Article

Luminescence Properties of Tetrahedral Coordinated Mn\(^{2+}\); Genthelvite and Willemite Examples

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Abstract: The cause of the split of \(4^4E(4G)\) Mn\(^{2+}\) excited level measured on minerals spectra is discussed. It is our view that \(\Delta E = 14E(4G) - 4A(4G)\) should be considered an important spectroscopic parameter. Among the possible reasons for the energy levels splitting taken under consideration, such as the covalent bond theory, the geometric deformation of the coordination polyhedron and the lattice site’s symmetry, the first one was found to be inappropriate. Two studied willemite samples showed that the impurities occur in one of the two available lattice sites differently in both crystals. Moreover, it was revealed that the calculated crystal field \(D_q\) parameter can indicate which of the two non-equivalent lattice sites positions in the willemite crystal structure was occupied by Mn\(^{2+}\). The above conclusions were confirmed by X-ray structure measurements. Significant differences were also noted in the Raman spectra of these willemites.

Keywords: Mn\(^{2+}\); luminescence; energy of excited level; crystal field parameters

1. Introduction

The luminescence of synthetic materials subsidized with manganese ions, especially (2+), is still intensively researched and has been for many years [1,2]. The emission color of subsidized Mn\(^{2+}\) compounds is usually green or orange to red. It depends on the strength of the crystal field, i.e., the coordination number, the type of ligand and the distance between the ligand and the manganese ion. Various materials with a halides, oxides, phosphates and silicate matrix are synthesized in the form of glass, ceramics, and crystals, sometimes as nanomaterials or coatings. Many synthetic materials are doped not only with Mn\(^{2+}\) but also with lanthanide ions. Then, between the Mn\(^{2+}\) and 4\(^{2+}\) ions, the phenomenon of energy transfer takes place [3]. This makes it possible to obtain efficient light emitters of various colors, including white light. Moreover, some of these materials exhibit a persistent luminescence phenomenon [4,5].

It is believed that the study of the spectroscopic properties of natural materials containing Mn\(^{2+}\) could be inspiring to create an optical material with the desired parameters. Divalent manganese ion is one of the most common and well-known activators of minerals’ luminescence.

The present research has demonstrated some properties of the luminescence spectra of Mn\(^{2+}\)-bearing minerals. First, attention was paid to the splitting of the \(4^4E(4G)\) excited level. The absorption/excitation bands corresponded to Mn\(^{2+}\) transitions were usually measured in the 300–580 nm range and these bands sometimes have not been single. On these spectra, the \(v_3\) band of \(6S \rightarrow 4E(4G)\) transition is usually distinguished due to its intensity and sharpness. It was also often measured, but not clarified, that this band is double. A review of available absorption/excitation spectra for Mn\(^{2+}\)-bearing minerals and synthetic materials concludes that \(\Delta E = 4E(4G) - 4A(4G)\), i.e., splitting of these levels is an important spectroscopic parameter. In the current article, an attempt to
indicate the factors affecting the $\Delta E$ value for two minerals that contain Mn$^{2+}$ in tetrahedral coordination: genthelvite Be$_3$Zn$_4$(SiO$_4$)$_3$S and willemite Zn$_2$SiO$_4$ was made.

For all minerals and an overwhelming number of synthetic phosphors, Mn$^{2+}$ occurring as a high-spin complex possessing the unique electronic configuration ($t_{2g}^3$,$e_g^2$) with a single occupation of all five d orbitals and Crystal Field Stabilization Energy (CSFE) equal to zero [6]. As a consequence, Mn$^{2+}$ can be equally likely present in both octahedral and tetrahedral coordination. Tanabe–Sugano diagram for d$^5$ ion is presented in Figure 1a. The ground term is $^6S$ and the ground level is $^6A_1$ with the five 5d electrons orbitals ($t_{2g} \uparrow)^3(e_g \uparrow)^2$. In order of increasing energy, the excited terms are: $^4G$, $^4P$, $^4D$, $^4I$ and $^4F$. Due to the crystal field, the terms split into levels. For example, the first excited term $^4G$ splits into levels $^4T_{2g}$ and $^4T_{1g}$, whose energy strongly depends on crystal field parameter $Dq$ and two levels $^4A_1$ and $^4E_g$, which are independent on $Dq$. For an ion in tetrahedral coordination, the letter “g” in the subscript is not written. Figure 1b shows the electron configuration of the ground level and some of the excited crystal field levels of d$^5$ ion in tetrahedral coordination.

![Energy Levels of d$^5$ Ion and Electronic Configuration](image)

**Figure 1.** The energy levels of d$^5$ ion: (a) simplified Tanabe–Sugano diagram (sketched after [7]); (b) electronic configuration of d$^5$ ion, high spin (HS) and tetrahedral coordination.

The transitions between ground and excited states according to the solution of the Tanabe–Sugano theory are as expressed in Equation (1). In the visible region, there are five transitions measured as $\upsilon_1$-$\upsilon_5$ bands listed below in the order of increasing energy:

\[
\begin{align*}
    \theta_1 : & \quad ^6A_1(S) \rightarrow ^4T_{1g}(^4G) = -10Dq + 10B + 6C - 26\frac{B^2}{10Dq}, \\
    \theta_2 : & \quad ^6A_1(S) \rightarrow ^4T_{2g}(^4G) = -10Dq + 18B + 6C - 38\frac{B^2}{10Dq}, \\
    \theta_3 : & \quad ^6A_1(S) \rightarrow ^4E_g(^4A_{1g}(^4G) = 10B + 5C, \\
    \theta_4 : & \quad ^6A_1(S) \rightarrow ^4T_{2g}(^4D) = 13B + 5C + x, \\
    \theta_5 : & \quad ^6A_1(S) \rightarrow ^4E_g(^4D) = 17B + 5C,
\end{align*}
\]

(1)

where $B$ and $C$ are the Racah parameters. From these equations, the $B$, $C$ and $Dq$ parameters could be calculated. Usually, the $B$ parameter is calculated first, from the difference among $\upsilon_5$ and $\upsilon_3$ bands. However, if the $\upsilon_3$ and/or $\upsilon_5$ band is not a single band, but rather a split one, determining the values of parameters $B$ and $C$ becomes problematic. The $Dq$...
parameter is calculated from \( \nu_2 \) or \( \nu_1 \) transition, the band which is better distinguished in the spectrum. Then Equations (2) or (3) are used:

\[
100Dq^2 = (14B + 5C - E(\theta_2)(22B + 7C - E(\theta_2)) + 12B^2 \frac{(E(\theta_2) - 22B - 7C)}{(13B + 5C - E(\theta_2))})
\]

(2)

\[
100Dq^2 = (10B + 7C - E(\theta_1)(10B + 5C - E(\theta_1)) + 36B^2 \frac{(E(\theta_1) - 10B - 5C)}{(19B + 7C - E(\theta_1))})
\]

(3)

The \( ^4E^4A_1 \) level is the efficient level for the excitation of the emission of the Mn\(^{2+} \). Therefore, it has been concluded that the previously known theories explaining the causes of this level splitting should be considered. In general, the reasons of the complex nature of absorption/excitation band may be as follows:

(a) The excited states have a mixed nature; for example, the \( ^4G \) level is influenced by \( ^4D \) or \( ^4P \) levels. The \( ^4A_{1g} \) (\( ^4G \)) level is expected to be less affected than the \( ^4E_g \) (\( ^4G \)) level by slight changes in the metal-ligand distances. The mixed nature of the excited states was assumed for Mn\(^{2+} \) site in apatite [8] and then the non-zero \( \Delta E \) was calculated. However, this assumption was not made in the current study.

(b) The electron d-d transitions are strongly coupled with lattice vibrations, so the \( \nu_1 \) and \( \nu_2 \) transitions would not be single only at room temperature and the emission band should become narrower at low temperatures. However, it was sometimes difficult to unequivocally prove whether the measured \( \nu_1 \) and \( \nu_2 \) bands were single or complex. Accordingly, this effect could not be recognized as an important factor for \( \Delta E \) value.

(c) Mn\(^{2+} \) occupies more than one inequivalent crystal site. If the Mn\(^{2+} \) with the same or similar quantities occupies two sites with different \( Dq \) values, the \( \nu_1, \nu_2 \) and \( \nu_4 \) transitions would not be single. Such effect should be observed not only at low temperature but also at room temperature. This case was found for T1 and T2 sites of willemite by Halenius et al. [9]. Despite the significant difference of \( \nu_1, \nu_2 \) and \( Dq \) values for these sites, Halenius et al. [9] did not mention whether the emission band was double or not. In addition, the same \( B \) and \( C \) parameters were assigned for T1 and T2 sites [9]. According to [9], the difference of occupied sites does not imply a difference in the nature of the bond. Such a case is discussed in Section 3.5.

(d) In this work, we have also verified whether the \( \Delta E \) value depends on the geometrical deformation of coordination polyhedron. For each lattice site which Mn\(^{2+} \) can occupy, the following parameters were calculated: quadratic elongation \((\ell)\), bond angle variance \( (s^2) \), distortion index \( (s) \) [10] and mean quadratic elongation \( \Delta \) [11] defined for coordination CN = 4 as \( \ell(CN = 4) > \frac{1}{4} \sum_{i=1}^{4} \left( \frac{L_i}{l_0} \right) \), \( s^2 = \sum_{i=1}^{6} \left( \frac{\theta_i - 109.47^\circ}{s} \right) \), \( \sigma(CN = 4) = \sqrt{\frac{1}{4} \sum_{i=1}^{4} (l_i - l_0)^2} \) and \( \Delta = \frac{1}{4} \sum_{i=1}^{4} \left( \frac{L_i - L_0}{l_0} \right)^2 \). The \( l_i \) is individual Me-O bond length, \( l_0 \) is the main bond length for each site, and the \( \theta_i \) is individual O-Me-O angle. The emission band could be a single band for each site. These deformation parameters are discussed in Section 3.5.

