On some controversially-discussed Raman and IR bands of beryl

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Abstract. Natural and synthetic beryl, $Al_2Be_3Si_6O_{18}$, from various deposits and manufacturers were investigated with Raman, IR spectroscopy, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Electron Microprobe Analysis (EMPA). The Raman-band at 1067-1072 cm^{-1} and the IR-band at 1071-1207 cm^{-1} have been assigned till now either to Si-O or to Be-O by different studies. Following the findings in this study that the position and Full Width at Half Maximum (FWHM) of these bands were related to the concentration of silicon but not that of beryllium, it stated that these bands were generated by the vibration of Si-O.

Keywords: Raman, Infrared spectroscopy, FWHM, band position, beryl.

1. Introduction

In this study we focused on one Raman band at about 1067-1072 cm^{-1} and one IR band at about 1071-1207 cm^{-1} of the cyclo-silicate mineral beryl, $Al_2Be_3Si_6O_{18}$ (SiO_2-67 wt%, Al_2O_3-18,9 wt%, BeO-14,1 wt%, theoretically). The study aimed to obtain a better understanding of vibrational features of beryl and to assign precisely the presented bands to the vibrations. There have been many studies using factor group analysis to calculate lines (Adams & Gardner, 1974, [1] Hofmeister et al., 1987, [2] Kim et al., 1995 [3]). Nevertheless, assignment of observed bands to certain vibrations was always one of the most challenging tasks in vibration spectroscopy,

such as Raman and Infrared (Nasdala et al. 2004 [4]). As calculated by Kim et a. (1995) [3] and described by Moroz et al (2000) [5], the Raman band at 1067-1072 cm^{-1} has been assigned to Be-O vibration. However, this band was attributed by Adams & Gardner [1] and mentioned in the study of Charoy et al. (1996) [6] to the Si-O bond. Similarly, the IR band at 1071-1207 cm^{-1} has been assigned to Be-O vibration by Plyusnina [7], Plyusnina & Surzhanskaya [8] and to Si-O vibration by Aurisicchio et al. [9], Manier-Glavinaz et al. [10], Hofmeister et al. [2], Adams & Gardner [1], Gervais & Pirou [11]. According to our study, the features of both Raman and IR bands (band position and band width) were clearly related to the concentration of Si in the samples. The band width was shown to be broader in the samples containing a lower amount of silicon;

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moreover, the Raman shift appeared at lower frequency in the samples with higher silicon content and the IR band was at a higher position in these samples. Such relations were not found between these bands and Be concentration. We were therefore able to confirm the assignment of these bands to Si-O vibration.

2. Material and experimental methods

Narural beryls from Brazil (Carnaiba, Capoeirana, Itabira, Santa Terezinha, Socoto), Colombia (Chivor), Austria (Habachtal), Russia (Ural), Madagascar (Mananjary), South Africa (Transvaal), Zambia (Kafubu), Nigeria (Gwantu), China (Malipo) and synthetic ones from Tairus, Biron (hydrothermally-grown), Gilson, Chatham, Lennix (flux-grown) were collected in order to cover a wide range of chemical components. Eighty single crystals and facetted stones were chosen for Raman measurement and Raman spectra were obtained from their surfaces. Then, thirty six crystals chosen from among those already analysed by Raman underwent chemical analysis by LA-ICP-MS and EMPA. From the purest eighteen inclusion-free crystals and facetted stones, 2 mg of powder were scraped using a diamond point for IR measurements.

All Raman spectra were recorded at room temperature using a Jobin Yvon (Horiba group) LabRam HR 800 spectrometer. The system was equipped with an Olympus BX41 optical microscope and a Si-based CCD (charge-coupled device) detector. Spectra were excited by Ar^+ ion laser emission with 514 nm as a green laser with a grating of 1800 grooves/mm and a slit width of 100 µm. Due to these parameters and the optical path length of the spectrometer a resolution of 0.8 cm^{-1} resulted. The spectra acquisition time was set at 240 seconds for all measurements. Geometrical

factors were strongly controlled in all Raman measurements. One polarizer was used allowing only the laser beam with definitive vibrational direction (N-W) to pass through. Experiments were then conducted with the normal orientations of the beryl crystal (i.e orientations of c axis) with regard to E, the electric vector.

