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Marcasite revisited: Optical absorption gap at room temperature

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ABSTRACT

Jagadeesh and Seehra published in 1980 that the marcasite band gap energy is 0.34 eV. However, recent calculations and experimental approximations accomplished by several research groups point out that the marcasite band gap energy should be quite similar to that of pyrite (of the order of 0.8–1.0 eV). By using diffuse reflectance spectroscopy (DRS) we have determined that marcasite has no optical absorption gap at photon energies $0.06 \leq h\nu \leq 0.75$ eV and that it has two well defined optical transitions at ~ 0.9 eV and ~ 2.2 eV quite similar to those of pyrite. Marcasite optical absorption gap appears to be $E_g \cong 0.83 \pm 0.02$ eV and it is due to an allowed indirect transition.

1. Introduction

Marcasite (FeS_2) is a polymorph of pyrite that crystallizes in the orthorhombic system (space group P_{nnm}). It appears to be metastable with respect to pyrite at low temperatures but at ~ 700 K it suffers an irreversible exothermic transformation [1–3]. Similar behavior is observed at high pressures (~ 3.7 GPa) [4]. Marcasite to pyrite conversion seems to be favored by the presence of Na in the prepared material [5].

Marcasite band gap energy was determined by Jagadeesh and Seehra [6] in 1980 and a value of 0.34 eV was obtained. The authors accomplished electrical resistivity vs. temperature measurements by heating the samples up to 370 K. However, several papers published in recent years [4,7–9] yield serious doubts (mainly from the theoretical point of view) about the real value of the marcasite band gap energy. Most of the published calculations predict that marcasite should have an energy gap quite similar to that of pyrite (around 0.8–1.0 eV [10–15]), although former theoretical approaches by Bullet [16] yielded 0.7 eV for the pyrite band gap and 0.4 eV for that of marcasite.

Therefore, it seems quite convenient to make additional experimental determinations of the marcasite band gap energy. It is important to try to clarify this matter for several fundamental and practical reasons. Marcasite very often appears as a secondary phase when pyrite is grown (see, for example [5]) both as bulk material and as thin films. Pyrite is considered a potentially useful photovoltaic and photoelectrochemical semiconductor. Then, marcasite would be a non-convenient contaminant of pyrite that could contribute to an effective reduced band gap energy of the photovoltaic material. In fact, some authors have considered that marcasite could be segregated to the grown pyrite surface and explain the low photovoltage presented by pyrite. As a consequence, efforts are done by researchers in order to eliminate marcasite traces from the pyrite preparations.

Therefore, we have tried to measure the marcasite band gap energy by using optical spectroscopy techniques. In particular, we have applied Diffuse Reflectance Spectroscopy (DRS) to investigate natural materials (minerals). In addition to marcasite, we have worked with two other metal sulphides as reference materials in different optical ranges (IR, VIS-UV): galena (PbS) with a well-established energy gap at 0.37–0.41 eV [17–22] due to a direct allowed transition and pyrite itself.

We have found that marcasite has no optical absorption gap at photon energies $0.06 \leq h\nu \leq 0.75$ eV what it is in open contradiction with the published experimental result [1]. In addition, we have found that both, pyrite and marcasite, behave quite similarly in the VIS–NIR region. Marcasite optical absorption edge appears to be at $E_g \cong 0.83 \pm 0.02$ eV, quite close to that of pyrite. However, optical absorption coefficients of pyrite seem to be much higher than those of marcasite at the investigated light wavelengths.

Abbreviations: DRS, diffuse reflectance spectroscopy; EDX, energy dispersive X-ray spectroscopy; SEM, scanning electron microscopy; XRD, X-ray diffraction; DRIFTS, Diffuse Reflectance Infrared Fourier Transform Spectra

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2. Experimental section

Natural materials (minerals) from different Spanish mines have been used in this work. Marcasite from Reocin mine, Santander (Cantabria, Spain), pyrite from Navajun mines, Logroño (La Rioja, Spain) and galena from Linares mines, Jaén (Andalucía, Spain). Powders (particle sizes $\sim 10-20\,\mu m$) were obtained from the natural pieces by grounding them in an agate pestle and mortar and the resulting powders put through one sieve to select the size distribution. The obtained powders were used in the IR optical spectrometer. For measurements in the NIR–VIS region the mineral powders were deposited (by drop coating) on glass or amorphous silica plates (a suspension of the powder in ethanol was prepared and then deposited on the substrates which were slightly and carefully heated to allow the ethanol evaporation). The thickness of the deposited layer was $\sim 40\,\mu m$. These deposited samples were also used in the other characterization techniques applied in this work.

Confirmation of the identity of the minerals through their crystallographic structure, chemical stoichiometry and impurity content was done by means of several experimental methods. X-ray diffraction (XRD) was accomplished with an X'Pert PRO Panalytical diffractometer. Sample composition was obtained by EDX (Oxford instruments, model INCA x-sight) coupled to a SEM (Hitachi, S-3000N). Raman spectra were obtained with a Labram HR Raman Spectrometer (Horiba Scientific).