(e) The contribution of covalence participation in Mn-ligand bonding. The degeneracy of states \( ^4E \) (\( ^4G \)) and \( ^4A_{1g} \) (\( ^4G \)) could be lifted by covalence in the crystal. The removal of degeneracy can be explained by the differential expansion of \( (2\phi) \) and \( (e\phi) \) orbitals due to differing covalence between \( t_2 \) and \( e \) orbitals. Curie et al. [12] and Stout [13] proposed to introduce parameters taking into account the participation of the covalent bond. These are: the Koide–Pryce parameter \( \epsilon \), the Racah–Trees parameter \( a \), and finally, the \( N_t \) and \( N_e \) normalization parameters. The values of the Racah \( B \) and \( C \) parameters as well as the energy values of the energy levels change (Equation (4)):

\[
\theta_1 : -10Dq + 10B + 6C = \frac{26B^2}{10Dq} + 22a, \quad \theta_2 : -10Dq + 18B + 6C = \frac{38B^2}{10Dq} + 26a, \quad \theta_3 : 10B + 5C + 20a
\]

\[
\theta_4 : 13B + 5C + 8a, \quad \theta_5 : 17B + 5C + 6a, \quad B = \frac{94a}{\sqrt{49(\theta_4 - \theta_3)^2 - 768a^2}}, \quad C = \frac{\theta_5 + \theta_1 - 27B - 26a}{10}
\]

(4)
According to [12], the possibility of Mn being present in two non-equivalent lattice sites in willemite samples. Palumbo and Brown [14] measured several excitation spectra of Mn-bearing crystals. The splitting of almost all Mn ions, Vaida [18,19] showed two sets of energy levels in willemite, and Zn-spinel. After [14], the excitation of 4E4A(4G) level exhibits 3 lines, for Zn$_2$SiO$_4$: 0.06 Mn with $\Delta E = 147$ cm$^{-1}$. Calculation of the energy of excited levels whose orbital degeneracy has been removed due to low symmetry of occupied site or coordination polyhedron is presented as a solution of the following crystal field Hamiltonian $H = \sum_{p=2} B^p \cdot O^p_{\text{h}}$. Energy values of the excited levels, without imaginary terms, can be obtained for a symmetry of position lower than orthorhombic. In other cases, the approximation of the orthorhombic field is used. Such calculations are successfully performed for 4$^p$ ions. Brik et al. [17] for LiAlO$_2$:Mn$^{2+}$ (0.034 at%) and C$_2$ symmetry measured that $\Delta E = 616$ cm$^{-1}$, while calculated only $\Delta E = 428$ cm$^{-1}$. For Mn$^{2+}$ in willemite, Vaida [18,19] showed two sets of $B^p$ parameters and calculated energy levels. These data are presented in Table 7. In the previous one [18], splitting energy levels was neither observed nor calculated, contrary to Su et al. [20]. While the proper value of $B$ (622 cm$^{-1}$), $C$ (3504 cm$^{-1}$), and $Dq$ (562 cm$^{-1}$) parameters have been obtained. In the second [19], with changed $B^p$ parameters, a complete split of energy levels was observed, but the obtained values of parameters $B$ (945 cm$^{-1}$), $C$ (2851 cm$^{-1}$), and $Dq$ (340.5 cm$^{-1}$) are rather not credible. Both of the above examples [17–19] showed that this method of calculation energy of excited levels of Mn$^{2+}$ present in a low symmetrical lattice site does not give results consistent with the experimental data. Due to the low symmetry of the lattice site and the insufficient amount of experimental input data, especially the position of the v$_1$ band, no such calculations were made for the minerals studied in this work.

In this article, we present a discussion of the influence of the following factors on the value of $\Delta E$, i.e., (4E4A(4G)) splitting—geometric deformation of lattice site, participation of covalent bond and, only qualitatively, a low position symmetry. We also discuss the possibility of Mn$^{2+}$ being present in two non-equivalent lattice sites in willemite samples.

2. Materials and Methods

All studied here minerals showed an intense green luminescence (Figure 2).

Two specimens of genthelvite Be$_2$Zn$_4$(SiO$_4$)$_3$S from Poudrette quarry Mont Saint-Hilaire (Quebec, QC, Canada) have been studied in the current research. They have light yellow (G1) or yellow (G2) color and are tristetrahedrons, most probably tetrahedrally-shaped [112] and [114] (Figure 2, photo 1a, b). These crystals’ sizes are relatively small, up to 2.5 mm. Genthelvite belongs to tectosilicates and may be considered as a member of the sodalite Na$_4$(Si$_3$Al$_3$)O$_{12}$Cl subgroup, where Be is playing the role of Al. The crystal structure of genthelvite was resolved by Hassan and Grundy [21]. Crystal space group is $P4_3n$, number of formula unit $Z = 2$, the lattice unit recognized as a standard $a = 8.1091(4)$ Å for the sample with minimal Mn-content 0.95 wt.%. The SiO$_4$ and BeO$_4$ polyhedrons are
linked and make up the cages with central sulphur, the common apex for two ZnO$_2$S tetrahedra. It is believed [22] that Mn substitutes for Zn in ZnO$_6$S trigonal pyramid, coordination number CN = 7, with three Zn-O bond lengths 1.948 Å, three other 3.1076 Å and one Zn-S equal 2.3628 Å. However, it is most often assumed that Zn has the subsequent four ligands O$_2$S, with a mean Zn-ligand distance equal to 2.0615 Å, but an effective coordination number of Zn is equal to 3.3608 [21]. Wyckoff’s position of all atoms in genthelvite structure is 8e, the site symmetry of Zn atoms is rather high—C$_3$. The sketch of the genthelvite crystal structure is presented in Figure 3a.

Two willemite Zn$_2$SiO$_4$ specimens from the Franklin deposit (Franklin, Sussex County, NJ, USA), were studied here. The first one, named W1, forms a mass of fine grains of a prismatic or lamellar habit and dark red (maroon) color. The second, W2, forms colorless, small—up to 1.5 mm—prismatic crystals (see photos 2a, b). Willemite belongs to orthosilicates, is trigonal, space group $R3$, the number of formula unit $Z = 18$ and lattice parameters refined as the standard [23] are $a = 13.948(2)$ Å, $c = 9.315(2)$ Å, $Z = 18$. In the references [24, 25], the zinc positions are named the opposite of Klaska et al. [23]. The Zn$_1$ tetrahedrons (orange) are smaller ($<\text{Zn}_1\text{-O}> = 1.9495$ Å) than Zn$_2$ (grey) $<\text{Zn}_2\text{-O}> = 1.9613$ Å. Zn$_1$O$_4$ tetrahedrons form 6-membered rings with each other and also 4-membered
rings with SiO$_4$ and Zn$_2$O$_4$ tetrahedrons. Zn$_2$O$_4$ forms 6-membered rings with SiO$_4$ and 4-membered rings with SiO$_4$ and Zn$_1$O$_4$ tetrahedrons. The average distances are Zn$_1$-Zn$_1$ ~3.14 Å, Zn$_1$-Zn$_2$ ~3.50 Å, Zn$_2$-Zn$_2$ ~5.25 Å. Each oxygen is bonded to three tetrahedral cations, one silicon (Si$^{4+}$) and two zinc (Zn$^{2+}$, Zn$^{2+}$). All ions occupy an 18f position, and the site symmetry of the Zn$^{2+}$ is triclinic C$_1$. The sketches of the willemite crystal structure are presented in Figure 3b.

The Measurements’ Conditions

The preliminary chemical compositions of willemite W1, W2 and genthelvite G1, G2 were examined using a scanning electron microscope Phenom XL equipped with an EDS (energy-dispersive X-ray spectroscopy) detector (Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Sosnowiec, Poland). Quantitative chemical analyses of both minerals were carried out on a Cameca SX100 electron microprobe (Institute of Geochemistry, Mineralogy, and Petrology, University of Warsaw, Poland) at 15 kV and 10 nA and using the following lines and standards: Si K$_\alpha$, Mg K$_\alpha$ = diopside; Zn K$_\alpha$ = sphalerite; S K$_\alpha$ = chalcopyrite; Mn K$_\alpha$ = rhodonite; FeK$_\alpha$ = Fe$_2$O$_3$. Beam diameter was 5 µm for willemite and 10 µm for genthelvite.

The powdered sample of genthelvite (G1, G2) and willemite (W1, W2) were examined by X-ray powder diffraction (XRD). A PANalytical PW 3040 diffractometer was used (Bragg-Brentano, theta- theta geometry), using Co K$_\alpha$1 radiation (filtered by Fe filter placed on the diffracted beam path). The generator settings for the X-ray tube were: tension = 40 kV, current = 40 mA. The measurements conditions were: scan range: 5–110 2θ degree time limit was set to 300 sec, and the scan speed was 0.02 2θ degree. The Rietveld method was applied to refine collected patterns using the HighScore+ software (version 4.9, Malvern Pananalytical B.V., Almelo, The Netherlands.

The Raman spectra of genthelvite samples were recorded on a WITec alpha 300R Confocal Raman Microscope equipped with an air-cooled solid laser 532 nm and a CCD (closed-circuit display) camera operating at −61 °C. The laser radiation was coupled to a microscope through a single-mode optical fiber with a diameter of 3.5 µm. An air Zeiss (LD EC Eppllan-Neofluan DIC-100/0.75NA) objective (Carl Zeiss AG, Jena, Germany) was used. Raman scattered light was focused by an effective Pinhole size of about 30 µm and a monochromator with a 600 mm$^{-1}$ grating. Integration times of 5 s with an accumulation of 30 scans and a resolution of 3 cm$^{-1}$ were chosen. The Raman spectra of willemite samples W1 and W2 were recorded on a WITec alpha 300R Confocal Raman Microscope equipped with an air-cooled solid laser 633 nm and a CCD (closed-circuit display) camera operating at −61 °C. The laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of 50 µm. An air Zeiss (LD EC Eppllan-Neofluan DIC-100/0.75NA) objective) was used. The scattered light was focused on multi-mode fibre (100 µm diameter) and a monochromator with a 600 mm$^{-1}$ grating. Raman spectra were accumulated by 30 scans with an integration time of 20 s and a resolution of 3 cm$^{-1}$. In both cases, the monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm$^{-1}$).

All Raman spectra processing was performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, Salem, NH, USA), while the baseline correction and cosmic ray removal were conducted using WitecProjectFour software (version Four, WITec Company, Ulm. Germany). The Raman bands were fitted using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process.

Luminescence spectra were determined at room temperature using a Jobin-Yvon (SPEX) FLUORLOG 3-12 spectrofluorimeter with a 450 W xenon lamp, a double-grating monochromator and a Hamamatsu 928 photomultiplier. Luminescence decay curves were measured utilizing a pulsed excitation delivered by a Continuum Surelite optical parametric oscillator (OPO) pumped with the third harmonic of an Nd:YAG laser. The decays were measured with a Hamamatsu R-955 photomultiplier connected to a Tektronix Model MDO.
4054B-3 digital oscilloscope. For low-temperature measurements, samples were placed in a continuous-flow liquid-helium cryostat equipped with a temperature controller.

3. Results and Discussion

3.1. Chemical Analyses

The results of electron microprobe analyses for genthelvite and willemite crystals are presented in Tables 1 and 2, respectively. The obtained results indicate that studied crystals are chemically homogeneous and show extremely little variation in cation content.

