Properties of artificially grown single crystals of galena

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The growth of high quality single crystals of PbS from natural galena is reported. From ESR spectra the presence in the lattice of isolated Mn^{2+} ions and an Fe^{3+} rich phase for the correspondingly doped crystals is inferred.

1. Introduction

Naturally occurring single crystals of PbS known as galena have been employed in the past as detectors in radioreceivers. Later, the production of high quality PbS crystals was stimulated by the interest in tunable lasers [1] and infrared detectors [2]. More recently, in studies related to the separation of galena from ores, the need for large single crystals of good quality arose [3]. For this purpose we decided to grow PbS single crystals directly from natural galena, to be used in such studies when large natural single crystals are not available.

Single crystals of PbS have been prepared by the Bridgman–Stockbarger technique [4–6] and by sublimation from vapours [7], using as the starting material elemental lead and sulphur. To our knowledge the successful use of PbS in growing single crystals has not been attempted. This paper reports the results of a study concerning the preparation and properties of single crystals of PbS grown directly from natural galena.

2. Experimental details

Use was made of relatively large (up to a few cm^3) pieces of native galena as the starting material for the PbS crystal growth. By visual inspection it was possible to select pieces of galena with a minimum amount of macroscopic inclusions and relatively flat cleavage surfaces (Fig. 1).

Cylindrical ampoules with a conical bottom made of fused silica were loaded up to 2 cm below the top with freshly crushed galena, about 25 g per charge. Immediately afterwards the ampoule was evacuated to 10^{-5} mm Hg, baked at about 250°C and sealed. It has been found that ampoules containing crushed galena which was kept in air for longer periods before sealing, usually exploded around 950°C. This phenomenon, due to oxygen adsorption and the formation of $PbSO_4$, could be avoided by reduction with hydrogen [8].

Crystal growth was performed by the Bridgman technique using standard crystal growth equipment [9]. The following parameters were used in the growth process: maximum temperature in the furnace $1140 \pm 10°C$, lowering speed 3 mm h^{-1}, temperature at the end of the growing phase 1000°C, travelling distance during the crystal growth 8 cm. The annealing time down to room temperature, after the power switch off, took about 20 h.

The single crystals were grown from natural galena to which 0.01 mol % of manganese or iron (Specpure from JMC Ltd., England) was added for the doping experiments.

3. Results and discussion

PbS single crystals with a diameter of 1.1 cm and typical length of 3 cm were obtained by this procedure. Contrary to the case of some PbS single crystals grown from elemental lead and sulphur in silica ampoules [7], in our case the single crystals did not stick to the wall, resulting in crackfree crystals with smooth outer surfaces. The cleavage could be done easily, resulting in extremely flat mirrorlike (100) faces, without macroscopic inclusions or inhomogeneities. Fig. 2 exhibits the picture of a single crystal of PbS of which the upper 1 cm was removed by cleavage. To illustrate the flatness of the cleavage faces, the image by reflection of a smaller piece of crystal has been taken in the same picture. The similar sharp Laue patterns obtained at various points on (100) faces
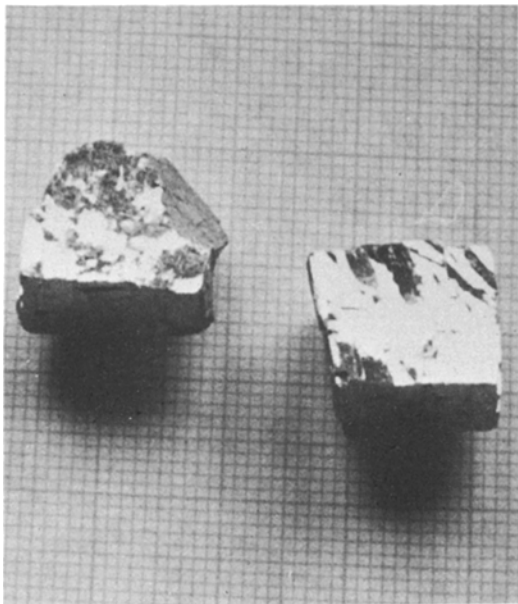
Figure 1 Selected pieces of natural galena used for growing PbS single crystals.

Figure 2 PbS single crystal grown from natural galena (on a mm scale paper).

as well as the narrow ESR (electron spin resonance) transitions of the isolated Mn^{2+} ions, to be discussed later, are also indications that a good crystal lattice was obtained. No specific assessment of the crystal lattice perfection has been attempted.

