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ON THE PROBLEM OF THE OCCURRENCE OF DISPERSED BUNSENITE (NiO) IN CHRYSOPRASES

Abstact. UV-VIS-NIR spectroscopic investigations of chrysoprases of different crystallinities were performed to determine sites of the localization of nickel ions and confirm the origin of their green colouration. The spectroscopic results can be explained assuming that the Ni^{2+} ions are grafted to the fine-crystalline SiO_2 matrix in extraframework positions of distorted octahedral symmetry. The coordination sphere of Ni^{2+} ions being partly formed by water molecules is labile and easily affected by thermal treatment. The green colour of the samples is determined by the absorptions in the red (654.0 nm) and the blue (389.0 nm) regions of the visible spectrum (transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively). The presence of dispersed bunsenite (NiO) phase in the investigated samples has been excluded because of the absence of the corresponding charge transfer band.

Key-words: chrysoprase, nickel, UV-VIS-NIR spectroscopy, coordination

INTRODUCTION

It is well known that the green colour of chrysoprase is mainly due to its nickel content. A comprehensive review of different forms of nickel occurring in this mineral was published, among others, by Sachanbiński (1985). Some authors postulate a substantial role of dispersed NiO (bunsenite) as a pigment of chrysoprases (Sinkankas 1959; Barsanov, Jakovleva 1981; Heflik et al. 1989). However, this opinion is based on doubtful results of the TEM investigations of replicas taken from some chrysoprase surfaces. Gaweł et al. (1997) have shown that even in the case of chrysoprases with a relatively high Ni content, no X-ray pattern of bunsenite is observed. This, however,

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does not exclude the possibility of the NiO occurrence in the form of very fine particles, not detectable by the XRD method.

In this study a new insight into the role of bunsenite as a possible pigment of the chrysoprase was obtained by use of UV-VIS-NIR spectroscopy.

EXPERIMENTAL

Materials

Four samples of chrysoprase coming from the mineralogical collection of the University of Mining and Metalurgy in Cracow were investigated. The light-green sample from Szklary (Lower Silesia, Poland) with the smallest content of Ni (0.23 wt.%) and high crystallinity of the silica matrix was labeled K-1, an apple-green chrysoprase from Szklary labeled Z-5, an emerald-green specimen from Marlborough Creek (Australia) labeled Z-7 and a dark-green sample from unknown locality in Africa labeled Z-8. All the samples, with exception of K-1, display low crystallinity index (quartz) of the silica framework, especially the samples Z-7 and Z-8 (Gaweł et al. 1997). A mechanical mixture of NiO and silica, containing 6 wt.% of NiO, was used as a reference sample.

Methods

Diffuse Reflectance Spectroscopy (DRS)

The UV-VIS-NIR spectra of the chrysoprase samples were recorded in the diffuse reflectance mode on a Cary 5E spectrometer working in the 200–2500 nm range, equipped with an integration sphere coated with polytetrafluoroethylene (PTFE). PTFE was also used as a reference.

TABLE 1

Abundance of selected transition metal ions in the chrysoprase samples

Sample locality	Ni [wt.%]	Fe [wt.%]	Mn [wt.%]	Cr [wt.%]	Cu [wt.%]	Crystallinity index
K-1 Szklary, Poland	0.23	n.d.	n.d.	n.d.	n.d.	6.3
Z-5 Szklary, Poland	1.71	0.65	0.004	0.001	<0.001	2.3
Z-7 Marlborough Creek, Australia	0.98	0.10	<0.001	0.001	<0.001	0
Z-8 Africa, unknown	4.38	0.05	<0.001	0.003	<0.001	n.d.

n.d. — not determined.

Atomic Absorption Spectrometry (AAS)

The chemical analyses of the samples were performed by means of the AAS technique. The contents of Ni and some other transition metals, which may influence the hue of the green colour of chrysoprase, are given in Table 1. X-ray crystallinity index was determined according to Murata and Norman (1976).