Table 1. Chemical composition (wt.%) of genthelvite Be$_3$Zn$_4$(SiO$_4$)$_3$S.

| Constituent | Sample G1 | Sample G2 |
|-------------|-----------|-----------|
|             | Mean      | S.D.      | Range     | Mean      | S.D.      | Range     |
| n = 12      | n = 12    |           |
| SiO$_2$     | 30.74     | 0.19      | 30.48–31.11 | 30.77     | 0.20      | 30.44–31.12 |
| BeO         | 12.70 *   |           |           | 12.70 *   |           |           |
| MnO         | 1.87      | 1.54      | 0.38–5.16  | 3.36      | 1.78      | 1.39–6.77  |
| ZnO         | 52.22     | 1.81      | 49.27–54.71| 50.77     | 1.87      | 47.56–53.06|
| S           | 5.45      | 0.06      | 5.32–5.54  | 5.45      | 0.01      | 5.43–5.47  |
| $\text{O} = \text{S}$ | −2.72 | −2.72 | |
| Total       | 100.26    |           |           | 100.33    |           |           |

Calculated on the basis of 13 anions (12O + S)

| Si$^{4+}$       | 3.02 | 3.02 |
| Be$^{2+}$       | 3.00 | 3.00 |
| Mn$^{2+}$       | 0.16 | 0.16 |
| Zn$^{2+}$       | 3.79 | 3.79 |
| Sum M           | 3.95 | 3.95 |
| S$^{2-}$        | 1.00 | 1.00 |

Note: * Calculated on the basis of stoichiometry; S.D. = 1σ = standard deviation; n = number of analyses.

Table 2. Chemical composition (wt.%) of willemite Zn$_2$SiO$_4$.

| Constituent | Sample W1 | Sample W2 |
|-------------|-----------|-----------|
|             | Mean      | S.D.      | Range     | Mean      | S.D.      | Range     |
| n = 12      | n = 12    |           |
| SiO$_2$     | 28.37     | 0.37      | 27.68–28.85| 27.80     | 0.12      | 27.53–27.93|
| FeO         | 0.29      | 0.12      | 0.05–0.50  | 0.03      | 0.04      | 0.00–0.12  |
| MgO         | 2.38      | 0.88      | 0.87–3.30  | 0.25      | 0.05      | 0.20–0.30  |
| MnO         | 3.40      | 0.56      | 2.42–4.25  | 6.49      | 0.57      | 4.91–7.10  |
| ZnO         | 65.99     | 1.53      | 64.10–68.31| 65.74     | 0.77      | 64.44–67.46|
| Total       | 100.43    |           |           | 100.31    |           |           |

Calculated on the basis of 4 O

| Si$^{4+}$ | 1.01   | 1.01   |
| Fe$^{2+}$ | 0.01   | <0.01  |
| Mg$^{2+}$ | 0.13   | 0.01   |
| Mn$^{2+}$ | 0.10   | 0.20   |
| Zn$^{2+}$ | 1.74   | 1.77   |
| Sum A     | 1.98   | 1.98   |

Note: S.D. = 1σ = standard deviation; n = number of analyses.

Both studied genthelvite samples are from Mont-Hilaire. The Mn content in these samples is lower than that found by Halenius [22], i.e., 6.27 wt.% but slightly higher than Hassan and Grundy [21] have shown for crystals from the same locality, i.e., 0.95 wt.%. Moreover, no impurities of other elements such as Fe, Al, Mg, or Ca were found in the tested crystals, as it was demonstrated for different samples, also from other localizations [26,27].
For example, the Mn-content up to 7.66 wt.% and 5.61 wt.% was reported in Fe-poor samples by [28] and [29], respectively. Antao and Hassan [28] found in Mt St. Hilaire genthelvite crystal a two-phase intergrowth with Mn-poor phase, up to 0.14 wt.% and Mn-rich phase contain Mn to 2.45 wt.%.

The Mn-content in crystal G1 is higher than in crystal G2. The empirical formulas of these samples can be written as sample G1: Be$_{3.00}$(Zn$_{3.68}$Mn$_{0.28}$)$_{3.96}$Si$_{3.02}$O$_{12}$S, sample G2: Be$_{3.00}$(Zn$_{3.79}$Mn$_{0.16}$)$_{3.95}$Si$_{3.02}$O$_{12}$S.

Both studied willemite samples are from Franklin deposit (Franklin, Sussex County NJ, USA). The chemical composition of the W1 sample is more complex than that of sample W2. Whereas the dominant admixture in sample W2, unlike in sample W1, is Mn. The MnO and FeO contents for willemite from Franklin deposit were determined as 0.12–8.96 wt.% and 0.81 wt.%, respectively [29]. For other localities, MnO content was equal to 0.03–1.22 wt.% [27], while FeO up to 0.15 wt.% [30]. The empirical formulas of studied willemite crystals can be written as: sample W1 (Zn$_{1.74}$Mg$_{0.13}$Mn$_{0.10}$Fe$_{0.01}$)$_{1.98}$Si$_{1.01}$O$_4$ and sample W2: (Zn$_{1.77}$Mn$_{0.20}$Mg$_{0.01}$)$_{1.98}$Si$_{1.01}$O$_4$.

3.2. XRD Diffraction Patterns

The results of X-ray powder diffraction analyses of studied genthelvite and willemite crystals are presented in Tables 3–5.

The unit parameter $a = 8.1090(0)$ Å of genthelvite was determined by Hassan and Grundy [21] for 0.95 wt.% MnO and $a = 8.1493(5)$ Å for 10.79 wt.% FeO and 1.93 wt.% MnO. For two-phase Mn-poor and Mn-rich intergrowth in genthelvite crystal from the same locality, i.e., Mt. St. Hilaire, the $a = 8.119190(7)$ Å and $a = 8.128914(9)$ Å, respectively [28]. The values of the lattice $a$ parameter measured in the current study correspond to its variability with the content of Mn.

Table 3. Crystal data and data collection information for genthelvite and willemite samples.

| Sample | Genthelvite | Willemite |
|--------|-------------|-----------|
|        |             | G1        | G2        | W1        | W2        |
| Space group (No.) | $P4_{3}3n$ | $R3$      |           |           |           |
| $a$ [Å] | 8.12745(3)  | 8.11944(1) | 13.9500(3) | 13.9647(2) |
| $b$ [Å] | 8.12745(3)  | 8.11944(1) | 13.9500(3) | 13.9647(2) |
| $c$ [Å] | 8.12745(3)  | 8.11944(1) | 9.3254(2)  | 9.3359(1)  |
| alpha [°] | 90         | 90        |         |         |
| beta [°] | 90         | 90        | 90      | 90      |
| gamma [°] | 90        | 90        | 120     | 120     |
| V [10$^6$ pm$^3$] | 536.8626   | 535.2769  | 1571.6100 | 1576.6990 |
| V ESD [10$^6$ pm$^3$] | 0.002234   | 0.0008744 | 0.0474664 | 0.0290179 |
| R expected | 3.420      | 2.879     | 7.11093  | 3.92045  |
| R profile | 6.402      | 6.403     | 6.63224  | 5.83627  |
| R weighted profile | 9.701      | 10.074    | 9.08086  | 8.53544  |
| GOF     | 2.837      | 3.498     | 1.270    | 2.177    |

Klaska et al. [23] measured unit cell parameters for hydrothermal synthesized α-Zn$_2$SiO$_4$ to be $a = 13.948(2)$ Å and $c = 9.315(2)$ Å. The unit cell parameters of other synthesized willemite samples are similar: $a = 13.9468(3)$ Å, $c = 9.3177(1)$ Å [25]. For the willemite sample from the Franklin deposit, Simonov et al. [31] have refined its structure and determined $a = 13.971(3)$ Å, $c = 9.334(1)$ Å; however, the content of the impurities was not specified. No other data on the lattice parameters of the willemite mineral have been found in existing literature. For nanocrystalline willemite powder with the highest Mn-content, i.e., Zn$_{1.5}$Mn$_{0.5}$SiO$_4$, the following unit cell parameters were measured: $a = 13.946(5)$ Å, $c = 9.315(2)$ Å [32]. Thus, it can only be concluded that the studied samples W1 and W2 satisfy the relation of increasing the values of parameters $a$ and $c$ with an increase of Mn content. It was also checked if Mn uniformly occupy Zn$_1$ and Zn$_2$ sites. The EPR data [33] and luminescence results [34] showed a clear preference of the Zn$_2$ site over
the Zn\textsubscript{1} site in the most common 2:1 ratio. On the other hand, Kim et al. \cite{15} diffraction data showed that for the synthetic Zn\textsubscript{2}SiO\textsubscript{4} samples Zn\textsubscript{2-x}Mn\textsubscript{x}SiO\textsubscript{4} (0.01 \leq x \leq 0.05), the preference of Zn\textsubscript{2} site over Zn\textsubscript{1} was evaluated to be close to 10, with the best Rietveld refinement and Goodness of Fitting (GOF) parameter equal 2.28.

The samples studied here—willemite W1 and willemite W2—contain much more Mn than was noted in previous publications. The performed calculations for the W1 sample ended with GOF = 1.270 showed that Mn occupies only the Zn\textsubscript{1} site. For the W2 sample, almost equally good fit was obtained for two cases. For the first it was calculated in accordance with Klaska et al. structural model \cite{23}, obtained GOF = 2.18 when Mn occupied only Zn\textsubscript{2} site. For the second, with Hang et al. \cite{35} structural data, obtained GOF = 2.17 when 5% Mn and 1% Mg were presented at Zn\textsubscript{1} site, while 95% of Mn occupied Zn\textsubscript{2} site. The calculations put in Tables 4 and 5 show that there is a preference of the lattice sites in both samples and that this preference is different in them.

### Table 4. Refined structural parameters for W1 sample Zn\textsubscript{1.74}Mg\textsubscript{0.13}Mn\textsubscript{0.10}Fe\textsubscript{0.01}\textsubscript{1.98}Si\textsubscript{1.01}O\textsubscript{4} obtained from the Rietveld refinement using X-ray powder diffraction data at room temperature.

| Atom | Wyck. | s.o.f. | x     | y     | z     | B \times 10^4 (pm\textsuperscript{2}) |
|------|-------|--------|-------|-------|-------|---------------------------------------|
| Zn1  | 18f   | 0.76(5)| 0.017430 | 0.209100 | 0.084650 | 0.511026                             |
| Zn2  | 18f   | 1.000000 | 0.230600 | 0.215030 | 0.418600 | 0.518746                             |
| Si   | 18f   | 1.000000 | 0.211640 | 0.195570 | 0.249400 | 0.218623                             |
| O1   | 18f   | 1.000000 | 0.106000 | 0.216400 | 0.250500 | 0.513483                             |
| O2   | 18f   | 1.000000 | 0.344670 | 0.015530 | 0.084330 | 0.689644                             |
| O3   | 18f   | 1.000000 | 0.209200 | 0.125600 | 0.392600 | 0.496288                             |
| O4   | 18f   | 1.000000 | 0.205600 | 0.128300 | 0.103600 | 0.657360                             |
| Mn1  | 18f   | 0.10(2) | 0.017430 | 0.209100 | 0.084650 | 0.511026                             |
| Mg1  | 18f   | 0.14(5) | 0.017430 | 0.209100 | 0.084650 | 0.511026                             |
| Fe1  | 18f   | 0.02(1) | 0.017430 | 0.209100 | 0.084650 | 0.511026                             |

W.P.—Wyckoff position; s.o.f.—site occupation factor; B—isotropic atomic displacement.

