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Spectroscopic characterization of manganese minerals

**S.Lakshmi Reddy[1], K.Padma Suvarna[2], G. Udayabhaska Reddy[1],
Tamio Endo[4] and R.L.Frost[3]**

1. Dept. of Physics, SVD College, Cuddapah 516 003, India.
2. Dept. of Physics, Jawaharlal Nehru Technologicl University College of
   Engineering, Anantapur, India.
3. Faculty of Engineering, Mie University, TSU, Mie 514 8507, Japan.
4. School of Chemistry, Physics and Mechanical Engineering, Science and
Engineering Faculty, Queensland University of Technology, GPO Box 2434,
Brisbane Queensland 4001, Australia.

Abstract

Manganese minerals ardenite, alleghanyite and leucopoenicite originated from
Madhya Pradesh, India, Nagano prefecture Japan, Sussex Country and Parker
Shaft Franklin, Sussex Country, New Jersey respectively are used in the present
work. In these minerals manganese is the major constituent and iron if present
is in traces only. An EPR study of on all of the above samples confirms the
presence of Mn(II) with g around 2.0. Optical absorption spectrum of the
mineral alleghanyite indicates that Mn(II) is present in two different octahedral
sites and in leucophoenicite Mn(II) is also in octahedral geometry . Ardenite
mineral gives only a few Mn(II) bands. NIR results of the minerals ardenite,
leucophoenicite and alleghanyite are due to hydroxyl and silicate anions which
confirming the formulae of the minerals.

Key words: Alleghanyite, ardenite, leucophoenicite *minerals, Mn(II), EPR, Optical
absorption, near infrared spectral studies.*

1.Introduction

Most of the silicates, oxides or hydroxide minerals contain maily the two
transition metals, Fe and Mn. Manganese minerals are very important constituents in
soils because Mn is an essential element for plant and nutrition. Also these minerals
have a high sorption capacity for many metals [1].

1.1 Alleghanyite

Alleghanyite is silicate mineral of manganese and iron belongs to humite
group. It is pink to reddish brown in colour. The crystal structure of
alleghanyite $[Mn_5(OH)_2(SiO_4)_2]$ mineral from North Carolina is reported . Its
belongs to space group $p2_1/c$ having cell constants a= 8.2747, b= 4.8503, c=
10.7193 A. In the structure, Si occupies tetrahedral site and Mn occupies (three

types of highly distorted) octahedral site. In first the site, Mn is surrounded by five oxygens and one OH and in the second site, Mn is surrounded by four oxygens and two OH groups. In the third site, Mn is surrounded by six oxygens.[2] The compositional analysis of different origin alleghanyites have been reported which reveal that manganese is the major constituent of the mineral and iron is almost zero.

1.2. Ardennite

Ardennite is a rare arsenic manganous variety of gem silicate mineral. In India this mineral is first identified by Nayak [3]. Its formula is $Mn_4(Al,Mg)_6(Si_5O_{18})$ $(As,V)O_4(OH)_6$. It belongs to orthorhombic with space group P_{nmm} having cell constants a = 8.712, b =18.512 and c= 5.8108 A. The chemical analyses of ardennite from Belgium, France and Greece were reported and indicate that MnO is about 20 wt% and iron is almost in traces [4].

1.3. Leucophoenicite

Leucophenicite is a silicate mineral. Leucophoenicite crystals are very rare. Its formula is leucophenicite[$Mn_7 (SiO_4)_4 (OH)_2$][5-7]. Leucophoenicite group of minerals and humite groups minerals are similar in structure. The difference between the structures were studied by Welch et al., [8]. Hydrogen positions in lecophoenicite obtained from Frankilin, Sussesx country was studied [9] confirming that the formula of the mineral contain hydroxyl groups. The crystal structure of leucophoenicite was refined by Moore and Dunn [10,11]. The mineral crystallises in the monoclinic crystal system, space group 2/m with unit cell parameter a = 10.84Å, b = 4.82Å, c = 11.32Å, β= 103.93°. The identification of this mineral has been determined by single crystal XRD and Raman spectroscopy. The compositional analysis of different localities leucophoenicite had been reported [4] and reveal that MnO about 60 wt% and FeO is in traces. The mineral from other sources have all most the same composition. Single crystal XRD, Raman and IR spectral studies on leucophenicite originated from Franklin, New Jersey is reported [12,13].

In this study, the authors made an attempt to determine the structure of these minerals, valence state of manganese and the site symmetry using electron

paramagnetic resonance (EPR), optical absorption and near-infrared spectroscopic techniques. The samples of alleghanyite is obtained from Hamayokokawa mine, Tatund Cho, Nagano prefecture, Japan and leucophenicite is obtained from Parker Shaft Franklin, Sussex Country, New Jersey are used in the present work. Both the minerals are supplied by Mineralogical Research Company, 15840 East Alta Vista Way, San Jose, California 95127, USA. Ardennite is obtained from Kajlidongri mine, Jhabua district, Madhya Pradesh, India and gifted by Prof. Herman Goethal, Belgium are used in the present study.

2.Experimental

EPR spectra of the powdered samples are recorded both at liquid nitrogen and room (RT) on JEOL JES-TE100 ESR spectrometer operating at X-band frequencies (υ = 9.38520 GHz for alleghanyite, 9.38064 GHz for ardenite and 9.4321GHz for leucophoenicite), having a 100 KHz field modulation to obtain a first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g factor calculations. Optical absorption spectra of alleghanyite, ardenite and leucophoenicite minerals are recorded at RT on Carey 5E UV Vis-NIR spectrophotometer in the range 200-1500 nm in mull form.

Band component analysis is undertaken using the Jandel "PEAKFIT" software package which enabled the type of fitting function to be selected and specific parameters to be fixed or varied accordingly. Band fitting is carried out using a Lorentz–Gauss cross product function with a minimum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results are obtained with squared correlations of r^2 greater than 0.9975.

