International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.06, pp 183-189, 2018

Spectroscopic Interrogations and Study on the Insulating Property of Magnesite

D.Gopinath[1]* and S. Gunasekaran[1]

St. Peter's Institute of Higher Education and Research, St. Peter's University, Avadi, Chennai-600 054, India.

Abstract : Abstract :Magnesite is a magnesium carbonate mineral because of its thermal stability and inertness. All the three grades of magnesite both in raw and sintered forms have vast applications. The FTIR spectra of raw magnesite and sintered magnesite samples have been recorded in the mid - infrared region of 4000-450 cm-^{1}. In general, vibrational spectroscopy detections can qualitatively and quantitatively distinguish the spectral assignment of specific bands between corresponding bonds and functional groups, as also the observation of spectral profiles can be used to define and differentiate the magnesite The present work is aimed to make an investigation with reference to the insulating property of the magnesite. The dielectric measurements were carried out to analyze the insulating property of magnesite. It is observed that dielectric constant and dielectric loss of magnesite decrease with increase in frequency. However magnesite it is noted that there is an increase in the dielectric strength of the material, as it possess low dielectric constant as well as dielectric loss.

Keywords : Magnesite, FTIR, LCR Meter.

Introduction

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). Large Mineral deposits of magnesia are in Austria, Brazil, Canada, China, Common wealth of Independent States, former Czechoslovakia, Greece, Turkey, North Korea, former Yugoslavia and the US . The commercial production of magnesia in India was started during the World War I, when imports of magnesium chloride was ceased and in indigenous resources must be developed to meet the needs of industry (4). The bitterns from marine salt works provided a convenient source material for magnesium chloride and the pioneer magnesia works limited Kraalhead, started production in 1916.

The Chemical name of magnesite is magnesium carbonate ($MgC0_3$) (i.e) Magnesite is a carbonate of magnesium. When pure, it contains 52.4 % carbon di-oxide (CO_2) and 47.6% magnesium oxide (MgO) (3).The magnesium and calcium bearing carbonates represent an important mineral group which is mined extensively. It is usually white, but it may be light to dark brown if iron bearing. Magnesite is an important industrial mineral.

D.Gopinath *et al* /International Journal of ChemTech Research, 2018,11(06): 183-189.

DOI= http://dx.doi.org/10.20902/IJCTR.2018.110623

Various types of magnesite are produced by different thermal treatments and it is used in the production of calcined, dead- burned .Magnesite is converted to calcinedmagnesite when it heated between 700 ^{0}Cand 1000 ^{0}C temperatures. Calcined magnesite is used in the manufacture of paints, paper, plastic, rubber, oil, pharmaceutical, fertilizer, animal feed, building materials and as a fire retardant. If calcinedMagnesite is heated to 1500 ^{0}C to 1800 ^{0}C, it will convert to dead- burned magnesite which is known as sintered magnesite and it is used predominantly for refractory bricksare widely used in many industrial sectors e.g. pharmaceutical and cosmetic industries, paint formulations and bulk applications including concrete and magnesia (MgO) production. There have been a considerable number of studies suggesting that magnesite should be considered when evaluating the role of carbon in the earth's mantle. Magnesite is indeed a very good candidate for hosting oxidized carbon in the mantle, since experiments or calculations indicate that magnesite is, among all carbonates the most stable at high pressure and high temperature (6-11). Numerous experiments have been dedicated to determine the compression properties of magnesite, as these govern to some extent to its stability versus the composition into a mixture of oxides MgO and $CO_{2.}$ Recently the high-pressure behaviour of magnesite has been studied with angle dispersive X-ray diffraction by Fiquet et al and Reynard et al (12-15). Ross et all carried out even the structural refinement of megnesite at high pressure in 1997(16). Though many research works were carried out in magnesite at high pressure not much work was reported at high temperature. Here an attempt is made to study the behaviour of the ceramic (MgO) at different temperatures, using infra red.

Experimental and Methods:

FT- IR Spectral Analysis

Natural samples of Raw Magnesite, LBM, HBM and different grades of DBM have been procured from TANMAG(Tamil Nadu Magnesite Limited), Salem, India. The FTIR spectra were recorded in the range 4000-400 cm^{-1}using BrukerIFS 66V FTIR spectrophotometer at SAIF, IIT, Chennai, India. Since the samples were not soluble in solvent and also the preparation of the film was very difficult, the IR spectra were recorded by the use of KBr pellet method. .

Dielectric Analysis:

The dielectric measurement was carried out at Department of Physics, Loyola College, at Chennai. The dielectric studies of magnesite were analyzed using HIOKI model 3532-50 LCR HITESTER with a conventional two terminal sample holder. The dielectric studies were carried out for varying frequencies from 50Hz to 5MHz at room temperature .

