

Spectroscopic properties of halite from Kłodawa salt mine, central Poland

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Abstract The dynamics of colour centre transformation was investigated in blue halite single crystals from Kłodawa Salt Mine, Central Poland, using UV–vis spectroscopy. The following colour centres were considered: F, R₁, R₂, as well as plasmons and M centres. The R₂ centres predominated in navy blue (A) and pale blue (B) halites. Other relatively large populations were plasmons found in all examined samples. In purple (C) halite samples the plasmon population is the highest one among others and R₁ centres appeared to be equally significant, whereas M centres were almost absent. For A and C samples unidentified bands were observed at 26,500 to 26,200 cm⁻¹, respectively. The bleaching process of the blue halites was investigated using temperature dependent UV–vis and micro-Raman spectroscopies. In micro-Raman 300–100 cm⁻¹ region three very intense sharp bands were attributed to the colour centres and colloidal Na precipitation in A and B halites. The one broad band in the range 3,500 to 500 cm⁻¹, which was characteristic even for the colourless sample D but absent in the spectra of colourless NaCl obtained after recrystallization of sample A, requires further study.

Introduction

The occurrence of natural blue or purple crystals of halite has been the subject of interest for many scientists. The early

works on this topic are dated on the second half of 19th century. From among numerous works of 20th century the publication by Howard and Kerr (1960), a series of four papers on radiation damage in NaCl by Weerkamp et al. (1994), Seinen et al. (1994a,b), and Groote et al. (1994), as well as a review article by Sonnenfeld (1995) should be emphasized. Recently some examples of naturally occurring variety of colour centres in NaCl crystals from Kłodawa Salt Mine were identified by Wesełucha-Birczyńska et al. (2012). Interest in halite appeared again in connection with microbial life found in hypersaline environments such as those present on early Mars according to the research conducted by NASA's astrobiology program (Azua-Bustos et al. 2012; Edwards et al. 2006).

The present paper is one of an article series devoted to halites from Kłodawa Salt Mine. UV–vis spectroscopy was used for detection of colour centres in blue halite single crystals and their bleaching under heating. It concerns the spectroscopic properties of blue halite whereas the previous one dealt with lattice deformation of blue halites, their chemical composition, optical properties and solid state inclusions (Zelek et al. 2014).

Samples and experiments

Geological setting - origin of minerals and sample description

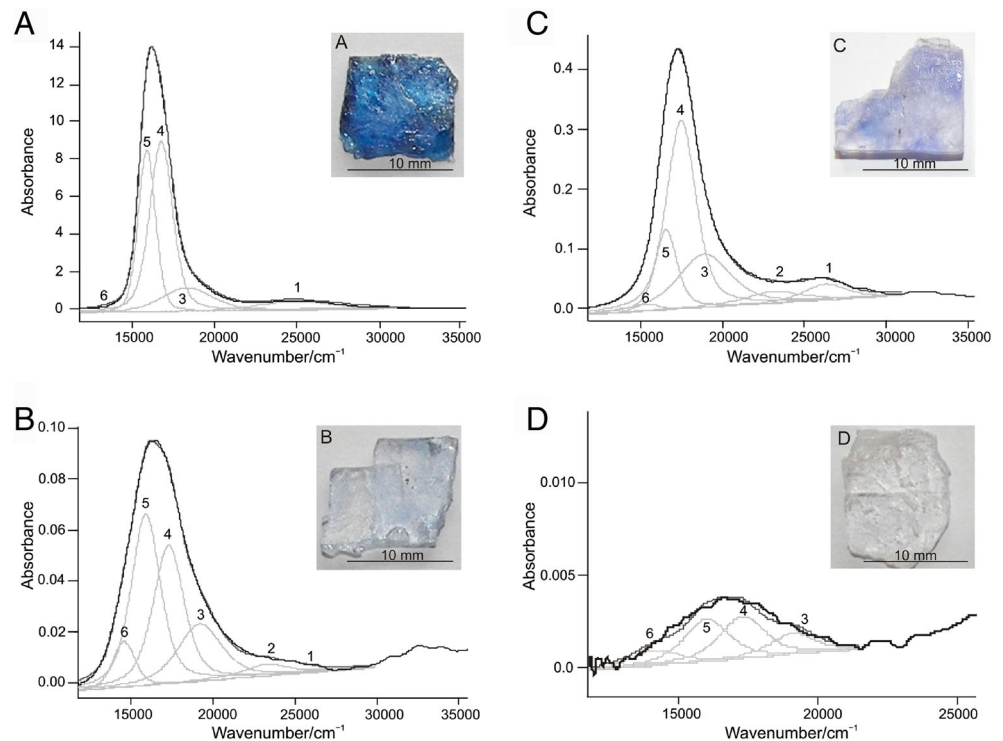
The occurrence of blue and purple forms of halite associated with potassium minerals typical for Zechstein salt formations were found in Kłodawa salt dome belonging to the Polish Zechstein Basin. The halite beds are accompanied by sylvinite veins (Natkaniec-Nowak and Tobała 2003; Tobała et al. 2007; Janiów et al. 2008; Wesełucha-Birczyńska et al. 2008) with the high

