

Upgradation and studies on semiconducting properties of pyrite (FeS_2) for device applications

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Pyrite (FeS_2) is a promising semiconductor material for photovoltaic applications. The paper reports the results of a systematic investigation of its various semiconducting properties in naturally occurring and upgraded form. The suitability for using this as an efficient thermoelectric generator material has been examined.

1. Introduction

Polycrystalline iron pyrite (FeS_2) is one of the candidate materials for photoelectrochemical and photovoltaic applications [1–3]. FeS_2 crystals in contact with an iodine/iodide-containing electrolyte have a high quantum efficiency [3]. The material is a semiconductor with an indirect bandgap of 0.9 eV. Its high electron mobility ($230 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [4] and high optical absorption coefficient ($\alpha > 6.0 \times 10^5 \text{ cm}^{-1}$ for $h\nu > 1.3 \text{ eV}$) are very favourable parameters for its application as a solar cell material. High contribution of d-states of the valence band have made this material important for photoelectrochemical application with high corrosion stability [5,6]. But no systematic attempts have so far been made to study the electrical, optical, thermoelectric, thermal, structural and other properties of this material in a comprehensive manner. On the other hand, a potential candidate material for solar energy applications need to be produced in large quantities at reasonable cost. In the light of the above facts and figures, a comprehensive programme has been undertaken in our laboratory to develop a low-cost high-volume technology for production of reasonably pure

FeS_2 material and to explore the possibility of using this material as an efficient thermoelectric generator material. This paper reports the results of the studies on structural, electrical, optical, thermal and thermoelectric properties of the material and its upgradation by a simple process as the first phase of our programme.

2. Experimental

Naturally occurring FeS_2 specimens in the form of cubes (1.5 cm^3) were collected from Amjor mines of Orissa, India. The specimens were thoroughly cleaned by mechanical separation of undesirable contaminants on its outer surfaces and then crushed into fine powders ($10 \mu\text{m}$) with the help of a porcelain jar ball mill. This mass was further grinded by a ball mill under wet condition (water). The slurry material obtained after grinding operation was then transferred to a flotation cell of a froth flotation apparatus for beneficiation (upgradation); see fig. 1. During flotation, sodium silicate was added to depress the silica gangs present in the slurry and then a few drops of potassium ethyle xanthate (PEX) was added for

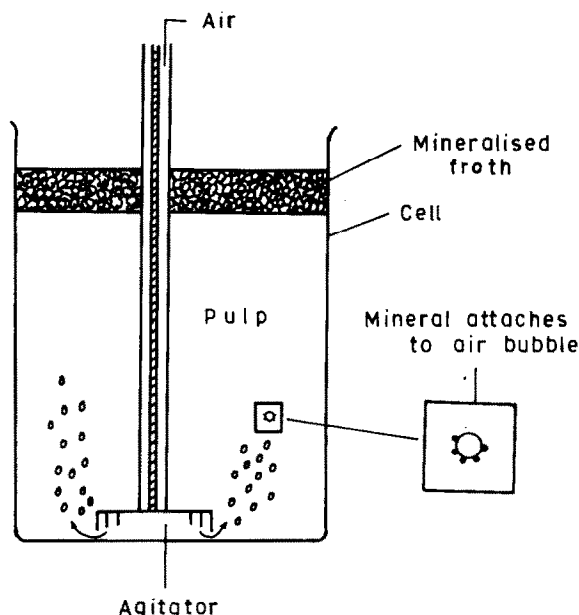


Fig. 1. Schematic diagram of the froth flotation apparatus.

aggregating the FeS_2 particles. During this operation the pH of the pulp was maintained at 9.5 by adding a calculated amount of NaOH. The material obtained from the froth was washed with deionised water. This beneficiated material was then pelletised by a hydraulic press applying 4 ton/square inch pressure. X-ray diffraction studies on both the natural and beneficiated material were undertaken using a Philips X-ray diffraction unit (model PW 1710, Mo $K\alpha$ radiation). In order to examine the defect in a typical natural specimen, the surface of the crystalline block was chemically etched applying a chemical etchant ($\text{CH}_3\text{COOH}:\text{HF}:\text{HNO}_3 = 1:1:1$) for about 30 s. The etched surface was then rinsed with deionised water. Immediately after the drying of the etched surface, its scanning electron micrograph was taken (Camscan, series 2 DV with link system). The chemical composition of naturally occurring and beneficiated materials were also ascertained by EDX analysis studies. Studies on the temperature variation of their resistivities were conducted by adopting a two-probe technique. Silver paint contact was found to be Ohmic for both the samples. The thermoelectric power of the natural specimen block was measured in the temperature range 300–425 K. DTA and TGA analyses of both specimens were undertaken

from room temperature to 523 K using a thermal analyser (Stanton Redcraft thermal analysis system). The reflectance of a typical natural specimen was studied in the spectral range 0.7–1.8 μm with the help of a spectrophotometer (Beckman UV-VIS-NIR-5270).

