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MINERALOGICAL CHARACTERISTICS OF KYANITE FROM PRILEPEC, REPUBLIC OF MACEDONIA

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A b s t r a c t: This paper gives mineralogical characteristics of kyanite from village of Prilepec, R. Macedonia. Several samples were collected for research. The kyanite was identified by Scanning electron microscopy (SEM), coupled with an energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD) and Infra red spectroscopy (IR). The use of these three methods showed that they are very useful methods for rapid mineral analysis contributing important analytical information.The results of the X-ray powder pattern, SEM analysis and Infra red spectroscopy enable straightforward identification of the studied mineral sample as kyanite. Kyanite is located east of village of Prilepec in micashist rocks which have lepidoblastic structure and schistose texture. It occurs in blue thin-bladed triclinic crystals and crystalline aggregates. Cleavage is perfect on {100}, good on {010}. Fracture is splintery. Kyanite is transparent to translucent. Lustre is vitreous or sub-vitreous. Hardness lengthwise 4–5, crosswize 6–7. Density 3.53–3.67 g/cm^3. The colour is blue. Origin on blue colouris due to the charge-transfer process $Fe^{2+} \rightarrow Fe^{3+}$, $Fe^{2+} \rightleftharpoons Ti^{4+}$ or Cr^{3+}. In our samples concentration of Fe is 0.05–0.18 wt%, Ti concentration is 0.03–0.11 wt%, while Cr concentration is 0.02–0.13 wt%.

Key words: kyanite; scanning electron microscope (SEM); X-ray diffraction; infrared spectroscopy (IR)

INTRODUCTION

Kyanite is named in 1789 by Abraham Gottlieb Werner from the Greek word "kyanos", meaning "blue," the common color of the species. Kynanite is a triclinic polymorph of the aluminosilicates having the chemical formula Al_2SiO_5. Colour is blue (Fig. 1). Cleavage is perfect on {100}, good on {010}. Fracture is splintery. Kyanite is transparent to translucent. Lustre is vitreous or subvitreous. Hardness lengthwise 4–5, crosswize 6–7. Density 3.53–3.67 g/cm^3.

Crystalize in triclinic system, class 1 – Pinacoidal, a = 7.1262(12) Å, b = 7.8520(10) Å, c = 5.5724(10) Å, α = 89.99(2)°, β = 101.11(2)°, γ = 106.03(1)°, V = 293.60 Å^3, Z = 4. Under cross nicol it shows gry to black colour. Its relief is high and interference colours up to first order red. Pleoshroisam is weak. X = colorless, Y = violet-blue, Z = cobalt blue. n_α = 1.712–1.718, n_β = 1.720–1.725, n_γ = 1.727–1.734, $2V$ = 82°–83°.

Fig. 1. Kyanite from village of Prilepec

The crystal structure of kyanite was first deduced by Naray-Szabo et al. (1929), and refined by Burnham (1963) from single crystal X-ray diffraction data. Winter and Ghose (1979) studied the structural variations of kyanite, sillimanite, and andalusite with temperature. Studies on the crystal structures of the three Al_2SiO_5 polymorphs have been summarized by Papike and Cameron (1976),

Winter and Ghose (1979), Ribbe (1980), Kerrick (1990), Yang et al. (1997a) and Comodi et al. (1997). Kyanite commonly found in medium- to high-grade metamorphic regional rocks of areas subjected to minimum pressure of about 3 Kbars which is known as kyanite stability field in the phase diagram of andalusite-kyanite-sillimanite. (Hurlbut and Klein, 1977). Kyanite is often associated with garnet, staurolite and corundum. It is located east of village of Prilepec in micashist rocks which have lepidoblastic structure and schistose texture. The geological characteristics, mineralogical composition, genesis and reserves of the kyanite from Prilepec were reported by (Stojanov R., 1974; Barić Lj., 1956, Marinković S., 1955).

EXPERIMENTAL METHODS

The kyanite was identified by Scanning electron microscopy (SEM), coupled with an energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD) and Infra red spectroscopy (FTIR). The use of these three methods showed that they are very useful methods for rapid mineral analysis contributing important analytical information. SEM is especially useful because it gives elemental, mineralogical and morphological data at the same time. Scaning electron microscopy model VEGA3 LMU and EDS-X-act: 10 mm^2 connected with INCA 250 EDS software was used.

X-ray diffraction (XRD) is known as the best method for the identification and quantification of minerals.The used instrument was XRD Shimadzu 6100. It was used copper radiation CuK_α = 1.54178 Å, the voltage of the generator 40 kV, and the current was 30 mA..$2\theta = 2°$/min.