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Fig. 1 The representative UV–vis spectra for navy blue (a), pale blue (b), purple (c) and colourless (d) halite samples from Kłodawa Salt Mine. Band components are described by the numbers according to Table 1. Note different scale for absorbance values in each case



contents of potassium-40 (Zelek 2012; Zelek et al. 2014). The potassium isotope could be considered as the source of radiation necessary for the production of scattered F-centres. All single crystals used in the research (A, B, C and D types) were taken from the blue halite outcrops localized in the ventilating gallery between chambers KS39 and KS38 (on the level 562 m).

The single crystals samples were prepared using cleavage properties of halite and the measured surfaces were not actually modified by grinding and polishing. In ambient conditions the single crystals of halites were relatively stable. Selected fragments were isolated from the rock according to colouration which was defined using UV–vis spectra and assigned the following sym-

Table 1 Description of UV–vis absorption bands: experimental band positions (cm^{-1}), FWHM (cm^{-1}), N_F population according to Weselucha-Birczyńska et al. (2012)

Sample	Distance Na–Na/Å (Zelek 2012)		Position of absorption band/ cm^{-1}					
			1 Unidentified band	2 F band	3 $R_1(F_3)$ band	4 $R_2(F_3)$ band	5 Plasmon band	6 $M(F_2)$ band
A	2.8185(2)	λ_{exp}	24,900	–	18,300	16,800	15,900	14,200
		FWHM	6,000	–	3,600	1,700	1,200	100
		Population N_F	1.23×10^{16}	–	2.11×10^{16}	7.21×10^{16}	5.12×10^{16}	9.71×10^{12}
B	2.8191(1)	λ_{exp}	25,200	23,200	19,200	17,300	15,900	14,600
		FWHM	1,200	3,500	3,200	2,200	2,100	1,600
		Population N_F	6.45×10^{12}	1.07×10^{14}	4.88×10^{14}	8.31×10^{14}	9.69×10^{14}	1.94×10^{14}
C	2.8207(1)	λ_{exp}	26,300	23,100	18,900	17,500	16,600	15,400
		FWHM	3,100	4,100	3,800	2,100	1,600	1,800
		Population N_F	1.31×10^{13}	1.01×10^{14}	4.78×10^{14}	6.50×10^{14}	5.91×10^{14}	1.82×10^{14}
D	2.8208(1)	λ_{exp}	–	–	19,100	17,300	16,000	14,200
		FWHM	–	–	1,900	1,900	1,900	1,900
		Population N_F	–	–	9.98×10^{12}	1.98×10^{13}	1.97×10^{13}	7.07×10^{12}

Estimated standard deviations of band positions are in the range $70\text{--}200 \text{ cm}^{-1}$ and those of FWHM: $70\text{--}130 \text{ cm}^{-1}$ for well defined maxima

bols: A – navy blue, B – pale blue, C – purple and D – natural colourless fragments of rock salt (shown in Fig. 1 as insets). The saturation of blue hue in the halite aggregates was not homogeneous (compare Fig. 1 and examples in Zelek et al. 2014). These crystals displayed zones of navy blue hue, pale blue or purple hue alternate with colourless ones.