IR spectra of beryls were recorded using a PERKIN ELMER FT-IR Spectrometer 1725X with 100 scan and 4 cm^{-1} resolution. The samples were prepared as pellets made out of 2 mg of powdered beryl mixed with 200 mg KBr powder to minimize the polarization effects. Peak analysis for both IR and Raman measurements was performed with an Origin-lab 7.5 professional software package. The single and overlapping peaks were smoothed using the Lorentz-Gauss function.

Chemical analyses were carried out by means of LA-ICP-MS and EMPA. The use of LA-ICP-MS served to identify Li, Be, B, Na, Mg, Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, La and Ta. EMPA was used to identify the main element Si and other elements as well in order to have a reference matrix between LA-ICP-MS and EMPA measurements.

Ablation was achieved with a New Wave Research UP-213 Nd:YAG laser ablation system, using a pulse repetition rate of 10 Hz and 100 µm crater diameters. Analyses were performed on an Agilent 7500ce inductively coupled plasma - mass spectrometer in pulse counting mode (one point per peak and 10 ms dwelling time). Data reduction was carried out using Glitter software. The amount of material ablated in laser sampling was different for each spot analysis. Consequently, the detection limits were different for each spot and were calculated for each individual acquisition. Detection limits generally ranged between 0.001 and 0.5 ppm (µg/g). ^{28}Si was used as the internal standard.

Analyses were calibrated against the silicate glass reference material NIST 612 using the values of Pearce et al. [12], and the US Geological Survey (USGS) glass standard BCR-2G was measured to monitor accuracy.

Microprobe analyses were achieved with a JEOL JXA 8900RL - electron beam - microprobe with wavelength dispersive analysis technique. The chemical composition of each sample was then corrected by PAP program. The samples were measured by an acceleration voltage of 20 KV and 20 nA filament current. The detection limits differed for each element and were affected by the overall composition of a sample and the analytical conditions. For most elements, the detection limit for wavelength-dispersive (WD) spectrometers was between 30 and 300 parts per million. The precision depended on counting statistics, particularly the number of X-ray counted from the standard and sample, and the reproducibility of the WD spectrometer mechanisms. The minimum obtainable precision was about 0.5 percent, although it was higher for elements at trace concentrations. Therefore, EMPA was specially used in this study for detecting main elements.

3. Results and Discussion

3.1. Raman band at 1076-1072 cm^{-1}

As introduced, this band has been attributed to the Si-O bond in the studies of Adams and Gardner [1], Charoy et al. [6] but to the Be-O bond in the studies of Kim et al. [3], Moroz et al. [5] instead. According to our experimental results, in all synthetic beryls the position of this band was around 1067-1068 cm^{-1}, in Colombian and Nigerian samples the Raman shift was around 1068-1070 cm^{-1} and in samples from Austria, Brazil, China,

Madagascar, Russia, South Africa, Zambia, the Raman shift was around 1069-1072 cm^{-1}. In other words, this band shifted to higher frequency in natural samples than in synthetic ones (Figure 1.). Moreover, the width of this band also varied among samples of different provenances. The FWHM varied from 11 cm^{-1} to 14 cm^{-1} in synthetic samples, from 12 cm^{-1} to 15 cm^{-1} in samples from Nigeria and Colombia and from 17 cm^{-1} to 26 cm^{-1} in samples from Austria, Brazil, China, Madagascar, Russia, South Africa and Zambia. Figure 2. showed the plot of the peak position versus the FWHM for beryls of different origins. Based on the FWHM values and the Raman positions of this band, we could separate the samples studied into two ranges: Range I including synthetic beryls as well as natural Nigerian and Colombian ones were those with low FWHM and low band position; range II including all other investigated natural beryls.

