

FT- Raman Spectra of Raw Magnesite

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Abstract- Raman spectroscopies are rapid an analytical techniques used to detect vibrations in molecules Both of the techniques are based on interaction with light i.e. inelastic scattering and absorption for RS respectively. The Raman have been measured on natural raw magnesite minerals are characterized by the Raman wave numbers at 214 and 333 cm^{-1} and the infrared absorption bands at 712 and 728 cm^{-1} , respectively. The diagnostic peaks at 214 and 333 cm^{-1} in the Raman spectra indicate the existence of Magnesite structures in the samples.

Keywords: Magnesite, FTR...

Introduction

It has been recognized that magnesite might be a major reservoir for carbon in the Earth's mantle. Magnesium is one of most widely distributed elements in the earth crust of which it constitute nearly 2.7 percent and so occupies the sixth place on list (1) magnesium carbonate occurs in nature as magnesite and in association with calcium carbonate as dolomite. The majorly of magnesium oxide produced today is obtained from the processing of naturally occurring minerals such as magnesite (magnesium carbonate) (2).The Chemical name of magnesite is magnesium carbonate(MgCO₃)(i.e) Magnesite is a carbonate of magnesium. When pure, it contains 52.4 % carbon di-oxide (CO₂) and 47.6% magnesium oxide (MgO) (3).But pure magnesite is rarely found in nature. It is usually associated with small percentage of calcium, silicon, iron and aluminium, totals going up to 10%. These elements are called impurities (4)

Large minerals deposits of magnesite are located in Austria, Brazil, Canada , china and India Magnesite is found in nature usually as secondary deposit formed due to alteration of ultramafic rocks(5) (mostly serpentine) as is found in Chalk hills, Salem, and Dodkanya Mysore in Karnataka.

1.1 Sample preparation and material methods



Magnesium carbonate due to the materials wide reactivity range industrial applications are quite varied and include plastics, rubber, paper and pulp processing steel boiler additives and acid neutralization to name just a few.MgCO₃ is present as a major compound along with few percent of CaO, Fe₂O₃, SiO₂,Al₂O₃ as impurities.

The permissible impurities in magnesite that is to be dead burned vary depending on whether The ultimate use is to be as grain magnesite or as a constituent of magnesite brick. The effective sintering of magnesite is greatly felicitated by the presences of a few percentage of iron oxide Fe_2O_3 .

If the percentage of iron in the minerals is inadequate for efficient sintering, it is usually augments by the addition of iron ore or roll scale to the crushed magnesite before calcination. the alumina Al_2O_3 is interchangeable to some extent withFe₂O₃and in maintenances grade magnesia a higher content may be allowed

Raw magnesite

The minerals for the present study have been collected rock samples magnesite we get geographical location N11°45.354'E78°09.396' from TANMAG (Tamil Nadu Magnesite Limited) Salem Tamil Nadu India . The mineral rocks were crushed by hand using an agate mortar and pestle. The powdered different grade samples were subjected to analysis to get a grain size of the order of 53 μ m. The raw sample of magnesite looking colour white.

1.2 Experimental and Methods:

1.2.1 FT- RAMAN Spectral Analysis

The FT Raman spectrometer uses a laser of wavelength 1064 nm as an excitation source. As the spectrometer accepts various kinds of sample (bulk solids, powders, liquids, tablets, polymers, paper, etc.) only a very little or no sample preparation is required. An interferometer converts the Raman signal from the sample into an interferogram, permitting a detector to collect the entire Raman spectrum simultaneously. Usually, indium gallium arsenide nitrogen liquid cooled or germanium detectors are used signal detectors. Application of the Fourier transform algorithm to the interferogram converts the results into a conventional Raman spectrum. In the present investigation, FT Raman spectra of Magnesite



were recorded using BRUKER RFS 27: Standalone FT Raman Spectrometer, at SAIF, IIT Madras. Natural sample of raw magnesite LBM, HBM,and DBM different grade have procured from TANMAG (Tamil Nadu Magnesite Limited) Salem India. The mineral rocks were crushed by hand using an agate mortar and pestle. The powdered samples were subjected to sieve analysis to get a grain size of the order of 53 µm.

1.3 Result and discussion

. FT-RAMAN ANALYSICS

The FTR spectra of raw magnesite and sintering magnesite sample presented in Fig 1.1.Differents grade of DBM spectra are present in Fig 1.2 .Recently the FTR spectra have been utilized as an analytical tool by chemists and mineralogists. Many researcher collected the characteristics Raman spectra of minerals and rocks for identification of known minerals and DBM spectra are characteristic Raman Spectra mixtures (21-24). RAMAN technique was also applied to characterise the water and hydroxyl ions in the basic magnesium carbonate minerals by white (25). The thermal behaviour of calcite, kalonite and dolomite

In ceramics were reported recently (26-28). The analysis of magnesite sample investigation under the spectral show interesting relationship with its mechanical and electrical properties .the Raman spectrum of raw sample show a very strong This band is identified by Laitha et al (30) at 1450 cm in sample to confirm the presences of CO₃ a ions. As the sintering process takes place the band slightly shifts to 1445 cm with less absorbances.