3.Theory

The ground state electronic configuration for Mn(II) is $Ar(3d^5)$. In a cubic crystal field, these five d-electrons are distributed in t_2 and e_g orbitals with three in t_{2g} and two in e_g orbitals. Hence the ground state configuration is $t_2^3e^2$. This

configuration gives rise to the free ion terms ^6S and ^6G and several other quartet and doublet states, of which ^6S is the ground state. In an octahedral crystal field ^4G splits into $^6A_{1g}(G)$, $^4E_g(G)$, $^4T_{2g}(G)$, $^4T_{1g}(G)$. Of these $^6A_{1g}(G)$ lies lowest according to Hund's rule. Thus all the absorption bands of Mn(II) result from the spin forbidden transitions. Therefore, the intensity of transitions is weak. The energy matrices for all the states are given by Tanabe and Sugano.

Under the influence of external magnetic field the ground ^6S of Mn(II) splits into six equally spectral levels with g factor very close to 2.00.

4.Results and Analysis

4.1.EPR Spectra

The EPR spectrum of alleghanyite, ardenite and leucophoenicite powdered samples recorded at room temperature are shown in Fig.1, Fig.2 and Fig.3 respectively. Even at low temperature the structure could not be observed. This is due to very high concentration of manganese present in the minerals. However only a single resonance peak with g = 2.0 could be noticed in all three spectra at room temperature. As the mineral compounds contain a very high percentage of manganese, the hyperfine lines due to Mn(II) could not be resolved. This g value is similar to other manganese containing minerals [14]. Even though iron is present in the samples in traces its EPR signal is not noticed. This is be due to manganese resonant signal may be superimposed on iron signal if any present.

4.2.Optical absorption spectroscopic analysis

The optical absorption spectrum of alleghanyite, ardenite and leucophoenicite are analysed based on reported chemical analysis and EPR studies. The optical absorption spectrum of these minerals were recorded in the mull form in the range of 200−1500 nm. The band component analysis was conveniently divided into two ranges, as shown in Figs. 4(a) &(b) for alleghanyite, Fig.5(a) &(b) for ardenite and Fig.6(a) &(b) for leucophoenicite. Fig. 4(a) presents the band component analysis spectrum of alleghanyite in the range of 200−800 nm, consisting of bands at 224, 278, 410, 515, 555,623 and 688 nm. Fig. 4(b) presents the spectrum in the range of 800−1500 nm, spanning energies at 829, 929, 973,1209,1373,1438 and 1477 nm. These spectral features are similar to Mn(II) when it is present in compounds [14-17]. Fig. 5(a) represents the band component analysis spectrum of ardenite mineral in the range 200-800 nm. It has two charge transfer bands at 225,279 nm and in addition to band

component at 626 and 645 nm. The band at 626 (15975 cm^{-1}) and 645 nm (15500 cm^{-1}). Fig.5(b) presents the spectrum of ardenite in the range of 800-1500 nm showing three groups of energies at 928,1015, 1206,1359,1382,1440 and 1479 nm.

The bands of alleghanyite are conveniently divided into two sets the bands observed at 12060, 16950,19420 cm^{-1} as first set and 14535,18020,24390, 35970 44640 cm^{-1} as second set. These two are belonging to two different sites of Mn(II). The band observed at 12060 cm^{-1} (829 nm) in the first set and 14535 cm^{-1} (688 nm) in second set were assigned to the transition $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, whereas the band at 16050 cm^{-1} (623 nm) and 18020 cm^{-1} (555 nm) were assigned to the transition $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$. The third band ($v_3$) in the first set at 19420 cm^{-1} (515 nm) and 24390 cm^{-1} (410 nm) in the second set were assigned to the $^4A_{1g}(G) \rightarrow {}^4E(G)$ transition. The assignment of each band to a transition is very difficult. So the energy matrices for the d^5 configuration were solved for different values of crystal field splitting parameter Dq, and Racah parameters B and C. The parameters that provided a good fit to the experimental data were $Dq = 975$ cm^{-1}, $B = 625$ cm^{-1}, $C = 2500$ cm^{-1} and $\alpha = 90$ cm^{-1} for set I and $Dq = 900$ cm^{-1}, $B = 680$ cm^{-1}, $C = 2700$ cm^{-1} and $\alpha = 90$ cm^{-1} for set II. The band headed data, their assignments and the calculated values are presented in Table 1.These results are also further supported by X-ray structural analysis given in literature [2].

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zTable 1

Band headed data with assignments for Mn(II) in the alleghanyite

$Dq = 975$ cm^{-1}, $B = 625$ cm^{-1}, $C = 2500$ cm^{-1} and $\alpha = 90$ cm^{-1} site I

$Dq = 900$ cm^{-1}, $B = 680$ cm^{-1}, $C = 2700$ cm^{-1} and $\alpha = 90$ cm^{-1} site II

and

leucophenicite

$Dq = 900$ cm^{-1}, $B = 600$ cm^{-1}, $C = 2500$ cm^{-1} and $\alpha = 90$ cm^{-1}

</div>

Leucophenicite			Alleghanyite						Transitions
Wavelength (nm)	Wavelength (cm^{-1})		Wavelength (nm)		Wavenumber (cm^{-1})				from $^6A_{1g}$
	Observed	Calculated	Site I	Site II	Observed		Calculated		
					Site I	Site II	Site I	SiteII	
813	12300	12528	829	688	12060	14535	12029	14427	$^4T_{1g}(G)$
617 629 698	16210 15900 14325	16331	623	555	16050	18020	16073	18560	$^4T_{2g}(G)$
		20263	515	410	19420	24390	20514	25365	$^4E(G)$, $^4A_{1g}(G)$
333	30030			278		35970		34940	$^4A_{2g}(F)$
280	35710								$^4T_{1g}(F)$
274	36500				-	44640	-	-	$^4T_{2g}(F)$

| 225 | 44440 | | | 224 | | | | | CT |
| 207 | 48310 | | | | | | | | CT |

Fig. 6(a) presents the band component analysis spectrum of leucophenicite in the range of 200−800 nm, consisting of bands at 207, 225, 274,280,333,617,629 and 698 nm. Fig. 6(b) presents the spectrum in the range of 800−1500 nm, spanning energies at 813, 919,953, 1066, 1192, 1216,1387,1435 and 1477 nm. These spectral features are similar to Mn(II) when it is present in other mineral compounds [14-17]