Result and discussion

Since the samples were not soluble in solvent and also the preparation of the film was very difficult, the IR spectra were recorded by the use of KBr pellet method. The FTIR spectra ofthe raw magnesite and the sintered magnesite samples are presented in Figs. 3.1 Different grades of DBM Spectra are presented in Figs.3.2 Recently the IR spectra have been utilized as an analytical tool by chemists and mineralogists. Many researchers collected the characteristic IR spectra of minerals and rocks for identification of known minerals and mixtures (20-24). IR technique was also applied to characterize the water and hudroxyl 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 samples under the spectral invesitgation show interesting relationship with its machencial and electrical properties. The infrared spectrum or raw magnesite shows a very strong broad band at 1446 cm^{-1}due to the asymmetric C-O stretching vibrations and it is in good agreement with the literature value (29). This band is identified by laitha et al (30) at 1450 cm^{-1} in apatites sample to confirm the presence of CO_3 ion. As the sintering process takes place, this band slightly shifts to 1455 cm^{-1} with less absorbance. In DBM it completely disappears to show the absence of CO_3ion.

Another intense band at 856 cm^{-1} is characteristic of the CO_3asymmetric deformation as expected. This band appears with less intensity in LBM and disappears in both DBM. Similarly the weak bands at 1080cm^{-1} and 680 cm^{-1} may be due to the C-O symmetric and CO_3 symmetric deformation vibration. Following the frequency assisgnment done by Nakamoto (29), the bands at 1446 cm^{-1}, 856cm^{-1}, 1080cm^{-1} and 680cm^{-1} are confirmed as fundamental modes of CO_3ion present $MgCO_{3.}$ These four bands that are due to the CO_3ion present in the raw magnesite ($MgCO_3$) sample disapper one by one in sintered magnesite sample to prove that the CO_2 gas is explelled completely in the process of calcination at high temperature (1750°C). The frequency interpretation is tabulated for raw and sintered magnesites in Table 3.2. The values within the brecket gives the corresponding absorbance.The strong band near 887 cm_{-1} is due to the Mg-O stretching vibration (29) and this is active in all grads of DBM. The observed fundamentals along with their assignments for different grades of DBM are presented in Table 3.3.Values of the absorbance of the characteristic bands corresponding to the components present are given within the parenthesis in the table. The spectra of different grades of DBM give rise to more or less same infrared characteristic bands since there is a very small variation in the percentage of components present in it. Comparing the percentage of MgO with other components of DBM it is very high and varies between 72% and 89% and thus leads to a variation of absorbance in the range 0.33% to 0.70%. The second major contribution in DBM is due to SiO_2 and shows absorbance up to 0.59%.

The IR absorbance for SiO, Si_2O_2 molecules are observed at 1224 cm^{-1} (SiO), 805 cm^{-1}, 766 cm^{-1} (Si_2O_2), 973 cm^{-1}, 632 cm^{-1}, 312 cm^{-1} (Si_3O_2) by Ogden and Anderson(31). The peaks around 839 cm^{-1}, 987 cm^{-1} and 471 cm^{-1} are invariably present in all the grades of DBM, caused by a symmetrical stretching (32,33), asymmetric stretching (34,35) and bending vibrations (36,37) of Si-O group confirms its presence.Yousuf (38) ascribes the stretching vibrations of AI-O around 1000 cm^{-1} and the same is identified at 987 cm^{-1} in DBM grade samples and gives more or less the same value of absorbance. The stretching vibrations of Ca-O occur normally at 650 cm^{-1} (39) and here it is observed around 614 cm^{-1}. The absorbance of this peak isverysmall compared to the other impurities like AI_2O_3value .The strong band near 887 cm_{-1} is due to the Mg-O stretching vibration (29) and this is active in all grads of DBM. The observed fundamentals along with their assignments for different grades of DBM are presented in Table 3.2

