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Solid State Ionics 123 (1999) 19–24

**SOLID  
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IONICS**

## Brightness degradation in electroluminescent ZnS:Cu

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*Dedicated to Professor Michael O'Keefe on the occasion of his 65th birthday*

Received 22 January 1999; accepted 25 March 1999

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### Abstract

Monte Carlo simulations using crystal chemical constraints have been used to elucidate the copper diffusion mechanisms in copper-doped zinc sulfide. Relaxation around the ZnS|Cu<sub>2-x</sub>S interface allows facile copper diffusion, particularly in the presence of substitutional oxygen or sulfur vacancies. Copper diffusion is responsible for the brightness degradation in this electroluminescent material. Reducing sulfur vacancies and substitutional oxygen species are outlined as ways to reduce the luminescence decay. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Electroluminescence; ZnS; Bond valence; Monte Carlo; Diffusion

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### 1. Introduction

Many lighting sources suffer from diminishing intensity as they are used. Most of the reduction in luminescence is due to surface reactions, such as coking, poisoning, or oxidation, and to internal reaction and rearrangement within emitting particles. To mitigate the former sources, one often uses barrier layers or vacuum systems to reduce gas–solid diffusion. To reduce internal reactions, one must understand the solid–solid diffusion in these materials and reduce the corresponding driving potentials.

Such a tremendous amount of information is known about diffusion in solids that even textbooks

have been written on the subject [1]. Although many mechanisms are known and can be precisely modeled, it remains problematic to fashion a complete understanding of a given system, especially one in which multiple phases are incorporated within a single particle. One such fascinating system is ZnS:Cu,Cl. Although its chemical formula is unassuming, commercial examples contain both the Wurtzite and Sphalerite forms of ZnS, as well as Cu<sub>x</sub>S inclusions and perhaps even domains of enriched metallic and nonmetallic impurities. Optimization of its light output by manipulating its composition and physical properties continues [2,3].

Microscopy has shown that the majority of the luminescence from ZnS:Cu emanates near sharp features, such as stacking faults [4] or Cu<sub>x</sub>S inclusions [5–7]. Computer simulations on pure ZnS have elucidated the energetics of the Wurtzite-Sphalerite

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phase transition [8] and have suggested that zinc diffusion takes place by an interstitial mechanism while sulfur diffusion occurs through vacancies [9]. We previously reported, however, that the electroluminescent aging mechanism in this system is dominated by diffusion in and around the  $\text{Cu}_x\text{S}$  inclusions [10]. We report here on efforts to extend these studies to include the dynamics around the  $\text{ZnS}|\text{Cu}_{2-x}\text{S}$  interface, using Monte Carlo techniques.

## 2. Computational method

Monte Carlo methods have been used in a variety of modeling strategies [11–14]. Generally this stochastic technique is applied to an energy minimization function, but it has been used successfully to model ion distributions using crystal chemical rules [15,16]. We recount some of the salient features of using bond valence criteria in the following.

The primary *ansatz* of the bond valence method is that an atom partitions its bonding power among individual bonds, such that associated with each bond distance,  $d$ , is a unique bond strength or valence,  $v$ . The sum of the individual bond valences totals the atomic valence,  $V$ . As a consequence of the connectivity of atoms within a crystal, certain rules evolve due to the complementary nature of the cations and anions. These constraints can be expressed in the following equations

$$v_{ij} = \exp \left[ \frac{R_{0,ij} - d_{ij}}{b} \right]$$

$$V_i = \sum_{j=1}^Z v_{ij} = \sum_{j=1}^Z \exp \left[ \frac{R_{0,ij} - d_{ij}}{b} \right]$$

$$\text{loop} = \sum_{k=1}^{2n(n \geq 2)} (-1)^k w_k \exp \left[ \frac{R_{0,k,k+1} - d_{k,k+1}}{b} \right] = 0$$