Chemical data showed that samples of range I contained a higher amount of silicon than those of range II. The silicon concentration in beryls of range I varied from 65 wt% to 66,9 wt% (from 66,1 wt% to 66,9 wt% in synthetic samples - approximately approaching the theoretical concentration, and from 65 wt% to 66,3 wt% in Nigerian and Colombian samples) while silicon concentration in beryls of range II varied from about 62,5 wt% to 65 wt%. **Error! Reference source not found.** showed the correlation between the content of silicon and band position and FWHM for beryls of different origins. This meant that in the samples where the silicon content was high the band position and FWHM were low and in the samples where the content of silicon was low the band position and FWHM were high. We therefore agreed with the authors who assigned this band to vibration of Si-O, since there was no such correlation between beryllium concentration and band data (Figure 4.).
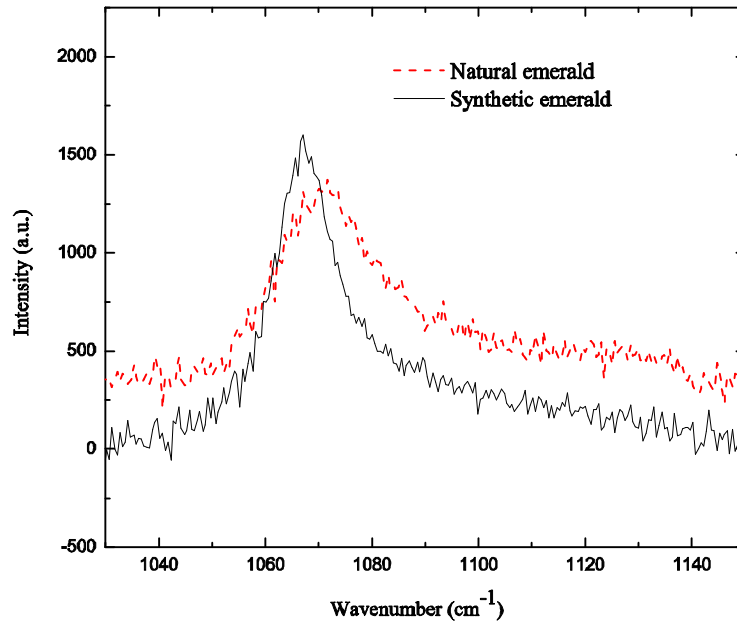
Figure 1. Raman shift at 1067-1072 cm^{-1} of synthetic (solid line) and natural beryls (dot line).
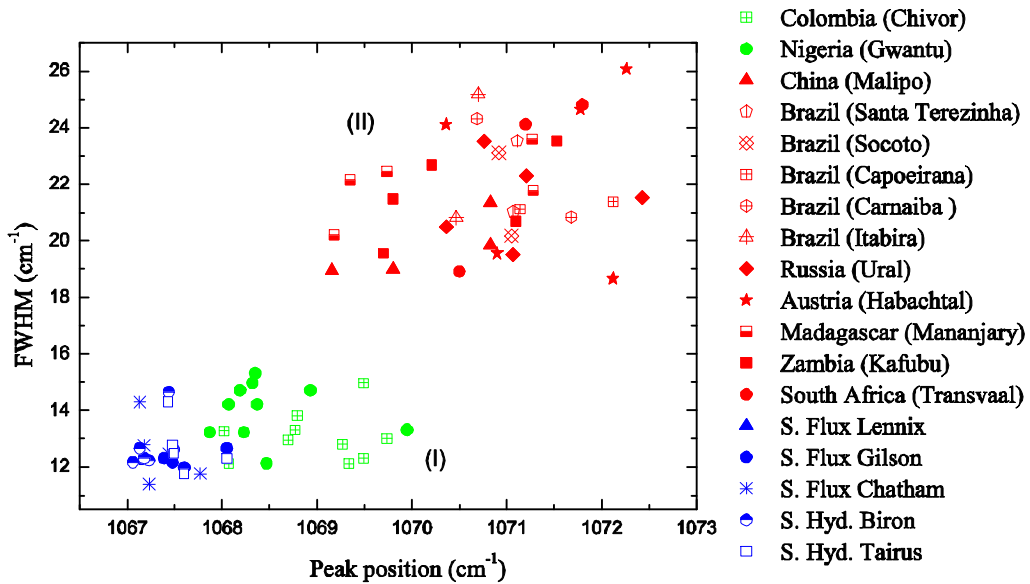