Infrared spectroscopy was performed using IR Prestige 21 spectrometer (Shimadzu, Japan) with DATLGS detector.The spectra were recorded in spectral range 400–4000 cm^{-1} with resolution of 2 cm^{-1} and 45 scans. For spectra manipulation IR-Solution 1.5 software (Shimadzu Corporation) was used. Two methods were employed in these measurements:

a) *The KBr pellet method*. The pellets (4 mm dia) were prepared by mixing 0.5–1 mg of the sample powder and about 100 mg of the KBr.

b) *The Diffuse reflectance method*. Reflectance spectroscopy measurements were performed by use of DRS 8000 (Shimadzu, Japan) accessory. Using this method the infrared spectra were obtained by measuring the diffuse reflected light that was emerged from the powder sample surface after first being absorbed inside the sample and reflected among the particles. The powdered samples were diluted to about 5% by weight in KBr and placed into the sample holders (2 mm dia with 1 mm deep). The resultant spectra were converted to Kubelca-Munk function (Griffiths, 2007) to make them more comparable to the absorption spectra.

RESULTS AND DISCUSSION

The summary of the chemical analysis result of the representative samples is represented in Table 1.

In comparison with the analytical values reported by Faye and Nickel (Table 2) these samples have the higher content of Ti and Cr, while concentration of Fe is nearly equal.

Figures 2, 4, 6, 8, 10, 12 and 14 show SEM images of kyanite, while EDX spectrum of kyanite is given on Figs. 3, 5, 7, 9, 11, 13 and 15.

The blue colour of the kyanite, has also been attributed to the presence of traces of Ti^{3+} by White and White (1967). Published analyses (Pearson and Shaw, 1960; Deer, Howie and Zussman, 1962; Herz and Dutra, 1964; Albee and Chodos,1969) indicate that the blue colour of kyanite does not correlate well with titanium concentration. According to Faye (1968a); Faye, Manning and Nickel (1968); Manning and Nickel (1969) the blue colour and visible pleochroism of this mineral were due to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process, a phenomenon which strongly influences the optical properties of many other minerals. That $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer may be associated with blue kyanite has been suggested by Robbins and Strens (1968), but they did not attemp to validate this speculation experimentally. According to Wenk and Bulakh (2004) origin of blue colour is result of charge transfer $Fe^{2+} \rightleftharpoons Ti^{4+}$. According to Wildner (2013) the blue colouration of kyanite solely is due to Cr^{3+}cations.

With X-ray the five alues – *d* and intensitites *I*: 3.35(100), 3.18(20), 2.70(40), 2.51(50), 1.960(50), 1.929(80).

The most intense registered maxima in the studied powder diagram (Fig. 16) were compared

with the corresponding maxima in the diagram of kyanite sample JCPDS card 01 083 1567. The comparison has shown that the X-ray powder pattern of the natural kyanite taken from the JCPDS card are practically identical with the studied diagram.

The experimental results obtained by Infrared spectroscopy are summarized in Table 3.

T a b l e 1

Chemistry of kyanite from village of Prilepec

Element	Weight (%)						
	Sample 1			Sample 2		Sample 3	
O	70.92	71.50	72.01	60.15	63.68	68.03	73.40
Al	19.82	17.61	18.09	19.59	23.75	21.31	17.95
Si	8.82	8.60	9.22	19.76	11.23	10.44	8.68
Ca	0.08	–	0.19	0.10	0.10	–	–
Ti	0.11	–	0.03	0.06	–	0.05	–
Cr	–	0.13	0.10	0.02	0.02	–	–
Fe	–	–	–	0.54	0.18	0.09	0.05
Ni	0.14	–	0.07	–	–	–	–
Cu	–	–	–	0.20	–	0.08	–
Sr	0.18	2.20	0.54	–	1.26	–	0.06
Ba	0.07	0.30	–	0.14	–	–	0.26
Co	0.05	0.04	–	–	–	–	–
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

T a b l e 2

Chemistry of kyanite from Minas Gerais, Brazil (Faye and Nickel)

Blue kyanite Minas Gerais, Brazil	Weight (%)		
	Fe	Ti	Cr
Pale blue	0.17	0.01	0.02
Medium blue	0.15	0.01	0.03
Deep	0.13	0.01	0.03

T a b l e 3

IR spectral analysis of the absorption spectra (Ab) and Kubelca-Munk converted spectra (KM)

