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# CRYSTAL GROWTH, CHARACTERIZATION AND PHOTOELECTROCHEMICAL PROPERTIES OF $Zr_{1-x}Ti_xS_3$ ($0 < x < .33$)

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ABSTRACT : We report crystal growth conditions, transport properties and preliminary photoelectrochemical properties of $Zr_{1-x}Ti_xS_3$ crystals of composition x = .07, .15, .25, .33. Their properties are compared to those of pure $ZrS_3$. It has been found that resistivity decreases with increasing titanium content, and the onset of photoresponse shifts to lower energies with a significant rise in quantum efficiency. We suggest that these results are related to the formation of a lower energy band consisting of titanium-like orbitals

## INTRODUCTION

Recently, lamellar compounds of the stoichiometry $MX_2$, such tungsten and molybdenum disulfide and diselenide (1), have received considerable attention as possible electrode materials for the conversion of solar energy in photoelectrochemical cells; however, relatively little is known about other lamellar semiconductors which might be suitable for the same application. The group IV A transition metal trichalcogenides such as $ZrS_3$ and $TiS_3$ crystallize with lamellar structures which are similar and show a wide range of optical and electrical properties. For example, the lowest optical transition of $TiS_3$ is around 1eV, while that of $ZrS_3$ is around 2eV (2). The room temperature resistivity of $TiS_3$ is around .1Ωcm, but there are conflicts concerning the electrical properties of $ZrS_3$. It has been reported to be greater than or equal to $10^3$Ωcm (3,5) except for one report of 15Ωcm (4).

The existing electrochemical studies on $ZrS_3$ (5) and $TiS_3$ (6) indicate that although $ZrS_3$ is somewhat stable in acidic media, the photocurrents are small. On the other hand, $TiS_3$ has larger photocurrents, but lacks stability in aqueous solution. These results suggest that an investigation of titanium substituted $ZrS_3$ might reveal a material having both larger quantum efficiencies in the region of the solar spectrum and reasonable stability in aqueous solution.

## EXPERIMENTAL

Single crystals of $ZrS_3$ and titanium substituted $ZrS_3$ were grown by chemical vapor transport using bromine.Sulfur powder (Johnson Matthey 99.999%) was purified by vacuum sublimation before use.Titanium powder (Johnson Matthey 99.99%) ana zirconium powder (Ventron 99.9%) were used as received. The composition of the ∿ 1.5g charge consisted of stoichiometric ratios of Zr or Ti and sulfur or a mixture of zirconium and titanium and sulfur. A concentration of 0.5 mg/cc $Br_2$ was used in 20cm X 10 mm id silica tubes. The charge compositions, product composition and growth conditions are summarized in table 1. Crystal growth proceeded for one week, after which the ampoules were air quenched to room temperature. The crystals were then removed from the tube, rinsed with acetone, and air dried. The composition of all samples was determined by microprobe analysis.

The electrical resistivity of all samples was measured using the four probe Van der Pauw technique. Ohmic contacts to the crystals were made by ultrasonic soldering of pure indium metal. The mobility of conducting samples was determined by D.C.Hall voltage measurements, and the carrier type was verified by qualitative Seebeck coefficient measurements.

X-ray diffraction studies were done using a Guinier camera (Enraf-Nonius FR - 552) employing Cu $k\alpha_1$ radiation with silicon as an internal standard. Cell parameters were calculated using a least squares refinement program with the aid of a computer.

