Ferromanganese oxide ores of western Koira Valley, Orissa, India: An infrared spectroscopy study

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Abstract

Ferromanganese oxide ores collected from three captive mines, viz., Koira, Kusumdih, Dengura, located in the western part of the Koira Valley, Sundargarh district, Orissa (India) have been investigated for their infrared absorption. Mineralogical assignment of the ore samples was made by infrared spectroscopic studies vis-a-vis XRD — microscopic interpretations. The common feature in all the IR Spectra is the presence of three major absorption bands in wave number regions of 1120-800, 710-410 and 350-250 cm\(^{-1}\). The ores in general, exhibit three broad spectral patterns which when correlated with their respective composition are found to represent three categories of samples corresponding to high, medium and low grade types. The effect of temperature (calcination) on the characteristics of IR absorption spectra has also been discussed. The IR results have been of value in characterising the manganese ores of the Koira region in general.

Introduction

Infrared spectroscopy (IR) is an important physical method used extensively to identify and study the structure of various terrestrial minerals. IR spectroscopy often gives better information than X-ray diffraction because of its sensitivity to amorphous minerals and the mineral assemblages with both high and low concentration ranges.

IR spectra of various crystalline modifications of MnO\(_2\) was first studied by Glemser et al. (1961). White and Roy (1964) used IR spectra in correlating the metal oxygen bond lengths in oxides with their corresponding absorption frequencies. Kolta et al. (1971) also studied the IR spectra and characterised different manganese oxide samples with the help of ratio of two strong bands at 585 and 530 cm\(^{-1}\). Potter and Rossman (1979) compiled the IR spectra of naturally occurring tetravalent and trivalent manganese oxides in both ordered and disordered forms and compared the results with synthetic manganese oxides. Parida (1981) has characterised IR spectra of synthetic MnO\(_2\) of various crystalline modifications. Frenzel (1980) and Ostwald (1988) have made noteworthy contributions on IR characteristics of manganese ore minerals. Hawker and Thompson (1988) used IR technique as one of the identification methods in the
study of manganese-iron enriched residue from Graskop region of South Africa. Limited attempts have also been made (Elderfield and Glasby, 1973; Perseil and Jehanno, 1981) in the past to use IR spectroscopy for investigating marine ferro-manganese nodules. IR characteristics of various calcined products of nodule sample have been recorded by Mohapatra et al. (1989). Most of the earlier workers have, however, published infrared spectra of either synthetically prepared or naturally occurring pure manganese oxide minerals. The present authors have studied the IR spectra of unequivocally complex ‘ferromanganese oxide ores’ from western Koir Valley of Orissa. The ores of this region, forming a part of Iron Ore Group of rocks of Precambrian age, occur as lentiformal bodies and are surfacially lateritised.

This paper elucidates the IR spectra of seventeen ferro-manganese ore samples of Koir Valley region. The absorption peaks of these spectral bands are compared either with the published values or with the results obtained by exposing mineralogically known ore sample with a view to examining if the spectra are sensitive to differences in manganese ore mineralogy. Since IR spectroscopy is not a primary structural technique, it was necessary to corroborate the mineralogic findings obtained by X-ray diffraction and optical microscopic methods.

**Materials and methods**

Selective ore samples were collected from three quarries, namely, Dengura (D), Kusumdih (KU) and Koir (KO) located in the western part of Koir Valley (Table-1), Sundargarh district, Orissa (India) for this investigation. All the samples were adequately ground to avoid any possible variation due to difference in particle shape and size (Rendon et al., 1981; Farmer, 1974) and then subjected to XRD, IR and partial chemical analysis.

The XRD study was carried out by means of an automatic Phillips Diffractometer (PW-1400) using CuKα radiation, divergence slit and graphite monochromator operated at 40 kV and 20 mA. The characteristic reflection peaks (‘d’-values) were matched with the JCPDS data file (1980) and different minerals were identified.