RESULTS AND DISCUSSION

The UV-VIS-NIR spectrum of a representative sample of the chrysoprase (Z-8) is shown in Figure 1. Three distinct regions corresponding to charge transfer (CT) transitions in the SiO_2 framework, Ni^{2+} *d-d* transitions and to overtone and combination bands of the OH vibrations of water, can be distinguished. Following the literature, the most intensive maximum near 205 nm is assigned to $O^{2-} \rightarrow Si^{4+}$ CT transition. The weaker three bands at 1124 nm, 654.0 nm (with a shoulder at 733.4 nm) and 389.0 nm can be attributed to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively (Lever 1984). It is worth noting that the 1124 nm band, corresponding to the crystal field parameter 10Dq, is much broader than the other *d-d* bands. The green colour of the samples is traced to the absorption in the red and the blue portions of the visible spectrum (transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$). In the near-IR

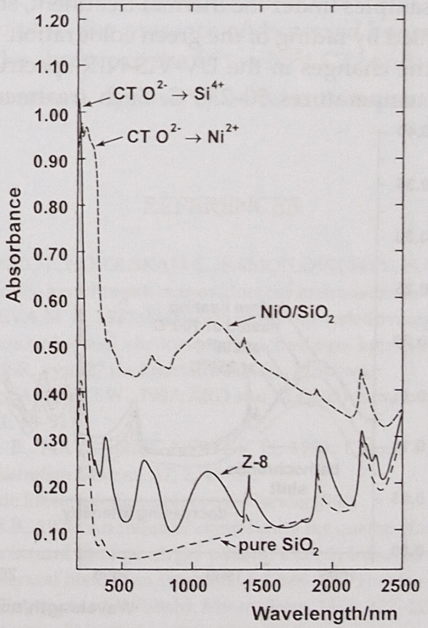

Fig. 1 UV-VIS-NIR diffuse reflectance spectra of Z-8 chrysoprase and of reference samples: pure SiO_2 and NiO/SiO_2 (6 wt.% of NiO), recorded at ambient conditions

region pronounced bands appeared at 1410 nm [ν(OH) overtone], 1910.4 nm [ν(OH) + + δ(OH) combination], both being associated with adsorbed H_2O (OH bond). The band at 2211.2 nm and a weaker one at 2313.6 nm may be ascribed to the ν(OH) + δ(OH) in free OH (Perry, Li 1991).

Generally, Ni^{2+} ions in chrysoprase could occur in three different forms. These are Ni^{2+} ions occupying octahedral extraframework sites, crystalline micro-inclusions of Ni silicates, or finely dispersed bunsenite (NiO). Tetrahedral coordination of Ni would be expected if the Ni^{2+} ions could have been incorporated into the SiO_4 framework tetrahedra, as it was observed for instance in the case of Fe^{3+} in α-quartz (Weil 1984). The $[FeO_4]^-$ centres are presumed to substitute for SiO_4 in such a case. However, in the case of nickel, a similar substitution has never been observed and our data also exclude this possibility (*fide* infra).

As the investigated samples are XRD-monophasic, the presence of a significant amount of crystalline bunsenite should be excluded. Comparison of the UV-VIS-NIR spectrum of chrysoprase with the NiO/SiO_2 reference sample indicates that amorphous NiO particles are also absent. The reference sample shows a CT transition $O^{2-} \rightarrow Ni^{2+}$ at about 200 nm due to finely dispersed bunsenite particles which was clearly absent in the chrysoprase samples. The lack of such a band indicates that in all the investigated chrysoprases bunsenite inclusions are essentially absent, within the sensitivity limit of the UV-VIS-NIR method. Thus, the chalcedony extraframework sites are the most probable localization centres of nickel. This attribution is supported by the behaviour of the samples under the thermal treatment, since the dehydration of the samples is accompanied by fading of the green colouration.

Figure 2 represents the changes in the UV-VIS-NIR spectrum of Z-8 chrysoprase upon heating in air at temperatures 50–250°C. Such treatment leads to partial dehydration of the sample. A bathochromic shift of the band at 1124 nm, corresponding to the parameter 10Dq, was observed upon dehydration together with decrease of the intensity of NIR bands (1410 nm, 1910.4 nm and around 2200–2300 nm) due to gradual elimination of water. The observed shift indicates that water is directly bonded to nickel and its removal by dehydration causes changes in the crystal field strength around Ni^{2+} ions. Simultaneously, a small bathochromic shift of the red portion of the band at 654.0 nm in the visible part of the spectrum is observed, evidencing a relationship between colouration of chrysoprase to the presence of water. These effects speak in favour of the localization of Ni^{2+} ions in the extraframework positions of chrysoprase where they assume distorted octahedral symmetry coordinating interfacial water. This observation confirms the former opinion of Balakirev et al. (1979, *fide* Sachanbiński 1985).

