Absorption of light by exchange coupled pairs of tetrahedrally coordinated divalent manganese in the helvite-genthelvite solid solution

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Abstract

Intensified colours in the helvite-genthelvite solid solution series are demonstrated by means of single crystal optical absorption and electron microprobe techniques to be due to absorption of light by exchange coupled $^{IV}Mn^{2+}$-$^{IV}Mn^{2+}$ pairs. The absorption bands caused by the pair transitions occur at energies, 21100, 22600, 23800, 26800 and 28400 cm^{-1}, that are comparable to those recorded for spin-forbidden single ion transitions in $^{IV}Mn^{2+}$, but the absorption coefficients of the bands are proportional to the square of the Mn-contents of the samples instead of simply showing a Lambert-Beer relationship to the Mn-content. The helvite structure, comprising four corner sharing MnO_3S tetrahedra with a common sulphur anion apex, represents a favourable situation for formation of exchange coupled 3d-cation pairs. However, several common Mn-rich minerals, as, e.g., rhodonite, have comparably favourable structures that contain corner, edge or face sharing 3d-cation centred polyhedra. Consequently, may Mn^{2+}-Mn^{2+} pair absorption be a frequent cause for colour intensification in minerals.

Key words: helvite; genthelvite; electronic spectroscopy; electron microprobe analyses.

Introduction

Members of the sodalite mineral subgroup are cubic or tetragonal species that crystallise with structures comprising frameworks of TO_4 tetrahedra linked into four- and six-membered rings, creating zeolite β cages, commonly called "sodalite cages" (Liebau, 2003), that contain a central cluster of atoms. In the cubic beryllosilicates danalite, $Fe_4(Be_3Si_3O_{12})S$, helvite, $Mn_4(Be_3Si_3O_{12})S$, and genthelvite, $Zn_4(Be_3Si_3O_{12})S$, linked SiO_4 and BeO_4 tetrahedra make up the cages and the central cluster consists of a sulphur anion (Figure 1) coordinated tetrahedrally by four cations (*Me*₄S-cluster). Hence, in helvite, the S anion is the common apex of four corner sharing MnO_3S tetrahedra (Figure 1) with three Mn-O distances of ca. 2.07 Å and one Mn-S distance of ca. 2.45 Å and the Mn-Mn distance between adjacent MnO_3S tetrahedral equals ca. 4.01 Å (Hassan and Grundy, 1985).

Materials with sodalite type structures are chemically very diverse comprising substances
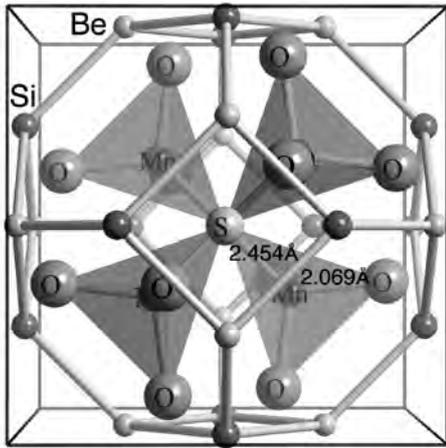
Figure 1. Projection of the helvite crystal structure highlighting the sodalite cage of interconnected SiO_4 and BeO_4 tetrahedra and the central sulphur anion that constitutes the common apex ligand for MnO_3S tetrahedra within the cage.

with, e.g., Be, Al, Si, P, Ga and Ge at the framework T-sites and a large range of monovalent or divalent cage anions or anion complexes such that the group includes several hundreds of members (Fischer and Bauer, 2009), although just some tens of these are so far known from nature. These structures are of interest for many reasons including applications as ion exchangers, catalytic materials, pigments, jewels and fluorophores.