Kyanite (Ab.)	Kyanite (KM)	Suggested assignment
435	557 m	Si-O-Si (banding)
638 m	601 w	
	630 w	
466	667 m	Al-O-Si (banding)
505		
673 m		
732 m	729 m	Al-O-Si (streching)
898 w	914	Si-O-Si (streching)
941	999 m	
997 m	10553 7 w	
1033 m		
	1658 w	H_2O (banding)
3448 w		H_2O (streching)
	3620 m	OH (bending)
	3653 m	
	3693 m	

w – weak; s – strong; m – medium

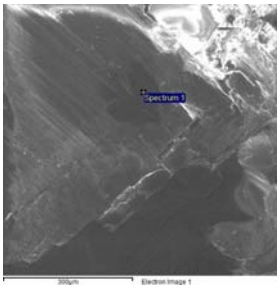

Fig. 2. SEM images of kyanite (sample 1)

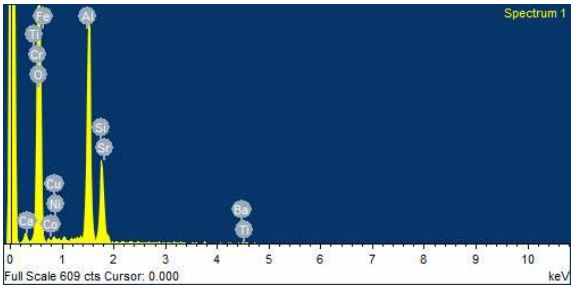

Fig.3. EDX spectrum 1 of kyanite (sample 1)

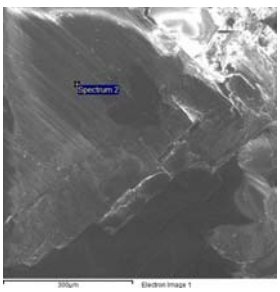

Fig. 4. SEM images of kyanite (sample 1)

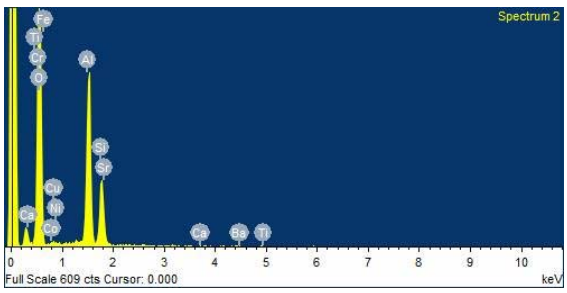

Fig.5. EDX spectrum 3 of kyanite (sample 1)

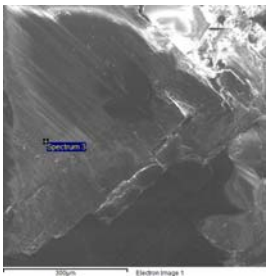

Fig. 6. SEM images of kyanite (sample 1)

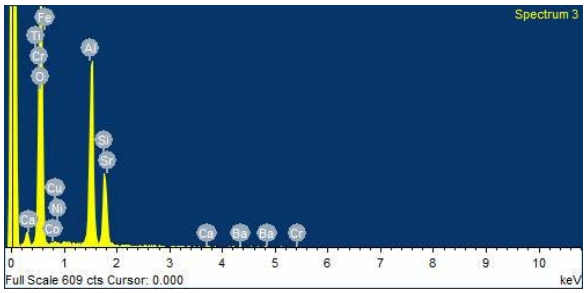

Fig. 7. EDX spectrum 4 of kyanite (sample 1)

Fig. 8. SEM images of kyanite (sample 2)

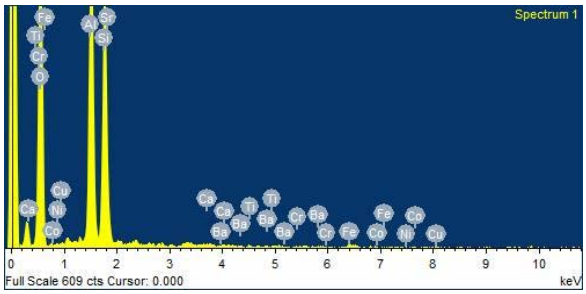

Fig. 9. EDX spectrum 5 of kyanite (sample 2)

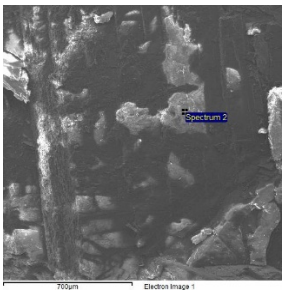

Fig. 10. EDX spectrum 5 of kyanite (sample 2)