$$w_k = \frac{1}{\frac{V_k}{Z_k} + \frac{V_{k+1}}{Z_{k+1}}}$$

where  $V$  is the formal valence of an atom,  $v$  is the individual bond valence,  $d$  is the bond distance,  $R_0$  is an empirically derived parameter for each type of bond  $ij$ ,  $b$  is a universal constant set at 0.37,  $Z$  is the

number of near neighbors, and  $w$  is a weighting factor related to the Pauling bond strength. Suitable bond valence parameters,  $R_0$ , are available in the literature [17,18]. An excellent review of the bond valence technique [19] and some early work on modeling defects in crystals [20] were provided by Brown.

For defective crystals, there is no unique solution to these equations, so Monte Carlo sampling is used to minimize the deviations from these criteria. Specifically, we minimize the following:

$$Q = \exp \left[ -s_1 \left( \sum |V_i - \sum v_{ij}|_{\text{new}} - \sum |V_i - \sum v_{ij}|_{\text{old}} \right) - s_2 \left( \sum |\text{loop}|_{\text{new}} - \sum |\text{loop}|_{\text{old}} \right) \right] > 1$$

where  $s_1$  and  $s_2$  weight the atomic valence and the loop closure criteria. The exponential is compared to a random number generated between 0 and 1 before acceptance to allow for a number of ‘bad’ configurations to be admitted. This allows the possibility of climbing from a metastable configuration to a more stable one. At each step, an atom is either displaced within a certain radius or displaced and exchanged with a neighbor. The technique enables, therefore, both large-scale atomic segregation and short-range diffusion.

Our calculations used a 0.03 Å displacement, 60% probability of exchange, 5000 Monte Carlo steps, and weighting factors appropriate for cubic crystals [21],  $s_1=20$  and  $s_2=10$ . Atomic models were generated within a  $3 \times 3 \times 3$  supercell (about  $4600 \text{ \AA}^3$ ) of eutactic (‘cubic closest packed’) sulfur atoms for variants of  $\text{Cu}_2\text{S}$  and a  $4 \times 4 \times 4$  supercell (about  $11\,000 \text{ \AA}^3$ ) for the two-phase case. The metal atoms were placed in all or  $\frac{1}{2}$  of the tetrahedral sites for  $\text{Cu}_2\text{S}$  and  $\text{ZnS}$ , respectively. The models, therefore, include  $\text{Cu}_2\text{S}$  as a coherent precipitate within the  $\text{ZnS}$  matrix. The volume was allowed to vary, but the shape was constrained to be a cube. For the  $\text{Cu}_{2-x}\text{S}|\text{ZnS}$  interface, the space was divided equally between the two materials. Calculations on 700 atom ensembles took about 10 h on a Pentium processor running at 150 MHz under a Microsoft FORTRAN compiler. Some models included 10% vacancies or atomic substitutes (e.g., O for S) which were ran-

domly generated. Contour plots were generated along [1–10], since this particular projection has more open space than its other high-symmetry counterparts [10].

### 3. Results

We calculated the  $d(\text{Cu-S})$  bond distances for each model as a check on the Monte Carlo simulations. It is satisfying that the median distance in all models is 2.40–2.41 Å which corresponds to the expected bond valence (strength) of  $\frac{1}{4}$ . The mean values vary, since they are influenced greatly by

outlying long and short distances near defects. The means vary from 2.37 to 2.40 Å.

It is our continuing thesis that regions of low bond valence sums facilitate atomic diffusion in crystals. In particular, regions where the bond valence sums are near unity (shown in yellow in the figures) would be likely routes for  $\text{Cu}^+$  diffusion. The bond valence contours in stoichiometric  $\text{Cu}_2\text{S}$  and nonstoichiometric  $\text{Cu}_{1.9}\text{S}$  are quite similar (see Fig. 1). The unsatisfied sulfur atoms at the edges are artifacts of the finite model constructed but bind tightly to the underlying Cu atoms, so the diffusion pathways are slightly more hindered than in previous static calculations [10].