The analysis of the bands for Mn(II) in the spectrum is as follows. The band observed at 12300 cm^{-1} (i.e. 813 nm) was assigned to the transition $^6A_{1g}(S) \rightarrow$ $^4T_{1g}(G)$, whereas the band at 16055 cm^{-1} is the average of 15900 and 16210 cm^{-1} (i.e., 629, 617 nm) and was assigned to the transition $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$. The third band ($\nu_3$) at approximately 24000 cm^{-1} (i.e. 415 nm) was assigned to the $^4A_{1g}(G) \rightarrow {}^4E(G)$ transition, which was not observed in the compound. It is very difficult assign each band to a transition. So the energy matrices for the d^5 configuration were solved for different values of crystal field splitting parameter *Dq*, and Racah parameters *B* and *C*. The parameters that provided a good fit to the experimental data were *Dq* = 900 cm^{-1}, *B* = 600 cm^{-1}, *C* = 2500 cm^{-1} and α = 90 cm^{-1}. The band headed data, their assignments and the calculated values are also presented in Table 1.

4.3. NIR spectroscopic analysis

The two bands observed at 10775 (928 nm) and 9850 cm^{-1} (1015 nm) in ardenite [shown in Fig. 5(b)] and 10765 cm^{-1} (929 nm) and 10260 cm^{-1} (973 nm) in alleghanyite [shown in Fig. 4 (b)] were broad and intense and they were assigned to the two band components of the same transition, $^5T_{2g} \rightarrow {}^5E_g$, of Fe^{2+} in the mineral. The average of these bands, i.e. 10313 cm^{-1} (i.e. 969 nm), in ardenite and 10512 cm^{-1} (951 nm) in alleghanyite was taken as 10Dq. The splitting of the 10Dq band resulted from the Jahn-Teller effect in the excited ^5E_g state because the splitting value was an intermediate value between 100 and 2000 cm^{-1} [18,19]. This band might be due to the presence of trace amounts of iron present in the minerals.

Water has C_{2V} symmetry and has three fundamental vibrational modes. These modes are ν_1, ν_2 and ν_3, which represent the symmetric OH stretch, the antisymmetric OH stretch and the H-O-H bending, respectively. In the vapor phase, ν_1, ν_2 and ν_3

occur at 3652, 1595 and 3756 cm^{-1}, respectively [20]. In liquid phase, these vibrational modes are shifted to 3219, 1645 and 3445 cm^{-1}, and in solid phase, they are shifted to 3200, 1640 and 3400 cm^{-1}. The shifts of ν_1 and ν_3 modes towards lower frequencies and the shift of ν_2 mode towards higher frequencies are characteristic of hydrogen bonding [21]. The very sharp band observed at 8290 cm^{-1} (1206 nm) in ardenite and a band at 8270 cm^{-1}(1209 nm) in allegyanite were assigned to the combination of $\nu_1 + \nu_2 + \nu_3$ (3200+1640+3400 = 8240 cm^{-1}) of water molecule. The moderate sharp intensity band observed at 7360 cm^{-1} (1359 nm) with a component at 7235 cm^{-1} (1382 nm) in ardenite and similar band at 7280 cm^{-1} (1373 nm) in alleghanyite are due to first overtone of $2\nu_{OH}$. The OH stretching mode gives rise to the most common features in near-infrared region. Hydroxyl exists as part of the structure and the stretching mode appears whenever water is present in any form. The υ_{OH} overtone ($2\upsilon_{OH}$) gave rise to a band in the NIR spectrum [21]. Accordingly the very sharp band with high intensity at 6940 cm^{-1} (i.e.1440 nm) and the component band at 6760 cm^{-1} (i.e. 1479 nm) in ardenite and similar bands at 6950 cm^{-1} (i.e.1438 nm) and the component band at 6770 cm^{-1} (i.e. 1477 nm) in were assigned to the first overtone of OH.

NIR spectrum of leucophenicite is shown in Fig. 6(b). The two bands observed at 10890 and 9380 cm^{-1} (i.e. 919 and 1066 nm) were broad and intense and they were assigned to the two band components of the same transition, $^5T_{2g} \rightarrow {}^5E_g$, of divalent iron in the mineral. The average of these bands, i.e. 10135 cm^{-1} (i.e. 985 nm), was taken as 10Dq. Accordingly, the Dq value was 1014 cm^{-1}. The splitting of the 10Dq band (10890 – 9380 = 1510 cm^{-1}) resulted from the dynamic Jahn-Teller effect in the excited ^5E_g state because the splitting value was an intermediate value between 100 and 2000 cm^{-1} [18,19]. This band was a result of an impurity in the mineral during its formation in the earth crust.

The very sharp band observed at 8390 $cm^{-1}$with a component at 8220 cm^{-1} is assigned to the combination of $\nu_1 + \nu_2 + \nu_3$ (3200+1640+3400 = 8240 cm^{-1}) of water molecule. The moderate sharp intensity band observed at 7210 cm^{-1} (i.e 1387 nm) is due to first overtone of $2\nu_{OH}$.

The OH stretching mode gives rise to the most common features in near-infrared region. Hydroxyl exists as part of the structure and the stretching mode appears

whenever water is present in any form. The υ_{OH} overtone ($2\upsilon_{OH}$) gives rise to a band in the NIR spectrum [18]. Accordingly the sharp band with moderate intensity centered at 6965 cm^{-1} (i.e.1435 nm) and the component band at 6770 cm^{-1} (i.e. 1477 nm) are assigned to the first overtone of OH.