The IR spectra of all the samples were taken using KBr pellet technique by means of Pye-unicam IR Spectrometer at the rate of 7 min. scanning speed. All the spectra were taken in the region of 4000-200 cm⁻¹. Some differential spectra were also obtained after calcining one ore sample (KU/10) at different elevated temperatures. In addition to this, one iron ore sample from the adjacent Barsua Iron Mine (B/1) was also exposed. The samples B/1, KO/3, constituting single (as determined by XRD) mineral phase of iron and manganese respectively were used as reference in addition to the standard results available in the literature. The magnitude of the spectral peaks in the unknown then yields by comparing the approximate percentage of the minerals in the known. The chemical analysis of iron, manganese and alumina was taken up by routine

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<th>Sample Code</th>
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Titration method, silica by gravimetric method and the results are given in Table-1.

Results and interpretation

Mineralogy of ferromanganese ores was brought out by combined studies of optical microscopy and X-ray diffraction techniques. The mineral species of all the samples are given in Table-1. The detailed mineralogy of individual deposits was reported by the authors elsewhere (Mohapatra et al., 1989).

Optical Microscopy

Cryptomelane, pyrolusite, lithiophorite form the chief manganese minerals though occasionally romanechite, manganite and braunite are recognised. Iron is mostly present in three oxyhydroxide phases: hematite, goethite and lepidocrocite. Limonite, another complex hydrous phase of iron is ubiquitously noticed in Dengura samples. Kaolinite and quartz are the silicate minerals noted in these ore types.

Fabrics of different minerals observed indicate colloform, replacement, banded, open-space filling, brecciated and intergrowth textures. More than one generation of cryptomelane, pyrolusite and goethite are recognised. Braunite probably represents the
part of primary mineralogy. Pyrolusite occurring as irregular patches and finely felted ice-flower within cryptomelane is of supergene nature. In the depositional sequence lithiophorite and limonite are the last minerals to have formed during lateritisation process.

**X-ray Diffraction**

X-ray powder diffraction obtained for different samples are illustrated in Figs. 1b, 2b and 3b. Different manganese minerals identified through this technique are pyrolusite

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**FIG. 1.** IR spectra (a) and X-ray diffraction pattern (b) of high grade (A-type) manganese ore samples (P-Pyrolusite, C-Cryptomelane, G-Goethite, Q-Quartz, L-Lithiophorite).

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**FIG. 3.** IR spectra (a) and X-ray diffraction pattern (b) of low grade (C-type) manganese ore samples (H-Hematite, M-Magnetite, G-Goethite, K-Kaolinite, L-Lithiophorite, C-Cryptomelane, Q-Quartz).
(3.10Å), cryptomelane (3.39Å) and lithiophorite (4.75Å). The iron minerals generally include goethite (4.19Å) and hematite (2.69Å) with doubtful presence of magnetite (KU/1 and KU/2). Silicate minerals recorded are quartz (3.33Å) and Kaolinite (7.20Å).

It can thus be summarised that mineralogically the Koirala samples are pyrolusite rich, Dengura ores are hematite rich whilst Kusumdh hill comprise mixed phases of cryptomelane and hematite with minor pyrolusite. Eventually the mineralogy broadly divides the ferro-manganese ores of western Koirala Valley into three domains i.e., manganese rich, iron rich and intermediate between these two. With this background information, all the samples were exposed under IR spectrometer.