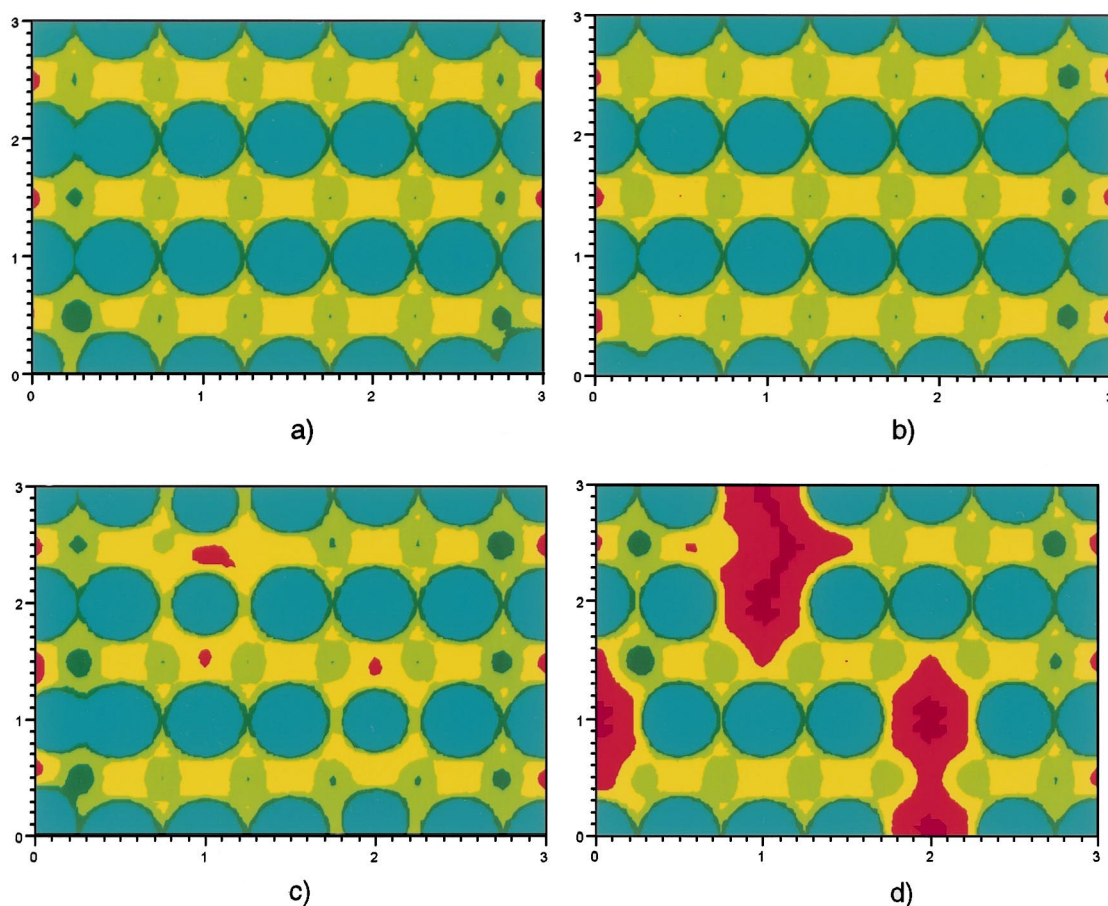


Fig. 1. Bond valence sums of Cu viewed along [1T0]. The horizontal axis is  $x=y$  and the vertical one is  $z$ . a)  $\text{Cu}_2\text{S}$ , b)  $\text{Cu}_{1.9}\text{S}$ , c)  $\text{Cu}_2\text{S}_{1.9}\text{O}_{0.1}$ , d)  $\text{Cu}_2\text{S}_{0.9}$ . For c) and d) the oxygen atoms or vacancies are located at (2,0), (2,1), (1,2), and (1,3). Red, orange, yellow, pale green, green, and blue contours correspond to regions where the bond valence sums are 0,  $\leq 0.5$ ,  $\leq 1.0$ ,  $\leq 1.5$ ,  $\leq 2.0$ , and  $> 2.0$  respectively.

