranging in size from 2 to 1 4 cm are common in the gem-bearing class of pegmatites in the Shigar valley. During the field work, it was noticed that the gem-quality crystals are typically concentrated near the core-margin zone of pegmatites within the cavities and vugs. According to the local miners, morganite (pink-beryl) is also found from these pegmatites but the present X-Ray Diffraction studies showed that these so-called morganite crystals are actually apatite and not the beryl.

When the collected beryl crystals were analyzed on XRD, it became evident that these crystals are pure beryl. There are only slight differences between the chemical composition and d-values of the aquamarines and goshenite. This is the reason that the analyzed crystals can not qualify either for aquamarine or goshenite and are, therefore, characterized as beryl. (Fig. 3).

Foitite -Schorl [$NaFe_3^{+2}Al_6(BO_3)_3Si_6O_{18}(OH)_4$]

Schorl or foitite the "black tourmaline" is a ubiquitous gemstone in the gem-bearing class of the Shigar Valley pegmatite. Schorl or foitite is not as attractive as the other gem-varieties of tourmaline group such as rubellite, indicolite, dravites, achroite and bi and tri-colored tourmalines. During the field work though we could not collect best specimen but one gem-quality crystal was collected from a pegmatite exposed at Kashmol village. Other common associated minerals of the schorl in the Shigar valley pegmatites are albite, muscovite, aquamarine and quartz **(Fig. 3)**.

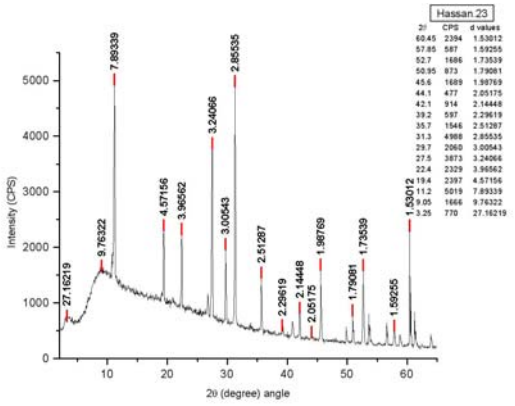


Fig. 3. X-Ray powder diffraction pattern of beryl from a pegmatite at Dassu, Shigar Valley.

only one variety is found but different types of tourmalines may be present even in a single pegmatitic body as is reported by Shearer *et al.,* (1984) from the Black Hills, South Dakota and Laurs *et al.,* (1998) from the pegmatites of Stak Nala, northern areas of Pakistan. Genetically, there are two types of tourmalines of the Shigar Valley pegmatites. Those, formed during the main pegmatitic evolution are the primary, while those formed during the hydrothermal or pneumatolytic action are secondary in origin (Hassan, 2007).

The collected tourmaline crystals are analyzed on the XRD and the results are given in Table 1 and (Fig.4). According to the Electron Probe Microanalyzer data mentioned by Hassan (2007) and Agheem *et al.,* (2011 in press) the tourmalines of the Shigar Valley are the iron-rich variety known as schorl but the present X-Ray diffraction studies favors another iron rich variety known as foitite (Fig. 4). On the basis of present XRD data, the main three intensive d-values are very close to the standard patterns of either foitite or foitite-schorl varieties **(Fig. 4)**. In case of foitite, the main and characteristic d-value is 3.45 and it is present in all the analyzed tourmalines. The second highest peak present in the analyzed crystals is 2.57, which is the common d-value in all the varieties of tourmalines. The third intensive and characteristic peak of foitites is 6.33 and this is also present in the analyzed tourmalines. The fourth intensive peak is 2.96 and this is present

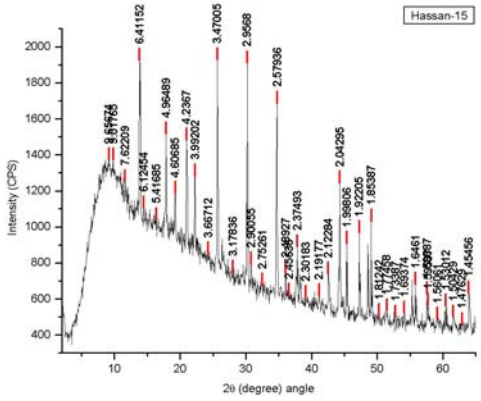


Fig. 4. X-Ray powder diffraction pattern of the tourmaline (var. schorl-foitite) from a pegmatite, Kashmol, Shigar Valley.

in some of the tourmalines, especially in the foitite-schorl end-member. So the present X-Ray Diffraction studies indicate that the tourmalines of the Shigar valley are either foitite or foitite-schorl instead of pure schorls.