### Table 5. Refined structural parameters for W2 sample Zn\textsubscript{1.77}Mn\textsubscript{0.20}Mg\textsubscript{0.01}\textsubscript{1.98}Si\textsubscript{1.01}O\textsubscript{4} obtained from the Rietveld refinement using X-ray powder diffraction data at room temperature.

| Atom | W.P. | s.o.f. | x     | y     | z     | B \times 10^4 (pm\textsuperscript{2}) |
|------|------|--------|-------|-------|-------|---------------------------------------|
| Zn1  | 18f  | 0.96(9) | 0.017100 | 0.208700 | 0.084400 | 0.000000                             |
| Zn2  | 18f  | 0.91(9) | 0.023400 | 0.213500 | 0.418500 | 0.709822                             |
| Si   | 18f  | 1.000000 | 0.211800 | 0.196300 | 0.249000 | 0.850365                             |
| O1   | 18f  | 1.000000 | 0.208500 | 0.126700 | 0.391800 | 0.769829                             |
| O2   | 18f  | 1.000000 | 0.205900 | 0.129500 | 0.104500 | 0.769829                             |
| O3   | 18f  | 1.000000 | 0.107500 | 0.217500 | 0.249600 | 0.799833                             |
| O4   | 18f  | 1.000000 | 0.345170 | 0.016830 | 0.082630 | 0.990119                             |
| Mn1  | 18f  | 0.004(2) | 0.017100 | 0.208700 | 0.084400 | 0.000000                             |
| Mg1  | 18f  | 0.17(1) | 0.023400 | 0.213500 | 0.418500 | 0.000000                             |
| Mn1  | 18f  | 0.06(3) | 0.017100 | 0.208700 | 0.084400 | 0.000000                             |

W.P.—Wyckoff position; s.o.f.—site occupation factor; B—isotropic atomic displacement.

### 3.3. Raman Spectra

Until now, the Raman spectra of genthelvite have been cited on the rruff.info website (https://rruff.info/genthelvite/display=default/ on 15 September 2021) and this is the only source material. In literature, there is no description or even qualitative characteristics of the spectrum of this mineral. In genthelvite lattice, three types of tetrahedron BeO\textsubscript{4}, ZnO\textsubscript{4}, and SiO\textsubscript{4} form a skeleton connecting by oxygen corners. Genthelvite Be\textsubscript{3}Zn\textsubscript{4}(SiO\textsubscript{4})\textsubscript{2}S belongs to tectosilicate, and it is a member of helvine group Be\textsubscript{3}M\textsubscript{4}(SiO\textsubscript{4})\textsubscript{2}S (M = Fe\textsuperscript{2+}, Mn\textsuperscript{2+} and Zn\textsuperscript{2+}) together with danalite (Be\textsubscript{3}Fe\textsuperscript{2+4}(SiO\textsubscript{4})\textsubscript{2}S) and tugtupite (Na\textsubscript{4}BeAlSi\textsubscript{4}O\textsubscript{12}Cl). Genthelvite can be considered as a member of the sodalite subgroup where Be is playing the role of Al in sodalite Na\textsubscript{4}(Si\textsubscript{3}Al\textsubscript{3})O\textsubscript{12}Cl lattice. In genthelvite structure, the number of formula units per unit cell Z = 2, so then 138 normal modes are predicted to \textit{P}\textsuperscript{43}n space.
The most intense bands in Raman spectra of genthelvite and willemite come from SiO\(_4\) tetrahedra because the Si-O bond is the most covalent one. Both studied minerals have SiO\(_4\) and ZnO\(_2\) tetrahedra, in genthelvite also BeO\(_4\) tetrahedrons, thus, the Raman spectra may show some similarities as well as differences. Therefore, the following qualitative description of Raman spectra of the studied minerals is proposed. The two genthelvite samples G1 and G2 are from the same locality (Mont Saint-Hilaire in Quebec, QC, Canada) and differ in Mn content (Table 1). The Raman spectra of the studied genthelvite are showed in Figure 4. The differences in the number, frequency, and intensity of the bands in both spectra are infinitesimally small, practically negligible. The most intense band at 887 cm\(^{-1}\) is assigned to Si-O stretching \(\upsilon_1\) (A) vibration. The four bands on the higher frequency side (911–1031 cm\(^{-1}\)) can be identified as asymmetric stretching Si-O band \(\upsilon_3\) (F\(_2\)). The bands at 609–635 cm\(^{-1}\) and 418–445 cm\(^{-1}\) could be assigned as Si-O bending \(\upsilon_4\) and \(\upsilon_2\) vibrations, respectively. In turn, the ZnO\(_4\) tetrahedron \(\upsilon_3\) and \(\upsilon_1\) vibration could be recognized at 609–635 cm\(^{-1}\) and 539 cm\(^{-1}\), respectively. The bands at 575 cm\(^{-1}\) and 773 cm\(^{-1}\), which are not present in willemite spectra (Figure 5), could be recognized as symmetric \(\upsilon_1\) and asymmetric \(\upsilon_3\) stretching vibrations related to the BeO\(_4\) tetrahedrons. A very intensive band is visible at 170 cm\(^{-1}\), the lack of which in the willemite spectra and measured for helvine ([https://rruff.info/helvine/display=default/](https://rruff.info/helvine/display=default/ on 15 September 2021)) and danalite ([https://rruff.info/danalite/display=default/](https://rruff.info/danalite/display=default/ on 15 September 2021)) should be attributed to the Be-O vibrations.

The Raman spectroscopic analyses for two willemite samples (sample W1 and W2) from Franklin Mining District, Sussex County, NJ, USA, were performed, and the spectra are showed in Figure 5. Chemically, the samples differentiate in Mn, Mg, and Fe contents (Table 2). The most intense band noted in the spectra and centred at 874 cm\(^{-1}\) is assigned to the symmetric Si-O stretching \(\upsilon_1\) (A) vibration. Three bands in the range 900–950 cm\(^{-1}\), respectively at 903, 911, 951 cm\(^{-1}\) for sample W1 and 904, 910, 949 cm\(^{-1}\) for sample W2, are ascribed to the \(\upsilon_3\) (F\(_2\)) triply degenerate asymmetric stretching vibrations. The symmetric \(\upsilon_2\) (E) and asymmetric \(\upsilon_4\) (F\(_2\)) bending O-Si-O vibrations are observed in ranges 380–400 cm\(^{-1}\) and 470–510 cm\(^{-1}\), respectively. The assignation of the vibrations of (SiO\(_4\))\(^4\)\(^{-}\) groups in willemite samples from Franklin are in good agreement with Handke and Urban [48] for other orthosilicates [49–51]. The presence of a single band at 552 cm\(^{-1}\) (sample W1) and 548 cm\(^{-1}\) (sample W2), as well as bands in the range 600–625 cm\(^{-1}\), is disputable and not completely defined. Based on willemite IR spectroscopy results, we can assume that these bands could be assigned to symmetric stretching \(\upsilon_1\) (~550 cm\(^{-1}\)) and asymmetric stretching \(\upsilon_3\) vibrations of ZnO\(_4\) [43,45,52]. According to Griffith’s work [53], band ~550 cm\(^{-1}\) can also be related to asymmetric bending vibrations, where \(\upsilon_4\) was at 542 cm\(^{-1}\) [53], but in present work, this band is shifted to the higher wavenumbers. In both samples, Zn is replaced by atoms of lower mass with a similar total amount. However, there is more Mg than Mn in sample W1, hence the frequency of \(\upsilon_1\) ZnO\(_4\) is higher (552 cm\(^{-1}\)) than for
sample W2. The W1 sample has more atoms which are lighter than Zn, and shorter Zn-O bond lengths, than sample W2, which resulted in a higher frequency of the $\nu_1$ band than for sample W2, i.e., 552 cm$^{-1}$ and 548 cm$^{-1}$, respectively. The deconvolution of the $\nu_3$ band into its components looks different for the two samples. There are bands at 597 and 623 cm$^{-1}$ for W1 and 602 and 626 cm$^{-1}$ for the W2 sample, which is undoubtedly related to the different lattice sites occupation by Mn in these samples. In the lattice vibrations range, a slight distinction in the number or intensity of the bands can be noticed, which may be related to the differences in the content of impurity elements. The spectrum of willemite W2 in the range of lattice vibrations shows bands with frequencies 217 and 237 cm$^{-1}$, not measured for sample W1. They probably come from Mn(Zn$_2$)-O vibrations.

![Figure 4. Raman spectra of genthelvite samples.](image)

Figure 4. Raman spectra of genthelvite samples.
Figure 5. Raman spectra of willemite samples.

The Raman bands position and their assignment for genthelvite and willemite samples are indicated in Table 6.