. This band appears with less intensity in disappears DBM .Similarly the weak bands at 1100cm and 1091cm may be due to C-O Symmetric deformation vibration. Following the frequency assignments done by Nakamoto (29), the bands at 1446 cm ,733cm, 1091cm and 1100 cm are conformation as



fundamental modes CO₃ ion presented in MgCO₃

These four bands that are due to the CO₃ ion presented in the raw magnesite (MgCO₃) sample disappear one in sintered magnesite sample to prove that the CO₂. gas is expelled completely In the process of calcination at high temperature (1750°C). The frequency interpretation is tabulated for raw magnesite in table 3 and sintering magnesite in Table 4. The strong band near 1089 is due to the Mg-O stretching vibration (29). And this is active in all grade DBM . The observed fundamentals along with their assignments for different grade of DBM are presented in Table

Thus the table proves a direct relationship betweeen the percentage of occurrence and the absorbance even for the other compounds CaO, Fe₂O₃ and Al₂O₃.

The chemical composition of all magnesite sample accurately characterizes by physical chemical methods in Spectroscopy. These methods give a quantitative measurement of chemical groups. The vibration bands assignment had been made for all the fundamental modes of vibration of raw and sintered sample of magnesite and changes were discussed here.. The spectra of these sample absorption bands with differences in absorbance values .

The Raman spectrum of has been analyzed recently by Fiquent.G and Reynard(33) respectively . Lakshmi et al (23) identified these same bands inmagnesite samples around 1090 cm ⁻¹ , 716 cm ⁻¹ and 330 cm ⁻¹

According to Gadsden et al (15) four absorption were found in raw magneste in the 300 cm⁻¹ to 1500 cm⁻¹ region and the absorptions near 1089 is very large and fairly broad with a strong the shape on the high frequency side and it was also proved by omori te al (61) that no absorption band exist in the range 700 - 300 cm⁻¹

The band due to MgCO₃ vibrations are appreciable in raw magnesite Sample but it



improves as the sintering takes place . Further increase in calcination temperature up to 1750 ° C shows a absorption bant at 1090 cm⁻¹ is Mg-O is stonger than all other spectra;

This be may due to no phase transformation ,which takes place in magnesite sample at higher temperature. Since magnesite is a combination of an inorgain compound, only a limited number of absorption bands are appearing here .Many

researchers have identified the common magnesite peaks at 312, 730,1090,1440 cm⁻¹ (61-69).

The FTR spectra of all these three samples and also the comparison spetra are presented .The vibrational band assignments made on raw magnesite and sintered magnesite have been summarized in table . of raw magnesite .



Fig 1.1 FT-RAMAN spectral analysis on Raw magnesite Grade Table 1.1 FTRAMAN spectral analysis on Raw magnesite Grade



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Band assignment	Wave number cm - ¹	Wave number cm- ¹	Wave number cm - ¹
Mg-O symmetric Stg	1085	1083	1085
Mg-O Asymmetric Stg	334	330	332
Ca-O Stg	217	214	215
Symmetric CO Stg	1402	1406	1405
Asymmetric CO Stg	1448	1445	1440
Asymmetric CO ₃ def	1101	1106	1104
symmetric CO₃ def	1099	1096	1092

Conclusions



The combination of both Raman and IR spectra could be used in the analysis of raw Magnesite and sintering magnesite in the screening of materials. The band observed in the region 1425–1450 cm-¹ in infrared is strong and broad but it is weak in the Raman spectra. The symmetric stretching vibration, on the other hand, gives rise to a very strong Raman band at 1000–1100 cm-¹, which is normally inactive in the infrared. The diagnostic peaks at 214 and 333cm-¹ in the Raman spectra indicate the existence of Magnesite structures in the samples.

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[2]. Conley R T. Infrared spectroscopy, 2ndEdition, Allyn and Bacon, Boston (1972)/

[3]. Nakanishi, Koji, Soloman P H,
Infrared absorbance spectroscopy-Practical,
2nd Edition, Holden-Day, San Francisco (1977).

[4]. Colthup N D, Daly L H and Wiberley
 S.E, Introduction to infrared and spectroscopy, 2nd Edition, Academic press,
 New York and London (1975).

[5]. Jallo H N A and Jalhovn M G, Spectrochim Acta, 31A,265 (1975).