Fluorite (CaF_2)

In the Shigar Valley pegmatites, fluorite is generally found in the cavities near the core-margin zone which could be of pneumatolytic origin **(Fig. 5)**. It is pale to dark-green in color and is found

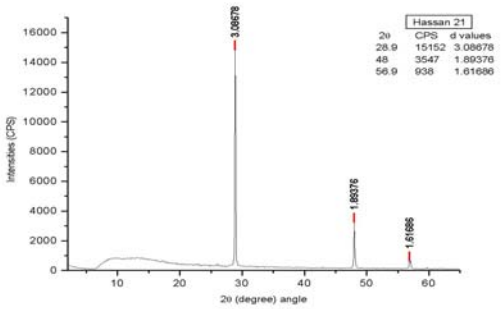


Fig. 5. X-Ray powder diffraction pattern of a fluorite from Kashmol mine, Shigar Valley.

at various localities such as Yuno, Mungo, Kashmol, Baha and Nyit Bruk. The average size of these crystals is 2 x 3 cm and they are typically associated with tourmaline, beryl, quartz, topaz and muscovite. Bill *et al.,* (1967) reported that the green color of fluorites is mainly due to the presence of either Dy or Sm. However, Bellanca *et al.,* (1981) are of the opinion that the green colored fluorites are generally rich in Sm and Eu then the blue, violet, or white varieties.

Gem-quality fluorite crystals are analyzed for their x-ray diffraction pattern on the XRD and the results are presented in (Fig. 5). The XRD data suggest that the studied fluorites are pure in nature. However, yttrian-fluorite variety has also been noticed. Hassan (2007) and Agheem *et al.,* (2011 in press) reported that like the minute crystals of fluorite observed in the thin sections, the large gem-quality green colored fluorites are also pure CaF_2.

Apatite [Ca_5 (PO_4)$_3$ (OH, F, Cl)]

Shigar Valley pegmatites are also the host rocks of pink to light-pink colored apatite. The local miners call these light pink-colored apatites as morganite (a variety of beryl). These gem-quality apatites were run on XRD and x-ray diffraction pattern are shown in **(Fig-6)** and d-values in Table 1.

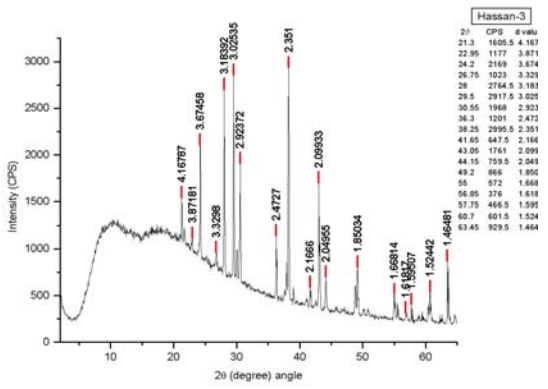


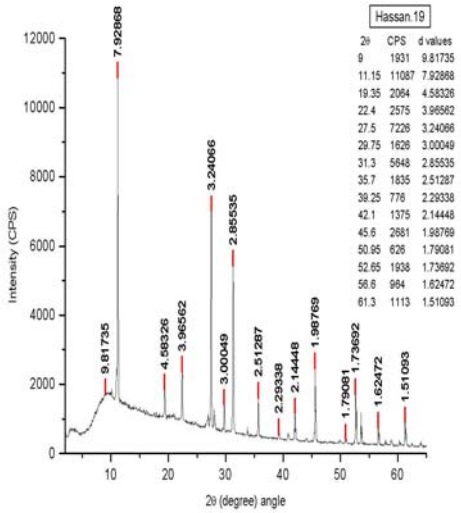
Fig. 6. X-Ray powder diffraction pattern of apatite from Yuno mine, Shigar Valley.

The X-Ray Diffraction data of these apatites indicate that these are pure apatites instead of morganite. The colorless apatites are also reported from the Shigar Valley pegmatites but these were not seen during the present studies. The best specimens having apatite and other associated gemstones occurring in the Shigar Valley are exported in the world gem-market. The gem-quality apatites are only present within the gem-bearing class of pegmatites but under the microscopic study minute crystals were also seen in the gem-barren class of pegmatites (Hassan, 2007).