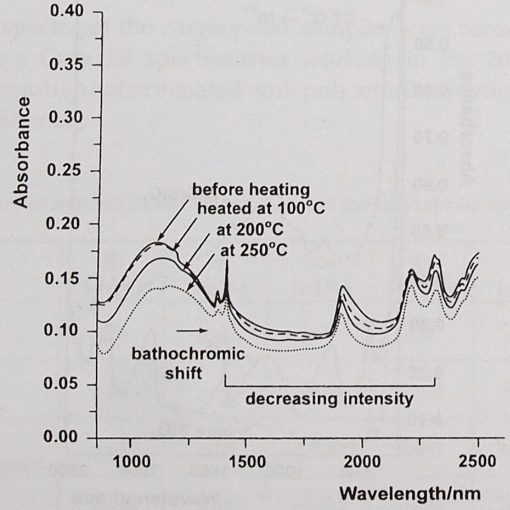

Fig. 2 UV-VIS-NIR diffuse reflectance spectra of Z-8 chrysoprase heated in air at various temperatures (50–250°C)

CONCLUSIONS

The UV-VIS-NIR spectroscopic investigations of chrysoprases coming from various localities were performed to determine the status of Ni^{2+} ions and explain the green colouration of this mineral. Analysis of the results indicates that in the investigated samples Ni^{2+} ions are accommodated chiefly at the extraframework positions of the chalcedony matrix, assuming a distorted octahedral symmetry. The coordination sphere of the grafted nickel ions is formed by nO (or OH) ions of $[SiO_4]$ groups and $(6 - n)$ water molecules. The absorption bands at 389.0 and 654.0 nm determine the green colour of the samples. The presence of dispersed bunsenite in our samples has been excluded due to the absence of the $O^{2-} \rightarrow Ni^{2+}$ CT band.

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PROBLEM WYSTĘPOWANIA ROZPROSZONEGO BUNSENITU (NiO) W CHRYZOPRAZACH

Streszczenie

Powszechnie wiadomo, że chryzopraz zawdzięcza swe zielone zabarwienie obecności niklu, jednak formy występowania tego metalu pozostają wciąż dyskusyjne. Niektórzy z autorów postulują istotną rolę rozproszonego NiO (bunsenitu) jako pigmentu chryzoprazów, jednak dotychczas nie przedstawiono na to przekonywającego dowodu. Autorzy tej pracy wykonali badania spektroskopowe w zakresie UV-VIS-NIR czterech próbek chryzoprazów o różnym stopniu uporządkowania matrycy krzemionkowej (chalcedonu). Stwierdzono, że zielone zabarwienie próbki jest związane z obecnością pasm absorpcji około 389 i 654 nm. Ewentualną obecność rozproszonego bunsenitu wyklucza brak odpowiednich pasm CT (charge transfer) $O^{2-} \rightarrow Ni^{2+}$. Analiza spektrogramów wskazuje natomiast na występowanie jonów Ni^{2+} w zdeformowanych pozasieciowych oktaedrach, utworzonych przy udziale drobin H_2O. Przemawia za tym m.in. przesunięcie pasma absorpcji związanego z parametrem pola krystalicznego 10Dq (1124 nm) w kierunku większych długości fali podczas dehydratacji zachodzącej w czasie ich ogrzewania w zakresie temperatur 50–250°C. Batochromowe przesunięcie pasma 1124 nm pod wpływem odwodnienia próbek wskazuje na silne oddziaływanie cząsteczek wody z jonami Ni^{2+} w sieci chryzoprazu. Równocześnie obserwowane jest niewielkie przesunięcie w kierunku dłuższych fal pasma 654 nm w widzialnej części widma. Efekt ten wskazuje na wpływ obecności koordynowanej przez nikiel wody na barwę chryzoprazu.