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Structural, optical, electron paramagnetic, thermal and dielectric characterization of chalcopyrite

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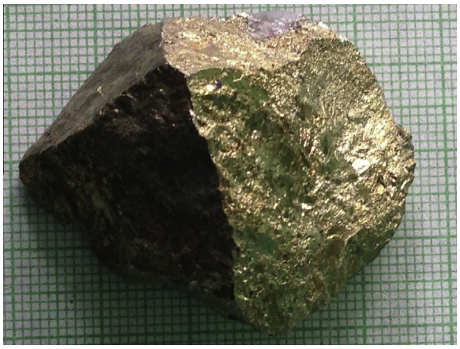
HIGHLIGHTS

- Optical absorption spectrum is due to Fe(II)/Cu(II) which is distorted octahedral symmetry.
- The EPR studies on chalcopyrite with iron and copper manganese is also present in traces.
- The FTIR and FT-Raman spectra were recorded and analyzed.
- TG–DTG curves at three different heating rates were carried out to find activation energies.
- Both dielectric constant and dielectric loss decreases with increase in the frequency.

GRAPHICAL ABSTRACT



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ABSTRACT

Chalcopyrite ($CuFeS_2$) a variety of pyrite minerals was investigated through spectroscopic techniques and thermal analysis. The morphology and elemental analysis of the chalcopyrite have been done by high resolution SEM with EDAX. The lattice parameters were from the powder diffraction data ($a = 5.3003 \pm 0.0089$ Å, $c = 10.3679 \pm 0.0289$ Å; the volume of the unit cell = 291.266 Å^3 with space group I42d (1 2 2)). The thermal decomposition behavior of chalcopyrite was studied by means of thermogravimetric analysis at three different heating rates 10, 15 and 20 °C/min. The values of effective activation energy (E_a), pre-exponential factor ($\ln A$) for thermal decomposition have been measured at three different heating rates by employing Kissinger, Kim–Park and Flynn–Wall methods. Dielectric studies at different temperatures have also been carried out and it was found that both dielectric constant and dielectric loss decreases with the increase of frequency.

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Introduction

Chalcopyrite is a copper ore and is the primary source of copper. Other names of chalcopyrite are chalcopyrite, copper pyrites, Cupropyrite, Towanite, yellow copper, yellow copper ore, yellow pyrite [1]. The name chalcopyrite is derived from the Greek words chalkos, means “copper” and pyrites means “strike fire” [2]. Fortunately, both structure and composition affect certain physical properties. It is through the proper use of these properties that minerals can reliably be identified. Over 9 million tons of copper are produced each year for mineral processing plants around the world [3]. It is the most commonly encountered copper mineral. Chalcopyrite is a composition sulfide of copper and iron (34.5% Cu, 30.5% Fe, 35% S copper pyrite). In India, the occurrences of chalcopyrite are reported from most parts of the country which includes Karnataka, Jharkhand and Orissa. It has its importance in the field of industry and therefore it is a well studied sulfide

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mineral. It is also used as an ore of copper for pipes, electrical circuits, coins, brass, and bronze.

Spectroscopic methods are the most direct and powerful means of obtaining experimental information on the electronic structure of materials. Moreover, Raman spectroscopy is considered a powerful tool in order to estimate the degree of structural order–disorder at short-range in different types of the materials [4]. In this paper, we study applications of spectroscopic techniques (UV, FTIR, FT Raman and EPR) to chalcopyrite. UV–visible and FTIR has been used to investigate the absorption mechanism of chalcopyrite. Interactions with higher energy forms of radiations are then considered with the use of X-rays in XRD study. Electron spin resonance is a branch of absorption spectroscopy in which radiation having a frequency in the microwave region absorbed by a paramagnetic substance (EPR study) to induce transitions between magnetic energy levels of electrons with unpaired spins [5]. Thus, the EPR technique only detects species that possess unpaired electrons—in this case, $[FeS_3 \cdot V_s^{\cdot\cdot}]$ or $[CuS_3 \cdot V_s^{\cdot\cdot}]$ sulfur complex clusters. The magnetic energy splitting is done by applying a static magnetic field. DPPH is used as internal standard ($g = 2.0036$). EPR technique is also employed in application for characterization of chalcopyrite and the g value can be calculated. Hence, the purpose of this work is to study the effect due to hydroxyl stretching modes and to determine the site symmetry of iron/copper and other impurities present in the mineral chalcopyrite natural. Moreover, the structures, optical and dielectric properties of mineral chalcopyrite natural were investigated.