Topaz (Al_2SiO_4 (OH, F)$_2$

Two varieties of topaz are reported from gem-bearing class of pegmatites from different localities in the Shigar Valley. During the present fieldwork only two colorless crystals of topaz (1x3 cm), one from Yuno and another from Kashmol were collected. The collected colorless crystals of topaz were run for their X-Ray patterns on the XRD and the results are shown in **(Fig. 7)**. The obtained X-Ray Diffractogram of colorless topaz indicate that these crystals are of pure topaz that is generally found in granitic pegmatites.

Fig. 7. X-Ray powder diffraction pattern of topaz from Kashmol, Shigar Valley.



Zoisite [Ca_2 (Al, Fe)$_3$ (OH) (SiO_4)$_3$]

All the gemstones found in the Shigar valley are not of pegmatitic origin but a few of them are either the product of metasomatism or thermal and regional metamorphism (Hassan, 2007). Gemstones such as the axinites, zoisites and clinozoisites being mined from Alchuri and Hashupa areas of the Shigar valley are of this variety as no pegmatite intrusions are found in this area. The colorless to light-green gemstones of epidote group collected from the Alchuri area is known as tanzanite among the local miners. These were analyzed by the XRD and the X-Ray Diffractogram and the d-values are shown in **(Fig. 8)** respectively. The x-ray pattern and the d-values clearly suggest that these are zoisite of green-quality and not tanzanite. Moreover, during the field work it was noticed that gem-quality zoisite is not found within pegmatite bodies but it is present along the margins or fractures of the metamorphosed mafic veins within the greenschist to amphibolite grade metamorphic rocks.

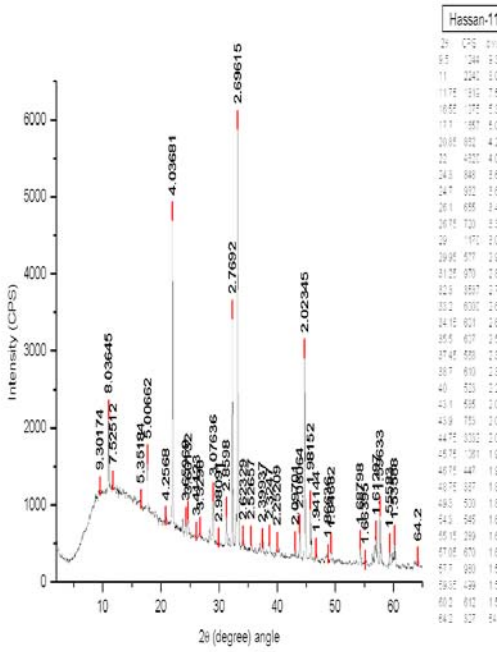


Fig. 8. X-Ray powder diffraction pattern of zoisite from Alchuri, Shigar Valley.

Clinozoisite [$Ca_2Al_3Si_3O_{12}$ (OH)]

Like the zoisite; clinozoisites are also being mined from those areas of the Shigar Valley, where granitic pegmatites are not exposed. The most productive and well-known localities for the occurrences of such gemstones are the Alchuri and Hashupa (Fig.1). The mineralization of epidote-clinozoisite is either in the form of veins or sometimes it occurs along the joints or fractures developed within the metamorphic rocks of greenschists or epidote-amphibolite facies. The gem-quality epidote crystals collected during the field work from the Alchuri and Hashupa areas are mostly brown to yellowish brown. Majority of the crystals are dark-brown and opaque but transparent to translucent greenish-brown to light-brown or yellowish green varieties are also being mined from these areas. Among the local miners and gem-dealers these varieties of epidote are known as Zabarjad. Therefore, these green-quality epidotes were run on the XRD for their proper nomenclature. The X-Ray Diffraction pattern **(Fig. 9)** and the d-values (Table 1) indicate that these are clinozoisite and not the zabarjad.