Figure 2. Peak positions versus FWHMs in natural and synthetic beryls from various origins.
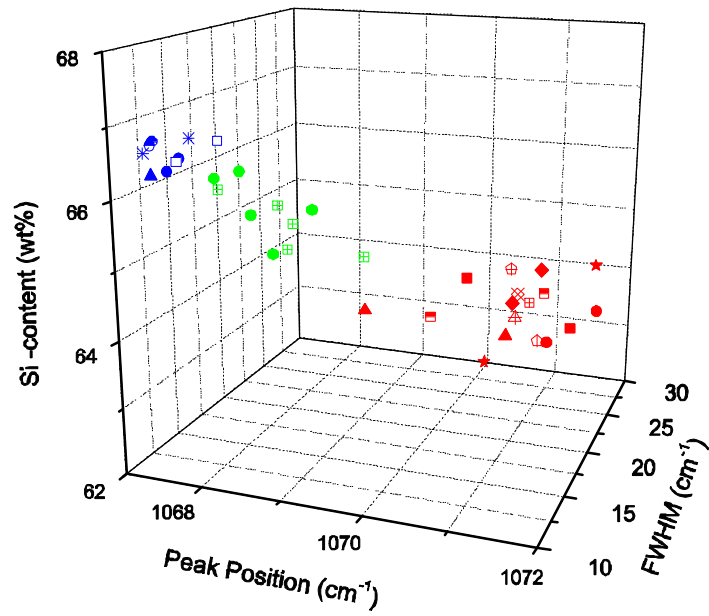
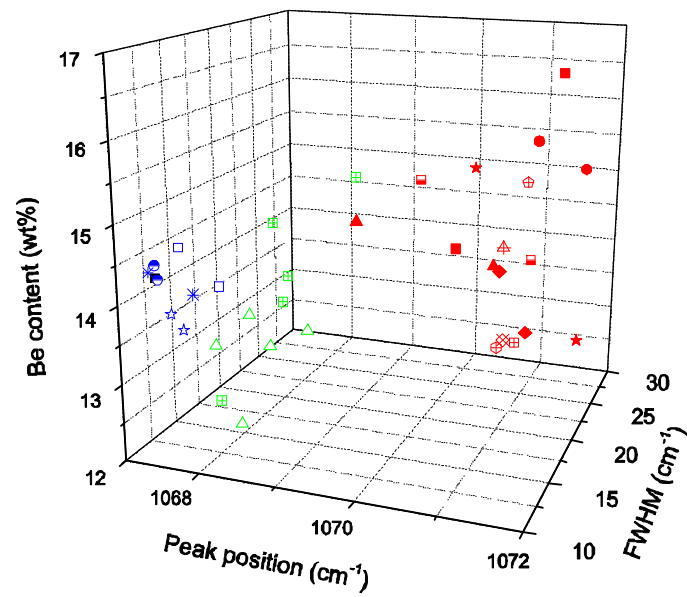Figure 3. Correlation silicon content, band position and FWHM.

Figure 4. Correlation between beryllium content, peak position and FWHM.