Potential electronic interactions between metal clusters (Me_4S) at the centre of adjacent β cages and hence applications as framework expanded semiconductors have been considered and been the theme for a number of explorative studies on synthesis and magnetic properties of the cubic beryllosilicates of the sodalite subgroup. A few of these studies have included Mössbauer spectroscopy (Sharp et al., 1985; Armstrong et al., 2003) or optical absorption spectroscopy on single specimen (Lin and Zhu, 1985; Dann et al., 1997). None of the studies have confirmed long-range magnetic interactions, but magnetic

susceptibility measurements have indicated strong antiferromagnetic coupling between neighbouring Mn^{2+} and Fe^{2+} cations in the Me_4S clusters of helvite (Dann et al., 1997) and danalite (Armstrong et al., 2003), respectively. The stronger interactions within the Me_4S clusters as compared to between the clusters may be explained by the shorter Me-Me distances of ca 4 Å as compared to a distance of ca. 7 Å between centers of neighbouring metal clusters (Dann et al., 1997; Armstrong et al., 2003). Dann et al. (1997) concluded that the susceptibility observed at 10 K suggested spin-glass freezing rather than long-range magnetic order.

In nature, helvite-genthelvite solid solution crystals occur in a range of colours, hues and colour intensities. The appearance of crystals in pale green or yellow via dark yellow to brownish or reddish yellow suggests that the colours in this solid solution series may be caused by more complex processes than single ion absorption by tetrahedrally coordinated Mn^{2+}.

In order to explore the nature of colour mechanisms and in particular to investigate potential absorption related to reported antiferromagnetic coupling between neighbouring Mn^{2+} cations in helvite (Dann et al., 1997), optical absorption spectra of a set of five chemically characterised helvite-genthelvite single crystals with different Mn-contents have been measured.

Samples and Experimental

Samples

The present helvite-genthelvite solid solution single crystals were selected from specimens in the mineral collections of the Swedish Museum of Natural History (NRM). The selected crystals were subhedral to euhedral in shape, highly transparent, showing homogenous coloration in the range pale yellowish green to reddish yellow and were virtually free of inclusions. The collection numbers (NRM #) and origin of the specimens are summarised in Table 1. Information

Table 1. Samples and their origin.

Sample no	Mineral	Origin
#g15206	Helvite	Schwarzenberg, Saxony, Germany
#530959	Helvite	Stokøy, Langesundsfjord, Norway
#530965	Helvite	Brevig, Langesundsfjord, Norway
#920775	Helvite	Utö, Stockholm, Sweden
#950099	Genthelvite	Mont Saint-Hilaire, Quebec, Canada

on the geology and mineralogy of sample localities and additional information on some selected physical and chemical properties of the beryllosilicate minerals at these localities may be found in Glass (1944), Dunn (1976), Larsen (1985) and Langhof et al. (2000), respectively.

Chemical analyses

Electron microprobe analyses of the present helvite-genthelvite solid solution crystals were obtained with a Cameca SX50 instrument operating at an accelerating potential of 20 kV and a sample current of 15 nA using a beam spot of ca 1µm in diameter. Standard samples were synthetic MgO (Mg), Al_2O_3 (for Al), $CaSiO_3$ (for Si and Ca), $MnTiO_3$ (for Mn), Fe_2O_3 (for Fe) and ZnS (for Zn and S). For raw data reduction, the PAP computer program was used (Pouchou and Pichoir, 1984). Analyses were performed on 6 to 10 spots distributed over each crystal area used for recording the respective optical absorption spectra. The presented analyses in Table 2 represent mean values of the recorded point analyses for each single crystal. Concentrations of all other elements with N>8 than those detailed in Table 2 were below the respective detection limits of the instrument in the present samples. BeO-contents were calculated assuming 3 atoms of Be per formula unit.

Optical absorption spectroscopy

Optical absorption spectra in the UV/VIS range (290-800 nm) were obtained at room temperature from double-sided polished single crystals. Absorber thickness was varied in response to the Mn-concentration of the crystals between 105 and 770 µm as determined by means of a digital micrometer. Spectra were recorded during three cycles at a spectral resolution of 1 nm with a Zeiss MPM800 single beam microscope-spectrometer equipped with Zeiss Ultrafluar 10x condenser and objective lenses, a 75W Xenon arc light source and a photomultiplier detector. The spot size of the incident light beam was 35 µm in diameter. The accuracy of wavelength readings in the spectral range below 29000 cm^{-1} is better than 40 cm^{-1} as monitored by spectral recordings of Ho_2O_3-doped and Pr_2O_3/Nd_2O_3-doped calibration standards (Hellma™ glass filters 666-F1 and 666-F7). The recorded spectra were fitted with Gaussian components using the Jandel Scientific software Peakfit 4.0. The UV-absorption edge was fitted by an exponential function.