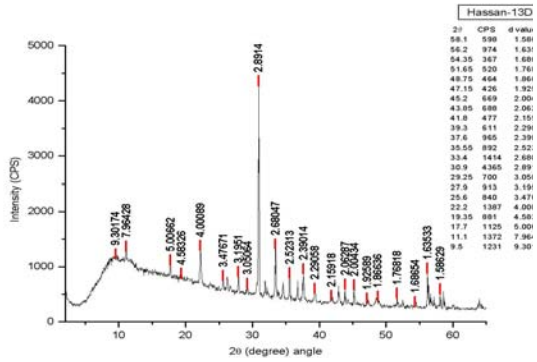


Fig. 9. X-Ray powder Diffraction pattern of clinozoisite from Hashupa mine, Shigar Valley.

Axinite [$(Ca, Fe, Mn, Mg)_3 Al_2BO_3Si_4O_{12}$ (OH)]

Axinite is a group of minerals such as ferroaxinite, manganaxinite, magnesioaxinite and tinzenite (Sanero and Gottardi, 1968; Milton *et al.*,1953; Jobbins *et al.*,1975). During the field work, some of the axinite crystals were collected from Alchuri and Hashupa areas (Fig.1). These axinite crystals are light-pink to brown in color. These axinites were analyzed by the XRD for their X-Ray Diffraction pattern **(Fig. 10 and d-values Table 1)**. It was found that these patterns are more similar to ferro-axinites instead of mangano-axinite.

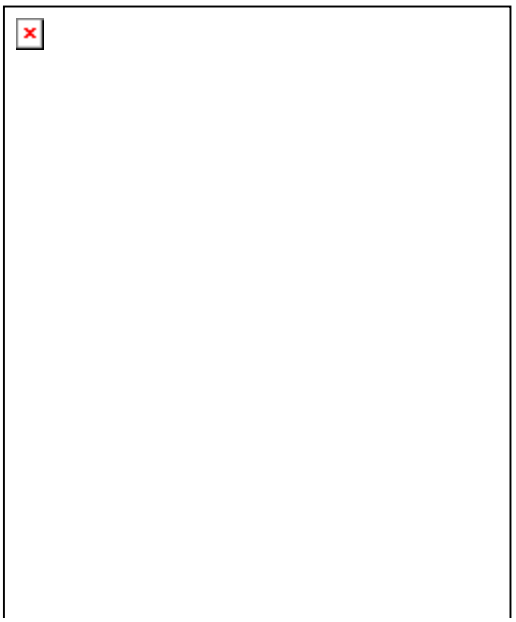


Fig. 10. X-Ray powder Diffraction pattern of axinite (var. ferroaxinite) from Alchuri, Shigar Valley.

Table 1. XRD data of the Shigar Valley gemstones with three major d-values.

S. No.	Sample No.	Name of the Locality	d - 1	d - 2	d - 3	Gemstone
1.	23	Dassu	3.45	2.56	6.33	Foitite
2.	20B	Dassu	3.45	2.56	6.32	Foitite
3.	15	Kashmol	3.45	2.57	6.32	Foitite-schorl
4.	13D	Alchuri	2.87	2.78	2.65	Clinozoisite
5.	10C	Alchuri	2.88	2.66	2.59	Clinozoisite
6.	22	Hashupa	2.57	3.96	2.88	Clinozoisite
7.	11A	Alchuri	2.68	2.02	4.03	Zoisite
8.	19	Kashmol	2.91	3.17	3.65	Topaz
9.	6	Yuno	2.92	3.02	3.65	Topaz
10.	3	Yuno	2.78	3.41	2.71	Dahlite
11.	7	Yuno	3.13	1.92	1.64	Fluorite
12.	21	Kashmol	3.13	1.96	1.64	Fluorite
13.	18	Kashmol	3.13	1.92	1.64	Fluorite
14.	4A	Yuno	2.85	3.24	7.89	Beryl
15.	8	Yuno	2.84	3.22	7.89	Beryl
16.	46	Dassu	2.85	3.23	7.89	Beryl
17.	54	Goyungo	2.85	3.23	7.86	Beryl
18.	50	Nyit	2.88	3.27	7.92	Beryl
19.	53	Nyit	2.85	3.24	7.93	Beryl
19.	58	Basha	2.85	3.24	7.89	Beryl
21.	48	Dassu	2.56	1.56	1.54	Almandine
22.	5	Yuno	2.54	2.83	1.51	Almandine

CONCLUSIONS

The nomenclature used for a variety of gemstones found in the Shigar Valley has been confirmed by using the X-Ray Diffraction technique.

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