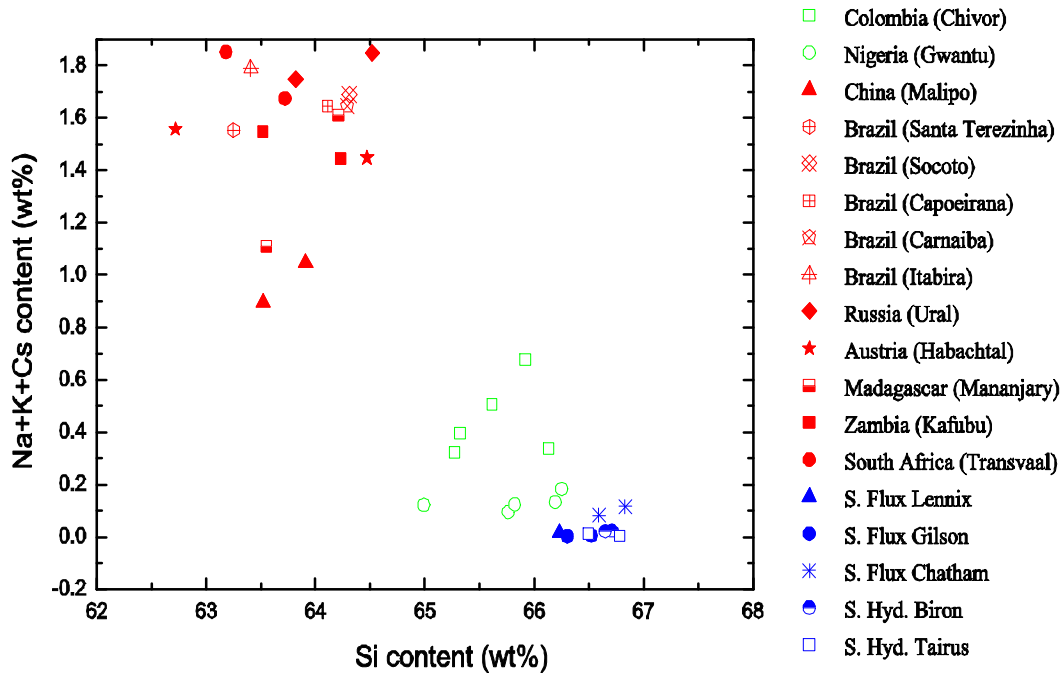In addition, the concentration of alkali ions (Na, K, Cs) was also variable among samples.

Figure 5. Alkali content versus Si content in natural and synthetic beryls from different origins.

The alkali amount of synthetic beryls varied from 0 wt% to 0,1 wt%, and from 0,1 wt% to 0,71 wt% in natural beryls of range I, from 0, 89 wt% to 1, 87 wt% in natural beryls of range II.

