

# Low-cost solar selective absorbers from Indian galena

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**Abstract.** The main thrust of our research is to prepare a low-cost solar-selective absorber from an indigenous semiconducting mineral, galena (galena aggregate and galena concentrate), for a solar thermoelectric generator. We report the results of preparation and characterization of solar-selective coatings made from galena aggregate and galena concentrate collected from the Zawar mines in Rajasthan, India. The coatings of galena are prepared by a thermal evaporation technique and exhibit high absorptivity ( $\alpha \sim 0.95$  and  $0.97$ ) in the solar spectral range and low emissivity ( $\epsilon$  375~0.21 and 0.27) in the thermal range. Finally, these coatings were compared with synthesized PbS coating prepared in our laboratory and found to be quite comparable. The structure and composition of the coatings were studied by x-ray diffraction and electron spectroscopy for chemical analysis. Reflectance and absorption studies were made in the 0.3- to 3.1- $\mu\text{m}$  spectral range.

*Subject terms:* solar thermoelectric generators; selective absorbers; galena; x-ray photoelectron spectra.

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## 1 Introduction

In recent years interest has increased in the production and characterization of high-thermal-stability selective surfaces that have high solar absorptance  $\alpha_s$  and low thermal emittance  $\epsilon_{th}$ . Different techniques such as thermal evaporation, spray pyrolysis, ion-beam sputtering, and chemical techniques have been utilized to prepare several coatings of high  $\alpha_s$  and low  $\epsilon_{th}$  values. Attempts have been made<sup>1–4</sup> with different types of interference stacks such as metal-dielectric, semiconductor-dielectric,<sup>2,3</sup> and dielectric-metal-dielectric<sup>1</sup> for use as solar-selective surfaces. Lead sulfide has application in the manufacture of Q-switches for lasers and solar-absorbing thin films where higher absorptance-to-emissivity ratios can be achieved than with other semiconducting materials.<sup>5–7</sup> Reddy et al.<sup>4</sup> studied the solar absorptance and thermal emittance of multistack PbS/CdS layers deposited chemically on different metal substrates such as copper and stainless steel. Martin, Netterfield, and Sainty<sup>8</sup> produced PbS films on glass substrates with aluminum base coats by the ion-beam deposition technique and improved the solar absorptivity and hardness of the films produced by other methods. Although different techniques such as vacuum evaporation,<sup>9</sup> dip-dry,<sup>10</sup> and spray pyrolysis<sup>6,11</sup> have been used to prepare pure lead sulfide films for use as selective absorbers, no such effort has been made to use Indian galena ore for solar-selective surfaces. Due to its large reserve ( $\sim 10^{10}$  kg), if galena can be used for solar-selective surfaces, the cost of the surfaces can be reduced considerably.

This work is an extension of our previous work<sup>12–16</sup> for the purpose of making low-cost solar thermoelectric generators from Indian galena.

In the present investigation, the viability of Indian galena ore for solar-selective surfaces is tested and the performance of the surfaces is compared with the performance of PbS films of synthesized material also prepared in our laboratory.

## 2 Experimental Methods

### 2.1 Raw Materials

The crystalline form of natural galena aggregate and galena concentrate obtained from the Zawar mines was used in the present study. Galena aggregate is available in certain pockets of the mines in the form of a vein or in chunk form. Galena concentrate is beneficiated galena obtained by the froth flotation technique and is generally used for manufacturing lead.

### 2.2 Synthesis of Lead Sulfide

Pure lead (99.99%) in the form of sheet was abraded in the presence of acetone to remove the oxide coating. A stoichiometric proportion of lead and sulfur (99.99%) was carefully weighed by a Mattler balance. Finally, lead and sulfur were poured into a quartz ampule and a tightly fitting quartz rod was pressed on the lead chips. Just above the quartz rod, a capillary was drawn out. The quartz tube was then evacuated to  $1.33 \times 10^{-3}$  Pa pressure and sealed. The ampule was heated at 970 K for 120 h in a tubular furnace and then quenched in a bucket of water. The ampule was broken and the charge (PbS) was ground in the presence of acetone.