3. Results

The X-ray diffractograms of natural and beneficiated FeS_2 were taken. The calculated d -values of all the diffraction lines for both the specimens were compared with their standard d -values and they are listed in table 1. All the diffraction peaks were found to correspond to FeS_2 and there were no peaks for excess Fe or S indicating complete reaction of the components. The scanning electron micrograph of an etched surface is shown in fig. 2. The micrograph revealed linear pits formed due to etching of impurities from the surface. EDX analysis of both the materials indicated that they were stoichiometric (S/Fe was 1.98). Beneficiation of the material resulted in a reduction of the concentration of impurities like Si, Ti, Cd, Al (table 2). However, the concentration

Table 1
Comparison between the standard d -values calculated from X-ray diffractograms of natural and beneficiated samples

Sample	Calculated d -values (nm)	Standard d -values (nm)
natural pyrite	0.3116	0.3128
	0.2667	0.2709
	0.0821	0.0826
	0.0819	0.0817
beneficiated pyrite	0.3122	0.3128
	0.2713	0.2709
	0.2421	0.2428
	0.2213	0.2212
	0.1921	0.1912
	0.1642	0.1632
	0.1573	0.1564
	0.1511	0.1503
	0.1457	0.1448
	0.1221	0.1211
0.1116	0.1106	
	0.1050	0.1043

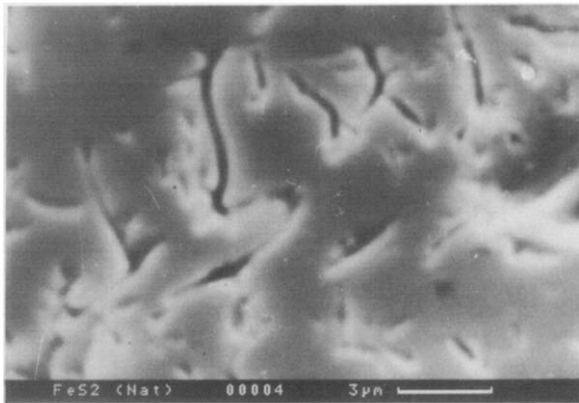


Fig. 2. Scanning electron micrograph of an etched surface of natural pyrite.

Table 2
Results of EDAX of natural and beneficiated samples

Elements present	At. %	
	natural FeS ₂	beneficiated FeS ₂
Fe	33.44	33.74
S	65.46	65.74
Si	00.72	00.13
Ti	00.14	00.05
Cd	00.08	00.06
Al	00.15	00.07
K	00.01	00.21

of K in beneficiated specimen was found to increase. The temperature variation of the conductivities is shown in figs. 3a and 3b. As compared to the natural sample the resistivity of the beneficiated sample was found to be higher at all temperatures. The thermal activation energies were calculated from those curves and they were found to be 0.096 and 0.0044 eV for the natural sample and 0.148 eV for the beneficiated sample. The temperature variation of the thermoelectric power of the natural specimen is shown in fig. 4. Fig. 5 shows the variation of the thermal conductivity with temperature of the same sample. Figs. 6a and 6b show the DTA and TGA records of the materials from 303 to 523 K. The reflectance spectrum of a polished natural sample is shown in fig. 7.

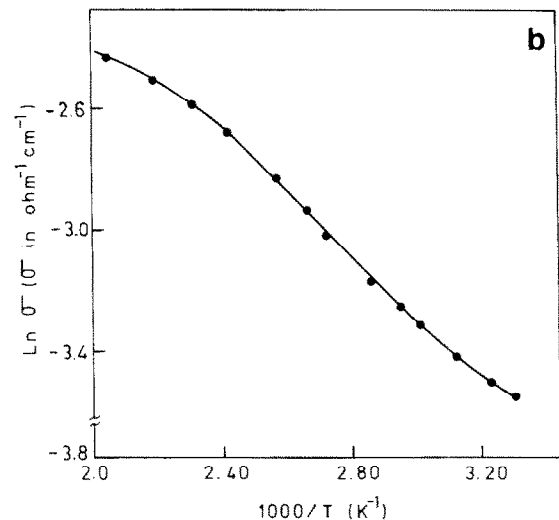
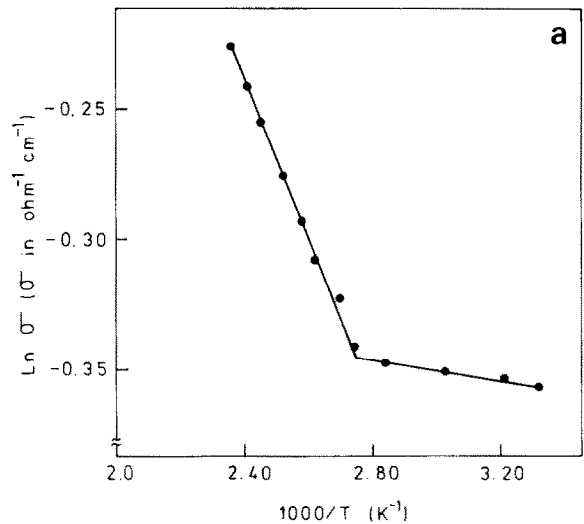