The impurity content in the starting material, as well as in the single crystals, has been determined by spectrographical analysis. The results of such measurements are presented in Table I. It is interesting to note that with the exception of antimony, the impurity content of the particular batch of natural galena used in our work was very low. Moreover, for the observed impurities the segregation effect is of little importance. (The presence of silicon in the as grown crystals is a contamination effect from the ampoule walls.) It should be noted that the above observations are strictly true for the middle part of the as grown crystals, for which the analyses were performed, and does not implicate that variations in the impurity content along the crystal axis were not possible.

In order to obtain information concerning the localization and charge state of the paramagnetic manganese and iron ions in the crystal lattice we performed electron spin resonance (ESR) measurements in the 9 GHz microwave frequency band by means of a JES-3M type of ESR spectrometer. No ESR spectra were observed at room temperature.
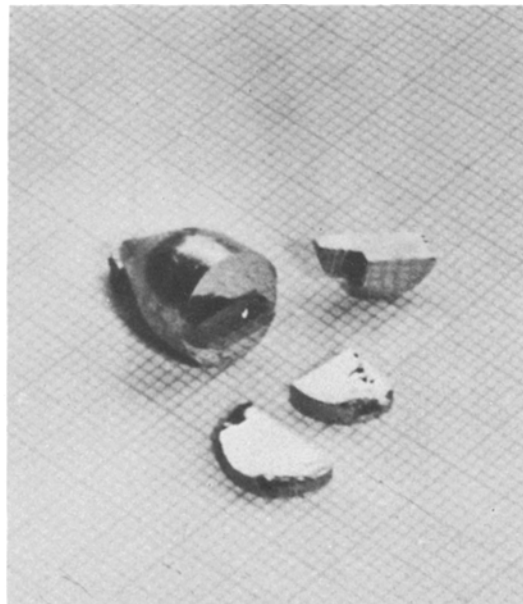
However, by decreasing the measuring temperature it has been possible to obtain ESR spectra from both types of impurities.

In the case of manganese doped crystals a characteristic 6 line isotropic structure (Fig. 3) due to the hyperfine components on the Mn^{2+} ions in the ^6S state, at cubic sites of the lattice [10], has been observed. The ESR spectrum can be described by the spin Hamiltonian

$$\mathcal{H}_S = g\beta\mathbf{HS} + A\mathbf{SI} \qquad (1)$$

The symbols employed have their usual meaning [10]. Based on the formula

$$H_m = H_0 - Am - \frac{A^2}{2H_0}\left(\frac{35}{4} - m^2\right)$$

describing the line positions H_m of the hyperfine components [11] and on their corresponding

TABLE I The impurities content (in ppm) of source material and resulting PbS single crystals as revealed by semiquantitative spectrographic analysis. The following elements were not detected: Be, Cr, Ni, Co, Bi, As, Ga, Ge, In, W, V, Mo, Tl, Te.

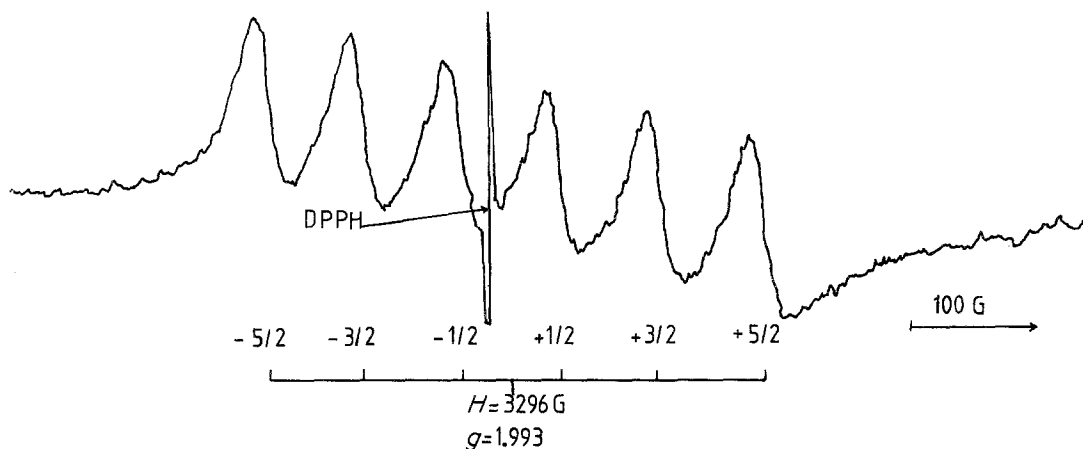| Material	Cd	Sb	Sn	Mn	Fe	Cu	Si
Natural galena	125	2160	22	–	–	38	–
Single crystal PbS	130	1900	55	–	–	28	50
Single crystal PbS 0.01 % Mn added	130	1950	50	165	–	30	50
Single crystal PbS 0.01 % Fe added	127	1970	52	–	130	32	50