The difference in the masses of atoms of the tetrahedrons adjacent to $\text{SiO}_4$ may influence the value of the frequency of Si-O vibrations. In genthelvite, for the $\text{SiO}_4$ tetrahedron, each apex oxygen is also common to the two $\text{BeO}_4$ and $\text{ZnO}_4$ tetrahedrons. While the former neighborhood may cause an increase in the frequency, the latter one decreases it. The reduced masses for the Si-Be, Si-Zn and Si-Si pair are 0.1465 and 0.0509 and 0.0712, respectively. It means that the neighborhood of Be, which increases the frequency, has greater influence. Indeed, vibrations of $\text{SiO}_4$ tetrahedron have higher frequencies for genthelvite ($887 \text{ cm}^{-1}, 418-445 \text{ cm}^{-1}$) than for willemite ($874 \text{ cm}^{-1}, 387-448 \text{ cm}^{-1}$). In addition, in the range below 300 cm$^{-1}$, a greater number of bands were measured for the willemite, usually with a lower relative intensity than for the genthelvite.
Table 6. Raman bands (position and assignment) of studied genthelvite and willemite samples.

| Bands Position (cm$^{-1}$) | Assignation | Bands Position (cm$^{-1}$) | Assignation |
|---------------------------|-------------|---------------------------|-------------|
| Sample G1                 | Sample G2   | Sample W1                 | Sample W2   |
| 1030                      | 1031        | 951                       | 949         |
| 948                       | 949         | 911                       | 910         |
| 926                       | 926         | 903                       | 904         |
| 911                       | 911         |                            |             |
| 887                       | 887         | 874                       | 874         |
|                            |             |                            |             |
| 773                       | 773         |                            |             |
|                            |             |                            |             |
| 636                       | 635         | 623                       | 626         |
| 614                       | 618         | 597                       | 602         |
| 575                       | 575         |                            |             |
|                            |             |                            |             |
| 537                       | 539         | 552                       | 548         |
|                            |             |                            |             |
| 444                       | 445         | 509                       | 488         |
| 427                       | 418         | 486                       | 469         |
|                            |             |                            |             |
| 436                       | -           |                            | unknown     |
|                            |             |                            |             |
| 398                       | 396         |                            |             |
| 384                       | 387         |                            |             |
|                            |             |                            |             |
| 294                       | 298         |                            |             |
| 282                       | 287         |                            |             |
| 304                       | 305         |                            |             |
| 293                       | 293         |                            |             |
| 243                       | 243         | 196                       | 195         |
|                            |             |                            |             |
| 190                       | 191         | 179                       | 177         |
| 137                       | 137         | 165                       | 164         |
| 129                       | 129         | 143                       | 144         |
|                            |             | 112                       | 111         |
| 170                       | 170         |                            | Be-O        |

3.4. Luminescence Spectra

3.4.1. Genthelvite

The emission and excitation spectra of the genthelvite G1 sample have been presented in Figure 6. At room temperature, the emission band was measured at $\lambda = 508$ nm, the full width at half maximum (FWHM) was $844$ cm$^{-1}$. At low temperature ($T = 77$ K), the emission band became narrower, FWHM = $655$ cm$^{-1}$ and asymmetrical from a longer wavelength. It could be related to lattice vibration; however, its maximum was measured at the same position, i.e., $\lambda = 509$ nm. At the same time, no significant shift of the excitation bands was found. The $\nu_3$ band is single also at low temperature (see inset in Figure 6a). It is worth noting that the $\nu_2$ band is wider than the $\nu_3$ band; full width at half maximum (FWHM) is equal to $460$ cm$^{-1}$ and $140$ cm$^{-1}$, respectively. Due to the interactions with phonons, the $\nu_5$, $\nu_4$, and $\nu_2$ bands at $T = 77$ K have a complex shape with a shoulder as a result of coupling with the intense lattice vibrations at $170$ cm$^{-1}$ (Figure 4). The position of the $\nu_1$ band is not precisely measured due to its proximity to the emission band. The
emission and excitation spectra for the genthelvite G2 sample were the same as for the G1 sample. Gorobets and Rogojine [54] measured the Mn$^{2+}$ emission band for genthelvite at 510 nm. The measured lifetimes of luminescence have values expected for spin-forbidden transition $^4T_1(^4G) \rightarrow ^6A_1(^6S)$. Their values equal 2.20 ms and 3.4 ms for samples G1 and G2 increased to 2.63 ms and 4.51 ms as the temperature was decreased (Figure 7). It means that that thermal quenching of the decay time takes place. A brief discussion of the luminescence decay times is included in Section 4.

Figure 6. Luminescence spectra of Mn$^{2+}$ in genthelvite, (a) left—excitation spectrum, right—emission spectrum. Inset: the $\nu_3$ excitation band measured at $T = 77$ K; (b) deconvolution of the $\nu_3$ and $\nu_2$ excitation bands measured at $T = 77$ K.

Figure 7. Luminescence decay curves for genthelvite samples G1 and G2 measured at $T = 300$ K and $T = 77$ K (red and blue line, respectively).
3.4.2. Willemite

Mn-doped Zn$_2$SiO$_4$ green phosphor is of particular interest because of its high luminescence efficiency, high photo-stability (especially under UV excitation), and stability to moisture. The alpha (rhombohedral) and beta (orthorhombic) Zn$_2$SiO$_4$ phases were synthesized by various methods, which often produce nanoparticles or thin films. For example, Bertail et al. [55] showed the maximum of luminescence efficiency and the longest luminescence lifetime 35 ms for the Zn$_{1.6}$Mn$_{0.4}$SiO$_4$ sample. Rivera-Enriquez et al. [56] found that the optimal Mn dopant concentration for the $\alpha$-Zn$_2$SiO$_4$ samples is approximately 3 mol%, and the decay time was determined to be 10.93 ms. The luminescence decay curves have been fitted to the double-exponential decay function. Kretov et al. [57] estimated luminescence lifetime for $\alpha$-willemite with 0.7 Mn moli% to be 22 ms. The emission measurement conducted at $T = 4$ K [34] showed two Zero-Phonon lines (ZPL) of Mn$^{2+}$ emission at 18,673 cm$^{-1}$ (535 nm; 2.32 eV) and 19,675 cm$^{-1}$ (508 nm; 2.44 eV) from Zn$_2$ and Zn$_1$ site. The ratio of the intensity of this second line to the intensity of the higher energy line was 1: 2–2.5 and did not change after heat treatment of the sample. They believed [57] that the emission band measured for $T = 300$ K and $T = 77$ K at 525 nm (19,047 cm$^{-1}$) is the sum of these two components. Since the higher emission energy of Mn$^{2+}$ corresponds to the lower value of $Dq$, i.e., the greater length of the Mn-O bond, i.e., corresponds to the Zn$_2$ site. Moreover, their measurements and calculations have shown that up to 0.7 wt.% of Mn, the occupancy ratio Zn$_2$:Zn$_1$ ~ 2 as was earlier demonstrated by EPR measurement [33].

Mineral willemite fluoresces brilliant, intense green, sometimes yellow-green. On several websites, some photos and data could be seen on, for example, http://www.fluomin.org/uk/fiche.php?id=199 (on 10 September 2021). A single and intense emission band at 525 nm was measured as $^{4}T_i(^{4}G) \rightarrow ^{6}A_i(^{6}S)$ transition. The intensity of this emission is slightly higher for the sample containing more Mn, i.e., for the W2 sample. The emission bands are a bit asymmetric (Figure 8). The distribution of these bands into its components is as follows: for sample W1, first maximum at 528 nm (18,927 cm$^{-1}$) and FWHM = 1166 cm$^{-1}$ and the second at 523 nm (19,120 cm$^{-1}$) and FWHM = 397 cm$^{-1}$. The second band can be recognized as the sum of the electronic transition, i.e., emission at 18,927 cm$^{-1}$ and lattice vibrations at 196 cm$^{-1}$ (see Figure 5). The emission band of sample W2 is more symmetrical. The decomposition of the W2 emission band is as follows: the first component at 523 nm (19,133 cm$^{-1}$) and FWHM = 603 cm$^{-1}$ and the second at 535 nm (18,663 cm$^{-1}$) and FWHM = 1365 cm$^{-1}$. Due to the nature of the fitting of this band, the component lines can be regarded as the sum (18,663 cm$^{-1}$ + 237 cm$^{-1}$) = 18,900 cm$^{-1}$ and the difference (19,133 cm$^{-1}$ − 217 cm$^{-1}$ = 18,916 cm$^{-1}$) the emission band at about 18,900 cm$^{-1}$ (529 nm) with lattice Mn-O vibrations at 217 cm$^{-1}$ and 237 cm$^{-1}$. There is a visible difference in the coupling of the electronic transition with vibrations for both subjects. At the present stage of research, the reasons for this cannot be established. The W1 and W2 samples differ in the amount of Mn and its different incorporations into the willemite structure. However, it is not known whether and how these factors caused the observed differences.

![Figure 8](image-url)  
**Figure 8.** Deconvolution of the Mn$^{2+}$ emission band for W1 and W2 samples.
The energy of Mn\(^{2+}\) transitions measured for natural and synthetic ZnSiO\(_4\) and calculated in the earlier studied was put in Table 7. The excitation spectra of samples W1 and W2, although similar, are not identical. For current researches, the emission and excitation spectra of willemite measured at room and liquid nitrogen temperatures have been presented in Figures 9–12. The \(v_3\), \(v_4\), and \(v_1\) band are not identical, as is clearly visible on the excitation spectrum measured at T = 77 K (Figures 9d and 11a). Splitting of some absorption bands on the absorption spectrum of Mn\(^{2+}\)-bearing willemite has been measured by Halenius [9], as well as on the excitation spectrum of synthetic Zn\(_2\)SiO\(_4\): Mn by Palumbo and Brown [14]. However, the authors give different reasons for this splitting. Palumbo and Brown [14] noticed the splitting not only of \(v_1\), \(v_2\), and \(v_4\) but also of \(v_3\) and \(v_5\) bands, which correspond to transitions independent of \(Dq\). They considered the low site symmetry of the Mn\(^{2+}\) in the willemite structure as the reason for this effect. The willemite W2 and W1 samples are a case of evident splitting the \(4E^4A_1(6G)\) level and with a very high value \(\Delta E = 577\) cm\(^{-1}\) and 598 cm\(^{-1}\), respectively. At T = 300 K, the level \(4E^4A(4G)\) splits into two components, while at T = 77 K it splits into three.

The intense band measured on the excitation spectrum at 279 nm (Figure 9c) is the charge transfer (CT) transition from the ground state \(6A_1(6S)\) of Mn\(^{2+}\) to the conduction band of Zn\(_2\)SiO\(_4\). It is a smaller energy gap value than the theoretically calculated or determined from the absorption edge. Probably in natural crystals, there are levels below...
the Fermi surface and associated with point defects, hence the lower value than 260 nm, i.e., 4.76 eV [58].

Figure 10. Luminescence decay curves for willemite sample W2 measured at T = 300 K and T = 77 K (red and blue line, respectively).

Figure 11. Luminescence spectra of willemite W1 sample: (a) emission and excitation of Mn$^{2+}$ measured at T = 300 K and T = 77 K; (b) deconvolution of $\nu_2$ and $\nu_3$ bands.

Figure 12. Luminescence decay curves for willemite sample W1 measured at T = 300 K and T = 77 K (red and blue line, respectively).
The measured luminescence lifetimes of both W2 and W1 samples are typical for Mn\(^{2+}\) emission (Figures 10 and 12). The lifetimes of sample W2 are shorter than those of sample W1. A proposal to explain the differences in the measured luminescence decay times is provided in Section 4.

