RB-123

# ANOMALOUS VARIATION OF BAND GAP WITH COMPOSITION IN ZINC-SULFO-AND SELENO-TELLURIDES


RADIO CORPORATION OF AMERICA
RCA LABORATORIES
INDUSTRY SERVICE LABORATORY

RADIO CORPORATION OF AMERICA

RCA LABORATORIES

INDUSTRY SERVICE LABORATORY

RB–123

# ANOMALOUS VARIATION OF BAND GAP WITH COMPOSITION IN ZINC-SULFO- AND SELENO-TELLURIDES

# Anomalous Variation of Band Gap with Composition in Zinc-Sulfo- and Seleno-Tellurides

For many binary solid solutions a monatonic variation of band-gap occurs with variation of composition. In the Group II–Group IV system, ZnS–ZnSe exhibits this behavior. However, recent experiments show that for ZnSe-Te and for ZnS-ZnTe, there exist anomalous minima in plots of band-gap versus composition of the solid solution.

## Introduction

Some measurements of the variation of band-gap energy with composition in isomorphous series of two-component solid solutions have been reported. Gisolf[1] has investigated the ZnS-CdS system, Johnson and Christian[2], the Ge-Si system, and Folberth[3], Group III-Group V materials. The results seemed to confirm a postulate that intermediate members of a two-component series have band-gap energies intermediate to those of the extreme members of the series. The present work reports results which show that although the system ZnS-ZnSe follows the above postulate, the systems ZnS-ZnTe, and ZnSe-ZnTe do not.

## Experimental

### *Synthesis of Materials*

Phosphor-grade zinc chalcogenides were used throughout the work. Powder mixtures of the pure ingredients (in the desired molar proportions) were dry ball-milled for six hours, to insure homogeneity of mixing. The materials were then transferred to silica boats, and crystallized in an atmosphere of purified nitrogen at 900 degrees C. The materials were cooled under nitrogen. Phosphor-type purity and precautions were maintained throughout the synthesis.

### *Analysis*

X-ray diffraction studies were carried out using a North American Philips diffractometer, with a copper target and nickel filter, to obtain monochromatic 1.54 $\mathring{A}$ radiation.

Chemical quantitative analyses of tellurium in solid solution were carried out by an electrometric titration method developed by Dr. M. C. Gardels of these laboratories[4].

### *Reflection Spectra*

In the absence of single crystals for direct absorption measurements, the diffuse reflectance of the microcrystalline powders was used to furnish a relative measure of the absorption. Light from either a xenon pressure-arc or a tungsten-filament lamp was passed through a 500 millimeter Bausch and Lomb monochromator, equipped with an automatic scanning control. The intensity of the diffusely reflected light from approximately 1 square centimeter of the specimen was measured with a 1P21 multiplier phototube. The intensity relative to that from a pressed disc of magnesium carbonate was plotted against wavelength. Values of the energy gap were calculated from the wavelength corresponding to the intersection of the straight-line extrapolation above and below the short wavelength knee of the curve. The diffuse reflectance spectra for several zinc seleno-telluride solid solutions are shown in Fig. 1.

### *Diffuse Transmission*

Measurements of diffuse transmission were made on several materials with a Cary recording spectrophotometer, Model 14. Small amounts of the materials to be tested were ground with potassium bromide (Harshaw, IR Quality) and pressed into translucent pellets. Energy gap determinations were made by extrapolations on the recorded curves of optical density (log transmission).

### *Results and Discussion*

A plot of band-gap as a function of composition for the three systems studied is given in Fig. 2. It is seen