**IR Spectra**

Due to poor spectral resolution at high frequency region, usually caused by OH stretching vibration, the area offers little promise for identifying minerals. Hence, lattice bands between 1400-250 cm⁻¹ corresponding to OH bending and metal-oxygen
stretching are discussed in greater detail. Nevertheless, the 4000-1400 cm\(^{-1}\) region is often diagnostic due to its association with the hydrous components of the oxides. Peaks around 3400 cm\(^{-1}\) and at 3600 cm\(^{-1}\) are attributable to pyrolusite and cryptomelane respectively (Ostwald, 1986). Absence of romanechite and ramsdellite in Koira Valley samples is indicated since their characteristic OH peaks around 1700 and 3580 cm\(^{-1}\) (Potter and Rossman, 1979) do not appear in any of the spectra. The occurrence of goethite in some samples is supported from the weak but sharp peaks around 3150 cm\(^{-1}\) (Cambier, 1986). Lewis and Farmer (1986) assigned peaks at 3620 cm\(^{-1}\) and near 3525 cm\(^{-1}\) to lepidocrocite. Present authors noticed these peaks only in two samples (KO/8 and D/1), though microscopically lepidocrocite is also recognisable in many others (Table-1). However, obtaining spectra by TIBr technique could have provided better resolution in this region.

The spectra in 1400-200 cm\(^{-1}\) region generally show strong absorption in three areas: (a) 1120-800 cm\(^{-1}\), (b) 710-410 cm\(^{-1}\), and (c) 350-250 cm\(^{-1}\). The IR spectra of all the samples are illustrated in Figs. 1a-3a.

(a) 1120-800 cm\(^{-1}\): Out of 17 samples examined, two each from Dengura (D/1 and D/2) and Kusumdih (KU/1 and KU/2) quarries and one from Koira quarry (KO/8) exhibit strong and sharp absorption in the region of 1120-800 cm\(^{-1}\). This band is usually resolved into five absorption peaks at 1100±10 (band 1), 1030±10 (band 2), 1005±10 (band 3), 910±10 (band 4) and 800±10 (band 5) cm\(^{-1}\) with varied intensities. These bands, moderate to strong and mostly sharp, are characteristic of O-H bending vibrations and assigned to hydroxide minerals like goethite, lepidocrocite and limonite, etc. The bands match well when compared with the IR bands of B/1 — a naturally occurring iron ore sample (Fe-62%) of Barsua mines (adjacent to Koira Valley). The disappearance of these bands at elevated temperature (Fig. 4) confirms them to be hydroxide minerals.

White and Roy (1964) distinguished goethite and lepidocrocite from their diagnostic OH bending peaks at 882 and 1013 cm\(^{-1}\) respectively. In the present case, peaks around 910±10 cm\(^{-1}\) and 1005±10 cm\(^{-1}\) could probably be attributed to goethite and lepidocrocite respectively. Further, the lattice band at 792 cm\(^{-1}\) corresponding to OH bending of goethite (Cambier, 1986) in present sample appears at 800±10 cm\(^{-1}\) in very low magnitude. Some specific peaks around 1100±10\(^{-1}\) can be ascribed to limonite (Van der Marel and Beutelspacher, 1976). The 1030±10 cm\(^{-1}\) peak (band 2) could be due to fine grained Kaolinite inclusions (Ostwald 1988).

The presence of all the bands (1-5) in higher intensity in the set of samples illustrated in Fig. 3a eventually reveals a good proportion of iron hydroxide minerals in them. Further, if the magnitude of these bands between different spectra are compared, it is
observed that D/1 and KU/1 contain higher concentration of iron hydroxides than those of D/2, KO/8 and KU/2. Lack of X-ray reflection lines diagnostic of iron hydroxide minerals in these samples (Fig. 3b) very likely indicate their occurrence in more or less amorphous state. A significant difference in spectra of this region between this set of samples with respect to other two sets (Figs. 1a and 2a) is observed. Scarcely presence or complete absence of hydrous iron minerals is evident in latter two sets where these peaks are either absent (KU/4, KO/3, KU/7) or partly present in weak dimension.