Fig. 3. (a) Temperature variation of conductivity of natural sample. (b) Temperature variation of conductivity of beneficiated sample.

4. Discussion

The X-ray diffraction results of both natural and beneficiated materials indicated that the materials were essentially polycrystalline. The appearance of a smaller number of diffraction peaks for a natural specimen suggested that in this material the grains were more oriented. The EDX analysis on the other hand indicated that both materials were stoichiometric. The beneficiation could upgrade the material

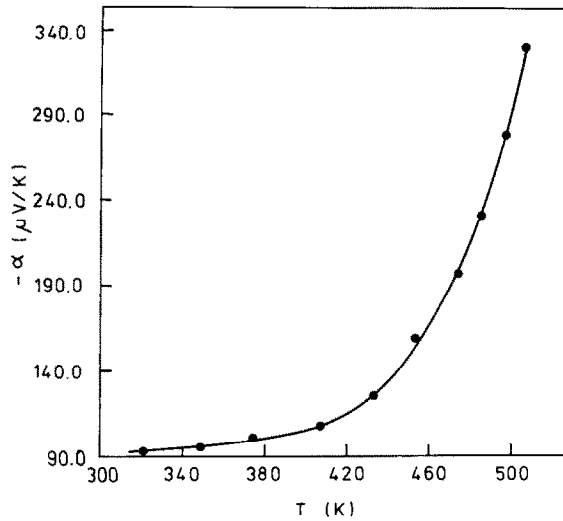


Fig. 4. Temperature variation of thermoelectric power of natural sample.

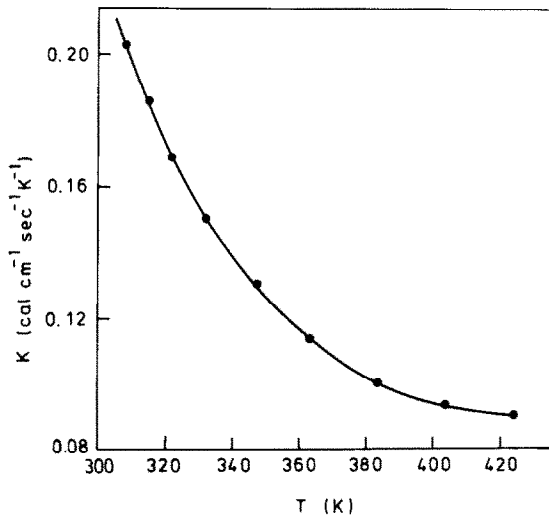


Fig. 5. Variation of thermal conductivity with temperature of natural sample.

which was revealed by the fact that beneficiation could substantially reduce the concentration of Si, Ti, Cd and Al impurities in the material (table 2). Increase in potassium content in the beneficiated product was due to the addition of potassium ethyle xanthate (PEX) in the process of beneficiation. However, it is believed that thorough cleaning of the material after beneficiation would eliminate the

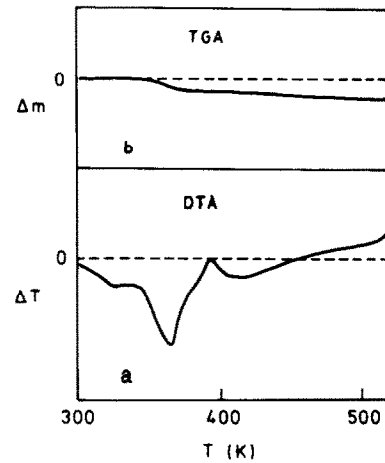


Fig. 6. (a) DTA and (b) TGA records of natural pyrite (FeS₂).