### Table 7. The measured and calculated Mn\(^{2+}\)-bands for natural and synthetic willemite.

| Transitions (cm\(^{-1}\)) | Zinc Silicate-Willemite Mineral | Vaida [18] | Curie et al. [12] | Su et al. [20] |
|-----------------------------|-------------------------------|------------|-------------------|---------------|
|                             | Current Study W1 Sample Excitation | Measured | Calculated | Measured | Calculated |
|                             | Palman and Brown [14] | T = 300 K | T = 300 K | T = 77 K | T = 300 K | ε = 0.0 | ε = 0.113 | T = 300 K Equation (1) |
| \(^{4}\)A\(_{1}\)(S\(_{1}\)) → \(^{4}\)T\(_{1}\)(E\(_{g}\)) | 20,570 | 20,570 | 20,462 | 20,794 | 20,109 | 20,109 | 20,041 | 20,540 | 20,563 | 20,367 | 20,465 ± 500 |
|                             | 21,230 | 21,230 | 20,811 | 20,794 | 20,475 | 20,475 | 20,469 | 20,540 | 20,449 | 20,563 | 20,367 | 20,465 ± 500 |
| \(^{4}\)A\(_{1}\)(S\(_{1}\)) → \(^{4}\)T\(_{2}\)(E\(_{g}\)) | 22,700 | 22,700 | 22,820 | 22,771 | 22,573 | 22,573 | 22,411 | 22,834 | 22,981 | 22,420 | 22,395 | 22,648 ± 600 |
| \(^{4}\)A\(_{1}\)(S\(_{1}\)) → \(^{4}\)E\(_{g}\),A\(_{1}\)(E\(_{g}\)) | 23,700 | 23,700 | 23,279 | 23,877 | 23,287 | 23,287 | 23,935 | 23,793 | 23,793 | 23,730 | 23,730 | 23,740 ± 450 |

#### 3.4.3. Is the \(\nu_2\) Band Double?

The luminescence spectra of the willemite W2 sample, measured at \(T = 300\) K and 77 K, were presented in Figure 9, and the positions of its bands are indicated in Table 9. Due to the existence of two non-equivalent lattice sites in the willemite structure, it should be verified whether the measured excitation spectra confirm the Halenius thesis [9], mentioned in Section 1. The excitation spectrum of sample W2 was chosen the first for this discussion as its MnO content is almost the same as for the willemite sample studied by Halenius [9]. The values of the Mn\(^{2+}\) absorption bands measured by him are presented in Tables 7 and 10. It has been shown [9] that the bands from \(\nu_1\), \(\nu_2\), and \(\nu_4\) transitions depending on the strength of the crystal field are not single but double. In particular, two \(\nu_2\) bands, at 22,700 cm\(^{-1}\) and 23,120 cm\(^{-1}\) have been distinguished as corresponding to the different crystal sites with \(Dq = 551\) cm\(^{-1}\) and 586 cm\(^{-1}\), respectively. For this reason, for the W2 willemite sample, it is necessary to decide whether or not the band at 22,770 cm\(^{-1}\) is the sole \(\nu_2\) band or one of the two, the other possible band being the one at 23,133 cm\(^{-1}\).

This assumption was found to be incorrect. The following data support this conclusion: (a) firstly, FWHM of bands at 422 nm (23,710 cm\(^{-1}\)) and 432.5 nm (23,133) are similar (326 cm\(^{-1}\) and 242 cm\(^{-1}\)) but quite different than that band at 439 nm (22,770 cm\(^{-1}\)), i.e., (1600 cm\(^{-1}\)) (see Figure 9b); (b) secondly, when the 23,133 cm\(^{-1}\) band was assumed to be the \(\nu_2\) band from the other crystal site, the calculated \(Dq_2\) value was equal 417 cm\(^{-1}\) (Table 9). Consequently, \(Dq_2/B = 0.68\), so the predicted emission band should have much higher energy and fall on about 472 nm. No emission band for such a short wavelength has been measured for willemite (dashed green line in Figure 13). For the sample W1 the \(\nu_2\) band is not double either. In particular, the additional \(\nu_2\) band for this sample is not the band at 429 nm (23,287 cm\(^{-1}\)). The justification for this is similar to those for sample W2. One only needs to compare the FWHM of the band’s component (Figure 11b) and the estimated value of the emission band from this hypothetical second lattice position. If we assume the 23,287 cm\(^{-1}\) as the \(\nu_2\) band of hypothetical T2 MnO\(_4\) tetrahedron, then \(Dq = 425.6\) cm\(^{-1}\) and \(Dq/B = 0.68\), then the expected emission band should fall on about 474 nm (Table 10). No emission band for such a short wavelength has been measured for this sample. These incorrect emission bands for W2 and W1 samples were marked in Figure 13 as dashed maroon and green lines, respectively. A discussion on the determined \(Dq\) and \(B\) parameters is developed in Section 3.5.2.
3.5. Calculations of $D_q$, Racah B and C Parameters, the Energy of Excited Levels, and Split the $^4E^4A_1(^4G)$ Level

The value of the $D_q$ parameter calculated from the position of band $v_1$ is burdened with a more significant error than those determined from the position of band $v_2$. It should be mentioned that the $^6A_1-^4T_1$ transition is forbidden by the group selection rules, whereas the $^6A_1-^4T_2$ is allowed. Due to this circumstance, the precise experimental determination of the $^4T_1$ level position from the excitation spectrum is rather ambiguous. Moreover, the $v_1$ band is often less visible because it is strongly coupled with lattice vibration; it is very close to Stokes shift associated with the strongest lattice vibration 900 cm$^{-1}$ for genthelvite, 870 cm$^{-1}$, and 850 cm$^{-1}$ for willemite W1 and W2 samples, respectively. For this reason, in present research, the $D_q$ values were determined from the $v_2$ band. A more appropriate Equation (2) was used.

In Figure 13, the $D_q/B$ and $^4T_{1g}(^4G) \rightarrow ^6A_1(S)$ transitions for genthelvite and two willemite samples are shown schematically.

3.5.1. Genthelvite

Using Tanabe–Sugano Formula (1) for data at $T = 300$ K it was calculated that $B = 633$ cm$^{-1}$, $C = 3497$ cm$^{-1}$ and $10Dq = 5305$ cm$^{-1}$ (Table 8). Then nephelauxetic ratio $\beta = B/B_0 = 0.659$ and $Dq/B = 0.796$. From data obtained at $T = 77$ K that $B = 636$ cm$^{-1}$, $C = 3404$ cm$^{-1}$ and $10Dq = 5025$ cm$^{-1}$. Then nephelauxetic ratio $\beta = B/B_0 = 0.662$ and $Dq/B = 0.790$. Halenius [22] reported for genthelvite the following values: $B = 663$ cm$^{-1}$, $C = 3408$ cm$^{-1}$, $10Dq = 5350$ cm$^{-1}$, so $Dq/B = 0.807$. 

![Figure 13](https://example.com/figure13.png)

**Figure 13.** Part of the Tanabe–Sugano diagram; genthelvite G1—yellow lines, willemite W1—maroon line, willemite W2—green lines; solid lines continuous lines for $D_q/B$ cases calculated from Formula (1), dashed line according to the text: yellow line for covalent bond participation, Formulas (4) and (5) from Table 8, green line—for $Dq_2$ in Table 9, wine line—for $Dq_2$ in Table 10.
Table 8. The measured and calculated Mn$^{2+}$-bands genthelvite G1 sample.

| Transitions/Band Position (cm$^{-1}$) | Halenius [22] T = 300 K | Current Study | Calculated |
|--------------------------------------|---------------------------|---------------|------------|
|                                      |                            | Measured      | Calculated |
|                                      |                            | T = 300 K     | T = 77 K   |
| $6^1A_1(6S) \rightarrow 4^2T_1(4G)$ | 20,930                     | 21,520        | ?          |
|                                      |                            |               |            |
| $6^1A_1(6S) \rightarrow 4^2T_2(4G)$ | 22,570                     | 22,750        | 22,530 (22,830 sh) |
|                                      |                            |               |            |
| $6^1A_1(6S) \rightarrow 4^4E, 4^2A_1(4G)$ | 23,670               | 23,817        | $^4A_1$: 23,471 |
|                                      |                            |               | $^4E$: 23,944 |
|                                      |                            |               | 23,104     |
|                                      |                            |               | 23,030     |
| $6^1A_1(6S) \rightarrow 4^2T_1(4D)$ | 26,670                     | 26,819        | 26,854 (26,853 sh) |
|                                      |                            |               |            |
| $6^1A_1(6S) \rightarrow 4^4E(4D)$  | 28,310                     | 28,286        | 31,137     |
|                                      |                            |               | 29,930     |
|                                      |                            |               |            |
| Spectroscopic parameters (cm$^{-1}$) | B = 663                   | B = 633       | B = 633    |
|                                      | C = 3408                   | C = 3404       | C = 3404   |
|                                      | $Dq = 535$                 | $Dq = 503.7$  | $Dq = 503.7$ |
|                                      | $Dq/B = 0.807$             | $Dq/B = 0.796$| $Dq/B = 0.796$ |
|                                      | $\Delta E = 0$            | $\Delta E = 0$| $\Delta E = 473$ |
|                                      | $\beta = 0.66$            | $\epsilon = 0.105$ |
|                                      | $\beta = 0.66$            | $\epsilon = 0.119$ |
|                                      | $N_t^2 = 0.895$           | $N_t^2 = 0.881$ |

The genthelvite case can be used as a reference for willemite minerals studied here. The excitation bands are single, so there is no ambiguity in calculating the $B$, $C$, and $Dq$ parameters. Consequently, $Dq/B$ marked in Figure 13 as a solid yellow line may be a reference for calculated values of other minerals.

For genthelvite samples, no splitting of $^4E, ^4A_1(4G)$ was observed. The probable causes of $^4E, ^4A_1$ level splitting, or rather of its absence, are discussed below.