The shifting and broadening (increasing in FWHM) of the Raman band were primarily the results of positional disorder. Since the band shifting and broadening were seen in low silicon-containing samples, there were actually other elements than silicon occupying the silicon position. The amount of positional disorder in each sample was the amount of lost silicon (in comparison with the ideal silicon amount). Other elements which could substitute Si are Al^{3+}, Be^{2+}, Li^+, etc. Charge compensator could be served by alkali ions (mainly Na^+, K^+, Cs^+) which existed in structural channels. That meant, the lost of silicon in beryl structure had to be compensated by other substituting elements (Al^{3+}, Be^{2+}, Li^+, etc.) together with charge compensating ions (Na^+, K^+, Cs^+). The correlation between Si- and alkali ion contents elucidated this fact, since in samples where the Si content was low, the alkali content was high (Figure 5.).
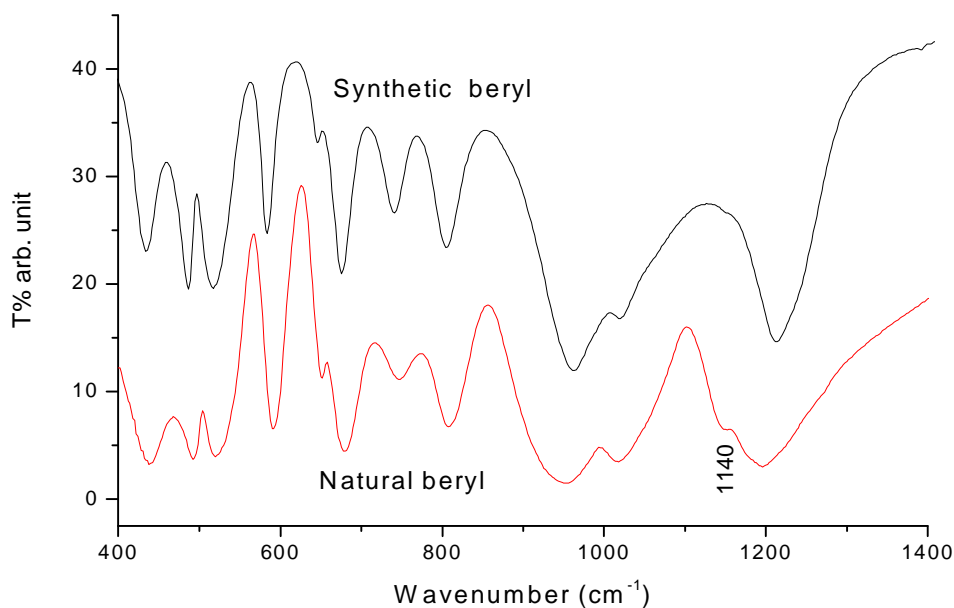
3.2. IR band at 1071-1207 cm^{-1}

Figure 6. IR spectra in the range 400-1400 cm^{-1} of beryls
(red line: natural sample from China; black line: synthetic Gilson sample).