Experimental details

Chalcopyrite mineral used in the present investigation was collected from Salem, Tamil Nadu, in India. The crystals were mechanically separated from the ore. The samples were hand picked, crushed and dry grounded with agate mortar to obtain in a fine powder form. The fine powder chalcopyrite sample was used for vibrational measurements. The morphological study was performed with a Jeol JSM-6360 SEM. The sample was glued onto aluminum tubes with colloidal graphite and then coated with a carbon film approximately 400 Å in thickness. The elemental analysis was carried out by employing EDAX.

Powder XRD analysis

Powder XRD was recorded with SEIFERT X-ray diffractometer with Cu Kα radiation ($\lambda = 1.540598$ Å), Cu Kα filter on secondary optics, 45 kW power 20 mA current in the Department of Nuclear Physics, University of Madras, Guindy campus, Chennai. Instrumental broadening as a function of 2θ is determined with a well crystallized quartz standard. The Gaussian standard deviation of the instrumental broadening was taken for 2θ value.

Vibrational spectral measurements

FTIR analysis was performed with Perkin–Elmer Model Spectrum one spectrometer at Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras. The powder chalcopyrite sample was analyzed using KBr pellet techniques. Spectrum was traced in the range 4000–450 cm^{-1} and the band intensities were expressed in the absorbance mode. The accuracy of the method may be compromised by any variation in the amount of powdered chalcopyrite sample successfully deposited on the KBr window, (9 mm diameter and 2 mm thickness) particularly with the manual sample preparation. The FT Raman spectrum of the mineral was recorded on a computer interfaced BRUKER IFS 66V model interferometer equipped with FRA-106 FT Raman accessories. The spectrum was measured in the Stokes region 3500–100 cm^{-1} using Nd: YAG laser at 1064 nm of 200 mW output as the excitation source and with a liquid nitrogen-cooled Ge-diode detector with the powder sample in a capillary tube.

Optical absorption measurements

UV–visible spectrum was recorded at Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras using Varian Cary 5E Model UV–visible NIS spectrophotometer. For UV–visible measurements the fine powder of chalcopyrite sample was used. The scanning range capability of the device was 200–1100 nm with an accuracy of 0.5 nm. The UV–visible spectrum of the mineral sample was the baseline corrected and the spectrum normalized to an acquire identical area under the curves and maximum absorbance values corresponding to characteristic bands were noted.

Electron paramagnetic resonance spectral measurements

EPR measurements were performed with EPR Spectrometer Model Varian E 102 at Sophisticated Analytical Instrumentation Facility IIT Madras. A part of the powder sample is taken into a quartz tube for EPR readings on a Varian E 102 EPR spectrometer operated at X-band frequencies having a 100 kHz field modulation and a phase sensitive detector to obtain a first derivative signal.

TG kinetics method of thermal degradation

A large number of mathematical models have been proposed and used for studying kinetics and mechanism of reactions using the TG data. Here, we studied the kinetics of the thermal decomposition of chalcopyrite at three different heating rates has been studied by three different multiple heating methods: Flynn–Wall, Kissinger and Kim–Park [6–8].

Flynn–Wall method

This is the simplest method for determining activation energies directly from mass loss against temperature obtained at several heating rates. This technique assumes that A, $(1-\alpha)^n$ and E_a are independent of T, A and E_a are independent of α.

$$\ln\beta = \ln(AE_a/R) = \ln F(\alpha) - E_a/RT \tag{1}$$

The value of the activation energy (E_a) can be calculated from the slope of the plot between ln β vs $1/T$ for a fixed mass loss.

Kissinger method

The activation energy for the decomposition of Chalcopyrite was calculated from the TG data using Kissinger Eq. (3):

$$\ln(\beta/T_p^2) = \ln[n(1-\alpha m)^{n-1}AR/E_a] - E_a/RT_p \tag{2}$$

where β is the heating rate, A is the pre-exponential factor, E_a is the energy of activation, R is the gas constant, T_p is the absolute temperature at the maximum rate of thermal decomposition and α_m is the mass loss at the maximum decomposition rate. This method assumes that ln $(1-\alpha_m)^{n-1}$ is independent of the heating rate (β). It also assumes that the reaction order remains constant and is very nearly equal to unity. The value of the activation energy can be calculated from the slope of the plot of ln $(\beta/T_p{}^2)$ vs $1/T_p$ at the maximum mass loss.

Kim–Park method

Kim–Park method assumes that α_m is independent of the heating rate β, activation energy E_a, and a pre-exponential factor A. The activation energy is calculated using the expression given below.

$$\ln\beta = \ln Z + (E_a/R) + \ln[1 - n + (n/0.944)]. \tag{3}$$

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