5. Conclusions

1. The compositional analysis indicate that MnO is two thirds of its constituents in leucophenicite and one fifth of its constituents both in ardennite and alleghanyite. FeO is almost zero in all the three minerals.

2. EPR spectra of all the minerals are similar and reveal the presence of Mn(II) showing no hyperfine splitting with almost same g value and confirming that manganese is in very high concentration.

3. Optical absorption spectrum of alleghanyite and leucophenicite is due to Mn(II) and is in octahedral environment. In these minerals Fe(II) is noticed in traces.

4. NIR results of all the three minerals are due to water fundamentals and confirming the composition of the minerals

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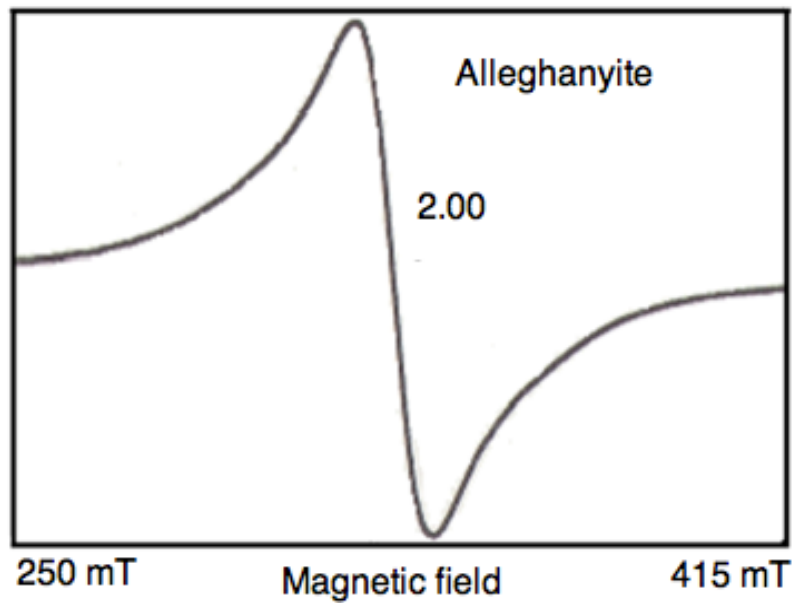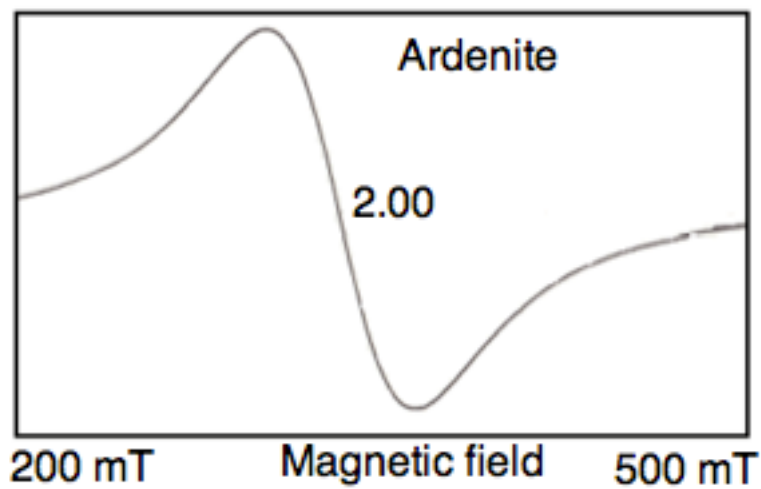Fig. 1 EPR spectrum of alleghanyite at room temperature
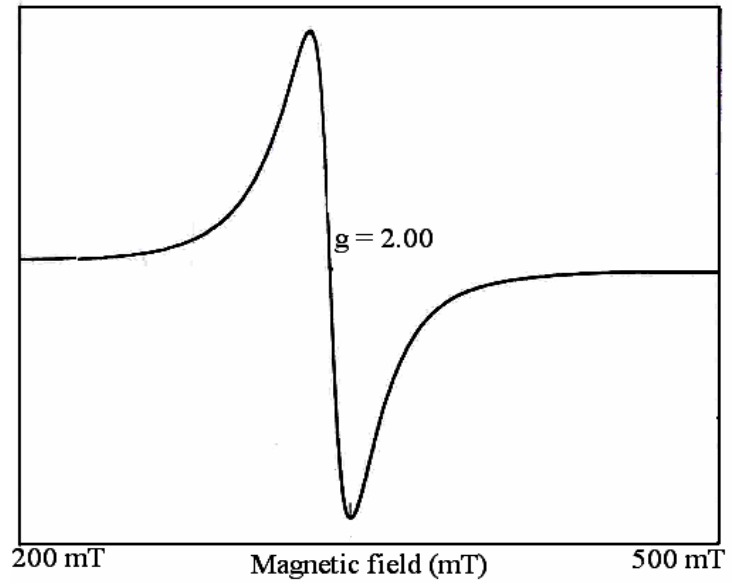
Fig.2. Room temperature EPR spectrum of ardenite