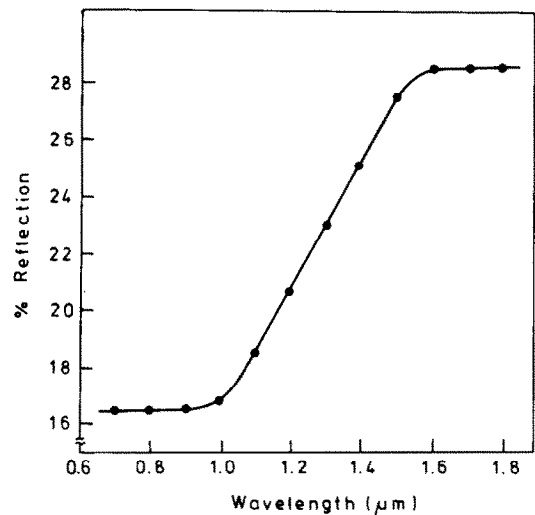


Fig. 7. Reflectance spectrum of polished natural sample.

presence of potassium even in traces in the material. The studies on temperature variation of resistivities of both the materials indicated the presence of shallow impurity states in the energy gap. The room-temperature resistivities of natural and beneficiated materials were found to be 1.4 Ω cm and 35 Ω cm respectively. The higher resistivity of the beneficiated and pelletised specimen may be attributed to a looser packing of the particles as compared to the natural specimen. Increase of pressure during pelletisation and annealing of the pellets in inert at-

mosphere would decrease the resistivity of this material. It may be mentioned here that both specimens, however, did not show any photoconductivity when shined with light of appropriate energy. The temperature variation of the electrical conductivity of the materials indicated that they were non-degenerate semiconductors. Both thermoelectric power measurement and hot probe test on the materials showed that they were n-type.

For a non-degenerate semiconductor, the variation of thermoelectric power (α) with carrier concentration is given by

$$\alpha = (k/q)[A + \ln(N_c/n)], \quad (1)$$

where A is a constant, k is Boltzmann's constant, q is the electronic charge and n is the carrier concentration. However, the value of A depends on the nature of carrier scattering. Considering the effect of temperature on thermoelectric power, eq. (1) can be written as

$$\alpha = (k/q)[A + (E_c - E_f)/kT]. \quad (2)$$

Differentiating with respect to T one gets

$$\frac{d\alpha}{dT} = \frac{k}{q} \left(\frac{dA}{dT} + \frac{1}{kT} \frac{d(E_c - E_f)}{dT} - \frac{E_c - E_f}{kT^2} \right). \quad (3)$$

Since dA/dT is not very high, the second and the third term inside the large parentheses in (3) will contribute more effectively to the value of $d\alpha/dT$. Again because of thermal generation of carriers at low and moderate temperatures, the term $d(E_c - E_f)/dT$ is expected to be negative causing a reduction of thermoelectric power with increase of temperature. But in our present investigation on FeS_2 this variation showed an opposite behaviour, i.e. the thermoelectric power increased with increase of temperature. Similar observations were reported earlier by Venkataraman [7] and Subba Rao [8] for p-type CuInSe_2 and SnSe respectively. Such contradiction may possibly be attributed to the fact that $d(E_c - E_f)/dT$ may sometimes be positive if electron traps play a dominant role at higher temperatures [7]. Apparently, however, the observed thermoelectric power variation in our material is found to be useful as thermoelectric generator material. The thermal conductivity of the naturally occurring samples on the other hand decreased with increase of temperature (fig. 5). This behaviour also suggests that the ma-

terial can be used as a thermoelectric generator material for a wide range of temperatures. The DTA and TGA analysis of FeS_2 clearly indicated the thermal stability of the material up to 523 K. When heated at a uniform rate the material showed an initial loss in weight which may be attributed to the moisture loss from the material. An endothermic peak in the DTA record around the same temperature range supported this viewpoint. On further heating, the sample did not exhibit any change in DTA or TGA pattern. The reflectance spectra (fig. 7) of the natural specimen showed a sharp edge around $1.3 \mu\text{m}$ which corresponds to an energy gap of 0.95 eV. Similar results in the spectral reflectance of synthetic polycrystalline FeS were also obtained by photoelectrochemical measurements by Ennaoui et al. [3] and in optical absorption measurement by Schlegel and Wachter [9].

5. Conclusion

The results of our investigations on naturally occurring and beneficiated FeS_2 material indicated that this material will in future find potential applications as a solar energy material, provided an appropriate technology for its mass scale production is developed. Further systematic studies on this material are needed on grown crystals to establish its suitability as an efficient thermoelectric generator material. Work in this direction is in progress in our laboratory.

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