Methods

The UV–vis spectra for halite crystals of A, B, C and colourless D from Kłodawa Salt Mine were recorded on spectrophotometer Shimadzu UV-3600 and Shimadzu UV-2101PC equipped with ISR 240 for measuring the reflection spectra. Absorption spectra in small areas (0.16 mm²) were also recorded using a spectrophotometer diode array of OceanOptics PC2000, during the gradual heating of single crystal samples from room temperature to 430 °C at a rate of 5 °C/min with Linkam LTS420E Thermal Stage.

The microscopic observations were performed with the registration of images using Nikon Eclipse E600 microscope equipped with a camera Nikon TV Lens C-0.45×. The observations were made during the annealing process of single crystal fragments, isolated from halite type A and C, during heating from room temperature to 430 °C at a rate of 10 °C/min.

All types of halite (A, B, C, D) in the form of single crystal samples were examined by Raman spectroscopy using Renishaw inVia spectrometer and Leica microscope with 50× magnification objective. The samples were excited with high power near-infrared diode lasers (HP NIR) using excitation at 785 nm (*ca.* 15–20 mW on a sample). Confocal microscope mode allows performing depth profile measurements and also 2-dimensional point-by-point mapping on micrometer scale. The experimental data were worked out using software GRAMS/32 AI ver. 6.0, 1991–2000 Galactic Industries Corporation and WiRE 2.0 service pack 9, Renishaw inVia Raman Microscope, 2002 Renishaw plc.

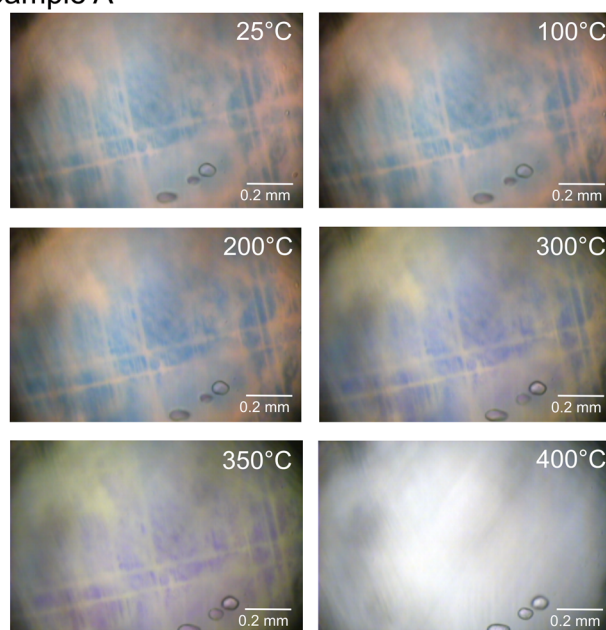
Decomposition of the experimental spectra was performed using the procedure described below. At first stage the 11,765–40,000 cm⁻¹ range was chosen for UV–vis, and two ranges, 300–100 cm⁻¹ and 3,500–500 cm⁻¹, were considered for Raman spectra. Secondly, the peak positions of components assigned according to the literature were imposed. The band shape of every peak was then fitted as Lorentzian-Gaussian type. And finally the sum of all calculated peak components were drawn to compare the calculated model of spectra with the experimental data.