Firstly, only one site is predicated for Mn$^{2+}$ in genthelvite structure, so there is no reason for the complex nature of the excitation spectrum. Second, the validity of the covalence theory was discussed. According to Equation (5), the calculated energies of $^4E, ^4A_1(4G)$ levels are different from those actually observed. The calculations were made for two cases. In the first $\alpha = 0$, so $B$, $C$, and $Dq$ parameters were taken from experimental data, and the $\epsilon$ parameter was equal to 0.105. In the second, the $\alpha = 65$ cm$^{-1}$ was adopted, at which point $B$, $C$, and $Dq$ had changed. In both cases, the $\Delta E$ parameter was not equal to zero. Let us note that the theoretical value of $^4A_1$ is greater than the value for $^4E$, as expected by Curie et al. [12] only after introducing the Koide–Pryce $\alpha$ correction. Applying only $\epsilon$ parameter does not yield such results (Table 8). The calculated energy values of levels $^4A_1(4G)$ and $^4E(4G, 4D)$ are not close to the experimental data. Additionally, a different $Dq$ value was calculated for the changed values of the $B$ and $C$ parameters. Consequently, the value of $Dq/B = 0.83$ is greater than that calculated from equation 2 (0.796). In that case, an emission band between 508 nm and 525 nm of willemite should be measured. These cases are marked in Figure 13 as yellow lines, solid and dotted, respectively. Therefore, this covalence theory approximation does not give results in sync with the experimental data for genthelvite. For this case, the difference in covalence of the orbitals $t_2$ and $\epsilon$ is not quite the same as was predicated for $LK = 4$ [12]. Perhaps the reason is that the fourth ligand around Mn is sulfur, a ligand weaker than oxygen.
3.5.2. Willemite W2 Case

The calculation values of the spectroscopic parameters B, C, Dq for Mn$^{2+}$ in the studied willemite W2 sample were presented in Table 9. The value of B and C Racah parameters must be computed from $v_3$ and $v_3$ transitions. First, it was checked whether the band at 23,121 cm$^{-1}$ is not a component of $v_2$ transition because in willemite, Mn$^{2+}$ can occupy two non-equivalent lattice sites. The Racah parameter have been calculated for 23,710 cm$^{-1}$ and 27,993 cm$^{-1}$ band, so $B = 612$ cm$^{-1}$, $C = 3512$ cm$^{-1}$. From equation (2) for T1 MnO$_4$ tetrahedron and $v_2 = 22,770$ cm$^{-1}$; it was calculated that $Dq = 512.8$ cm$^{-1}$ and $Dq/B = 0.84$. If we assume that band at 23,133 cm$^{-1}$ is the $v_2$ band of a hypothetical T2 MnO$_4$ tetrahedron, then $Dq = 417$ cm$^{-1}$. Such a value of $Dq$ is not controversial however, for this T2 site and value of $Dq/B = 0.68$, the emission line would have to be much shorter than the measured (525 nm), even shorter than for genthelvite (510 nm). It was estimated (Figure 13) that the emission should be a band at 480 nm, which was not confirmed by measurement. These two $Dq/B$ values were indicated in Figure 13 by a green line, solid and dashed, respectively. For this reason, the band at 23,133 cm$^{-1}$ cannot be considered as band $v_2$ from the other, second lattice site. These calculations were shown earlier in Section 3.4.3.

Previous calculations of B and Dq parameters were performed assuming that $v_3$ line is a single band at 23,710 cm$^{-1}$. However, for room temperature measurements, the $v_3$ band has two components: at 23,710 cm$^{-1}$ and 23,133 cm$^{-1}$. Different ways of the B parameter calculating were considered. The available literature data so far does not provide a solution. Ten two cases were proposed:

1. $E(4A_1) > E(4E)$ and we computed barycenter, so $v_3$ now is equal 23,517 cm$^{-1}$
2. $E(4A_1) < E(4E)$ and we computed barycenter, so $v_3$ now is equal 23,325 cm$^{-1}$

Neither case (1) nor (2) gives results similar to the experimental ones (Table 9). For each of these cases, the $Dq/B$ was too small to correspond to the emission at 525 nm. It can be noticed that it is even smaller than the $Dq/B$ for genthelvite (0.800), which exhibits an emission band at 509 nm. Therefore, the simplest output should be assumed: for Tanabe–Sugano equations (1), the parameter B should be calculated for the highest component value of the $v_3$ band.

For willemite W2 sample splitting of $^4E^4A_1(^4G) \Delta E = 577$ cm$^{-1}$ and 660 cm$^{-1}$ was observed at $T = 300$ K and $T = 77$ K, respectively. The probable causes of $^4E^4A_1(^4G)$ level splitting are discussed below.

The validity of covalence theory was discussed. According to equation (5) and for Koide–Price parameter $a = 0$ cm$^{-1}$, the calculated energies of $^4E^4A_1(^4G)$ and $^4E^4(D)$ are greater than measured; the $^4A_1(^4G)$ lies below $^4E(^4G)$, contrary to covalence theory conclusions. Only $\Delta E$ calculated value is close to the observed. For $a = 65$ cm$^{-1}$, $\epsilon = 0.137$, (I) in Table 9, the calculated energies of $^4E^4A_1(^4G)$ are now lower than measured, as a set of energy levels had now shifted to the opposite direction to the previous calculations. Contrary to covalence theory conclusions, the $^4A_1(^4G)$ lies below $^4E(^4G)$. Unfortunately, $\Delta E$ calculated value is much smaller than the measured one. For $a$ parameter less than 65 cm$^{-1}$, proposed $a = 30$ cm$^{-1}$, $\epsilon = 0.129$ (II) in Table 9, the calculated energies of $^4E^4A_1(^4G)$ are lower than measured; the $^4A_1(^4G)$ lies below $^4E(^4G)$, contrary to covalence theory conclusions. Only $\Delta E$ calculated value is close to the observed. For other often used parameters $a = 185$ cm$^{-1}$, $\epsilon = 0.161$ (III) in Table 9, the calculated energies of $^4E^4A_1(^4G)$ are now lower than for $a = 65$ cm$^{-1}$ and much lower than measured. The $\Delta E$ value looks better than for the previous calculation. However, the real root of the quadratic equation for the $Dq$ value is possible only for $a = 65$ cm$^{-1}$ and $Dq = 728.4$ cm$^{-1}$, $Dq/B = 0.99$. The emission bands should be measured at about 560 nm.

These calculations made according to the covalence theory [12] show a split of the $^4E^4A_1(^4G)$ level, but the calculated values of energy of these levels differ significantly from the experimental data. Therefore, it can be concluded that this theory does not correctly describe the Mn$^{2+}$ energy levels in willemite and does not explain the data obtained from the measurements.
Table 9. The measured and calculated Mn\(^{2+}\)-bands for willemite sample W2.

| Transitions/Bands Position (cm\(^{-1}\)) | Measured | Calculated |
|----------------------------------------|----------|------------|
|                                        | T = 300 K | T = 77 K   | Equations (1) and (2) | Equation (5) | Equations (4) and (5) |
|                                        |          |            | (Case 1) | (Case 2) | \(\alpha = 0\) | \(\epsilon = 0.1025\) | \(\alpha = 65\) |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{T}^{1}(\text{G})\) | 20,704–20,341 | 20,660–20,340 | 20,704–20,341 | 22,770 | 22,770 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{T}^{2}(\text{G})\) | 22,770 | 22,614 | T1: 22,770 | T2: 23,133 | 22,770 | 22,770 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{E},^{4}\text{A}^{1}(\text{G})\) | 23,133 | 23,110 | 23,710 | 23,133 | 23,133 | 23,133 |
| Spectroscopic parameters (cm\(^{-1}\)) | B = 612 | C = 3518 | \(\Delta E = 660\) | B = 639.5 | C = 3424 | \(\Delta E = 577\) |
|                                        | \(D_{q} = 520.5\) | \(D_{q} = 472\) | \(D_{q}/B = 0.85\) | \(D_{q}/B = 0.74\) | \(D_{q}/B = 0.85\) | \(D_{q}/B = 0.62\) |

3.5.3. Willemite W1 Case

The calculation results of the \(B, C, D_{q}\) parameters for Mn\(^{2+}\) in the studied willemite sample are presented in Table 10.

Table 10. The measured and calculated Mn\(^{2+}\)-bands for willemite sample W1.

| Transitions Band Positions (cm\(^{-1}\)) | Halenius et al. [9] | This Work Measured | This Work Calculated |
|----------------------------------------|---------------------|---------------------|---------------------|
|                                        | T = 300 K | T = 77 K | Equations (1) and (2) | Equation (5) | Equations (4) and (5) |
|                                        |          |            | \(\alpha = 0\) | \(\epsilon = 0.103\) | \(\alpha = 65\) |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{T}^{1}(\text{G})\) | T1: 20,370 | T2: 21,230 | 20,462 | 20,462 | 20,794 | 22,771 | T2: 23,287 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{T}^{2}(\text{G})\) | T2: 22,700 | T1: 23,120 | 22,820 | 22,771 | T1: 22,771 | T2: 23,287 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{E},^{4}\text{A}^{1}(\text{G})\) | T1: 23,700 | T2: 23,700 | 23,279 | 23,272 | 23,272 | 23,775 | 23,935 | 4\text{A}^{1}: 23,524 | 4\text{E}: 24,071 | 4\text{A}^{1}: 22,684 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{T}^{1}(\text{D})\) | T2: 26,320 | T1: 27,070 | 26,550 | 26,212 | 26,212 | 26,212 | 26,550 | 26,212 | 26,212 | 26,212 | 26,550 | 26,212 | 26,212 |
| \(^{6}\text{A}^{1}(\text{S}) \rightarrow ^{4}\text{E}(\text{D})\) | T1 and T2: 28,010 | 28,221 | 28,136 | 28,288 | 28,221 | 31,308 | 29,560 |
| Other parameters \(\Delta E\) not identified | \(\Delta E = 598\) | \(\Delta E = 663\) |

| Other parameters \(\Delta E\) not identified | \(\Delta E = 598\) | \(\Delta E = 663\) | \(B = 620.5\) | \(C = 3534\) | \(D_{q1} = 562.8\) | \(D_{q1}/B = 0.91\) | \(D_{q2} = 425.6\) | \(D_{q2}/B = 0.68\) | \(\Delta E = 547\) | \(B = 829.7\) | \(C = 2449\) | \(\Delta E = 62\) |
Using the previous discussion of calculations made for willemite W2, the bands at 28,221 cm\(^{-1}\) and 23,877 cm\(^{-1}\) were adopted for the B and C parameters calculations. Assuming the hypothesis about two Mn\(^{2+}\) lattice sites Halenius [9], two \(v_2\) bands should be selected. For T1 MnO\(_4\) tetrahedron and \(v_2 = 22,771\) cm\(^{-1}\), it was calculated that \(Dq = 562.8\) cm\(^{-1}\), \(Dq/B = 0.91\). If we assume the 23,287 cm\(^{-1}\) as the \(v_2\) band of hypothetical T2 MnO\(_4\) tetrahedron, then \(Dq = 425.6\) cm\(^{-1}\) and \(Dq/B = 0.68\). These cases were marked in Figure 13 as maroon lines, solid and dashed, respectively. Like the W2 case, the emission band should be measured at about 480 nm, which was not confirmed by measurement. For this reason, the band at 23,287 cm\(^{-1}\) cannot be considered as a band \(v_2\) corresponding to the other, second lattice site.