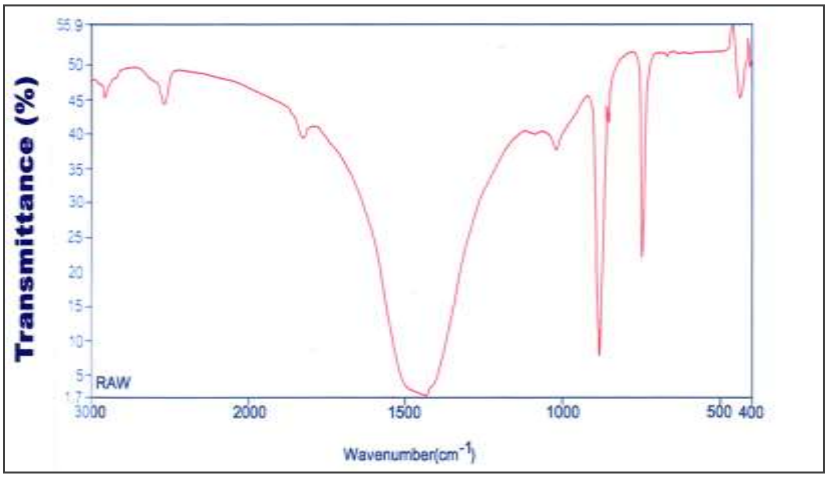

Fig 1 FTIR raw magnesite

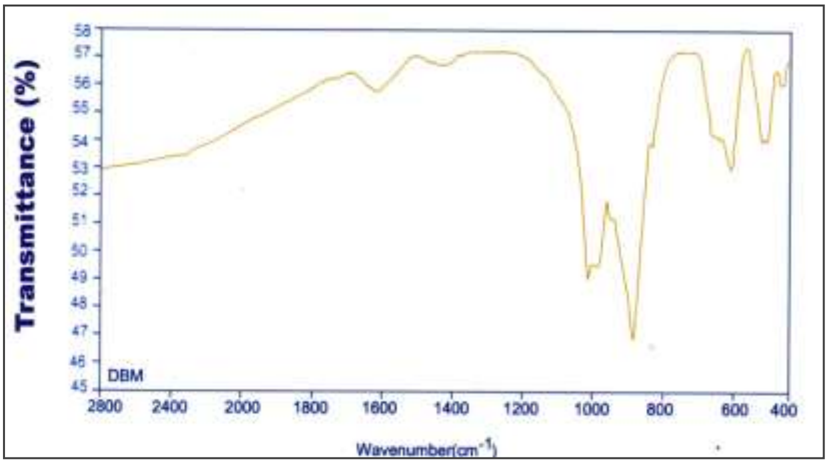

Fig 2 FTIR DBM magnesit

Table 1 FTIR spectral analysis on raw magnesite different Grades

Band assignments	**Grade 1 Wave number cm-^{1}**	**Grade 1 Wave number cm-^{1}**	**Grade 1 Wave number cm-^{1}**
Mg-O	885	885	885
SiO_2 Asymmetric Stg	1020	1020	1020
Asymmetric . CO stg	1446	1446	1446
Asymmetric CO stg	1080	1080	1080
Asymmetric CO_3 def	856	856	856
symmetric CO_3 def	680	680	680

Table 2 FTIR spectral analysis on Sintering magnesite different Grade

Band assignments	**Wave number cm-^{1}**	**Wave number cm-^{1}**	**Wave number cm-^{1}**
Mg-O	887	886	887
SiO_2 Asymmetric Stg	1017	1018	1017
Asymmetric CO stg	-	-	-
Asymmetric CO stg	-	-	-
Asymmetric CO_3 def	-	-	-
symmetric CO_3 def			-

Dielectric analysis of the magnesite

A graph was drawn between the calculated values of dielectric constant (ε’) and log frequency. Figures 3shows the variation of dielectric values with various frequencies for all the grade raw magnesite at different temperatures. we show the permittivity of fired magnesite samples as a function of log frequency, for different firing temperatures. The permittivity values of the samples range from 3 to 4. depending on the temperatures at 5 MHz frequency. It is clear that the permittivity depends on the sintering temperatures and the permittivity values of samples remain fairly stable at log frequency region between 4.5 and 6.5. Here, stable permittivity values are observed with low losses independent of frequency, its reason is the significance of interfacial effects between conjugated particles in powder compacts.The dielectric constant decreases with increase in frequency for all temperatures and this is termed as anomalous dielectric dispersion . This is a normal dielectric behaviour and can be understood on the basis of internal polarization process . The dielectric constant value depends on the degree of polarization charge displacement in crystals. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space- charge polarizations which depend on the frequencies. All these polarizations are active at low frequencies..The frequency dependence on dielectric constant of the magnesite is evaluated between 50Hz and 5MHz (45). The materials are analyzed at room temperature. From the dielectric study, it can be concluded that both dielectric constant and dielectric loss of the sample decreases with increase in frequency and attain a constant value beyond 1000 Hz (43,47). The results show that increased insulating property of magnesite is shown in Fig.3a. Moreover decreasing trend is noticed in the value of dielectric constant (ε_r) for magnesite which proves that the Dead burned magnesite is a better insulator than the magnesite