TABLE I

Preparation conditions for $Zr_{1-x}Ti_xS_3$ single crystals

| Charge | Product | T charge | T growth |
|---|---|---|---|
| $ZrS_3$ | $ZrS_3$ | 900 | 784 |
| $Zr_{.9}Ti_{.1}S_3$ | $Zr_{.93}Ti_{.07}S_3$ | 900 | 784 |
| $Zr_{.7}Ti_{.3}S_3$ | $Zr_{.85}Ti_{.15}S_3$ | 800 | 686 |
| $Zr_{.5}Ti_{.5}S_3$ | $Zr_{.75}Ti_{.25}S_3$ | 800 | 686 |
| $Zr_{.3}Ti_{.7}S_3$ | $Zr_{.66}Ti_{.33}S_3$ | 800 | 686 |
| $TiS_3$ | $TiS_3$ | 625 | 530 |

Electrodes of titanium substituted $ZrS_3$ were prepared by making electrical contact to the crystals with silver paste. All metallic surfaces were then insulated with a silicon rubber sealant (Dow corning RTV-3145) so that only the surfaces perpendicular to the crystallographic c axis of the crystals were exposed. All electrochemical measurements were carried out using a conventional three electrode system with a potentiostat. The counter electrode was platinum and the reference electrode was the SCE. All potentials are reported with respect to the SCE. All measurements were done in 1M $H_2SO_4$, and solutions were made up using analytical grade acid and purified deionized water. Photoresponse studies were done using standard potentiostatic lock-in techniques and white or monochromatic light from a 75 watt tungsten-iodine lamp chopped at a frequency of approximately 500 Hz. Spectral response studies were carried out with the aid of a calibrated silicon photodiode (EGG PV-215), and quantum efficiencies were calculated relative to the same diode.

## RESULTS

Crystals of $ZrS_3$ and titanium substituted $ZrS_3$ crystallize with a platelet morphology and have minimum dimensions of 2mm x 1mm x .02mm. Microprobe analysis showed all materials to be stoichiometric within limits of the analysis ( ∿ 1%) and gave the compositions listed in table 1. $ZrS_3$ is red and all other materials were dark red to black. An examination of Guinier powder photographs of ground single crystals showed that all materials appeared isostructural. The calculated all parameters are listed in Table 2. The values of the cell parameters for $ZrS_3$ and $TiS_3$ are in good agreement with literature values (7).

TABLE 2
Crystallographic datas for $Zr_{1-x}Ti_xS_3$

| | a (Å) | b (Å) | c(Å) | β(Å) | V(Å$^3$) |
|---|---|---|---|---|---|
| $ZrS_3$ (ref.7) | 5.124 | 3.624 | 8.980 | 97.28 | 165.4 |
| $ZrS_3$ | 5.119 | 3.622 | 8.999 | 97.28 | 165.5 |
| $Zr_{.93}Ti_{.07}S_3$ | 5.109 | 3.612 | 8.922 | 98.18 | 162.9 |
| $Zr_{.85}Ti_{.15}S_3$ | 5.092 | 3.591 | 8.961 | 97.43 | 162.5 |
| $Zr_{.75}Ti_{.25}S_3$ | 5.085 | 3.577 | 8.953 | 97.59 | 161.4 |
| $Zr_{.66}Ti_{.33}S_3$ | 5.069 | 3.554 | 8.981 | 97.68 | 160.3 |
| $TiS_3$ | 4.961 | 3.401 | 8.758 | 97.41 | 146.6 |
| $TiS_3$ (ref.7) | 4.958 | 3.400 | 8.778 | 97.32 | 146.8 |

a, b ± .003   c ± 0.1   β ± .07

The results of room temperature resistivity and Hall measurements are given table 3. Qualitative Seebeck coefficient measurements showed all materials to be n-type. $ZrS_3$ was found to be a high resistivity material ( $\rho > 10^5 \Omega cm$). Temperature dependent resistivity measurements of $Zr_{.93}Ti_{.07}S_3$ gave an activation energy of approximately .16 eV, indicating that these materials are extrinsic semiconductors.