Results and discussion

Absorption due to colour centres and bleaching process

The type of colour centres were characterized, using UV–vis spectroscopy in the following way: F centres – according the band at the 23,100–24,000 cm⁻¹; R₁(F₃) centres – the band in the range of 18,500–19,200 cm⁻¹; R₂(F₃) centres – the band in the range of 17,200–17,700 cm⁻¹; plasmons – the band in the range of 15,900–17,100 cm⁻¹; M(F₂) centres – the band in the range of 14,200–15,400 cm⁻¹ (Weselucha-Birczyńska et al. 2012; compare Ivey 1947 and Seinen et al. 1994a). The position of bands varied from sample to

Sample A



Sample C

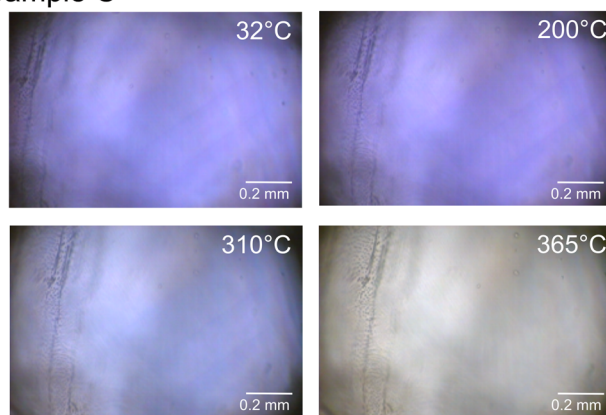


Fig. 2 The colour changes of single crystal fragments of halite A during heating from 25 °C to 400 °C and that of C during heating from 32 °C to 365 °C

sample in relatively narrow range but the set of components was characteristic for the particular type of halite. Estimated standard deviations of band positions were in the range $70\text{--}200\text{ cm}^{-1}$ and those of FWHM: $70\text{--}130\text{ cm}^{-1}$ for well defined maxima. These component bands are shown in Fig. 1. For each of the component bands the population for colour centres, given in Table 1, was evaluated according to Smakula's equation (Smakula 1930). The blue halite crystals undergo bleaching process during heating. The colour changes registered for a single crystal fragment of halite A during heating ($25\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$) and for halite C ($32\text{ }^{\circ}\text{C}$ to $365\text{ }^{\circ}\text{C}$) are shown in Fig. 2. The registration of UV–vis spectra along with the bleaching process was used for the interpretation of variability and dynamics of colour centre populations in the function of temperature (Fig. 3 and Fig. 4).

As can be seen in Fig. 4 the population of plasmons are predominated at room temperature for type A samples. However, it decreased with increasing temperature and disappeared at $300\text{ }^{\circ}\text{C}$, while the population of $R_2(F_3)$ centres increased to a maximum at the temperature of $250\text{ }^{\circ}\text{C}$, and subsequently a gradual band reduction was observed up to a complete disappearance at

$420\text{ }^{\circ}\text{C}$. With temperature increasing the population of plasmons in type B samples (Fig. 4) decreased from a maximum at $62\text{ }^{\circ}\text{C}$ concurrently to the population of $R_2(F_3)$ centres, which had a maximum at $250\text{ }^{\circ}\text{C}$. Both populations disappeared at $395\text{ }^{\circ}\text{C}$. In addition, for those types of halite samples (A and B) the relatively large population of $R_1(F_3)$ centres was observed with the maxima at $24\text{ }^{\circ}\text{C}$ and at $250\text{ }^{\circ}\text{C}$ for A and for B, respectively. For C samples the population of plasmons at $24\text{ }^{\circ}\text{C}$ was comparable to that observed for type A samples, while the population of $R_1(F_3)$ was predominant. With the increasing temperature the population of plasmons achieved a maximum value at $150\text{ }^{\circ}\text{C}$, and the population of $R_1(F_3)$ at $250\text{ }^{\circ}\text{C}$. Almost complete disappearance of the plasmons and R_1 populations was observed at $420\text{ }^{\circ}\text{C}$. In all types of halite the population of $M(F_2)$ centres was very small. It is worth noting that discreet F centres, in the investigated samples, were found at $23,600\text{--}24,000\text{ cm}^{-1}$, whereas the population of unidentified band at $26,200\text{--}26,500\text{ cm}^{-1}$ was negligible for all samples. Variability and dynamics of colour centre populations in the function of temperature derived from the graphical interpretation of the UV–vis spectra (Fig. 4) are in agreement with the colouration

