Calculation of quarzite crystallinity index by infrared absorption spectrum

Calculation of quarzite crystallinity index by infrared absorption spectrum

O Razva, A Anufrienkova, M Korovkin, L Ananieva and R Abramova
Tomsk Polytechnic University, Tomsk, Russia

Abstract. Quarzites retrieved from the Sopks-248 deposit and Belokamenka deposit, Antonovsk field cluster (Russia, West Siberia) were studied by the infrared spectroscopy method. The silicate thickness alteration rate was determined and the most crystalline quartzite variations were identified by defining the crystallinity index K_i according infrared absorption spectrum. To calculate "crystallinity index" the ratio of quintet peaks of 778 cm^{-1} as to peaks of 695 cm^{-1} were applied. It should be noted that the most crystalline quartzite variations are characterized by the relative value of crystallinity index.

1. Introduction

Due to the recently increased production of new materials and products from quartz, the demand for high-quality quartz raw materials has increased. Its application is rather diverse, including fiber optic communication systems, special glass, ceramic materials and unique products from silicon carbide (SiC) and silicon nitride (Si_3N_4).However, of great commercial importance is the silicon "solar" quality in manufacturing photovoltaic cells – solar panels.

In the context of increasing scarcity of rock crystal which was and is traditionally used as a high-purity quartz, the more and more attention is being paid to quartzites, which could be a potential high quality raw material source in high technology [1].

In this regard we have investigated the quartzites of Antonov field cluster (Russia, Western Siberia) [2]. According to its origin quartzites are sedimentary-metamorphic sediments being a lithification product formed under conditions of early metagenesis of quartz- sericite hydromica series [3]. As a result of biogenic siliceous strata metamorphism amorphous silica crystallization occurred and the highly pure crystalline alpha-quartz phase emerged.

To evaluate the quartzite alteration degree, the quartz crystallinity index k_i proposed by Murata & Norman [5] to determine the X-ray diffraction peak intensity (212) corresponding to $2\theta = 67{,}74°$ was used. At the same time [4] it was proposed to determine the quartz crystallinity index by infrared (IR) spectroscopy. It was observed that the change in the crystallinity degree of chalcedony and occurrence of the crystalline alpha -quartz phase, the absorption double peak within the range of 800...778 cm^{-1} in infrared absorption spectra was modified. For calculations the ratio of the weak peak value 778 cm^{-1} was proposed to be applied to its short wavelength shoulder. Another methodological approach [4, 5] was proposed to use the ratio of intensities of the IR absorption peaks at 778 cm^{-1} and 695 cm^{-1}, which belong to the vibrations of different symmetry types [6]. In [9] to calculate the crystallinity index the use of the peak intensity change of infrared absorption at 1145 cm^{-1} was proposed. However, in the IR spectra of studied fine-grained quartzite this peak was slightly distinguished (figure 1) and the proposed method, in this case, was inconclusive.

The topic of this research is to investigate the quartzite crystallinity index changes of different technological brands selected from ore deposits «Sopka-248» and Belokamenka, Antonov field cluster (Russia, Western Siberia) by infrared spectroscopy via a various calculation methods in determining this or that crystallinity index.