### 2.3 Preparation of Thin Films

The glass substrates were degreased with a warm soap solution and rinsed in water. Then the substrates were cleaned with warm chromic acid for 5 min and, finally, washed with deionized water. Galena aggregate, galena concentrate, and synthesized lead sulfide were deposited onto the glass sub-

strates under a vacuum of the order of  $10^{-4}$  Pa at a substrate temperature of 575 K with the help of a Hind Hivac Vacuum coating unit (Model 12-A4). The deposition rate for all the films was maintained the same ( $\sim 30$  nm/min). The thickness of the film was measured with the help of a Taylor-Hobson Form Talysurf. The mechanical and thermal stabilities of the films were tested by conventional testing methods.

#### 2.4 X-Ray Diffraction Studies

To identify the compounds present in galena aggregate, galena concentrate, and synthesized PbS films, x-ray diffraction studies were performed using a Rigaku Miniflex x-ray diffractometer. The diffractograms were recorded from 20- to 120-deg angles with  $\text{CuK}_\alpha$  radiation and a scanning speed of 2 deg/min. The  $d$  values were calculated from the peak positions using Bragg's law and compared with the standard  $d$  values as given in ASTM Powder Diffraction File, Card No. 5-0592. The observed  $d$  values are in good agreement with the standard values, which confirms that the materials are PbS.

#### 2.5 Composition Analysis

Electron spectroscopy for chemical analysis was used to study the composition of the prepared films. X-ray photoelectron spectra (XPS) were recorded by a VG ESCA LAB MK II spectrometer using  $\text{AlK}_\alpha$  (1486.6-eV) radiation operated at 12 kV and 10 mA. All the narrow scans were recorded at 50-eV pass energy while the analyzer chamber was maintained at  $1.33 \times 10^{-7}$  Pa. Before recording the spectra, the specimen was cleaned with  $\text{Ar}^+$  ions. For quantitative analysis, the areas under each of the photoelectron peaks were estimated after a correction for background. Atomic percentages were obtained with the published values of sensitivity factors.<sup>17</sup> Because of uncertainties in the published values of sensitivity factors and in the selection of background correction, the quantitative estimation is correct within 15 at. % within the XPS detection limit  $\sim 5$  nm from the surface.<sup>17</sup> Under the instrumental conditions employed, the energy resolution of the spectrometer was 0.92 eV. For the analysis, Pb ( $4f_{7/2}$ ) and S ( $2p_{3/2}$ ) photoelectron peaks were taken into consideration (Fig. 1). The peaks were identified with different electron-binding energy positions of pure elements. The binding energy of carbon, i.e., peak at 285 eV, was taken as the energy reference.<sup>18</sup>

#### 2.6 Absorptance and Emittance Measurements

Solar absorptance and thermal emittance (at 375 K operating temperature) were measured using an alphanometer (Model 1A) and emissometer (Model 1E) from the Devices and Services Co.<sup>19</sup> With these instruments, one can conveniently measure the solar-absorptance and thermal-emittance values of a solar-selective absorber over a large area. Those parameters were also measured after an interval of 6 months to ascertain their aging effect.

#### 2.7 Spectrophotometric Measurements

Optical absorption and total reflectance of the films were measured by a Carry 17D spectrometer for 0.3- to 3.1- $\mu\text{m}$  wavelengths. The band gaps of the samples were estimated from the absorption spectra of the films.

#### 2.8 Surface Morphology

The surface morphology of the films was studied with a scanning electron microscope (SEM) (Camscan Series, 2DV, AN 1258, Model No. 5108). The grains of the films were revealed well by vapor etching with Fackerd's solution. Typical scanning electron micrographs of galena aggregate, galena concentrate, and synthesized PbS films deposited on glass substrates are shown in Fig. 2.