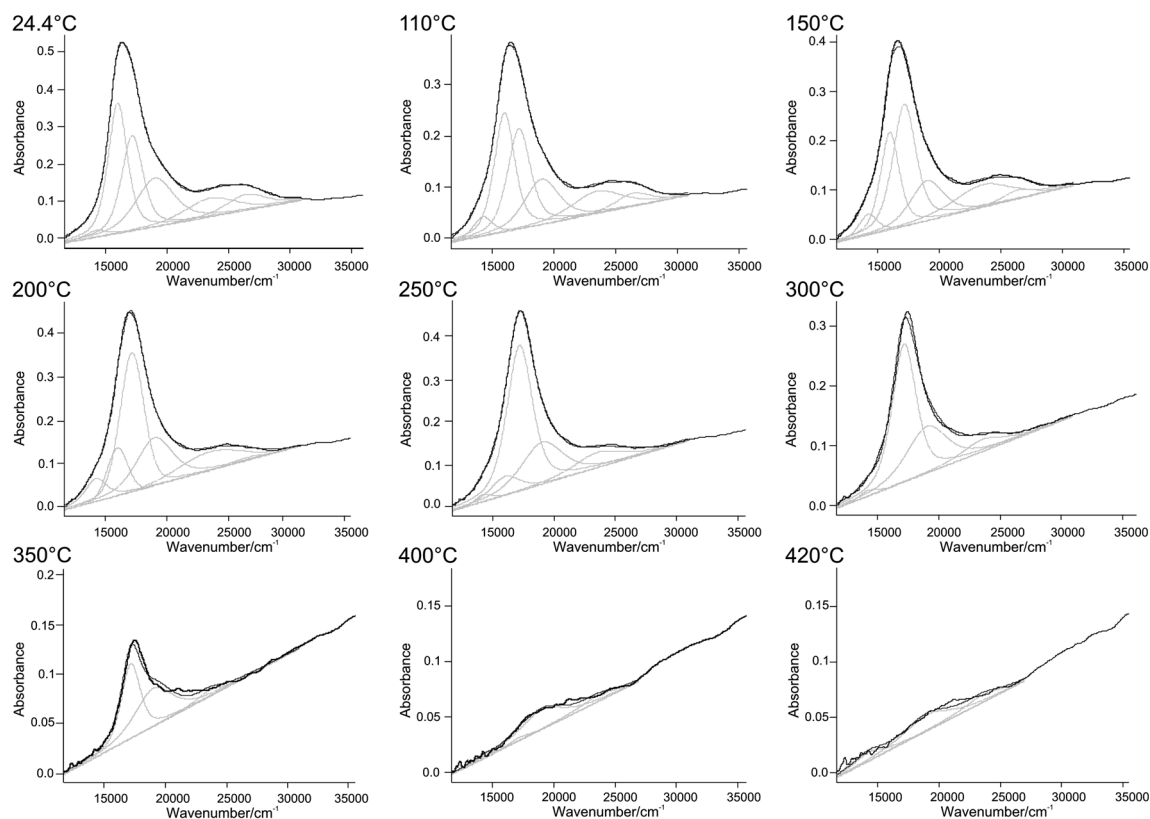