2. Research method and results

IR absorption spectra were recorded on the spectrophotometer Specord M40 within the range of 400...4000 cm^{-1} with a resolution of 0.01 cm^{-1} , and a spectrophotometer 21 IRPrestige (Shimadzu Co.) with Fourier conversion (FTIR-8400S) in the interval of 300 ... 4000 cm^{-1} with a resolution of 0.001 cm^{-1} (FT-IR) via software IRsolution. The test samples were prepared from selected quartzite samples under similar conditions. The test sample is grinded in an agate mortar to a fraction of less than 2 microns and mixed with both exclusively pure and purified for analysis KBr powders and then placed in a mold and compressed under high pressure into transparent thin disks. When measuring the IR spectra with spectrophotometer FTIR-8400S the weighed sample is 0.1...0.5 mg. Fragments of the infrared absorption spectra of quartzite are shown in figure 1.
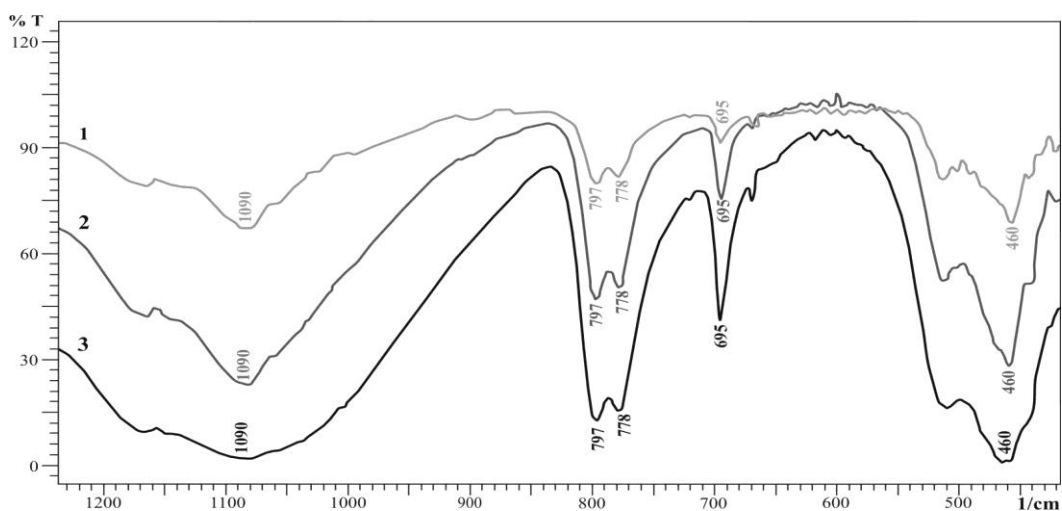
Figure 1. Fragments of infrared absorption spectra of samples on different quartz content basis.

With a further content increase of investigated material in prepared sample, a regular intensity increase of infrared absorption peaks was observed, and, in cases of high concentrations, more than 1.5 % their shape distorted and their magnitudes exceed the measurement limit range. In this case, the crystallinity index value calculated by various methods, also changes, including the IR intensity ratio of peaks at 778 and 695 cm^{-1} (table 1). Therefore, equal test sample mass was provided for an accurate comparative measurement analysis.

**Table 1.** Crystallinity index value (k_i) of samples on different quartz content basis.

№№ (measurement)	Weight of quartz on basis, %	k_i, (calculation by the method [5])	k_i, (calculation by the method [6,7])	Sample description
1	0.50	1.30	2.57	Belokamenka field. Quartzite of white colour, saccharoidal. Samples in binocular microscope
2	0.25	0.90	2.20	
3	0.75	0.50	1.74	
4	1.00	0.077	1.1	
5	1.25	0.047	0.95	

The calculation the quartzite crystallinity index was based on the methodology of Indian scientists [6, 7], who proposed the infrared absorption peak ratio of 778 and 695 cm^{-1}.

Crystallinity index calculation was performed according to the following formula:

$$k_i = a/b,$$

where, a/b – ratio peak intensity of 778 cm^{-1} to peak of 695 cm^{-1}, which were determined by the baseline method (figure 2).
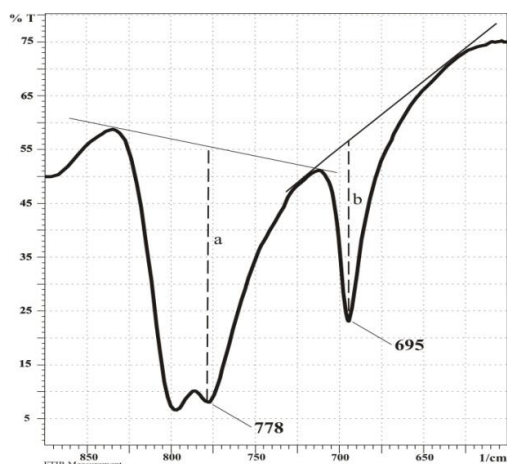
Figure 2. Calculation method of crystallinity index in relation to changes of absorption peaks 778/695 cm^{-1} in the infrared absorption spectrum.

Absolute crystallinity index values obtained by various methods differing to the absolute value are presented in table 2 for comparison. In all proposed methods crystallinity index value has a numeric value and is calculated directly from the measurements of the infrared absorption peak intensity and the magnitude of the IR absorption. These averaged values of crystallinity index obtained from three measured samples are presented in table 2. In all cases, a regular increasing trend of calculated crystallinity index values with quartzite conversion degree increase was observed, despite the fact that the calculated values of k_i are different.