Results and discussion

Electron microprobe analyses of the present crystals demonstrate that they are chemically homogeneous and that they display very small variations in 3d cation contents. For instance, the relative standard deviations for the analysed Mn-contents of the present crystals are less than 3% (Table 2). This is also the case for the crystal from Utö (NRM #920775), although helvite and genthelvite crystals from

Table 2. Microprobe analyses of the present helvite-genthelvite samples.

Sample no	#530965	#g15206	#530959	#920775	#950099
SiO_2 (wt %)	32.78	32.70	32.18	31.31	30.18
Al_2O_3	0.00	0.42	0.03	0.12	0.01
MgO	0.00	0.02	0.02	0.02	0.03
CaO	0.03	0.13	0.01	0.03	0.01
MnO	43.83	41.88	33.06	24.92	6.27
FeO	6.50	3.39	3.11	1.50	0.14
ZnO	0.88	5.62	16.40	26.01	49.19
S	5.92	5.58	5.77	5.65	5.46
BeO_{calc}	13.56	13.52	13.37	13.04	12.84
O=S	-2.95	-2.79	-2.88	-2.82	-2.73
SUM	*100.55*	*100.47*	*101.07*	*99.78*	*101.40*

Atoms per formula unit on the basis of 10 cations

Si	3.018	3.020	3.005	2.999	2.935
Al	0.000	0.046	0.003	0.013	0.001
Mg	0.001	0.002	0.002	0.003	0.004
Ca	0.003	0.013	0.001	0.003	0.001
Mn*	3.418	3.275	2.615	2.022	0.517
Fe	0.501	0.261	0.243	0.120	0.011
Zn	0.060	0.383	1.131	1.839	3.532
S	1.021	0.966	1.009	1.014	0.995
Be	3.000	3.000	3.000	3.000	3.000

*1s equals 0.075, 0.035, 0.003, 0.054 and 0.010 pfu, respectively.

this locality frequently display conspicuous zonation patterns (Langhof et al., 2000).

The recorded optical absorption spectra of the helvite-genthelvite solid solution single crystals show, in the spectral range above 20000 cm^{-1}, a set of six relatively narrow (*FWHM* ≈ 300-900 cm^{-1}) and weak (molar absorption coefficient, ε ≈ 0.06-2.8 l·mol^{-1}·cm^{-1}) absorption bands that increase strongly in intensity with increasing Mn-contents (Figure 2). Their energies, small widths and relatively low intensities are in general agreement with those of absorption bands caused by spin-forbidden electronic *d-d* transitions in Mn^{2+} in minerals (e.g., Burns,