Figure 3 The ESR spectrum of a PbS crystal doped in melt with 0.01 mol % manganese (PbS (0.01 % Mn), f = 9196 MHz, T = 110 K).

experimental values, the following values of the spin Hamiltonian parameters were obtained: $g = 1.993 \pm 0.003$ and $A = 7.6 \pm 0.05$ mT.

The hyperfine splitting parameter A is larger compared to the early determined [12] value of 7.18 mT, obtained from measurements at 1.3 K. This difference seems to be due to the temperature dependence of the hyperfine splitting [13]. From the above interpretation of the ESR spectra it results that the manganese ions are homogeneously distributed at isolated sites of the PbS lattice, very propably substituting the lead ions.

The single crystals grown from galena at which 0.01 mol % of iron was added in the melt exhibit an ESR spectrum consisting of a broad, isotropic line, at low values of the magnetic field (Fig. 4). The centre of this line (recorded as usual in ESR experiments as the derivative of the absorption) corresponds to an effective g value of 4.2 ± 0.1. The identification of the charge state and site localization of the iron is more difficult as several

such states are possible. Moreover no early experimental studies on iron doped PbS were reported. For this reason the general ESR properties of iron ions in crystal lattices have to be taken into consideration. The available data [10] suggest that the presence of either Fe^+ or Fe^{2+} states in our crystal are highly improbable. Due to a strong spin-lattice coupling, the ESR spectra of such ions could be observed only at lower temperatures (below 20 K). Trivalent iron exhibits a much weaker spin-lattice coupling, resulting in ESR spectra which could be observed in many cases even at room temperature and above [10]. The ESR spectrum arising from isolated Fe^{3+} ions consists of an odd number of relatively narrow lines, the central one being situated close to $g = 2$. However, this possibility is ruled out by our experimental results.

It is known from early studies [14, 15] that disordered structures like glasses doped with iron exhibit strong ESR transition situated at g values of 4.2 and 6. Such g-values have been explained as
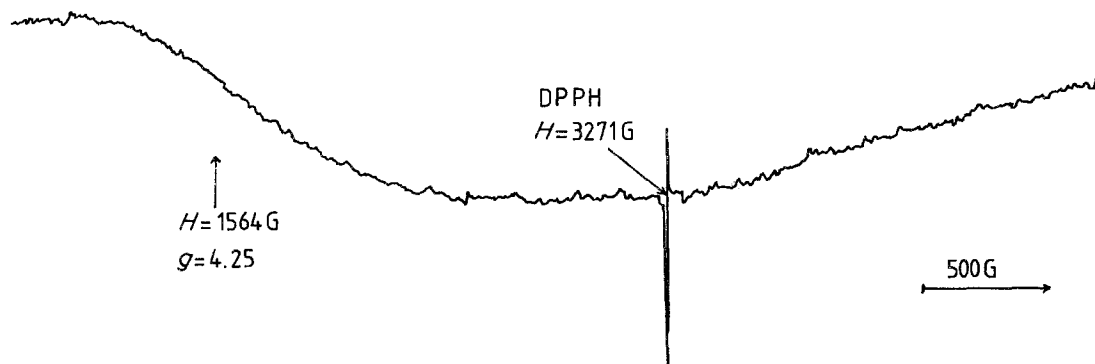

Figure 4 The ESR spectrum of a PbS crystal doped in melt with 0.01 mol % iron (PbS (0.01 % Fe), f = 9174 MHz, T = 110 K).

being due to the presence of local strong crystal fields with orthorhombic symmetry. Based on these results we conclude that the ESR spectrum observed in our iron doped PbS crystals is due to trivalent iron agglomerated as an iron rich phase in the crystal lattice. The resulting strong spin–spin interaction which occurs between the closed iron ions explains the large linewidth of the observed ESR spectrum.

We have attempted to study by X-ray powder diffractometry this iron rich phase but no supplementary reflexions from such a phase could be observed. The negative result was quite expected in view of the low iron content of our samples.

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