Cyclic voltammograms of $Zr_{1-x}Ti_xS_3$ ( $0 \leqslant x \leqslant .33$) photoanodes showed good diode-like behavior in aqueous solution, as is shown for $Zr_{.75}Ti_{.25}S_3$ in figure 1. The onset of photocurrent for all samples examined was more negative than -100 mV, indicating that the flat-band potential is more negative or equal to -100 mV for these materials. Increasing content

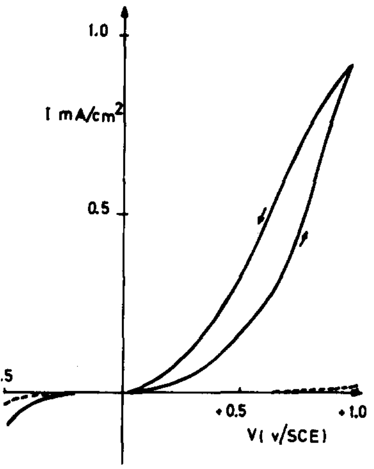

FIG. 1
Voltammogram of $Zr_{.75}Ti_{.25}S_3$ in 1M $H_2SO_4$ dark current (dash line) and photocurrent (solid line) v.s. SCE

of titanium in $Zr_{1-x}Ti_xS_3$ resulted in larger photocurrents as can be inferred from the results presented in the next section.

The spectral responses of $Zr_{1-x}Ti_xS_3$ were measured at two different anodic biases, IV and .5V, because the photoresponse of $ZrS_3$ is too small for spectral response measurements at .5 V.

The results are presented in figure 2 and figure 3, the small Hall mobility measurements indicate that the conditions under which quantum efficiency is proportional to the absorbtion coefficient were most likely satisfied; however, in general, the fits to the linear functions normally used to determine the energy of optical transitions, (in this case these are $(\eta h\nu)^{\frac{1}{n}}$ where n = 2 for indirect allowed transitions, n = ½ for direct allowed transitions) (8) showed irregularities at higher energies probably as a result of the complexity of the spectra. None the less, there is evidence of a new interband optical transition occuring before 2eV in all the substituted materials, and the magnitude of the quantum efficiency of this transition appears to be related to the degree of titanium substitution in $ZrS_3$. The spectra show that increasing titanium content in $Zr_{1-x}Ti_xS_3$ results in increased quantum efficiencies and, as observed, larger relative photocurrents under white light. Table 4 shows the approximate value of the lowest energy optical transition for he compositions studied. For x < .3 these transtions appears to be indirect. These values have a precision of about ± .05 eV and the values of the quantum efficiencies have a relative error on the order of 10%.

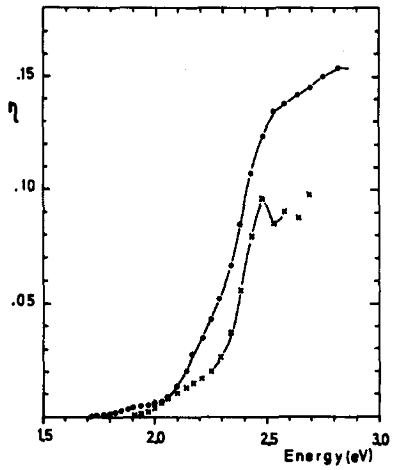

FIG 2
Quantum efficiency v.s. energy (ev) for $ZrS_3$ (x) and $Zr_{.93}Ti_{.07}S_3$ (°) at 1 v bias in 1M $H_2SO_4$.

TABLE 3

Transport properties of $Zr_{1-x}Ti_xS_3$

| | $\rho$ ($\Omega$cm) | $\mu$ ($cm^2$/V.s.) | n ($cm^{-3}$) |
|---|---|---|---|
| $ZrS_3$ | $>10^5$ | - | - |
| $Zr_{.93}Ti_{.07}S_3$ | ∿ 200 | 1.5 | $1x10^{16}$ |
| $Zr_{.85}Ti_{.15}S_3$ | ∿ 100 | 1.5 | $1.5x10^{16}$ |
| $Zr_{.75}Ti_{.25}S_3$ | ∿ 50 | 3 | $4x10^{16}$ |
| $Zr_{.66}Ti_{.33}S_3$ | ∿ 20 | 4 | $7x10^{16}$ |
| $TiS_3$ | ∿ .1 | 31 | $2x10^{18}$ |