### 3 Results and Discussion

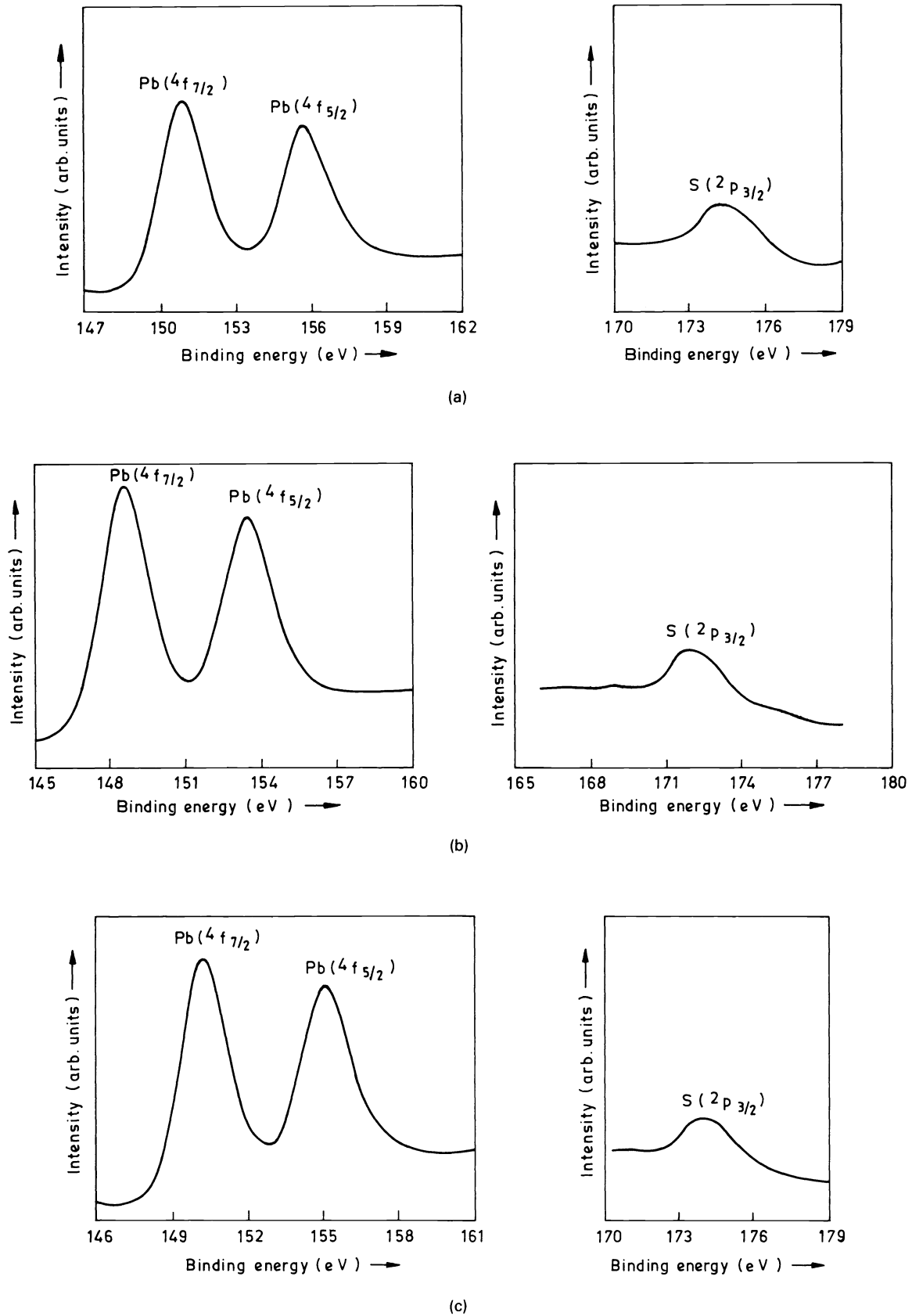
During the deposition of the films it was noted that the films deposited at room temperature or at lower temperatures and at higher deposition rates do not stick well to the substrates. A large number of pores appear within a few hours of removing the films from the evaporation chamber, even when they were kept in a vacuum desiccator. Similar observations have also been reported.<sup>20</sup> By trial method, a minimum substrate temperature of 575 K and a maximum deposition rate of about 30 nm/min were found to be satisfactory.