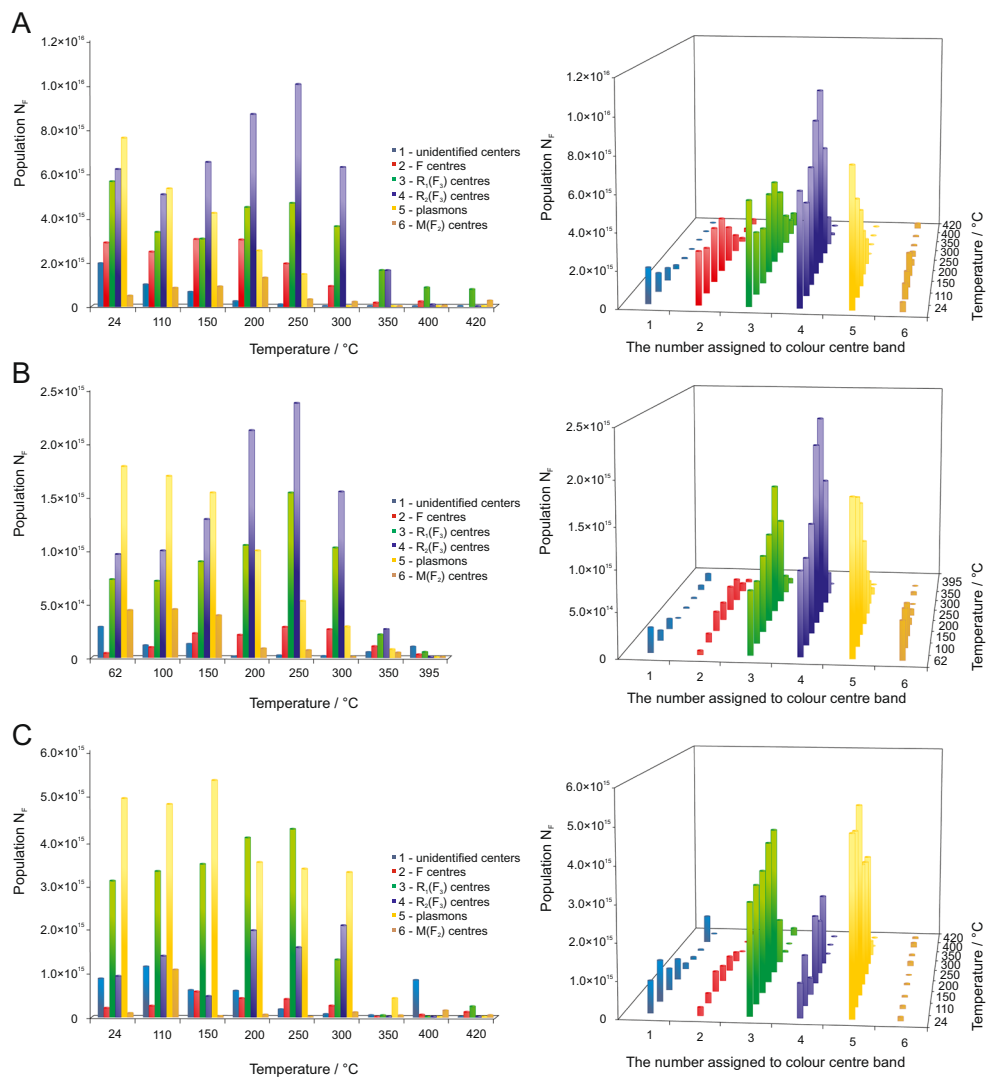