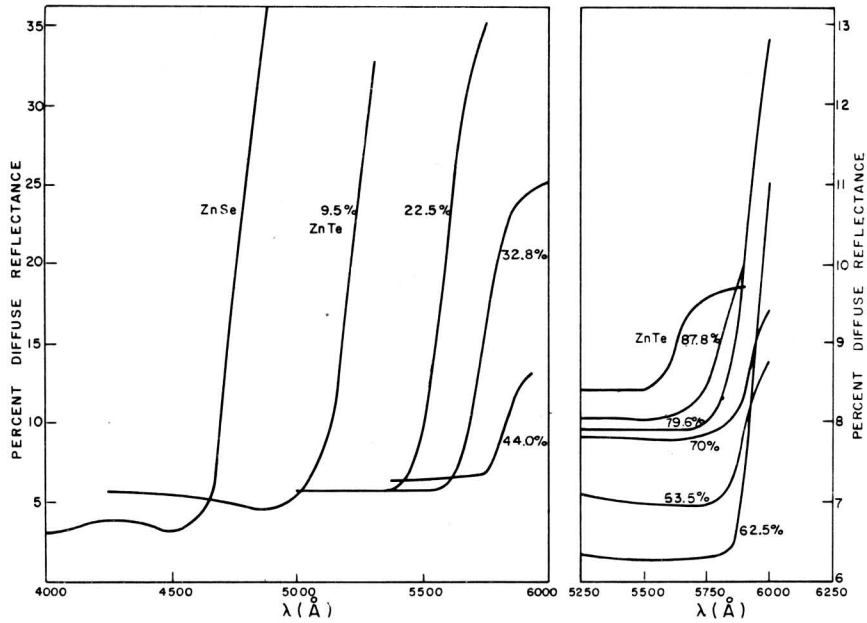


**Fig. 1 - Diffuse reflectance spectra of zinc seleno-tellurides. Figures indicate mole-percent zinc telluride.**

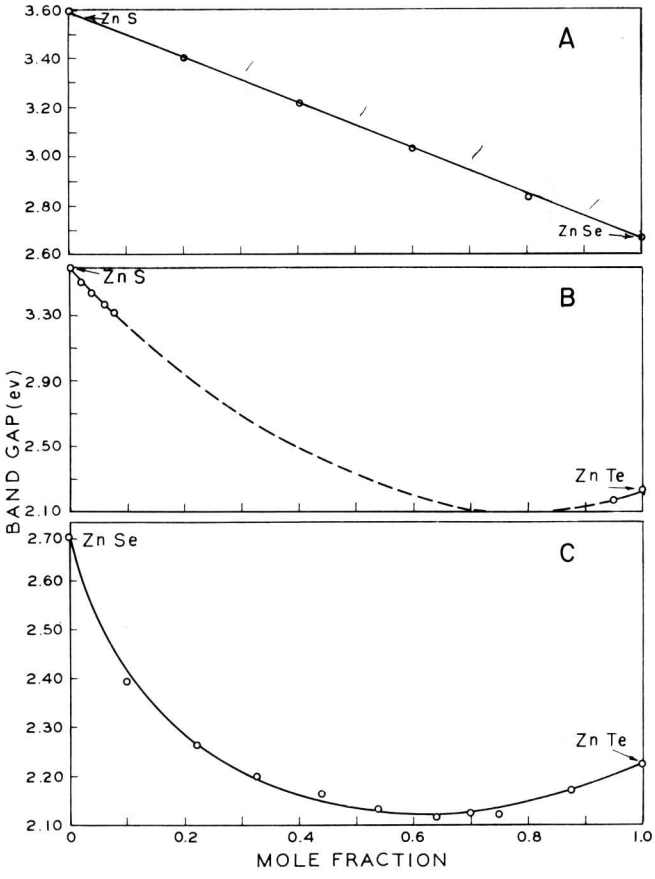


**Fig. 2 - Band gap as a function of composition of: A. zinc sulfo-selenides; B. zinc sulfo-tellurides; C. zinc seleno-tellurides.**

that a linear variation of band-gap with composition occurs for the system ZnS-ZnSe (Fig. 2A). Fig. 2B is a similar plot for ZnS-ZnTe. Solid solution in this system occurs only to the extent of about eight mole percent of ZnTe in ZnS, and about five mole percent of ZnS in ZnTe[5]. A similar plot for ZnSe-ZnTe solid solutions is shown in Fig. 2C. Measurement of the energy gap in this system by diffuse reflection and by diffuse transmission indicate a minimum near a composition of 66 mole percent ZnTe, without exhibiting a discontinuity of slope. A small systematic difference between the reflection and transmission values is attributed to the fact that diffuse reflectance and optical density do not have a simple relationship, so that extrapolations of the type described do not yield completely identical results. The trend however is unmistakable.

As seen from Fig. 2C, the variation of band-gap with composition for ZnSe-ZnTe, compared with that for Ge-Si, (1) is not linear, (2) is not monotonic, (3) does not have an abrupt change of slope, and (4) is concave. These features suggest that a band scheme other than that suggested by Herman[6,7] to account for the Ge-Si anomaly, should be sought. In particular, it would appear that some specific property peculiar to the tellurium atom (or ion) may bear directly on the behavior of solid solutions containing tellurium.