1993). In detail, the sharpness and energy of the band at ca 23800 cm^{-1} demonstrates that it represents the field-independent $^6A_1(S) \rightarrow {}^4E_g{}^4A_{1g}(G)$ transition in Mn^{2+} at a tetrahedrally coordinated site (Hålenius et al., 2007). The remaining absorption bands at ca. 21100, 22600, 26800, 28400, 28800 cm^{-1} are assigned in accordance with the general scheme proposed by Hålenius et al. (2007) to the spin-forbidden electronic *d-d* transitions $^6A_1(S) \rightarrow {}^4T_{1g}(G)$, $^6A_1(S) \rightarrow {}^4T_{2g}(G)$, $^6A_1(S) \rightarrow {}^4T_{2g}(D)$, $^6A_1(S) \rightarrow {}^4E_g(D)$ and $^6A_1(S) \rightarrow {}^4T_{1g}(P)$ in ^{IV}Mn^{2+}, respectively. These assignments are comparable to those proposed for the spectrum of one helvite
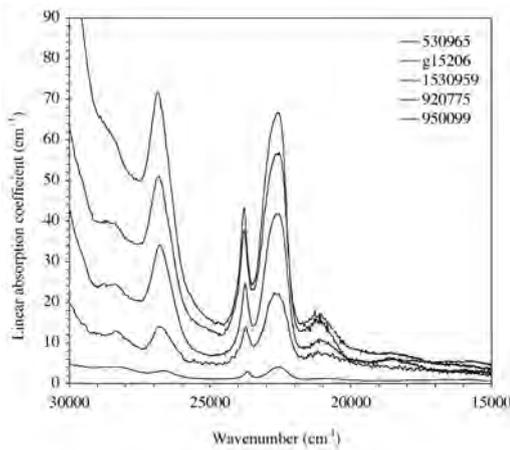
Figure 2. Optical absorption spectra of the present helvite-genthelvite solid solution crystals showing a strong increase in absorption band intensities with increasing Mn-concentration (bottom to top of the figure).

specimen recorded in the range 15000-27500 cm^{-1} by Lin and Zhu (1985), although they failed to observe bands caused by the high-energy transitions to the $^4E_g(D)$ and $^4T_{1g}(P)$ states because of a too limited spectral recording range. In contrast, Dann et al. (1997) assigned absorption bands observed in a diffuse reflectance spectrum of one synthetic helvite powder sample in a completely reversed order that results in unrealistic negative values for the crystal field splitting parameter (*10Dq*) and interelectronic repulsion *B*- and *C*-parameters of

$^{IV}Mn^{2+}$. Our spectra show no indications for a presence of Mn^{3+} or Fe^{3+}, but two very weak absorption bands observed in the spectral range below 20000 cm^{-1} are most likely caused by spin-forbidden *d-d* transitions in tetrahedrally coordinated Fe^{2+} (Lin and Zhu, 1985) that is present in subordinate concentrations in the present samples (Table 2). Considerably more intense and broader absorption bands cause by spin-allowed *d-d* transitions in tetrahedrally coordinated Fe^{2+} in genthelvite and other oxygen-based mineral structures have been demonstrated to occur at distinctly lower energies, typically below 7000 cm^{-1} (Rossman and Taran, 2001).

From the energies of the five recorded spin-forbidden $^{IV}Mn^{2+}$-bands (ν_1-ν_5), the crystal field splitting (10*Dq*) and interelectronic repulsion (Racah) *B* and *C* parameters for tetrahedrally coordinated Mn^{2+} in the respective helvite-genthelvite solid solution crystals (Table 3) are obtained by solving the Tanabe-Sugano equations (Lever, 1985):

ν_1	$^6A_1(S) \rightarrow ^4T_{1g}(G)$	$-10Dq+10B+6C-26B^2/10Dq$
ν_2	$^6A_1(S) \rightarrow ^4T_{2g}(G)$	$-10Dq+18B+6C-38B^2/10Dq$
ν_3	$^6A_1(S) \rightarrow ^4E_g{}^4A_{1g}(G)$	$10B+5C$
ν_4	$^6A_1(S) \rightarrow ^4T_{2g}(D)$	$13B+5C+x$
ν_5	$^6A_1(S) \rightarrow ^4E_g(D)$	$17B+5C$

The obtained values of these parameters for $^{IV}Mn^{2+}$ in the present samples are in excellent

Table 3. Energies (cm-1) of Mn2+ transitions (n1-n5), Racah (B and C) and crystal field splitting parameter (Dq) in the helvite-genthelvite solid solution.