(b) 710-410 cm\(^{-1}\): In this wave number region, the spectra of all the samples show strong absorption. This absorption band can be further split into six components at 700 ± 10 (band 6), 590 ± 10 (band 7), 560 (band 8), 540 ± 10 (band 9), 470 ± 15 (band 10) and 415 ± 5 cm\(^{-1}\) (band 11) out of which, the band 6 mostly appears as a shoulder. The absorption band of this region is characteristic of metal-oxygen stretching.
White and Roy (1964) described pyrolusite with the rutile structure to have a single broad band at 606 cm$^{-1}$. Parida (1986) recorded a strong peak at 615 cm$^{-1}$ along with four other bands at 725, 530, 400 and 340 cm$^{-1}$ and assigned these to be characteristic of synthetically prepared $\beta$-MnO$_2$. Potter and Rossman (1979) reported four spectra at 620, 530, 400 and 330 cm$^{-1}$ to be diagnostic of pyrolusite and indicated that the last two spectra uniquely and clearly distinguish this mineral from other manganese oxides. Groote Eylandt pyrolusite typically shows a sharp peak at 549 cm$^{-1}$ and smaller peaks centered about 390 cm$^{-1}$ (Ostwald, 1988). In the present investigation, however, a strong broad band 560 cm$^{-1}$ (band 8) with a satellite peak centered about 420 cm$^{-1}$ (band 11) is attributed to pyrolusite. Since the weak intensity band at 330 cm$^{-1}$ appears for both managanese and iron oxide phases, the same cannot be unequivocally used to distinguish pyrolusite from other oxide as mentioned by Potter and Rossman (1979). The two peaks diagnostic of pyrolusite appearing in sample KO/3 are in conformity with XRD interpretation. Non-existence of band 11 (415 ± 5 cm$^{-1}$) in some samples like D/9, KU/7, KO/4 probably suggests a lower concentration of pyrolusite in them. The shifting of band 8 gradually towards higher wave number region in some samples (KO/1, KU/10, KU/7, KU/6, KO/4 in Fig. 3a) indicates association of some other manganese oxides (cryptomelane as evidenced by XRD in Fig. 3b). This wave number region around 590 ± 10 cm$^{-1}$ is assigned band 7. As the cryptomelane content increases, the spectrum exhibits sharp and distinct doublet in the region of 590 ± 10 cm$^{-1}$ and 540 ± 10 cm$^{-1}$ (bands 7 & 9). The spectra of KU/6 is very similar to the cryptomelane standard No. 27 of Potter and Rossman (1979) not only in respect of band positions but also band intensities. In contrast, Ostwald (1988) reported a moderately sharp peak at 550.4 cm$^{-1}$ for essentially monominerallic cryptomelane.

Van der Marel and Beutelspachet (1976) recorded strong and sharp peaks at 574, 533, 477, 463, and 425 cm$^{-1}$ for hematite and 673, 477, 461 and 428 cm$^{-1}$ for goethite. Dessai (1980) assigned strong absorption at 463 and 425 cm$^{-1}$ and medium intensity bands at 496 and 460 cm$^{-1}$ to hematite and goethite respectively in the iron ores of Goa, India. Wilson et al., (1981) documented absorption maxima with a perpendicular band at 647 cm$^{-1}$ and in-plane bands at 519, 438 and 400 cm$^{-1}$ for platy hexagonal hematite. Some investigators (Rendon and Serna, 1981) noticed a shift of bands at 400 and 650 cm$^{-1}$ to lower wave numbers as the lath like morphology of hematite disappears. In the present investigation, strong and sharp absorption bands at 540 ± 10 (band 9) and 470 ± 15 cm$^{-1}$ (band 10) are due to vibration of hematite mineral ($\alpha$-Fe$_2$O$_3$). The presence of these bands are well exhibited in samples B/1, D/1, D/2, D/3 and KU/1 (all in Fig. 3a) which are in agreement with the XRD interpretations (Fig. 3b). Decrease of hematite content in KU/2 and KO/8 (Fig. 3a) is indicated by reduced intensities of these two bands.

Thus the band 9 (540 ± 10 cm$^{-1}$) is found to be a common absorption due to both
Ferromanganese oxide ores of western Koirai Valley

iron and manganese oxide phases. But from the precise character of the band, it is broadly possible to find out the relative dominance of Mn/Fe phase in an unidentified ferromanganese sample. In case of iron ores, the peak is very sharp whilst it appears broad in manganese ore samples.