TABLE 4

First observed transition in photoresponses

| Composition | eV |
|---|---|
| $ZrS_3$ | ∿ 1.95 |
| $Zr_{.93}Ti_{.07}S_3$ | ∿ 1.8 |
| $Zr_{.85}Ti_{.15}S_3$ | ∿ 1.7 |
| $Zr_{.75}Ti_{.25}S_3$ | ∿ 1.6 |
| $Zr_{.66}Ti_{.33}S_3$ | ∿ 1.5 |

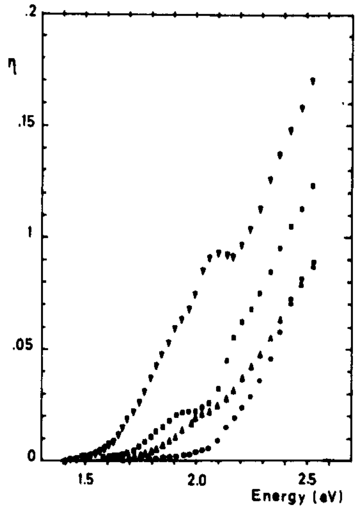

FIG. 3

Quantum efficiency vs energu (eV) for $Zr_{1-x}Ti_xS_3$ at. + .5 volts bias in 1M $H_2SO_{4=}$ : O , x = .07; Δ, x = .15; □ , x = .25; ∇, x = .33.

## DISCUSSION

Both $ZrS_3$ and $TiS_3$ crystallize with monoclinic lamellar structures having space group $P2_1/m$ (7). For simplicity only the structure of $ZrS_3$, illustrated in figure 4, will be dealt with here because the $TiS_3$ structure is related to it by a distortion of the coordination of the metal ion and a translation of the unit cell by one-half the length of the a axis. The $ZrS_3$ structure may be described in terms of layers consisting of a corrugated arrangement of linear chains of face-sharing trigonal prisms aligned parallel to the b axis.

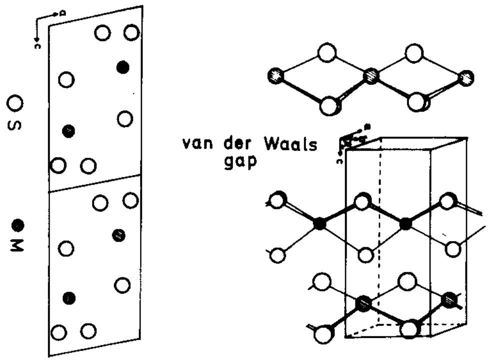

FIG. 4

Crystal structure of $ZrS_3$ : unit cell and a projection on (a, c) plane.

Crystallographic studies have indicated that the vertices trigonal prisms are made up of two types of sulfur groups,: four vertices are occupied by the sulfur atoms of sulfur-sulfur $S_2^{2-}$ pairs, and the remaining two vertices are $S^{2-}$ groups.The stoichiometry of the structure may thus be discribed as M (IV)($S_2^{2-}/S^{2-}$) giving the observed composition of M $X_3$. As a result of the arrangement of these chains of trigonal prisms within the layer, the Van der Waals surfaces of the structure which are roughly perpendicular to the c direction consist mainly of sulfur-sulfur pairs.

Due to the structural similarities of $ZrS_3$ and $TiS_3$, the possibility of the solid solution $Zr_{1-x}TiS_3$ exists, and expected contraction of the cell volume was observed.

The length of the a axis is an indication of the distance between chains in the structure, and the length of the b axis is indicative of the height of the trigonal prisms. The regular decrease in these two parameters, in addition to the monotonic decrease in the volume of the cell, verify that titanium is substituting for zirconium in the structure, but it cannot be verified if a significant amount of Ti is occupying insterstitial sites located, for example, in the Van der Waals gap.