Figure 6 showed the IR spectra in the range 400-1400 cm^{-1} for one alkali-free beryl (Gilson synthesis) and for one high-alkali-containing beryl (Chinese sample). We focused on the band at around 1200 cm^{-1} which has been assigned to the vibration of Be-O by Plyusnina [7], Plyusnina & Surzhanskaya [8] but to the vibration of Si-O by Manier-Glavinaz et al. [10], Hofmeister et al. [2], Adams & Gardner [1], Gervais & Pirou [11]. This band in fact varied in its actual position between 1171 cm^{-1} and 1203 cm^{-1} in natural beryls (low silicon content) and between 1200 cm^{-1} to 1207 cm^{-1} in synthetic beryls (high silicon content). A plot of band position versus Si content showed a trend, that in samples with high silicon content the band shifted toward high wave numbers (Figure 7.). In addition, this band was shown to be clearly more slender in synthetic samples than in natural ones. Again, both band width and band position were related to the concentration of silicon and did not show any relation to beryllium content. Therefore, the assignment of this band to Si-O vibration was preferred rather than to Be-O vibrations. This observation corresponded with the interpretation of the band at 1067-1072 cm^{-1} in Raman spectroscopy.
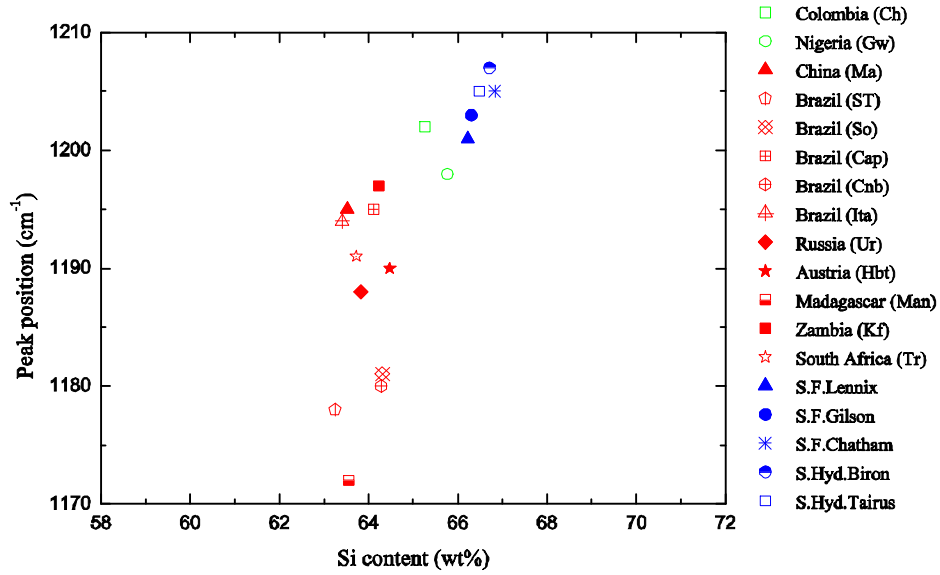
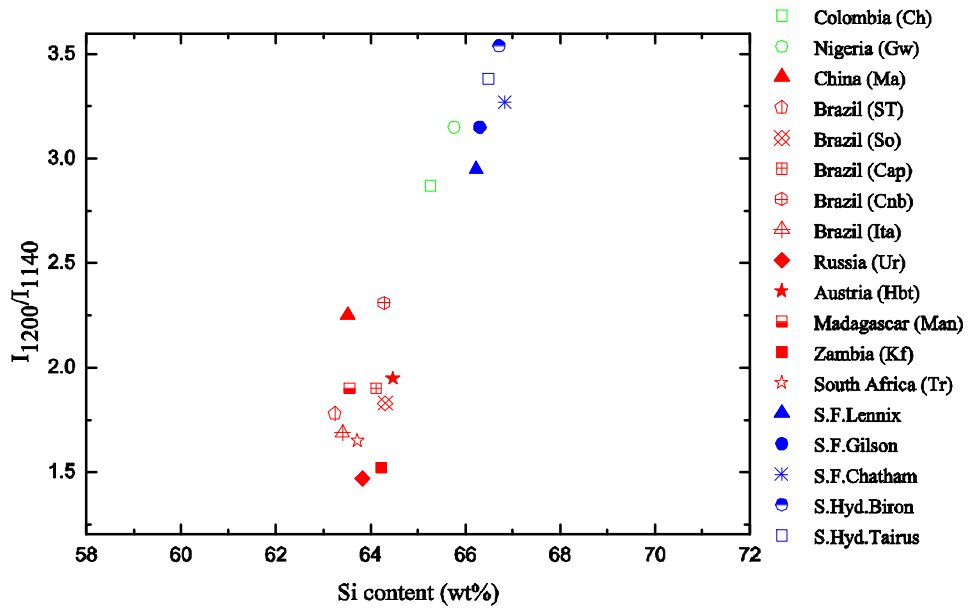Figure 7. Position of IR band at 1171-1207 cm^{-1} versus Si content.

Figure 8. Intensity ratio of band at 1171-1207 cm^{-1} and shoulder at 1140 cm^{-1} versus Si content.

One shoulder at about 1140 cm^{-1} was seen only in natural samples (with the exception of beryls from Nigeria where the alkali content was lower than 0,2 wt%) and was not seen in all synthetic samples or in samples from Nigeria. Plot of intensity ratios of band 1200 cm^{-1} and shoulder 1140 cm^{-1} versus Si content showed a positive linear trend, i.e. this intensity ratio was high in samples with a high Si content (Figure 8.). Therefore, not only band 1200 cm^{-1} but also shoulder 1140 cm^{-1} had a relationship with the Si content. Similarly, the plot of ratios of the band at 1200 cm^{-1} and the shoulder at 1140 cm^{-1} versus the alkali contents showed a negative