The calculated energy values of levels \(4A_1(4G)\) and \(4E(4G, 4D)\) with the covalent normalizing parameters did not bring results that are in line with the experimental data (just as was the case for the W2 sample). Moreover, similarly to that other sample, the modified values of B and C lead to the lack of a real root in the square equation of \(Dq\). For this reason, we recognize that, as seen before for genthelvite and W2 sample, the correction for covalent bonding does not describe the obtained measurement results well.

It is worth noting that for many \(a\) values (Tables 9 and 10), the energy of the \(4E\) level is greater than \(4A_1\), unlike that shown by Curie et al. [12]. The willemite specimens studied here did not form automorphic crystals, so it was impossible to make polarized spectra that could decide about the energetic order of the \(4E\) and \(4A_1\) levels. The components of the \(v_3\) band on the spectra measured at \(T = 77\) K for both W2 and W1 samples are separated in such a manner that the two higher energy bands lie closer to each other, and they probably belong to the \(4E\) sublevel. The third component, with the lowest energy, is perhaps the \(4A_1\) component. However, the lack of measurements in polarized light does not prove this.

4. Discussion

The probable causes of splitting of the \(4E^4A_1(4G)\) level are discussed below. Data related to this effect were included in Table 11.

| Possible Reason | Number of Non-Equivalent Crystal Sites of Mn\(^{2+}\) | Site Symmetry | \(<\text{MnO}_6>(\text{Å})\) | \(\text{Mean Quadratic Elongation (10}^{-3}\)) | Geometrical Distortion | \(\Delta E\) |
|-----------------|---------------------------------------------------|---------------|------------------|------------------------------------------|-----------------------------|-------|
| Genthelvite     | one                                               | C\(_1\)       | 2.0617           | 763 for O\(_2\)S                      | 2.0671                      | 1.0279 | 50.2929 | 74   |
|                 | two                                               | Zn\(_1\), Zn\(_2\) | C\(_1\)       | 1.9495                                   | 0.21                         | 0.00130 | 1.0050 | 19.8536 | W1: 62 |
|                 |                                                   | C\(_2\)       | 1.9613           | 0.00704                                  | 1.0045                      | 18.0387 | 13.9376 | W2: 39 |

The values in the table are based on the reference willemite data [23].

(1) The Zn (Mn) site’s geometric deformation indicators are higher for genthelvite than for willemite. However, the genthelvite excitation spectrum does not show \(4E^4A_1(4G)\) splitting. This means that the real symmetry of the lattice site does not determine the \(\Delta E\) value. For genthelvite, these geometric indicators have been calculated for O\(_2\)S, not for O\(_3\) coordination. If we take after [21] that a coordination number of Zn is equal to 3,3608 and the effective coordination of Zn in genthelvite is O\(_3\), then these geometric factors will become zero. On the other hand, when the sulphur atom as the fourth ligand is omitted, the Zn-O distance is shorter for genthelvite than for willemite, and by extension, \(Dq\) for genthelvite should be greater than for willemite, which is not actually the case. For willemite, the determined \(\Delta E\) value is higher for the W1 sample than for sample W2. Manganese ions occupy the Zn\(_2\) site in sample W2 and site Zn\(_1\) in sample W1. The geometrical deformation parameters are greater for the Zn\(_2\) site than for Zn\(_1\). This is either the opposite of the expected effect or the absence of a relationship between deformation and cleavage. Sample W2 contains two times more manganese than sample W1. In turn, in
sample W2, only Mn$^{2+}$ impurities were found, and in W1 an admixture of Mg$^{2+}$, exceeding the amount of Mn$^{2+}$ was found. The significant difference of the Mg$^{2+}$ and Mn$^{2+}$ ion radii (0.57 and 0.66 Å, respectively) may cause a greater local deformation around Mn$^{2+}$ in the structure of the W1 sample than for the W2 sample. In short, it can be said that the influence of the geometry of the coordination polyhedron on the value of ∆E is ambiguous.

(2) The calculations presented in Section 3.5 show that the theory of covalent bond participation does not give satisfactory results of the energies of the excited levels Mn$^{2+}$, nor the correct the values of the splitting of the $^4E_A^1(^4G)$ level.

(3) The reason for the splitting may be the low symmetry of the position of Mn$^{2+}$ in the crystal lattice: C$_1$ for willemite and C$_3$ for genthelvite. For spodumene LiAlSi$_2$O$_6$:Mn$^{2+}$ and C$_2$ site symmetry ∆E = 414 cm$^{-1}$ was observed [59]. However, the ∆E value for other minerals (talc, tremolite, poldervaarite, calcite, data in the study) with higher or lower local symmetry does not support this conclusion. However, incidentally, in calcite, where Mn$^{2+}$ occupies a position with C$_3$ symmetry, the ∆E = 325 cm$^{-1}$.

(4) There was a significant difference in the ∆E value for willemite as measured by Palumbo and Brown [14] and equal 147 cm$^{-1}$ and ∆E value about 600 cm$^{-1}$ in the current study. There is some doubt that it was possible to measure by [14], side-by-side, lines differing by 0.4 nm, i.e., 420.4 nm (23,787 cm$^{-1}$) and 420.8 nm (23,764 cm$^{-1}$) since it was stated that the spectroscopic resolution was not better than 0.6 nm (page 1186, ibid.). In this study, no band at about 23,300 cm$^{-1}$ was measured at all. Willemite studied by [14] contained four times less Mn. Despite the great interest in willemite as a photo-optical material, there is little data on the absorption or excitation bands for samples with different Mn content. All the data available so far has been discussed in the current paper.

The differences in the decay times for the G1 and G2 samples may be caused by different Mn content or by the presence of other lattice defects. Sample G2 contains two times less Mn$^{2+}$ than sample G1. For G1, they are located approximately in every second, and for sample G2 in every third unit cell. The difference between the decay time for W1 and W2 samples is caused by the higher Mn-content in sample W2. The measured lifetimes of studied willemite samples are shorter than of genthelvite samples. There are three reasons for this effect. The first is the greater number of manganese atoms in the unit cell of studied W1 and W2 samples. For 36 Zn-atoms of the unit cell, there are 1.8 or 3.6 Mn atoms, respectively. The second reason is the smaller Zn-Zn distance in the willemite (3.112 Å) than in the genthelvite (~4 Å). The third is a lower symmetry of Mn-crystal site in willemite than in genthelvite. In the current study, the longest lifetimes (~3 and ~4 ms) have been measured for sample genthelvite G2. It is the sample with the lowest Mn content. As a similar value of lifetime was measured earlier for spodumene crystals containing up to 100 times less Mn. Despite the great interest in willemite as a photo-optical material, there is little data on the absorption or excitation bands for samples with different Mn content. All the data available so far has been discussed in the current paper.

For almost all synthetic α-Zn$_2$SiO$_4$ with different Mn$^{2+}$ content, it has been shown that this ion occupies both lattice sites, usually preferring the larger Zn$_2$ site. The crystal field splitting parameter ($Dq$), as well as the Racah $B$ parameter for Mn$^{2+}$ derived for willemite samples W1 and W2, are not identical, and the difference in these values is significant. The comparison of the spectroscopic parameters is as follows:

- Sample W1: $B = 620.5$ cm$^{-1}$, $\beta = 0.65$, $C = 3535$ cm$^{-1}$, $Dq = 562.8$ cm$^{-1}$, $Dq/B = 0.91$.
- Sample W2: $B = 612.0$ cm$^{-1}$, $\beta = 0.63$, $C = 3518$ cm$^{-1}$, $Dq = 520.5$ cm$^{-1}$, $Dq/B = 0.85$.

The calculated crystal field parameter $Dq$ is higher for W1 than for sample W2. It can be concluded that the Mn-O distance for the W1 sample is shorter than for sample W2. Based on these spectroscopic data, it was hypothesized that manganese ions occupy site Zn$_1$ in sample W1 and Zn$_2$ in sample W2. The longer the Mn-O bond, the smaller $Dq$ is, and the bond is more covalent, also the Racah $B$ parameter has a smaller value; this is the case for sample W2. Thus, a comparison of the spectroscopic results with Rietveld’s structural data yields an elegant agreement. The energy of the $^4T_1(^4G)$ level from which the emission occurs depends not only on $Dq$ but also on $B$, in terms of Tanabe–Sugano on
Dq/B, and these values are similar for samples W1 and W2. For this reason, no significant differences in the position of the emission band were observed for both samples.

5. Summary and Conclusions

The calculations of the spectroscopic parameters B, C, and Dq, as well as the energy of the excited levels, were made after some preliminary assumptions. There is no absolute certainty that they are correct in all cases.

First, we adopted the values of B and C that are the most commonly used in the literature on mineral spectroscopy. They were B = 960 cm⁻¹ and C = 3325 cm⁻¹ although B = 860 cm⁻¹ is also used.

Second, there is no known method of determining the B parameter other than from the values of bands $\nu_3$ and $\nu_5$. The Mn²⁺ excitation or absorption spectra often show that the $\nu_3$ band is no single but complex. In the current study, the $\nu_3$ band component with the highest energy was selected for the calculation of B and C parameters. This was justified by the best fit of the Dq/B value on the Tanabe–Sugano diagram to the indisputable experimental value, i.e., the position of the emission band. However, the theoretical justification for this assumption is unknown.

Third, the electron Mn²⁺ transitions could couple with the lattice vibrations in a different way, maybe depending on the ion concentration or on the lattice site.

The discussion of the causes of the $^4E^1A_1(4G)$ level split can be summarized as follows:
1. The performed calculations and their discussion led to the conclusion that the explanation of the cause of the $^4E^1A_1$ level split on the basis of the theory of the covalent bond participation does not give a result consistent with the measured data. The Koide–Pryce correction $\alpha$ and Curie et al. [2] formulas do not even produce good qualitative results for studied minerals.
2. The geometric deformation of the coordination polyhedron is not the factor determining the $\Delta E$ value.
3. Local site symmetry seems to be a quite important factor influencing the studied $\Delta E$ parameter. In the structure of willemite, the Mn²⁺ site symmetry is very low, $C_s$ and $C_1$, while in genthelvite relatively high—$C_3$.
4. The presence, and perhaps the number of other point defects, apart from Mn, can be significant for willemite samples. This issue needs to be explored further.
5. The presented measured data, the results of the calculations, and the discussion mean that the $\Delta E$ value should be considered as an important spectroscopic parameter. So far, it is not known with what other parameters of the studied substances it is clearly and unequivocally related to. The greater number of experimental data obtained for samples with a different chemical composition and site symmetry of the manganese ion as well as the deformation of the coordination polyhedron should allow an assessment of the significance of the $\Delta E$ parameter and explain: (a) how to determine its value; and (b) what are the relevant factors at play. Some studies on calcite, talc, tremolite and poldervaartite are in preparation.

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