[6]. Dabrouski J, Spectrochim Acta, 19, 475 (1963).

[7]. Erskine R L and Waight E S, J.Chem.Soc., 3425 (1960).

[8]. Jakohsen R J and Bentley F F, App. Spectrosc, 18, 88 (1964).

[9]. Verdonck L et al, Spectrochim Acta, 30A, 813 (1973).

References



[10]. Higuchi S et al, Spectrochim Acta,30A 463 (1974).

[11]. Aruldhas G, Molecular structure and Spectroscopy, Prentice Hall of India (2001).

[12]. Smith A L, Applied infrared spectroscopy, Prentice Hall of India (2001).

[13]. Silverstein R.M. Bassler G C and Morril T.C, Spectrometric identification of organic compounds, John Wiley and Sons, New York (1991).

[14]. Albert N.L.KeiserW E and Sizymansky H.A, I R-Theory and Practice of Infrared spectroscopy, 2nd Edition, Plenum, New York (1967).

[15]. Bingel W A, Theory of MolecularSpectra, John Wiley and Sons, London(1969).

[16]. Miller R G J and Stace D C, Edision,
Laboratory methods in infrared spectroscopy
2nd Edition, Hayden and Sons, London
(1972).

[17]. Krishnan K, Hill S L and Gelpand LS, Proc.Soc.photo-opt. Instrum 553,338 (1985).

[18]. Krishnan K Proc.Soc.photo-opt.Instrum 665,252 (1986).

[19]. Krishnan Kand Kuehl D T, ASTM, Spec.Tech. Publ., 850, 325 (1984).

[20]. Adam S F, Microwave theory and application, Prentic-Hall, USA (1969).

[21]. Chatterjee R, Elements of Microwave engineering, affiliated to East –West Press, Pvt.Ltd, New Delhi (1984).

[22]. Chodoron M and Sussikind C,Fundamentals of MicrowaveElectronic, McGraw Hill, New York (1964).

[23]. Liao S Y, Microwave devices and circuits, Prentice Hall, Eaglewood Cliff, N.J.USA (1991).

[24]. D. A. Skoog, F. J. Holler, T. A.Nieman, "Principles of Instrumental Analysis"Saunders College Publishing, Philadelphia, USA (1998)

[25]. L. V. Azaroff, M. J. Buerger, "The Power Method in X-ray Crystallography", McGraw-Hill, New York, USA (1958)



[26]. B. D. Cullity, "Elements of X- Ray diffraction", Addison - Wesley, Boston, USA(1956)

[27]. H. P. Klug, L. E. Alexander, "X-ray Diffraction Procedures", 2nd ed., Wiley, NewYork, USA (1974)

[28]. M. M. Woolfson, "An introduction tox-ray Crystallography", Cambridge

University Press, Cambridge, USA (1997)

[29]. B. E. Warren, X - Ray Diffraction, Dover, New York, USA (1969)

[30]. C. Suryanarayana, M. Grant Norton,
"X - Ray Diffraction : A Practical Approach", Plenum press, New York, USA (1998)

[31]. P. P. Ewald, "Fifity years of X - RayDiffraction", IUCR XVIII Congress,Glasgow, Scotland (1999)

[32]. T. Irusan, D. Arivuoli, P. Ramasamy, Cryst Res Technol 25 (1990) K104

[33]. J. Drenth, "Principles of ProteinCrystallography", Springer, New York, USA

a. (2007)

[34]. R. S. Rowlett, "Protein X - Ray Crystallography Methods", Colgate University, New York, USA (2005) [35]. R. W. G. Wyckoff, R. B. Corey, J BiolChem 116 (1936) 51 [36]. C. R. Brundle, A. Charles, Jr. Evans, S. Wilson, "Encyclopedia of materials characterization", Butterworth- Heinemann Publications. Elsevier. Greenwich. UK (1992)[37]. D. B. Williams, C. B. Carter.

[37]. D. B. Williams, C. B. Carter, "Transmission Electron Microcopy: A Text book of Material Science", Springer, New York, USA (2009)

[38]. J. C. Delman: Low TemperatureFormation of Dolamite and Magnesite.Compact Disc Publications, Eindhoven,(2005) 2.33.

[39]. K. Wright, R.T. Cygan, B. Slater:
Structure of the (1014) Surfaces of Calcite,
Dolomite and Magnesite under Wet and Dry
Conditions. Phys. Chem. Chem. Phys. 3
(2001)839 - 844.

[40]. E. Tuncer, N. Bowler, I.J. Youngs,K.P. Lymer: Investigating Low FrequencyDielectric Properties of a Composite Usingthe Distributing of Relaxation Times



Technique. Philosophical Magazine Vol. **86** No 16 (2006) 2359 – 2369.