X-ray diffractograms of galena aggregate, galena concentrate, and synthesized PbS films deposited on glass substrates show a number of well-defined peaks corresponding to the peaks of cubic lead sulfide. These peaks indicate that the films are polycrystalline in nature. The  $d$  values corresponding to the peaks were calculated and compared with the standard  $d$  values of PbS. The calculated  $d$  values for these films are given in Table 1.

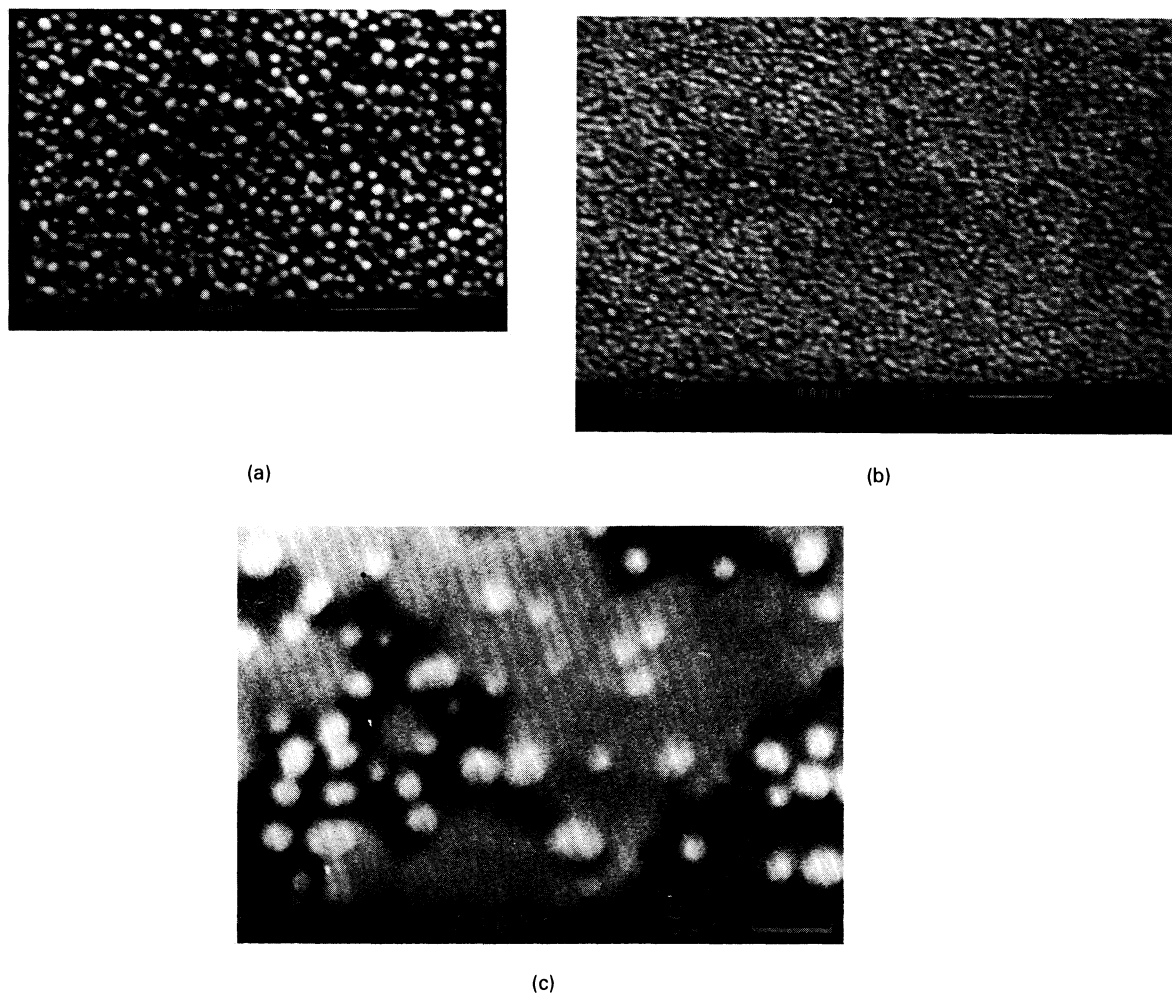
The surface morphologies of the typical films of galena aggregate, galena concentrate, and synthesized PbS SEM photomicrographs are shown in Fig. 2. Without etching, the surface texture of the film was not revealed. The texture of the film was revealed properly only after etching with Fackerd's solution vapor. All the films show a well-defined globular surface texture in SEM observation, of course with a difference in the dimension of the crystallites.