g = 2.00

200 mT   Magnetic field (mT)   500 mT

Fig.3 EPR spectrum of leucophoenicite mineral at RT.
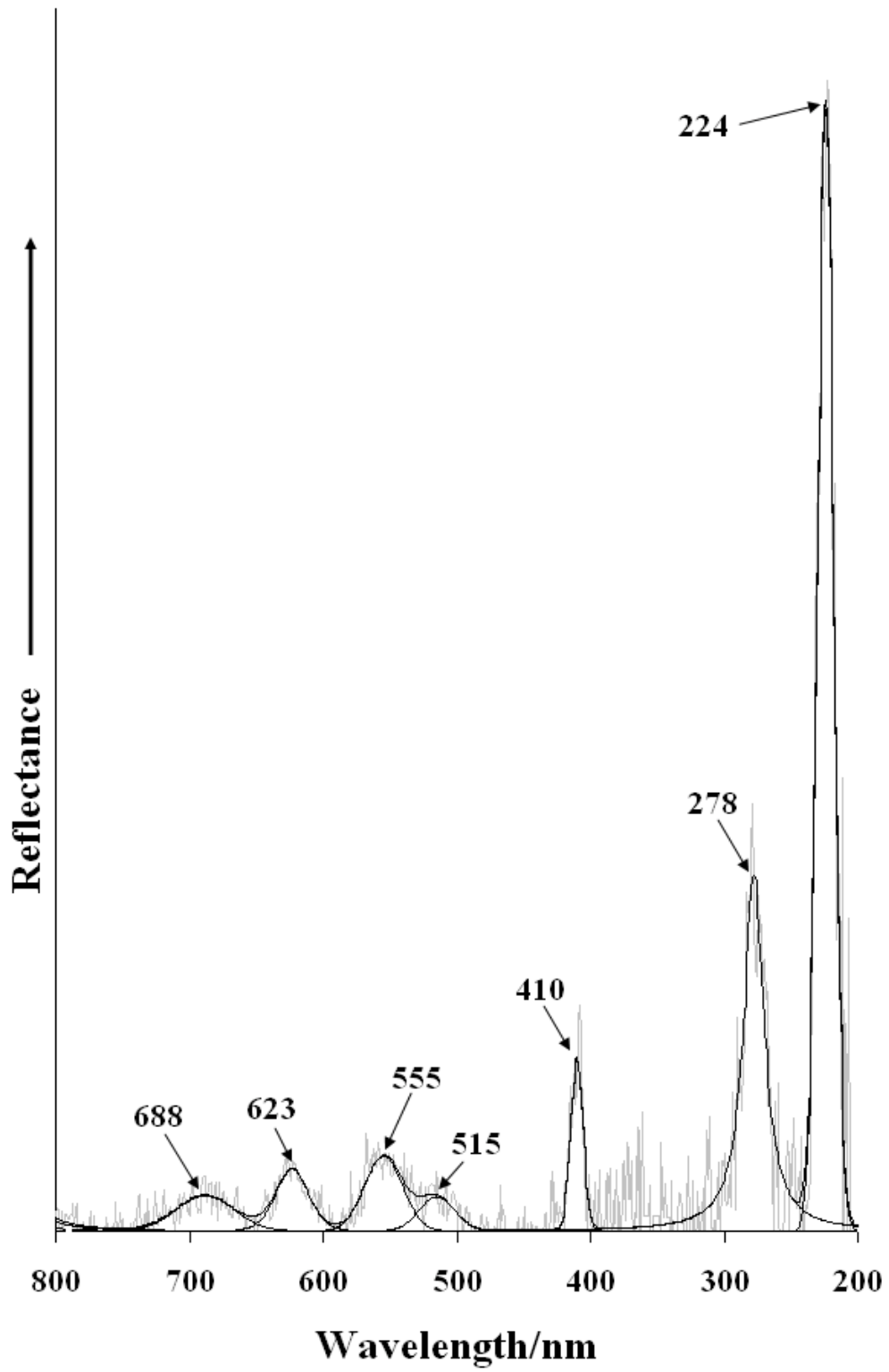
Fig.4(a) optical absorption spectrum of alleghanyite from 200-800 nm.
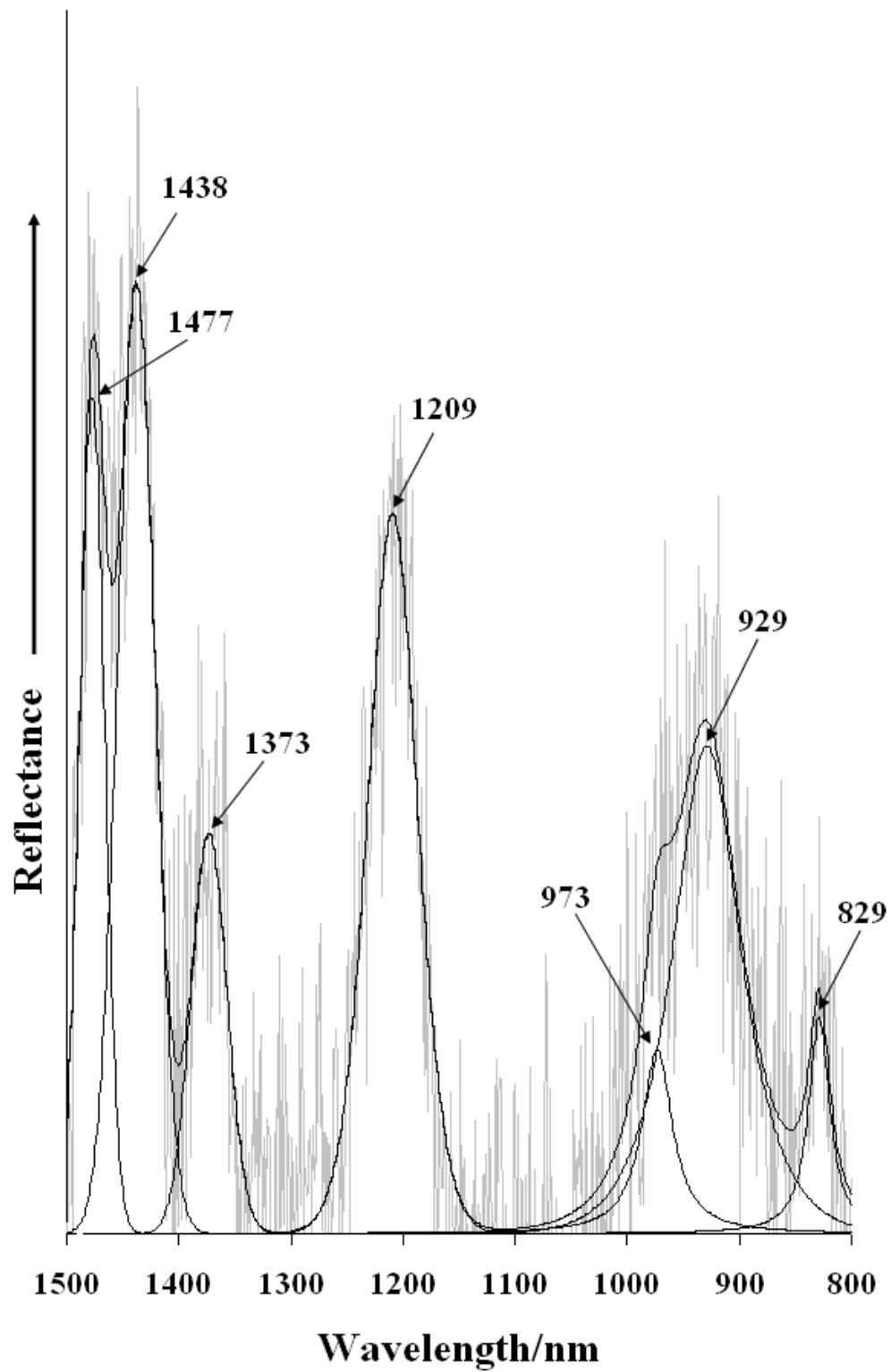
Fig. 4(b) Optical absorption spectrum of alleghanyite from 800- 1500 nm.