The electrical properties of $Zr_{1-x}Ti_xS_3$ indicate that these materials are extrinsic semiconductors. The large difference in thermal stability between $TiS_3$ and $ZrS_3$, in other words, that above 560°C $TiS_3$ gives of sulfur to form $TiS_2$ while $ZrS_3$ is stable above 900°C, suggests that the materials $Zr_{1-x}Ti_xS_3$ are probably slightly sulfur deficient. This would result in reduction of a small amount of titanium thus giving an n-type semiconductor.

Dark current v.s. applied voltage for $Zr_{1-x}Ti_xS_3$ $0 < x < 0.33$ photoanodes in 1M $M_2SO_4$ were similar to the previously described behaviour of $ZrS_3$ (6). At potential more negative than -200mv a cathodic dark current related to hydrogen evolution is observed. At potential more positive than -200 mv a photocurrent presumably due to oxygen evolution is observed with negligeable photocorrosion at potentials less than 1.0v.

The spectral responses given in figures 2 and 3 show clear increases in quantum efficiency with increasing titanium substitution in $Zr_{1-x}Ti_xS_3$. In the case of $ZrS_3$, shown in figure 2, the photoelectrolysis spectrum was found to be in good agreement with the optical absorption measurements and the thermomodulated reflectance spectrum of $ZrS_3$ found in the literature (2)(9). The peak found at around 2.5 eV has been attributed to an excitonic transition. Analysis of the spectral response indicated what appears to be an allowed indirect gap at $1.94 \pm .05$ eV, which is in good agreement with the proposed value of around 2 eV. The small quantum efficiency of $ZrS_3$ is most likely related to the high resistivity of the sample as it is found that 7% titanium substitution, which lowers the resistivity by a factor of $10^4$, produced an approximate doubling of the quantum efficiency in the region between 2.1 eV and 2.5 eV, as indicated in figure 2.

The evolution of the spectral response of $Zr_{1-x}Ti_xS_3$ with increasing titanium content is shown in figure 3. It is evident that the spectra show enhanced quantum yields with increasing titanium substitution and an extention of the spectral response, although still small, further into the visible; however, of particular interest is the variation of the spectra for each composition in the region between 1.5 and 2.1 eV. The results indicate that a new interband optical transition appears in the titanium substituted materials whose intensity appears to be dependent on titanium concentration. The band gap, as indicated by the lowest energy optical transition, decreases monotonically with increasing titanium content.

This new optical transition does not appear to substantially alter the position of the higher energy optical transitions appearing after 2 eV because the change in slope of the quantum efficiency spectra, which is indicative of the presence of additional optical transitions, always appears at the same energy of about 2.1 eV in all the spectra of the titanium substituted materials. This is similar to what has been observed in the spectral response of oxide solid solutions (10) where optical transitions at energies characteristic of the photoactive transition metal centers found in the solid solution are observed. By analogy to oxide systems, then, it seems plausible that the optical transition appearing in $Zr_{1-x}Ti_xS_3$ at energies less than 2 eV is due to the introduction of titanium centers in the $ZrS_3$ structures. This is consistent also with the observation that the lowest optical transition of $TiS_3$ lies at about 1eV. Unfortunately detailed optical spectral of $TiS_3$ and of the solid solution $Zr_{1-x}Ti_xS_3$ in this energy region appear to be lacking in the literature and comparison with the absorption spectra of other titanium chalcogenides is not valid due to the difference in coordination of the metal ion, (i.e., trigonal prismatic vs octahedral). The results presented here are somewhat unusual because chalcogenides, unlike the more ionic oxides, have covalent bonding characteristics which tend to strongly favor band formation.

## CONCLUSION

The photoelectronic properties of $ZrS_3$ have been improved by the substitution of titanium into the $ZrS_3$ structure. The improvements in the photoelectronic properties of the titanium substituted materials are an extension of the photoresponse further into the visible region of the spectrum and increases of the quantum efficiencies.A comparison of the spectral response of pure $ZrS_3$ and titanium substituted $ZrS_3$ shows that new interband optical transitions which may be attributed to titanium ions are present, a phenomenon similar to what has been observed in substituted oxide materials.

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