The films of synthesized PbS show a higher crystallite size than that obtained for galena aggregate and concentrate films. For the films of galena concentrate, the crystallite size is considerably small. However, the dimension of the crystallite for our films of synthesized material is remarkably bigger than the reported values of the same for thermally evaporated or ion-beam-sputtered films.<sup>8</sup>

From the optical absorption measurement, it is seen that the films have a strong absorption, ending at the long-wavelength end of the absorption spectrum at  $\lambda \approx 1.0 \mu\text{m}$  (corresponding to an energy of about 1.2 eV) at room temperature, and a weaker tail extending to 0.4 eV. Similar observations were also reported by Avery,<sup>21</sup> Gibson,<sup>22</sup> and Paul and Jones,<sup>23</sup> for PbS layers and single crystals. Plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for the films of galena aggregate, galena concentrate, and synthesized PbS are shown in Fig. 3, respectively. The absorption data fit well only for  $(\alpha h\nu)^2$  versus  $h\nu$  plots, which indicates that the transition corresponds to band-to-band transition. The direct band gaps for the materials are estimated from the  $x$ -axis intercepts and are listed in Table 2. The measured band gap for the galena aggregate material is slightly higher (0.477 eV) than the band gap measured for galena concentrate and synthesized PbS. The band gaps of galena concentrate and synthesized PbS (0.415 and 0.412 eV, respectively) are very close to the band gaps of PbS reported by Moss<sup>24</sup> and slightly higher than the value reported by



**Fig. 1** XPS peaks of lead and sulfur; full scales were 10 and 3 K for lead and sulfur, respectively: (a) galena aggregate, (b) galena concentrate, and (c) synthesized PbS.



**Fig. 2** Surface morphology of typical coated films: (a) galena aggregate, (b) galena concentrate, and (c) synthesized PbS.

Scanlon<sup>25</sup> from their optical and electrical measurements, respectively. However, a small variation in band gap for the three materials may be due to a variation of the Pb-to-S ratio. The values of the Pb to S atomic percent ratios for these films obtained from XPS study are also given in Table 2.

Figure 4 presents the total reflectance spectra for the films in the 0.3- to 2.1- $\mu\text{m}$  spectral range. From the spectra it is observed that the reflectance in the visible region for all the films is very small, and this is the primary and necessary condition for selective absorbers. The total reflectance for all the films increased considerably with the increase of wavelength. Throughout the region of measurement, the reflectance of the films of concentrated galena is higher than the same for the other films. However, the nature of variation of reflectance in all three films is the same.

The solar absorptance  $\alpha_s$ , thermal emittance  $\epsilon_{th}$ , and selectivity of typical vacuum-evaporated galena concentrate, galena aggregate, and synthesized PbS films are given in Table 2. From the results it is observed that  $\alpha_s$  and  $\epsilon_{th}$  for galena aggregate and galena concentrate are comparable and their selectivity is not too much less than the selectivity of the synthesized material. It is also observed from the results that the galena aggregate has a better selectivity than the

concentrated material. This might be due to the purity of the material. The percentage of PbS in galena aggregate is more than in the concentrate.<sup>26</sup>

From the environmental testing we observed that thermal shock and humidity did not degrade the films appreciably. Storage in air for 6 months also does not alter the optical properties much.