[41]. J. Li, K. Cho, N. Wu, A. Ignatiev:
Correlation between Dielectric Properties and
Sintering Temperatures of Polycrystalline
CaCu3 Ti4 O12.IEEE Transactions on
Dielectrics and Electrical Insulation Vol. 11
No. 3 (2004) 534 – 541.

[42]. E. Barsoukov, J. R. Macdonald:
Impedance Spectroscopy Theory,
Experiment, and Applications. A John Wiley
& Sons, Inc., (2005) 1 – 129.

[43]. W. D. Kingery, H. K. Bowen, D.R.Uhlmann: Introduction to Ceramics. WilleyInterscience Pub. (1975) 913 – 974.

[44]. C. R. Brundle, A. Charles, Jr. Evans,
S. Wilson, "Encyclopedia of materials characterization", Butterworth- Heinemann
Publications, Elsevier, Greenwich, UK (1992)

[45]. D. B. Williams, C. B. Carter, "Transmission Electron Microcopy: A Text book of Material Science", Springer, New York, USA (2009)

[46]. J. C. Delman: Low TemperatureFormation of Dolamite and Magnesite.Compact Disc Publications, Eindhoven,(2005) 2.33.

[47]. K. Wright, R.T. Cygan, B. Slater: Structure of the (1014) Surfaces of Calcite, Dolomite and Magnesite under Wet and Dry Conditions. Phys. Chem. Chem. Phys. **3** (2001)839 - 844.

[48]. E. Tuncer, N. Bowler, I.J. Youngs,
K.P. Lymer: Investigating Low Frequency
Dielectric Properties of a Composite Using
the Distributing of Relaxation Times
Technique. Philosophical Magazine Vol. 86
No 16 (2006) 2359 – 2369.

[49]. J. Li, K. Cho, N. Wu, A. Ignatiev: Correlation between Dielectric Properties and Sintering Temperatures of Polycrystalline CaCu3 Ti4 O12.IEEE Transactions on Dielectrics and Electrical Insulation Vol. **11** No. 3 (2004) 534 – 541.

[50]. E. Barsoukov, J. R. Macdonald:
Impedance Spectroscopy Theory,
Experiment, and Applications. A John Wiley
& Sons, Inc., (2005) 1 – 129.

[51]. W. D. Kingery, H. K. Bowen, D.R.Uhlmann: Introduction to Ceramics. WilleyInterscience Pub. (1975) 913 – 974.

[52]. Grinblat A., Bern F., Barzola - Quiquia
J., Tirado M., Comedi D., Esquinazi P.
2014, Electrical properties and luminescence of single ZnO/MgO core/shell nanowires,
Appl. Phys. Lett., 104, 103113.

[53]. IN-CHYUAN HO, UHUAN XU, JOHN D. MACKENZIE, 1997, Electrical and Optical Properties of MgO Thin Film



Prepared by Sol-Gel Technique, Journal of Sol-Gel Science and Technology, 9, 295. [54]. Yong Shin D., Nam Kim K., 2009, Electrical and optical properties of MgO films deposited on soda lime glass by a solgel process using magnesium acetate, Journal of Ceramic Processing Research, 10, 536.

[55]. Bondoux C., Prené P., Belleville P.,
Guillet F., Lambert S., Minot B., Jérisian R.,
2004, Sol - Gel MgO Thin Films for
Insulation SiC, Materials Science in
Semiconductor Processing, 7, 249.

[56]. Miranda E., O'Connor E., Hughes G., Casey P., Cherkaoui K., Monaghan S., Long R., O'Connell D., Hurley P. K., 2009, Soft breakdown in MgO dielectric layers, Reliability Physics Symposium, 26-30 April (2009), Montreal QC, 688-691.

[57]. Matousek, P., Towrie, M. and Parker, A. W. (2002) Fluorescence background suppression in Raman spectroscopy using combined Kerr gated and shifted excitation Raman difference technique. Journal of Raman Spectroscopy, 33, 238-242.

[58]. McKenzie, J. A. and Vasconcelos, G. (2009) Dolomite Mountains and the origin of dolomite rock of which they mainly consist: historical developments and new perspectives. Sedimentology, 56, 205-219.

[59]. Meng L. J., Andritschky M., Dos Santos M. P., 1993, The effect of substrate temperature on the properties of dc reactive magnetron sputtered titanium oxide films, Thin Solid Films, 223, 242.

[60]. Menzel, H. and Brückner, A. (1930)Studien an kohlensauren Magnesiumsalzen. I.Basische Magnesiumcarbonate. Zeitschriftfür Elektrochemie, 36, 63–87.

[61]. Mich., (1976).

[62]. Michal Barroom, Fundamentals of Ceramics, McGraw Hill, New York (1977).