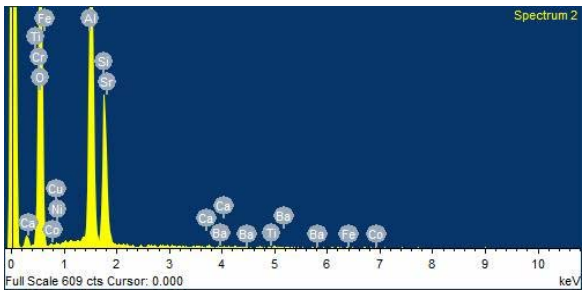

Fig. 11. EDX spectrum 5 of kyanite (sample 2)

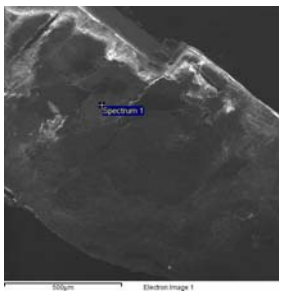

Fig. 12. EDX spectrum 5 of kyanite (sample 3)

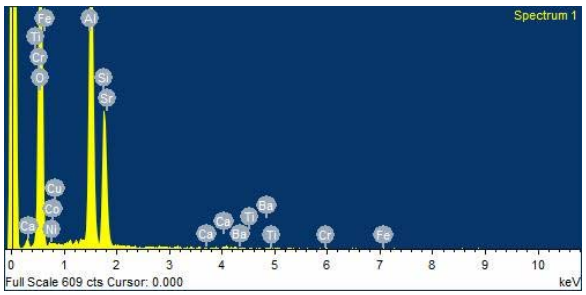

Fig. 13. EDX spectrum 5 of kyanite (sample 3)

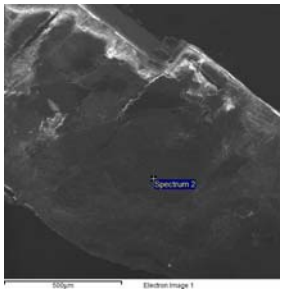

Fig. 14. EDX spectrum 5 of kyanite (sample 3)

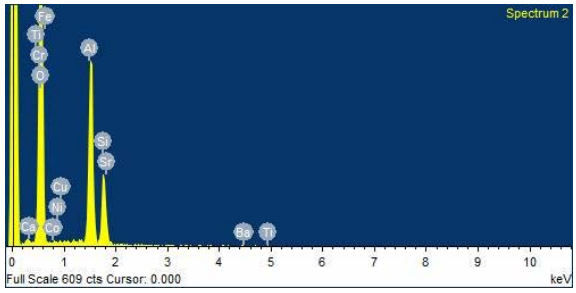

Fig. 15. EDX spectrum 5 of kyanite (sample 3)

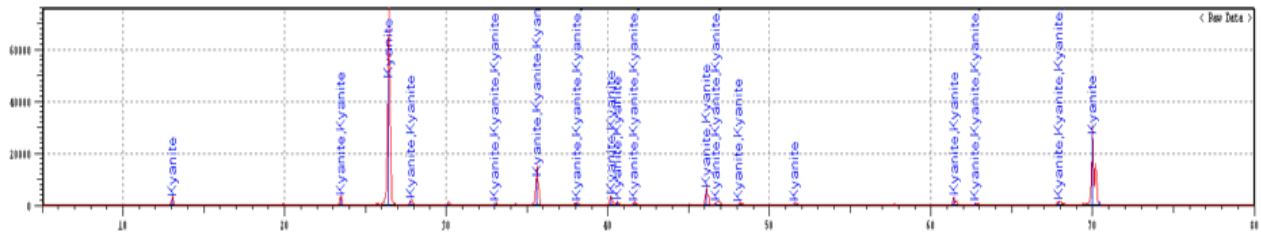

Fig. 16. X-ray diagram of kyanite

The kyanite was identified by the strong Si-O-Si stretching vibrations at 941 cm^{-1} accompanied with the bands at 1033, 997 and 898 cm^{-1} in the absorption spectrum (Fig. 17, Table 3). The bands at 435 and 638 cm^{-1} can be ascribed to Si-O-Si bending vibrations, while the bands at 673, 505 and 466 cm^{-1} (Fig. 17) relate to Al-O vibration. These results are in accordance with the reported data by Langer for the kyanite mineral (Al_2SiO_5) indicating the bands: 1032, 1009, 940, 898, 720, 674, 505, 467 and 438 cm^{-1} (Langer, 1975). The weak band at 3448 cm^{-1} (Fig. 17) ascribed the H_2O vibration. The most intensive bands attributed to the stretching (Si-O-Si) in the KM spectrum were assigned at 914, 999 and 1037 cm^{-1}. Direct comparison of the two spectra showed certain detection of the sharp peak at 729 cm^{-1} in the reflection spectrum contrary to the absorption spectrum (Fig.17).