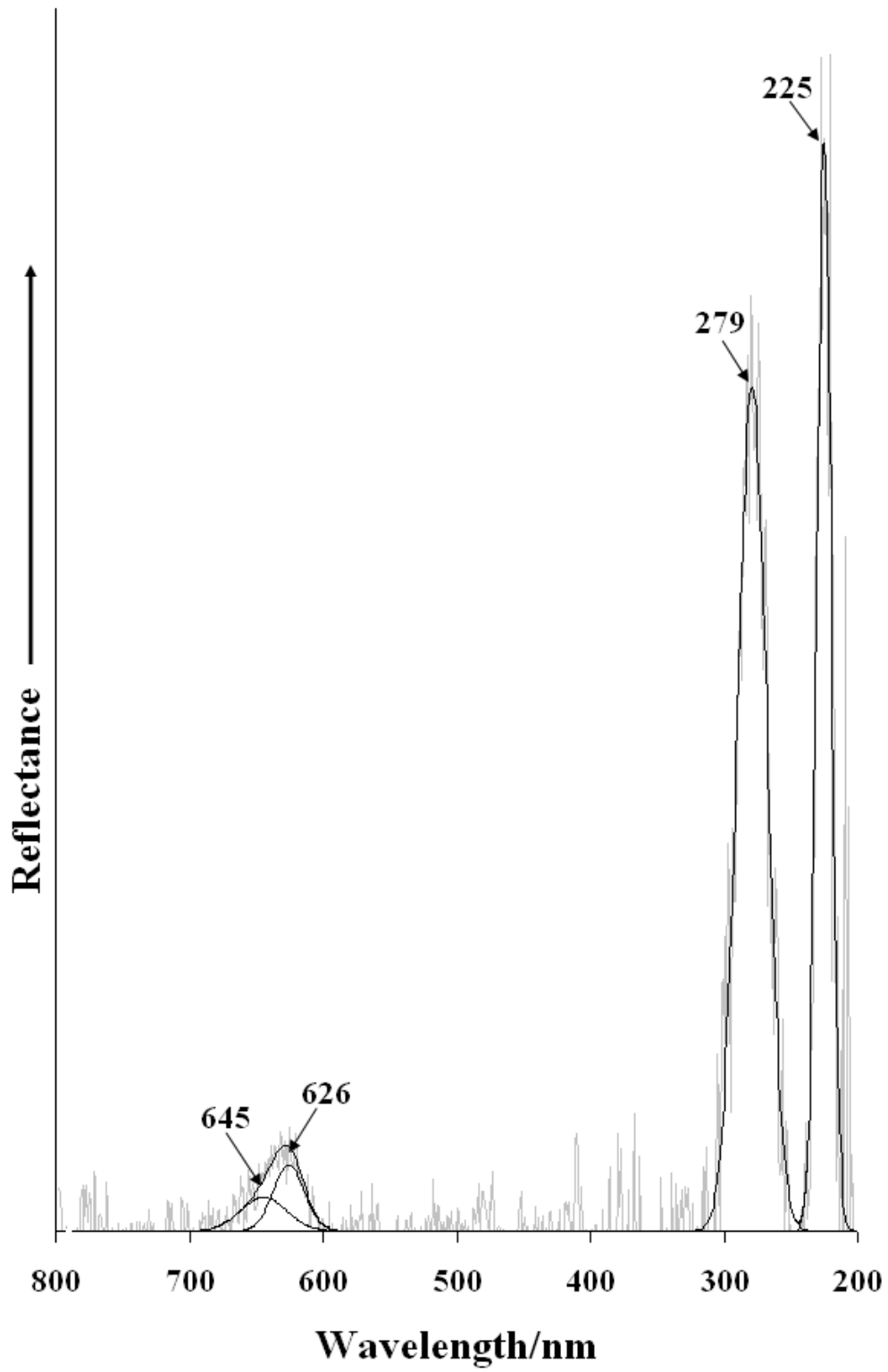
Fig. 5(a). Optical absorption spectrum of ardennite from 200-800 nm
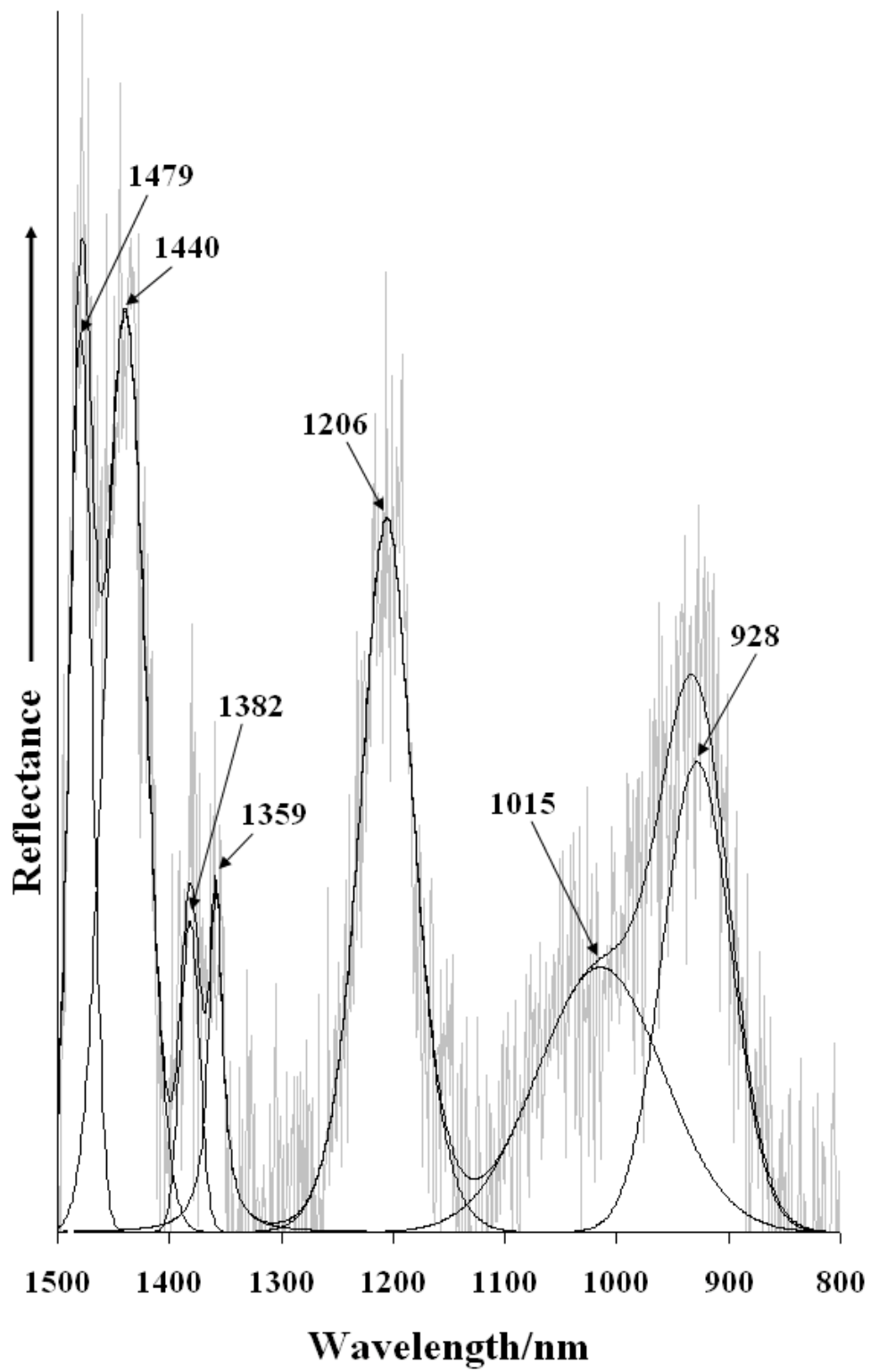
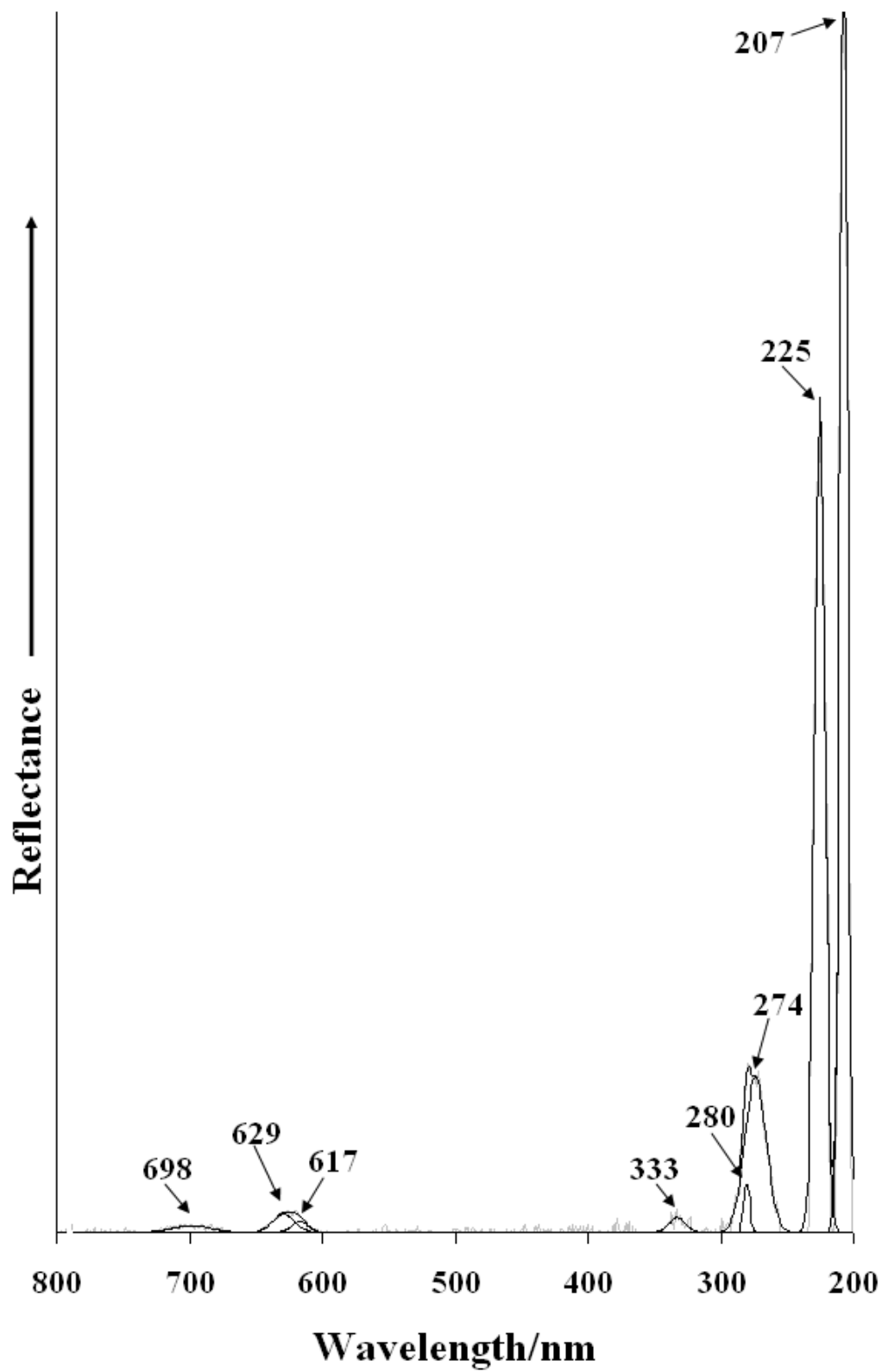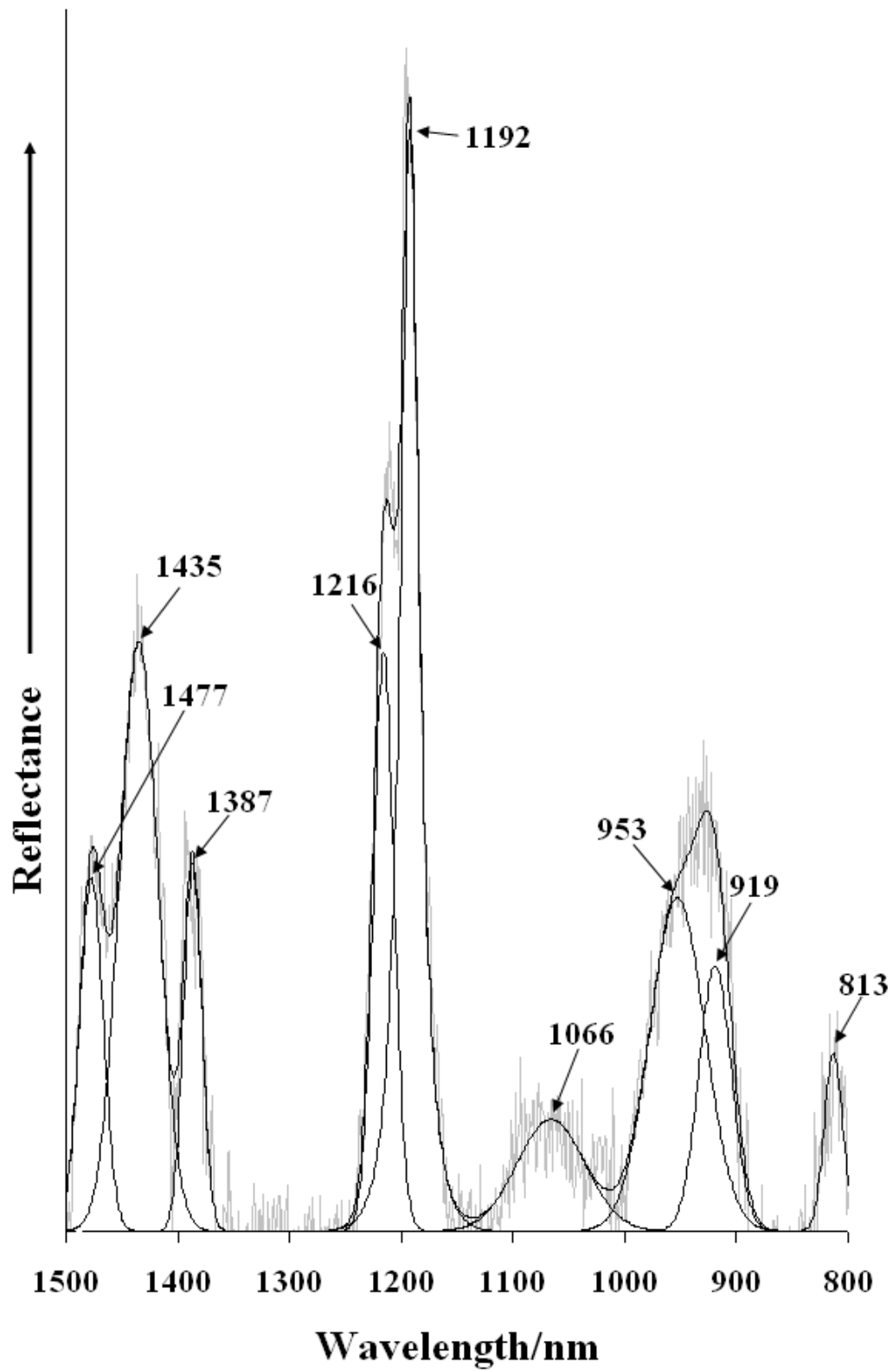Fig. 5(b) optical absorption spectrum of ardennite from 800-1500 nm.

Fig. 6(a) Optical absorption spectrum of leucophoenicite from 200 to 800 nm.

Fig.6(b) Optical absorption spectrum of leucophoenicite from 800 to 1500 nm.

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Table-1
Band headed data with assignments for Mn(II) in the

alleghanyite

$Dq = 975$ cm^{-1}, $B = 625$ cm^{-1}, $C = 2500$ cm^{-1} and $\alpha = 90$ cm^{-1} site I
$Dq = 900$ cm^{-1}, $B = 680$ cm^{-1}, $C = 2700$ cm^{-1} and $\alpha = 90$ cm^{-1} site II

and

leucophenicite

$Dq = 900$ cm^{-1}, $B = 600$ cm^{-1}, $C = 2500$ cm^{-1} and $\alpha = 90$ cm^{-1}