Some rather dramatic features are seen, however, in the models of  $\text{Cu}_2\text{S}_{1.9}\text{O}_{0.1}$  and  $\text{Cu}_2\text{S}_{0.9}$ . Analogous to the effects seen on sulfur atoms at the edge of the box, sulfur atoms adjacent to sulfur vacancies are displaced from their symmetric positions. Copper atoms near sulfur vacancies satisfy their bonding requirements by forming stronger bonds to their remaining sulfur partners. Larger diffusion pathways are seen near the small oxygen atoms which may substitute on sulfur sites. Sulfur-sulfur repulsions hold the anion network open, so the oxygen atoms cannot collapse around the areas of low bond valence sum.

Monte Carlo simulations on the interfacial  $\text{Cu}_{1.9}\text{S}|\text{ZnS}$  structure suggest that copper diffusion is more facile in  $\text{Cu}_{2-x}\text{S}$  than it is in ZnS (see Fig. 2). There are fewer ‘blocked’ regions in the copper region, and the benevolent regions near the sulfur atoms are larger. Surprisingly the copper vacancies at (0.75, 1.25) and (1.25, 1.25) do not greatly affect the bond valence profiles.

Since the many known copper sulfides vary primarily in their Cu:S ratio, we explored various stoichiometric variants. Fig. 3 shows the results of simulations starting with sulfur or copper vacancies along the interface. Areas near sulfur vacancies show features similar to those seen at the edge of the atomic array. Copper is assumed to diffuse freely along these extrinsic defects. As seen in the  $\text{Cu}_{1.9}\text{S}$  case, sulfur atoms near copper vacancies displace

towards other copper sites to increase their bonding complement. This results spatially in the opening of a large intrinsic defect which again should allow for facile copper diffusion.

In a final pair of simulations, substitutional atoms,  $\text{O}_\text{S}$  and  $\text{Cl}_\text{S}$ , were placed along the  $\text{Cu}_{2-x}\text{S}|\text{ZnS}$  interface (see Fig. 4). As seen in the static case, the substitution of chlorine for sulfur has little effect on the bond valence sum contours. Oxygen substitution for sulfur, however, opens up pathways for facile copper diffusion.

#### 4. Discussion

Dynamic Monte Carlo simulations confirm that reducing the diffusion of copper species in ZnS:Cu is a primary concern in mitigating brightness decay. Certain chemical strategies arise from this analysis, and these strategies are aligned with experimental observations.

It has been suggested that the reduction of sulfur vacancies,  $V_\text{S}$ , is critical, since diffusion is enhanced by their presence [9]. Sulfur atoms diffuse via these  $V_\text{S}$ , but we have shown in the current simulations, that the presence of  $V_\text{S}$  enhances the local diffusion pathways for copper atoms as well (see Table 1). Not surprisingly, therefore, firing materials in excess sulfur has shown some improvement in brightness maintenance [22].

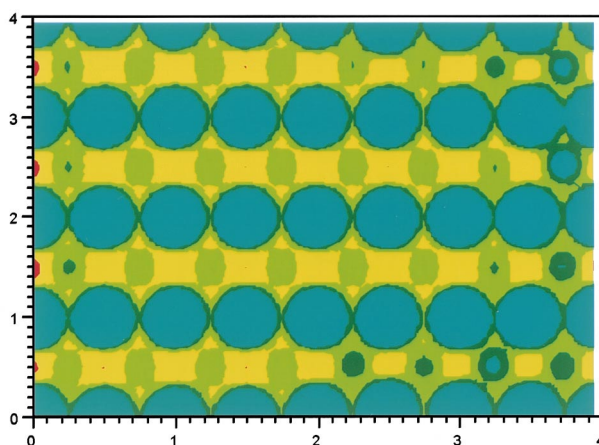


Fig. 2. Bond valence sums of Cu in  $\text{Cu}_{2-x}\text{S}|\text{ZnS}$  viewed along [1T0]. The  $\text{Cu}_{1.9}\text{S}$  region contains abscissa values under 2; the remainder is the ZnS region. The color scheme is the same as in Fig. 1.