The hydroxyl bands at 3693, 3653 and 3620 cm^{-1} are also detectable in the KM spectrum which were unrecognizable in the absorption spectrum.

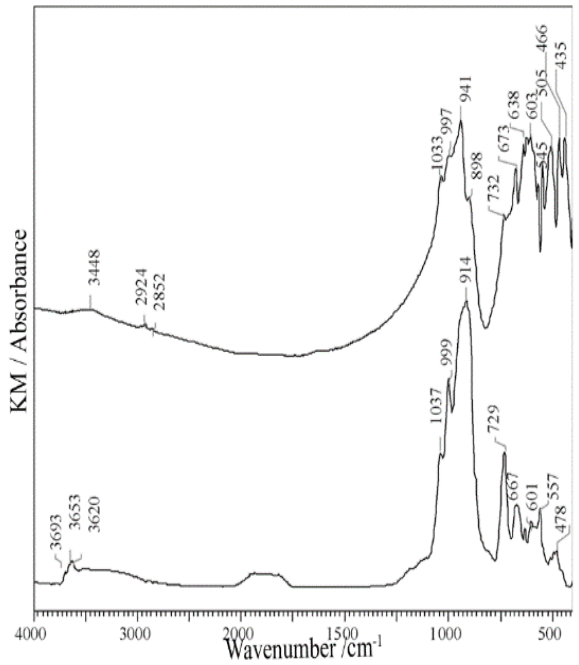

Fig. 17. Absorption spectra (upper) and reflection KM converted spectra (lower) of kyanite

CONCLUSION

Summarizing available data from this study we concluded that the investigated samples are kyanite. Kyanite is located east of village of Prilepec in micashist rocks which have lepidoblastic structure and schistose texture. It occurs in blue thin-bladed triclinic crystals and crystalline aggregates. Cleavage is perfect on {100}, good on {010}. Fracture is splintery. Kyanite is transparent to translucent. Lustre is vitreous or sub-vitreous. Hardness lengthwise 4–5, crosswize 6–7. Density 3.53–3.67 g/cm^3. The origin on blue colour were due to the charge transfer $Fe^{2+} \rightarrow Fe^{3+}$, $Fe^{2+} \rightleftharpoons Ti^{4+}$ or Cr^{3+}cations. In our samples concentration of Fe is 0.05–0.18 wt%, Ti concentration is 0.03 – 0.11 wt%, while concentration of Cr is 0.02 – 0.13 wt%.

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Р е з и м е

МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА КИЈАНИТОТ ОД СЕЛОТО ПРИЛЕПЕЦ, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: кијанит; скенирачки електронски микроскоп; рендгенска дифракција; инфрацрвена спектроскопија

Во овој труд се презентирани минералошките карактеристики на кијанитот од селото Прилепец, Р. Македонија. Испитувањата се вршени со SEM/EDS –скенирачка електронска микроскопија, X-ray-рендгенска дифракција и инфрацрвена спектроскопија (IR). Резултатите добиени со овие три методи дадоа јасна идентификација и потврдија дека испитуваниот примерок е кијанит. Тој се наоѓа источно од с. Прилепец во микашистните карпи кои имаат лепидопбластична структура и шкрилеста текстура. Се јавува во издолжени триклинични кристали и кристални агрегати. Кристалите се доста правилни и издолжени во правец на оската “c”. Застапени се призматични и пинакоидални рамнини {100}, {010}, {001}, {110}. Се среќаваат и близнаци по {100},{001}. Има совршена цепливост по {100} и нешто послабо изразена по {010}. Сјајноста му е стаклеста до седефаста. Прозирен е до провиден. Тврдоста во различни правци е различна. На рамнината {100} во правец на оската “c” тврдоста е од 4 до 5, а во правец на оската “b” од 6 до 7. Густината е од 3,5 до 3,7 g/cm^3. Има сина боја која најверојатно е резултат на трансфер на полнеж $Fe^{2+} \rightarrow Fe^{3+}$, $Fe^{2+} \rightleftharpoons Ti^{4+}$или Cr^{3+}. Концентрацијата на железо е 0,05 – 0,18 wt%, титанот е застапен со 0,03 – 0,11 wt%, а хромот со 0,02 – 0,13 wt%.