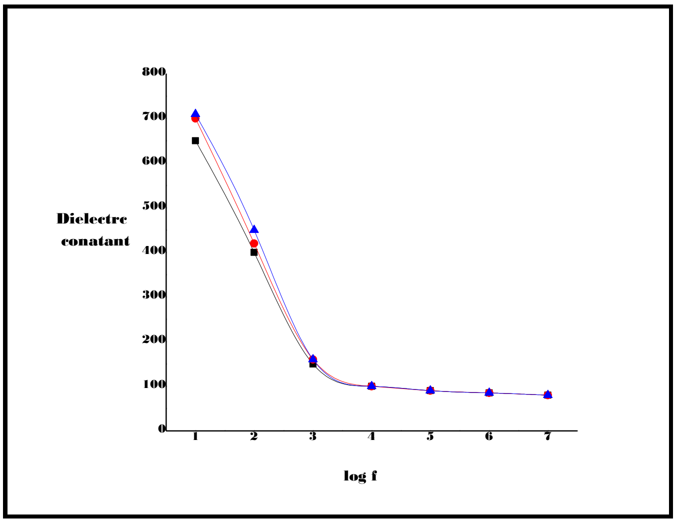

Fig 3 Dielectric constant of the magnesite

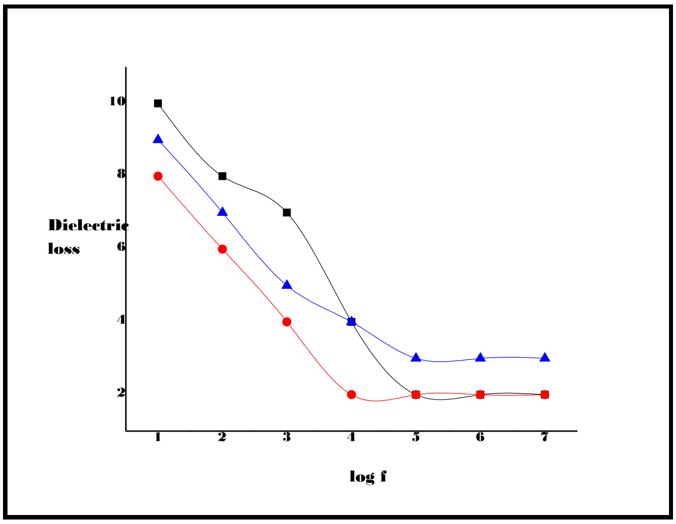

Fig.4 Dielectric loss of the magnesite

Conclusions

The FTIR measurement is used to analyze the samples of magnesite.. The FTIR technique is used to identify the characteristic bands of Silicate, aluminium, iron, present in the mineral, and a spectral analysis is also carried by FTIR. It is observed that the magnesite is more stable and has high mechanical strength , because of the presence of silica. The spectroscopic instrumentation techniques are used to conclude out of the three grade, the dead burned magnesite has higher insulation property than the magnesite. Furthermore increase of temperature the relative permittivity of the magnesite decreases, with confirms the increase of the insulating property. Hence the dielectric measurement on the sample proves that the dead burned magnesite becomes more insulation in its magnesite. They are in good agreement with the FTIR techniques and dielectric measurement results.

Acknowledgements

The authors are thankful to TANMAG(Tamil Nadu Magnesite Limited), Salem, India. for providing the samples and for their supported throughout the research. One of the authors Mr.Gopinath is thankful to St. Peter‟s University for providing the University Research fellowship to Carried out my Ph.D programme.

References

1. Robert M Silver stein, Spectrometric identification of organic compounds, John Wiley and Sons, New York (1981).
2. Conley R T. Infrared spectroscopy, 2nd Edition, 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, SpectrochimActa, 31A,265 (1975).
6. Dabrouski J, SpectrochimActa, 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, SpectrochimActa, 30A, 813 (1973).
10. Higuchi S et al, SpectrochimActa, 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 Molecular Spectra, 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 L S, Proc.Soc.photo-opt. Instrum 553,338 (1985).
18. Krishnan K Proc.Soc.photo-opt. Instrum 665,252 (1986).
19. Krishnan KandKuehl 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 Microwave Electronic,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 to x-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 - Ray Diffraction”, IUCR XVIII Congress, Glasgow, Scotland (1999)
32. T. Irusan, D. Arivuoli, P. Ramasamy, Cryst Res Technol 25 (1990) K104
33. J. Drenth, “Principles of Protein Crystallography”, 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, “Transmission Electron Microcopy: A Text book ofMaterial Science”, Springer, New York, USA (2009)
38. J. C. Delman: Low Temperature Formation 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 Frequency Dielectric Properties of a Composite Using the 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. Willey Interscience Pub. (1975) 913 – 974.
44. 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.
45. 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.
46. Yong Shin D., Nam Kim K., 2009, Electrical and optical properties of MgO films deposited on soda lime glass by a sol-gel process using magnesium acetate, Journal of Ceramic Processing Research, 10, 536.
47. 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.
48. 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.
49. Moses A., Jayachandran M., Sanjeeviraj C., 2010, Fabrication techniques and materials properties of dielectric MgO thin films, CIRP Journal of Manufacturing Science and Technology, 2, 92.

*****