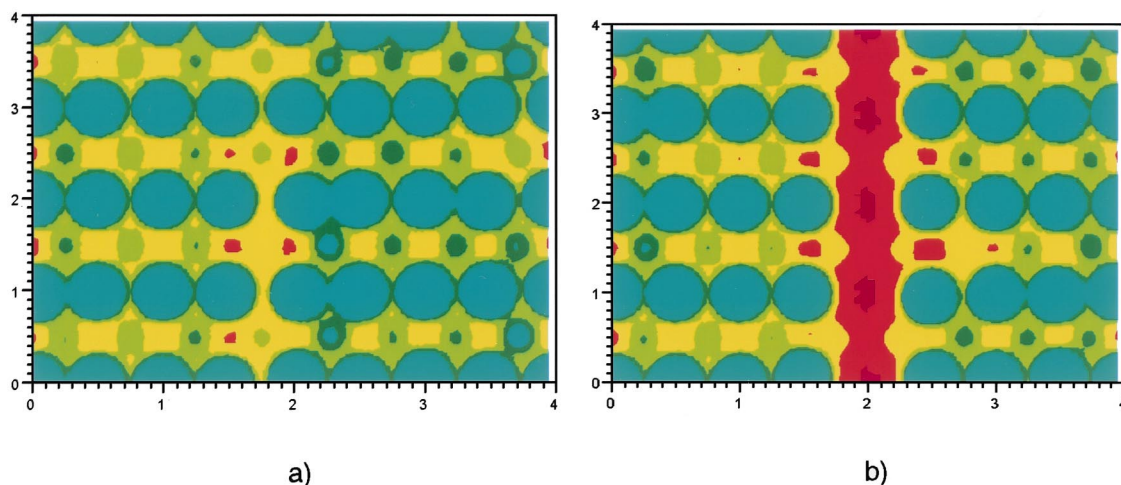


Fig. 3. Bond valence sums of Cu in  $\text{Cu}_{1.9}\text{S}/\text{ZnS}$  viewed along  $[1T0]$  with a) copper vacancies at  $x=y=1.75$  and b) sulfur vacancies at  $x=y=2$ . Again the copper region is on the left and the zinc region is on the right with the same contour coloring as used previously.