(c) 350-250 cm$^{-1}$: In the wave number region of 350-250 cm$^{-1}$, distinct peak appears only at 330 ± 15 cm$^{-1}$ (band 12). This peak has been assigned to mineral hematite. Presence of this peak is recorded in samples D/1, D/2, D/3 & KU/1, KU/2 (Fig. 3a). The appearance of band 12 with medium intensity in samples D/9 and D/5 (Fig. 2a) indicate low level concentration of hematite in them. Many minor peaks of weak magnitude also appearing in this region are difficult to be interpreted and assigned. However, medium intensity bands at 290 ± 10 cm$^{-1}$ in some samples support the presence of hematite (Cambier, 1986) in them and weak but sharp band at 345 cm$^{-1}$ in a few samples (especially KO/3) very likely indicates the presence of minor manganite (Ostwald, 1988).

Effect of Calcination on the IR Spectra

One manganese ore sample, namely KU/10 was calcined at different temperatures of 200$^\circ$, 400$^\circ$, 600$^\circ$ and 800$^\circ$ for a period of 4 hrs each. The IR spectra of all the calcined products were taken as usual in KBr matrix in the range of 4000-200 cm$^{-1}$. This is illustrated in Fig. 4.

The drying of above sample at 200$^\circ$C results in the removal of adhering moisture. The peaks at 1100, 1035 and 1010 cm$^{-1}$ exhibit lower intensity indicating some loss of H$_2$O from lattice position while the original weak peak at 910 cm$^{-1}$ distinctly appears at 915 cm$^{-1}$. The sharp and strong peaks at 580 & 540 cm$^{-1}$ get united and become a single broad band. The broadening of this absorption very likely indicates lattice disorder in oxide minerals. Weak band appears at 520 & 1115 cm$^{-1}$ (stray peaks) while the peak at 475 cm$^{-1}$ shows lower intensity.

At 400$^\circ$C calcination, the intensities of different bands in 1120-800 cm$^{-1}$ wave number region are further reduced. In 710-410 cm$^{-1}$ wave number region, two prominent bands, one as triplet around 600-580 cm$^{-1}$ and other as doublet around 545-535 cm$^{-1}$ appear alongwith a shoulder at 700-665 cm$^{-1}$. This together probably reveals that the metal oxides due to these absorption become more crystalline at this temperature. The stray stands at 520 and 1115 cm$^{-1}$ do not exhibit any change while the sharpness of original 475 cm$^{-1}$ peak is further reduced (480 cm$^{-1}$).

When the sample attains 600$^\circ$C heating, all the bands in the 1120-800 cm$^{-1}$ wave number region disappear. This indicates that the bands in this high frequency region for air-dried sample are due to hydrous components of the oxides and obviously therefore, these bands disappear at high temperature due to dehydroxylation. In the region of
710-410 cm$^{-1}$ the substantial reduction in intensity of 475 cm$^{-1}$ peak also supports dehydroxylation of iron hydroxides. 580 cm$^{-1}$ peak becomes very broad (575 cm$^{-1}$) and the stray band at 520 cm$^{-1}$ gains prominence. The length of the shoulder at 700-665 cm$^{-1}$ reduces at this temperature and exposes as a weak peak around 660 cm$^{-1}$. Most of the IR absorption peaks in the region of 350-250 cm$^{-1}$ practically remained unchanged on heating till 600$^\circ$C and therefore, are not related to structural water.

Calcined products at 800$^\circ$C do not show any change in the region of 1120-800 cm$^{-1}$. A doublet at 610-580 cm$^{-1}$ (new band at 610 cm$^{-1}$), probably diagnostic of bixbyite, appears indicating the conversion of $\beta$-MnO$_2$ to Mn$_2$O$_3$. X-ray diffraction pattern taken at 800$^\circ$C also confirms the above interpretation. The further broadening of peak around 520 cm$^{-1}$ (525-500 cm$^{-1}$) may suggest the lattice disorder in manganese oxide minerals. Most of the peaks of weak magnitude in the region of 350-250 cm$^{-1}$ disappear except a hook at 410 cm$^{-1}$ due to some structural change in metal oxides.