#### 4 Conclusions

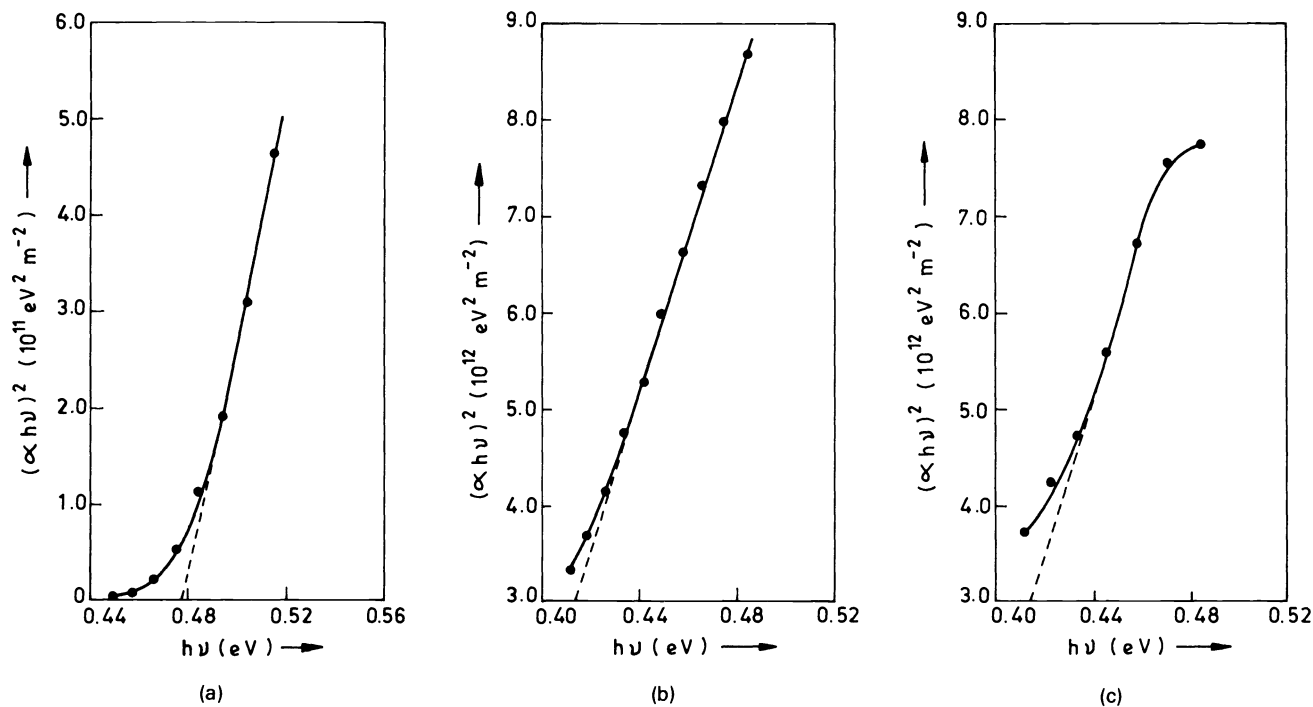
The results obtained in this study indicate that galena aggregate and concentrate can be used as low-cost high-temperature solar-selective surfaces and may be a good replacement for high-purity materials. The coatings possess good resistance to humid weather and temperature. Optical properties of the films are reproducible. Thus, it would be possible to prepare low-cost galena-based selective surfaces for high-temperature (up to 600 K) applications, which might be useful for solar thermoelectric generators.

The reflectance of the films in the visible range of the solar spectrum is considerably lower than the same obtained by Martin<sup>8</sup> and Reddy<sup>4</sup> for their ion-beam-sputtered and chemically deposited PbS films. The reflectance can be further reduced by using a thin antireflective coating.<sup>27</sup>

**Table 1** X-ray diffraction lines of a typical vacuum-coated galena aggregate, galena concentrate, and synthesized PbS film.