Fig. 3 An example of the variation of the absorption band with increasing temperature for sample A: black line – experimental data, grey lines – band components, graphite line – calculated fit. The temperature

increased from $25\text{ }^{\circ}\text{C}$ to $430\text{ }^{\circ}\text{C}$ during experiment, however the last sample state was registered at $420\text{ }^{\circ}\text{C}$

Fig. 4 The variability of the population of colour centres N_F with the temperature for halite type **a**, **b** and **c**. Red colour indicates F centre band, green – $R_1(F_3)$ centre band, purple – $R_2(F_3)$ centre band, yellow colour indicates plasmon band, orange colour indicates $M(F_2)$ centre band. The band at the range 26,200–26,500 cm^{-1} has not been interpreted yet



changes observed using optical microscope as colours complementary to light absorption (Fig. 2).

Micro-Raman spectra for colour centres and bleaching process

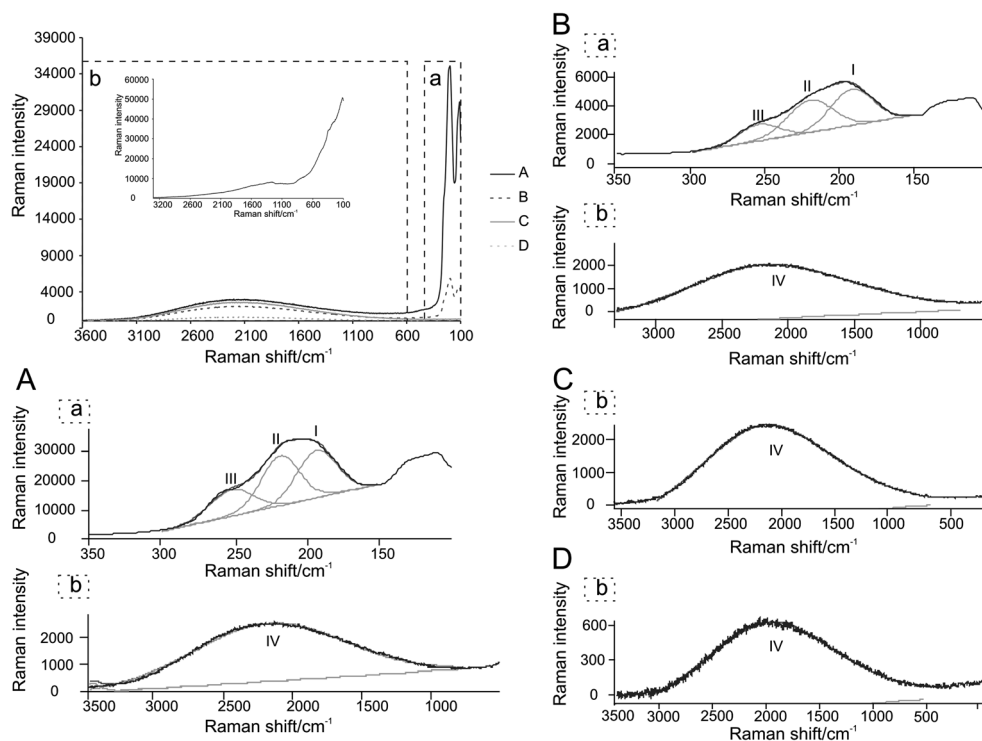
In the case of single crystals type A and B, very intense bands in the ranges of 191–193, 217–220, and 251–254 cm^{-1} as well as a broad band at *ca.* 2,160 cm^{-1} were observed (Table 2, Fig. 5). Estimated standard deviations of band positions were *ca.* 1 cm^{-1} and those of FWHM *ca.* 4 cm^{-1} for well defined maxima. The broad band was also observed for the halite single crystals of type C (2,180 cm^{-1}) and type D (2,160 cm^{-1}). The bands in the range of the 100–300 cm^{-1} indicate the presence of the colloidal Na precipitation (Duval et al. 1987). The observed values are within the frequency range of the phonon states in NaCl with phonon cutoff

Table 2 Bands position (cm^{-1}), FWHM (cm^{-1}), the intensity of the peaks and the area of the peaks in the micro-Raman spectra for single crystals of Kłodawa halites

Sample	Band components	Position of maximum	FWHM
A	I	193	32
	II	218	31
	III	251	35
	IV	2,160	1,270
B	I	191	33
	II	220	36
	III	254	32
	IV	2,160	1,530
C	IV	2,180	1,620
D	IV	2,160	1,530

Estimated standard deviations of band positions are *ca.* 1 cm^{-1} and those of FWHM *ca.* 4 cm^{-1} for well defined maxima

Fig. 5 Micro-Raman spectra for single crystal samples A, B, C and D with the spectrum of recrystallized A sample as inset. Band components are shown separately for two ranges: 300–100 cm^{-1} (a) and 3,500–500 cm^{-1} (b); black line – experimental data, grey lines – band components (enumeration according to Table 2), graphite line – calculated fit. In some cases all curves line up