Obtained by different methods, the purest white fine-grained quartzite diversity from «Sopka-248» [9] deposit is characterized by the lowest calculated crystallinity index value of – 2.21. Different quartzites from various local ore deposit areas, especially in high fragmentation areas, as result of supergene processes, undergo the following changes: quality deterioration, chemical composition and color alteration and the crystallinity index value also increases to 2.42...2.50.

Table 2. Quartzite crystallinity index.

Deposit	Sample	k_i, (calculation method [5])	k_i, (calculation method [6,7])
Sopka-248	White quartzite	2.21	2.21
	Gray quartzite with iron oxides adhesion	2.52	2.42
	Grayish quartzite with clay adhesion	2.66	2.49
	Black quartzite from periphery	2.75	2.50
	Jasper-like quartzite of brownish-cherry color with black veins	5.6	2.55
Belokamenka	White, saccharoidal quartzite	3.27	2.47
	White, transparent quartzite	3.8	2.67
Bural-Sardag	White coarse-grained quartzite	4.6	3.8

Fine-grained pure white quartzites of Belokamenka deposit are characterized by even higher crystallinity index values. To compare the quartzite alteration degree in Antonov field cluster, crystallinity index value of super-quartzites from Bural-Sardag deposit were examined. Super-quartzites from Bural-Sardag deposit are composed of larger grains with elongated porphyritic inclusions, subparallel orientation indicating that they have formed (recrystallized) in long-term dynamic stress conditions [1].

Super quartzites from Bural-Sardag deposit are characterized by high crystallinity index values in comparison to those of the Antonov field cluster ($ki = 3,8…4,6$).

3. Conclusion

Quartzite crystallinity index values calculated by different methods to infrared absorption spectra represent their conversion regularity despite the different values. Using these methods makes it possible to define and estimate quartzite recrystallization degree in different metamorphism stages including such as Antonov field fine-grained quartzites where traditional mineralogical and petrographic methods seem to be ineffective. Due to the fact that the purest samples are characterized by the lowest estimated crystallinity index values, such an evaluation could be applied in further mineralogical-technological mapping.

References

[1]   Nepomnyashchikh A I, Krasin B A, Vasilyeva I E, Yeliseyev I A, Yeremin V P, Popov S I, Sinitskiy V V, Fedoseyenko V A, Spiridonov A M, Vorobyev Ye I and Gnilusha V A 2000 Kremniy dlya solnechnoy energetiki *Bulletin of Tomsk Polytechnic University* **303** (1)176-190 [in Russian]

[2]   Zakharov V B 2000 Geologicheskoe stroenie Antonovskoi gruppi mestorogdeniy kvarcitov *Mining Journal* 7 7 [in Russian]

[3]   Ananyeva L G and Korovkin M V 2003 Mineralogo-geokhimicheskoye izucheniye kvartsitov Antonovskoy gruppy mestorozhdeniy *Bulletin of Tomsk Polytechnic University* 306 (3) 50-55 [in Russian]

[4]   Barsanov G P, Plyusnina I I and Yakovleva M E 1979 Osobennosti sostava, nekotorykh fizicheskikh svoystv i struktury khaltsedona (Moskov: Nauka) **28** 3-33

[5]   Murata K J and Norman II M B 1976 An index of crystallinity for quartz *American Journal of Science* **276** 1120-1130 [in Russian]

[6]   Ramasamy V and Suresh G 2009 Mineral Characterization and Crystalline Nature of Quartz in Ponnaiyar River Sediments, Tamilnadu, India *American-Eurasian Journal of Scientific Research* **4** (2) 103-107

[7]   Lazarev A N, Mirgorodskiy A P and Ignatyev I S 1975 *Kolebatelnyye spektry slozhnykh okislov* (Leningrad: Nauka) s 296 [in Russian]

[8]   Shoval S, Ginott Y and Nathan Y 1991 A new method for measuring the crystallinity index of quartz by infrared spectroscopy *Mineralogical Magazine* **55** 579-582

[9]   Korovkin M V, Ananyeva L G and Antsiferova A A 2012 Otsenka stepeni preobrazovaniya kvartsitov metodom infrakrasnoy spektrometrii *Bulletin of Tomsk Polytechnic University* **320** (1)16-18 [in Russian]