Line No.	Galena Aggregate		Galena Concentrate		Synthesised PbS		Standard values of * Lead Sulphide	
	2θ(deg)	d(nm)	2θ(deg)	d(nm)	2θ(deg)	d(nm)	Standard "d" in nm	Identification
1	26.20	0.3410	26.40	0.3376	25.95	0.3433	0.3429	PbS (111)
2	29.90	0.2988	30.53	0.2928	30.10	0.2969	0.2969	PbS (200)
3	43.00	0.2103	43.52	0.2079	43.05	0.2101	0.2099	PbS (220)
4	50.95	0.1792	51.45	0.1776	50.85	0.1795	0.1790	PbS (311)
5	-	-	53.96	0.1699	53.35	0.1717	0.1714	PbS (222)
6	62.50	0.1486	63.00	0.1475	62.50	0.1486	0.1484	PbS (400)
7	68.90	0.1362	69.50	0.1352	-	-	0.1362	PbS (331)
8	70.95	0.1328	71.485	0.1319	70.90	0.1329	0.1327	PbS (420)
9	79.10	0.1210	79.46	0.1206	-	-	0.1212	PbS (422)
10	84.85	0.11427	85.50	0.1136	-	-	0.11424	PbS (511)
11	102.40	0.09891	-	-	102.36	0.09894	0.09893	PbS (600)
12	110.50	0.09382	-	-	-	-	0.09386	PbS (620)

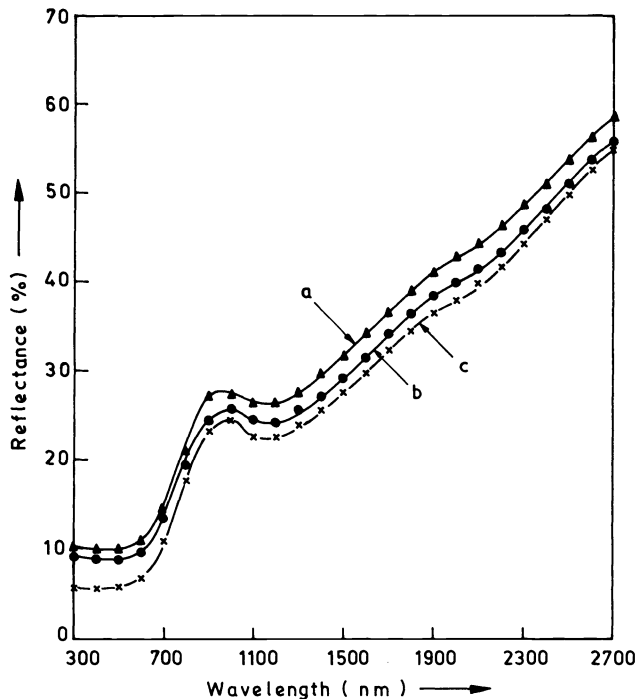
\* ASTM Powder Diffraction File, Card No. 5-0592



**Fig. 3** The  $(\alpha h\nu)^2$  versus  $h\nu$  plots of typical coated films: (a) galena aggregate, (b) galena concentrate, and (c) synthesized PbS.

**Table 2** Pb to S atomic percent ratio, band gap ( $E_g$ ), solar absorptance ( $\alpha_s$ ), thermal emittance ( $\epsilon_{th}$ ), and selectivity ( $S$ ) of typical vacuum-coated galena aggregate, galena concentrate, and synthesized lead sulfide film.

Material	Thick- ness, nm	Pb/S (atom%)	$E_g$ (eV)	$\alpha_s$	$\epsilon_{th}$ (at 375K)	Selectivity $S = \alpha_s / \epsilon_{th}$
Galena aggregate	195	1.32	0.477	0.95	0.21	4.52
Galena concentrate	205	1.70	0.412	0.92	0.27	3.41
Synthesised PbS	190	1.61	0.415	0.96	0.15	6.40



**Fig. 4** Reflectance spectra: (a) galena concentrate, (b) galena aggregate, and (c) synthesized PbS films.

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