Transport properties (Seebeck coefficient and electrical resistivity at R.T.) of the marcasite and pyrite powders were determined with some homemade equipments. Four points (Van der Pauw method) were used in the electrical resistivity measurements [23]. An instrument based in a differential method allowed to measure the Seebeck coefficient of the deposited powders. Temperature differences between the sample ends were $\sim 5-10$ K [24]. DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectra) were obtained with a BRUKER IFS 66 V spectrometer equipped with an integrating sphere (Praying Mantis DRA from BRUKER/HARRICK). Sample powder was placed in a cup where the thickness of the sample was ~ 2 mm. As a reference material KBr powder was used. In the NIR–VIS region a Perkin Elmer Lambda 9 Spectrometer with an integrating sphere (Labsphere, 150 mm) coated with Spectralon® was employed. We used powders of minerals deposited on glass or amorphous silica plates. So, thickness of the samples used in this wavelength range was $\sim 40\,\mu m$.

3. Results and discussion

3.1. Identification of samples and some properties.

Fig. 1 shows XRD patterns of the investigated minerals. Some diffraction planes according to standards (pyrite: JCPDS 00-042-1340; marcasite: JCPDS 00-037-0475; galena: JCDPS 00-005-0592) are indicated in Fig. 1(a)–(c). The three patterns confirm the identity of the minerals. They show a good crystallization although pyrite and galena present bigger crystallite sizes than marcasite according to the width of the diffraction peaks.

Raman spectra of the compounds are shown in Fig. 2 with indication of the main observed bands. Pyrite and marcasite show clear spectra with easily identifiable bands. Those marked in the figure (and their relative intensity) are in excellent agreement with published data ([15,25] and paper quoted there). On the contrary, PbS presents a rather diffuse spectrum what it is to be expected according to published data (see [26] and papers quoted there). Bands marked in Fig. 2 are in good agreement with those previously reported [26,27].

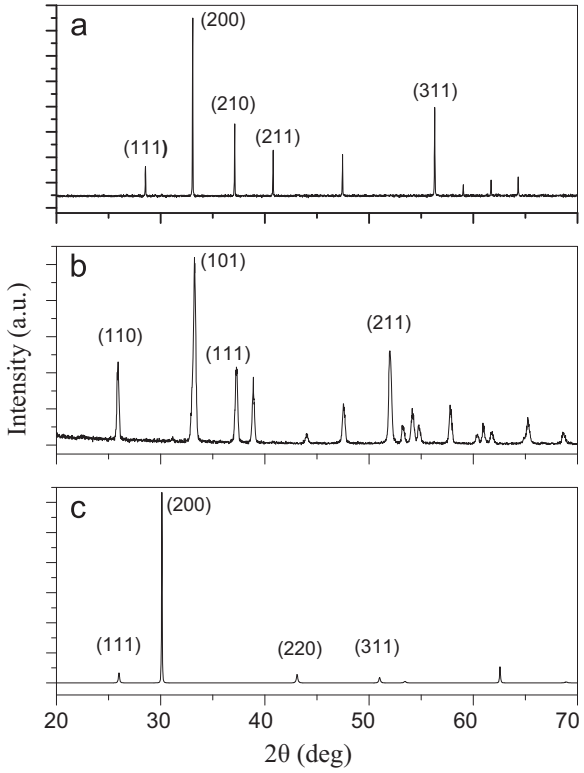

Fig. 1. XRD patterns of (a) pyrite (FeS_2), (b) marcasite (FeS_2) and (c) galena (PbS) natural powders. Quoted diffraction planes are from standards: pyrite (JCPDS 00-042-1340), marcasite (JCPDS 00-037-0475) and galena (JCDPS 00-005-05927).

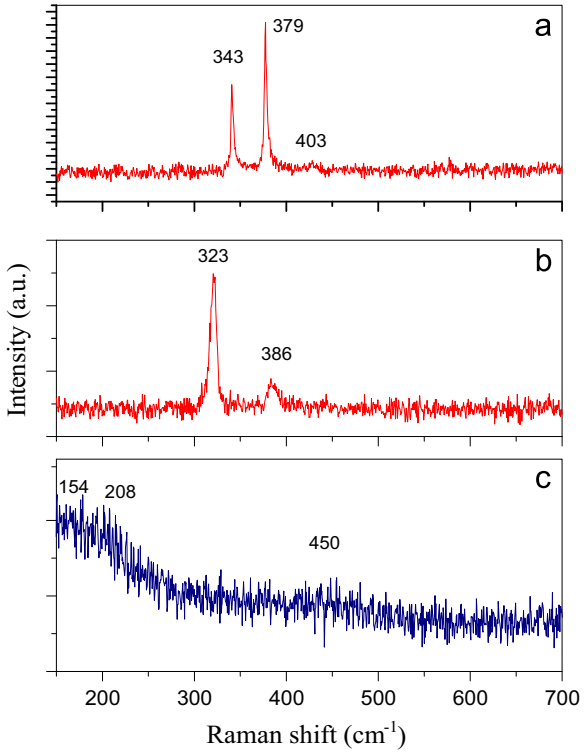

Fig. 2. Raman spectra of the three investigated minerals: (a) pyrite, (b) marcasite and (c) galena. Main obtained bands are indicated in the figure.

SEM observations proved that samples are homogeneous in particle size ($10-20\,\mu m$). EDX analysis of pyrite and marcasite showed the following results: marcasite appears under-stoichiometric ($\frac{S}{Fe} = 1.78 \pm 0.03$) i.e sulfur deficient as expected