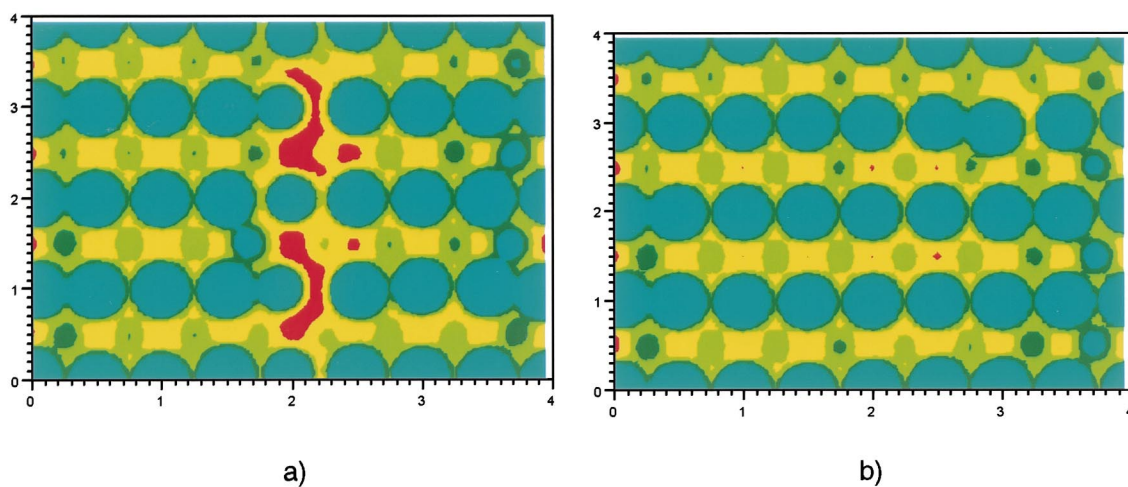


Fig. 4. Bond valence sums of Cu in  $\text{Cu}_{1.9}\text{S}/\text{ZnS}$  viewed along  $[1T0]$  with a) oxygen substitution at  $x=y=2$  and b) chlorine substitution  $x=y=2$ . Again the copper region is on the left and the zinc region is on the right with the same contour coloring as used previously.

Doped zinc sulfide emits a blue-green light, and it has been suggested that the blue emission is predominantly due to proximal  $(\text{Cu}'_{\text{Zn}}\text{Cu}'_1)$  pairs or  $V''_{\text{Zn}}$  while the green emission originates from distant donor  $(\text{Cl}'_{\text{S}})$ -acceptor  $(\text{Cu}'_{\text{Zn}})$  pairs [23–26]. The emission color would be expected to shift, if the emitting species diffused at different rates. Since no color change is observed, it is satisfying that the

simulations show little effect of  $\text{Cl}'_{\text{S}}$  substitution on copper diffusion.

It has been difficult to understand the role of oxygen atoms in the brightness degradation in  $\text{ZnS}:\text{Cu},\text{Cl}$ . Chemical analysis of these materials confirms the presence of oxygen, while X-ray diffraction, sensitive to perhaps the percent level, indicates oxygen is not present as zinc sulfate or zinc

Table 1

Area of projections with favorable bond valence sums; smaller numbers correspond to higher luminescence stability.

| Fig. | Composition                                       | $0.1 < \sum v_{ij} < 1.2$ | $0.5 < \sum v_{ij} < 1.0$ |
|------|---|---------------------------|---------------------------|
| 1a   | Cu <sub>2</sub> S                                 | 27.1%                     | 12.7%                     |
| 1b   | Cu <sub>1.9</sub> S                               | 27.6%                     | 13.1%                     |
| 1c   | Cu <sub>2</sub> S <sub>1.9</sub> O <sub>0.1</sub> | 27.8%                     | 14.4%                     |
| 1d   | Cu <sub>2</sub> S <sub>0.9</sub>                  | 30.9%                     | 13.8%                     |
| 2    | Cu <sub>1.9</sub> S ZnS                           | 33.4%                     | 18.7%                     |
| 3a   | Cu <sub>1.9</sub> S ZnS, Cu vac.                  | 32.4%                     | 18.4%                     |
| 3b   | Cu <sub>1.9</sub> S ZnS, S vac.                   | 38.1%                     | 19.4%                     |
| 4a   | Cu <sub>1.9</sub> S ZnS, O subst.                 | 33.6%                     | 18.5%                     |
| 4b   | Cu <sub>1.9</sub> S ZnS, Cl subst.                | 31.7%                     | 18.2%                     |

oxide. We have shown that the local diffusion of copper is greatly enhanced near oxygen. Brightness maintenance enhancements could be expected, therefore, if oxygen could be minimized. Examination of published recipes [3] suggests several strategies, including the removal of oxygen-containing reactants and the modification of the firing atmosphere.

### Acknowledgements

The Rohm and Haas Company assisted in meeting the publication costs of this article. N. Brese thanks S. Fitzwater for helpful discussions. G. Rohrer thanks the National Science Foundation for its generous support.

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