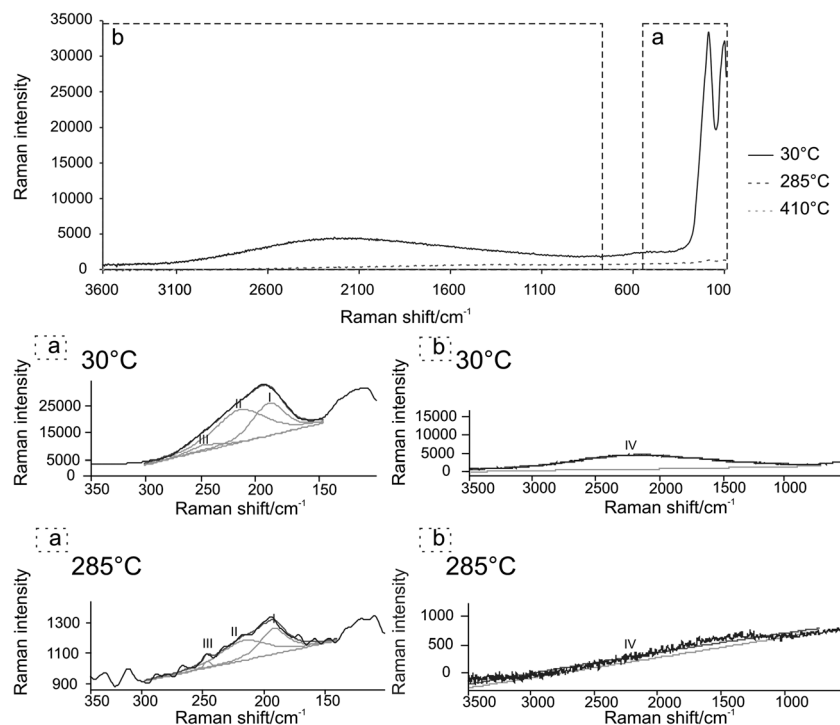


frequency at 260 cm^{-1} . The broad band around 2,160–2,180 cm^{-1} has not been taken into account in these considerations as it was also observed for colourless halite D. It is possible that in this case discrete F centres of very small population have gradually aggregated into unspecified clusters. For the recrystallized sample A the spectrum has

completely different character – typical for pure NaCl – what can be seen in the inset of Fig. 5 (note the Rayleigh component).

The micro-Raman spectroscopy was also used to examine the bleaching process. Blue halite single crystal sample (type A) was divided into three fragments which were then

Fig. 6 Variation of micro-Raman spectra for single crystal samples of A type showing bleaching process: at 30 °C (observed colour of sample was navy blue) and at 285 °C (the sample was purple). At 410 °C the sample was colourless and no bands were observed in micro-Raman spectra. Band components are shown for the ranges 300–100 cm^{-1} and 3,500–500 cm^{-1} both at 30 °C and at 285 °C



examined independently after heating up to 30 °C, 285 °C, and 410 °C, respectively. The obtained micro-Raman spectra were shown in Fig. 6. A complete bleaching was achieved at ca. 400 °C.

Conclusion

The experiments revealed high dynamics of identified colour centres different for each type of halite samples. In navy blue (A) and pale blue (B) samples the plasmons and $R_2(F_3)$ bands were predominated showing maximal populations at different temperatures: 24 °C and 250 °C, respectively. The blue component of the observed colouration fade away with increasing temperature, as can be seen under optical microscope. This process is due to the reduction of the population of plasmons, leaving exclusively purple component above the 300 °C. The purple sample (C) has the population of plasmons and $R_1(F_3)$ similar to those of navy blue A, however it has much lower population of $R_2(F_3)$ which is comparable to that in pale blue sample B.

In micro-Raman spectra the bands ca. 191 and 218 cm^{-1} observed for A and B halites in the 100–300 cm^{-1} range arose from the colour centres and Na colloids present in the samples (Sonnenfeld 1995; Worlock and Porto 1965; Henry 1966; Duval et al. 1987). All the samples (A, B, C, and D) had a broad Raman band with the maximum at about 2,100 cm^{-1} for which F-centre clusters of yet unrevealed structure were responsible. The band at ca. 190 cm^{-1} was not observed in the recrystallized colourless sample A, and it also disappeared during bleaching process under heating together with the other bands observed in the 100–300 cm^{-1} range.

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