linear trend, i.e. this intensity ratio was high in samples with low alkali content (Figure 9.). Therefore, the existence of the shoulder at 1140 cm^{-1} in all natural samples (except Nigerian ones) could also be related to alkali ions. The existence of this shoulder could be explained as follows: 1. The shoulder was generated by a vibration X-O in which X was a divalent or trivalent cation substituting in the Si position. The charge compensation was served by alkali ions (Na, K, Cs) in the channel. 2. The shoulder was generated by M-O in which M was the alkali ion in the channel.
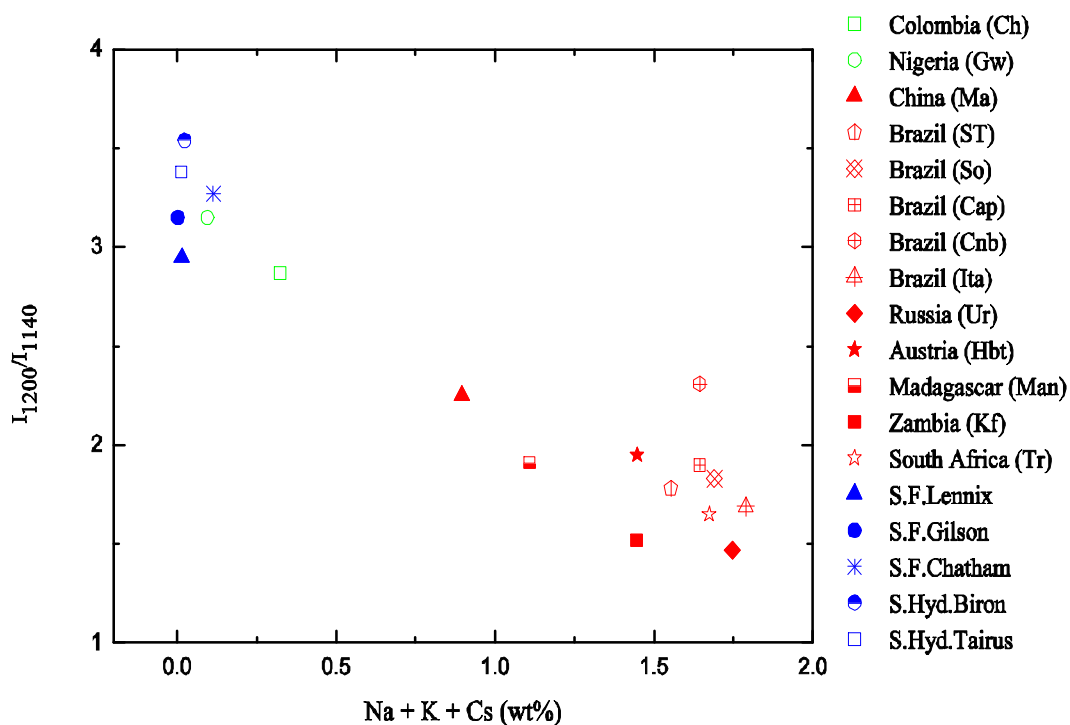

Figure 9. Intensity ratio of band at 1171-1207 cm^{-1} and shoulder at 1140 cm^{-1} versus alkali content.

4. Conclusion

In this study, based on chemical data we have shown that the features of the Raman band at 1067-1072 cm^{-1} and the IR band at 1071-1207 cm^{-1} depended on the concentration of silicon in the sample. We therefore agreed with the authors who assigned these bands to the vibrations of Si-O bonding. Moreover, by using features (FWHM, position) of these bands one is able to separate synthetic stones which were grown in free-alkali media from natural ones. Raman spectroscopy as a non-destructive method could be specially used in identification between natural gem and synthetic beryl, since in synthetic samples the position/FWHM of Raman band is at 1067-1068 cm^{-1}/ 11-14 cm^{-1} while these are very variable in natural ones: 1068-1072 cm^{-1}/12-26 cm^{-1}, respectively.

Acknowledgements

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