Spectra-chemistry correlation

Based on partial chemical analysis (Mn, Fe, SiO$_2$, Al$_2$O$_3$) of the samples as presented in Table-1, the ores of Koira and Dengura are broadly found to be manganiferous and ferruginous (-aluminous), respectively, while those of Kusumdhil are of intermediate nature.

The positions of the major peaks in the spectra with their band intensity in different ore samples were plotted against their manganese contents in order to correlate both the parameters. Closer examination of the plot reveals three distinct spectral patterns (say A, B & C).

In the spectral pattern of ‘A’ type, either two strong bands appear at 590 ± 10 cm$^{-1}$ and 540 ± 10 cm$^{-1}$ or a single band at 560/600 cm$^{-1}$. Strong absorption in region around 560-600 cm$^{-1}$ and disappearance of 470 ± 15 cm$^{-1}$ peak is characteristic of this type. The samples having larger proportion of Mn ( > 45%) exhibit such type of spectra and hence have been classified under high grade group.

The spectral pattern of ‘B’ type exhibits strong absorption at 540 ± 10 & 470 ± 15 cm$^{-1}$ with or without medium intensity band at 330 ± 15 cm$^{-1}$. This group has an intermediate composition (Mn — 25 to 45%) and the sample can be classified as medium grade.

The spectra of ‘C’ type show maximum number of strong to medium bands, in both low and high frequency region. Manganese poor samples of this group (Mn < 25%) have more resemblance with the spectrum of iron ore (B/1) and can be categorised as low grade.
Discussion

The systematic relationships established between optical microscopy, X-ray diffraction and IR spectra for ferromanganese oxides have considerably helped in elucidating the nature of a large number of ferro-manganese samples in Koir Valley region. A manganese ore sample with typical mineralogy exhibits a definite spectral pattern due to vibration in 1120-250 cm\(^{-1}\) wave number region.

In the first series of samples as illustrated in Fig. 1 the appearance of band between 560-600 cm\(^{-1}\) (band 7/8) region is significant. This band forms a doublet along with the peak at 540 ± 10 cm\(^{-1}\). While the intensity of 540 ± 10 cm\(^{-1}\) peak, probably due to the displacement of oxygen related to the manganese or iron ions, does not show any change the band 7/8 gets more and more pronounced as the manganese content of a sample increases. The Fig. 1a shows how gradually this band gain its importance and gets stronger sequentially from samples KO/4 to KU/6 → KU/7 → KU/10 as the peak intensity diagnostic of cryptomelane/pyrolusite gradually enhances in the adjacent X-ray diffractograms (Fig. 1b). Finally when the sample is very rich in pyrolusite, a broad spectrum appears around 500/600 cm\(^{-1}\) as observed in samples KO/1 and KO/3 (Fig. 1). Strong absorption at 470 ± 15 cm\(^{-1}\) as noticed in second and third series of samples gradually disappears as the ore changes to this group of samples. The band position vs. chemistry correlation indicates that the sample containing Mn above 45% or more (as high as 58%) show similar spectral pattern and can be grouped together in high grade sample category.

In the second series of samples like KU/4 and D/4, D/5, D/7, D/9 appearance of characteristic doublet at 540 ± 10 — 470 ± 15 cm\(^{-1}\) is documented (Fig. 2a). The absorption band at 330 ± 15 cm\(^{-1}\) in weak to medium magnitude in some samples (D/5 and D/9) can be accounted for the presence of hematite. Higher content of hematite in D/9 than D/5 is noted from the diagnostic X-ray reflection line (2.69 Å) and corresponding IR spectra band (Fig. 2). The band position vs. chemistry correlation reveals that the sample bearing Mn content upto 45% (Fe < 20%) exhibits similar spectral pattern and can be grouped together under medium grade category.