Sample no	ν_1	ν_2	ν_3	ν_4	ν_5	B	C	Dq
#950099	20930	22570	23670	26670	28310	663	3408	535
#920775	21050	22640	23740	26760	28390	664	3419	532
#530959	21100	22610	23750	26790	28400	664	3421	532
#g15206	21175	22600	23800	26850	28400	657	3446	545
#530965	21165	22600	23800	26850	28390	656	3449	548
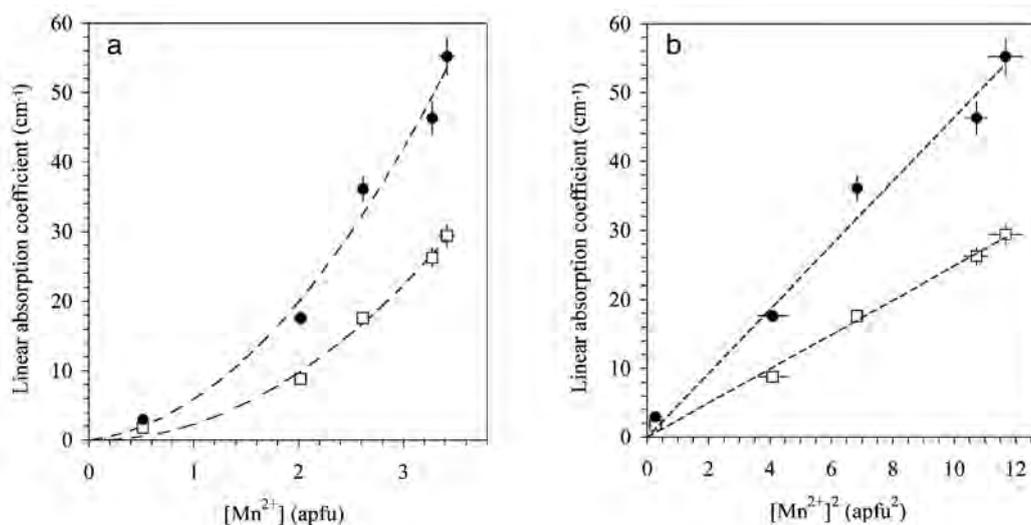
Figure 3. Plots of the linear absorption coefficients for the v_2 (filled circles) and v_3 (open squares) bands in the present spectra versus single ion Mn^{2+}-contents (a) and the square of the Mn^{2+}-contents (b). Thin broken lines representing square and linear functions are guides for the eye.

agreement with those retrieved from spectra of a number of minerals and inorganic compounds with tetrahedrally coordinated Mn^{2+} (Hålenius et al., 2007 and references therein).

The linear absorption coefficient, α, (i.e., absorbance divided by sample thickness) of all the Mn^{2+}-related absorption bands v_1-v_5 increases strongly with the Mn-content of the samples (Figure 2). Furthermore, it is evident that the absorption coefficients of these bands are not linearly dependent on the Mn-concentrations and consequently they don't obey the Beer-Lambert law (Figure 3a), as intensities of normal single ion spin-forbidden d-d absorption bands do. In fact, the absorption coefficients of the observed bands are directly proportional to the square of the Mn-concentrations of the samples (Figure 3b). This demonstrates that the Mn^{2+}-related absorption bands in helvite-genthelvite solid solution minerals are caused by electronic transitions in $^{IV}Mn^{2+}$-$^{IV}Mn^{2+}$ pairs. Strongly intensified absorption

bands caused by antiferromagnetically exchange coupled Mn^{2+}-Mn^{2+} pairs have been observed in a large number of Mn-rich compounds including synthetic equivalents of the minerals rhodochrosite ($MnCO_3$) and sphalerite (Mn-doped ZnS) (e.g., Lohr and McClure, 1968) and Fe^{3+}-Fe^{3+} pair absorption has been demonstrated in a variety of minerals (e.g., Rossman, 1975 and 1976; Andreozzi et al., 2001). However, this is the first recorded example of enhanced absorption and colour caused by $^{IV}Mn^{2+}$-$^{IV}Mn^{2+}$ pairs in naturally formed minerals. Although it may be argued that the helvite structure, comprising clusters of four corner sharing MnO_3S tetrahedra, provides an exceptionally favourable situation for formation of Mn^{2+}-Mn^{2+} pairs, it is still very likely that comparable pair transitions may be frequent causes for colour intensification in a large number of common Mn^{2+}-rich minerals with ligand sharing 3d-cation centred polyhedra as, e.g., rhodonite.

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