Comparison of the exact nature of the dependence of band-gap on composition suggests that each dependence may be categorized in one or more ways, as for example,

**Table I**

Types of Band-Gap Dependence

| Type of Variation | System | Reference |
|---|---|---|
| Linear | ZnS-CdS* | (1) |
| | InAs-InP | (3) |
| | ZnS-ZnSe | This work |
| Discontinuous slope or Monotonic convex | Ge-Si | (2) |
| Monotonic convex | GaAs-GaP | (3) |
| Non-monotonic concave | ZnS-ZnTe | This work |
| Non-monotonic concave | ZnSe-ZnTe | This work |

*Possible discrepancy in the band-gap value assigned to ZnS by Gisolf, makes it uncertain whether ZnS-CdS should be described as linear or monotonic concave.

**Table II**

Room Temperature Band-Gap Energies

| Material | Band-Gap | Method | Reference |
|---|---|---|---|
| Cubic ZnS | 3.64 | Absorption | (a) |
| | 3.60 | Luminescence | (b) |
| | 3.60 | Reflectivity | This work |
| Cubic ZnSe | 2.58 | Photoconductivity | (c) |
| | 2.66 | Luminescence | (b) |
| | 2.66 | Reflectivity | This work |
| | 2.64 | Transmission | This work |
| Cubic ZnTe | 2.15 | Absorption | (c) |
| | 2.10 | Photoconductivity | (d) |
| | 2.22 | Reflectivity | This work |
| | 2.26 | Transmission | This work |

(a) F. A. Kroger and J. E. Hellingman, *J. Electrochem. Soc.* 93, 156 (1948).

(b) R. E. Shrader, unpublished data.

(c) H. B. DeVore, unpublished data.

(d) R. H. Bube and E. L. Lind, *Phys. Rev.* 105, 1711 (1957).

**Table III**

Lattice Spacings of Zn(Se:Te)

| Initial Composition | Analyzed ZnTe Fraction | Lattice Spacing |
|---|---|---|
| ZnSe | – | 5.6684 |
| 0.9 ZnSe:0.1 ZnTe | – | 5.705 |
| 0.8 ZnSe:0.2 ZnTe | 0.226 | 5.761 |
| 0.7 ZnSe:0.3 ZnTe | 0.328 | 5.811 |
| 0.6 ZnSe:0.4 ZnTe | 0.440 | 5.857 |
| 0.5 ZnSe:0.5 ZnTe | 0.535 | 5.899 |
| 0.4 ZnSe:0.6 ZnTe | 0.633 | 5.940 |
| 0.3 ZnSe:0.7 ZnTe | 0.700 | 5.977 |
| 0.2 ZnSe:0.8 ZnTe | 0.793 | 6.022 |
| 0.1 ZnSe:0.9 ZnTe | 0.875 | 6.055 |
| ZnTe | – | 6.100 |

linear, non-linear but monotonic-concave (or -convex). Table I summarizes in this manner some available data on band-gap dependence.

Simon Larach

*Band Gap Determinations*

Several methods exist for the measurement of band-gaps in solids. These include: absorption, transmission, reflectance, photoconductivity and luminescence. Table II lists and compares the band-gaps obtained by the various methods with those obtained in this work.

Ross E. Shrader

*Lattice Spacings*

The lattice spacings of solid solutions of ZnSe and ZnTe follow Vegards law throughout the range. Table III lists the initial composition, prior to crystallization, the analyzed amount of ZnTe present after crystallization, and the lattice spacing of the solid solution.

Carl F. Stocker

## References


1: J. H. Gisolf, *Physica* **6**, 84 (1939).

2. *LB-949, Some Properties of Germanium-Silicon Alloys,* by E. R. Johnson and S. M. Christian, also *Phys. Rev.* **95**, 560 (1954).

3. O. G. Folberth, *Z. f. Naturf,* **10a**, 502 (1955).

4. Method to be published.

5. Larach, McCarroll and Shrader, *J. Phys. Chem.* **60**, 604 (1956).

6. *RB-27, The Electronic Energy Band Structure of Silicon and Germanium,* by F. Herman.

7. *RB-64, Semiconductor Alloys,* by F. Herman, also *Phys. Rev.* **95**, 847 (1954).