The third series of samples like D/1, D/2, D/3; KU/1, KU/2 and KO/8 exhibits maximum number of sharp peaks in both low and high frequency region (Fig. 3a). Weak to medium intensity bands at 1100 ± 10, 1030 ± 10, 1005 ± 10, 910 ± 10 cm\(^{-1}\) and strong sharp bands at 540 ± 10, 470 ± 15, 330 ± 15 cm\(^{-1}\) region are ascribed to iron hydroxide (FeO-OH) and iron oxides (α-Fe\(_2\)O\(_3\)) respectively.

Appearance of 1100 ± 10, 1005 ± 5 and 910 ± 10 cm\(^{-1}\) peaks in different intensities in a sample probably suggests mixture of limonite, lepidocrocite and goethite phases in variable proportion. Confirmation of these phases by IR is possible if the hydroxyl associated with their high frequency bands would have been exposed to D\(_2\)O vapour
and resulting thereby the appearance of specific O–D vibration peaks due to individual minerals (Lewis and Farmer, 1986). The 1030±10 cm⁻¹ peak is possibly due to fine grained kaolinite inclusions. The band position vs. chemistry correlation reveals that the samples having Mn content upto 25% (Fe 30 to 50%) exhibit similar spectral pattern and can be grouped together under low grade sample category. Poor absorption in the 1120-800 cm⁻¹ region in the sample D/3 indicates absence of any iron hydroxide mineral in it.

However, in general, the IR spectra of ferro-manganese ore samples have certain limitations. IR bands (doublet at 780-790 cm⁻¹ and 380-400 cm⁻¹) diagnostic of quartz (Moenke, 1974) did not prove useful for this type of mineralogically complex samples. Often lithiophorite recorded by XRD and supported by microscopic study (abundantly present in KU/4) does not exhibit 3400 and 1020 cm⁻¹ peaks as claimed by Potter and Rossman (1979).

Effect of temperature on ferro-manganese ore sample was brought out from the differential IR absorption spectra obtained for sample KU/10. The weak absorption bands at 1100, 1035, 1010, 910 and 475 cm⁻¹ gradually disappear on rise of temperature. Therefore, they have been attributed to lattice vibration in metal hydroxides. Similar bands dominate in the third series of samples (Fig. 3) and hence, the low grade manganese ore types comprise comparatively larger volume of metal hydroxides than the other two types. The absorption of 610 cm⁻¹ in the spectrum of sample calcined around 800°C is the result of decomposition of β-MnO₂ to Mn₂O₃ (bixbyite) which is in agreement with XRD interpretation.

The trends achieved by correlation between spectral band positions versus chemical composition of ore samples (17 Nos.) were subsequently used to infer the relative grade of unknown ore samples in Koirala Valley region to a reasonable approximation by comparing their IR results with the above three spectral patterns.

Conclusions

The IR spectroscopy is a well known technique for its ability to produce patterns diagnostic of a mineral phase and hence can be effectively used to determine the mineralogy of an unknown ore sample. Different oxides in ore sample can be characterised by absorption pattern due to vibration in the 1120-250 cm⁻¹ wave number region. The bands between 4000-1120 cm⁻¹ wave number region, attributable to absorption associated with hydrous components of the oxides are not found to be promising for Koirala group of samples. It is possible to make an approximate estimate of the relative proportions of iron and manganese content in a complex mixture of ferromanganese ores by means of IR analysis despite the fact that the variability of MnO₂ spectra precludes high accuracy. However, the IR studies of the samples have
not been rewarding in telling the mineralogy that contributes to SiO₂ and Al₂O₃. Nevertheless, IR spectroscopy has proved to be an essential supplement to XRD and microscopic findings for mineralogical analysis and finding out relative chemistry of manganese ore samples of Western Koira Valley, Orissa (India).

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