



## STUDY ON REVIEW OF LITERATURE ON CHALCOGENIDES

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**Abstract:** Owing to promising optical and electrical properties and better thermal and aqueous stability, chalcogenide perovskites have shown a wide range of applications. Chalcogenides belong to the 16<sup>th</sup> group of periodic tables and could be potential materials for the fabrication of efficient and stable (chalcogenide perovskite) solar cells. Generally, metal halide perovskites are used for the fabrication of solar cells. However, they have some grave problems like less stability and toxicity. In this context, chalcogenide perovskites (AB (S, Se)<sub>3</sub>) may be a better option due to their potential to solve the existing problems and hence could be deployed in the fabrication of high-performance solar cells. These chalcogenide perovskites have high stability (thermal and aqueous), along with their environment-friendly elemental composition. In this review, we present various techniques used for the synthesis of chalcogenide perovskites and their applications in the fabrication of solar cells. Furthermore, we have also studied the scope for the commercial development of chalcogenide perovskite-based solar cell.

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### Introduction:

In the past decade, the field of photovoltaics (PV) has been turned on its head by the arrival of “perovskite” materials. In this context, “perovskite” means hybrid organic–inorganic halides crystallizing in perovskite structures, and such materials have shown better intrinsic properties for PV applications than almost anything that has come before. High absorption coefficients allow efficient solar cells to be made from films in the range of 300–500 nm thick, while high mobilities for electrons and holes, and a lack of deep defects, allow long charge carrier diffusion lengths and lead to efficient collection of photoexcited electrons.<sup>[1,2]</sup> These properties have underpinned the rapid rise of certain halide perovskites to high efficiency in PV cells.

While very impressive single-junction solar cell efficiencies have been reached,<sup>[3]</sup> the “killer” application of PV perovskites in the near term is thought to be the augmentation of commercial crystalline silicon solar cells with wide-bandgap perovskite top cells, to create a tandem device. Si-perovskite tandem device efficiencies have reached 29%, which already exceeds the record for silicon technology alone, clearly demonstrating the promise of this concept.<sup>[4]</sup> Such tandem devices could be manufactured with high throughput, with some studies predicting lower per-Watt costs than existing technology.<sup>[5]</sup> Unsurprisingly, attempts to

commercialize this technology are already underway.<sup>[6]</sup>

Apart from their optoelectronic properties, a useful engineering factor for halide perovskites is the ability to deposit films at low temperatures, in the range of 80–150 °C.<sup>[7]</sup> The ability to form highly crystalline, large-grained halide perovskite layers at low temperature, using simple solution-based approaches, has been an integral part of the rapid improvement in device performance compared with other (inorganic) PV technologies.<sup>[7]</sup> Besides, a low deposition temperature allows for straightforward integration of halide perovskite top cells onto completed Si subcells without risk of damage to the latter.

Despite their advantages, halide perovskite solar cells face challenges in terms of their long-term stability, due to degradation of the perovskite bulk and interfaces under various combinations of internal and external stressors such as heat, light, humidity, and electric fields.<sup>[8-11]</sup> For any new PV technology aiming at mainstream applications, long term stability must meet or exceed the high bar set by existing (Si) technologies. Performance warranties from some Si module manufacturers are at 25 years with as little as 10% degradation, and this is expected to improve to 30 years within a decade.<sup>[12]</sup> Even a small compromise in the operational lifetime of a perovskite–silicon tandem PV module could offset efficiency gains,

erode cost reductions, and make the technology less attractive for investors.<sup>[5]</sup> The stability of halide perovskites might be enhanced by external means, such as encapsulation, but the ultimate solution lies in modifying the intrinsic properties of the perovskite materials themselves. To what extent this can be achieved with halide perovskites while retaining their good qualities is a question that is under intense research today.

Another family of PV materials, the chalcogenides, have already provided high-performance examples that have reached commercial applications in single-junction solar cells (principally Cu(In,Ga)(S,Se)<sub>2</sub> and CdTe), and this family could thus be an alternative source of tandem top cell materials. Unlike the halide perovskites, good environmental stability is a common feature of chalcogenide compounds, which is an important advantage and underpins their commercialization by companies such as First Solar, Inc and Avancis GmbH. The challenges here are different from the halide perovskite case. One issue is that the better stability tends to go hand-in-hand with higher temperature synthesis (>400 °C). While this can present problems for monolithic integration with Si cells, recent results have shown that this can be dealt with.<sup>[13, 14]</sup> A more serious issue is that none of the emerging chalcogenide candidates has shown sufficiently high efficiency. To achieve a Si-based tandem device with over 30% efficiency, the top cell must have efficiency in the range of 17–19% for bandgaps in the range of 1.7–1.8 eV.<sup>[15]</sup> To date, the best example from the chalcogenides is Cu(In,Ga)S<sub>2</sub>, with a 15.5% efficiency at an ≈1.65 eV bandgap.<sup>[16]</sup> compiles open-circuit voltage data from solar cells based on different material categories, compared to the band-gap dependent Shockley–Queisser (SQ) limit. Data are shown for chalcogenides in the chalcopyrite group (i.e., Cu(In,Ga)Se<sub>2</sub> and derivatives), “emerging” chalcogenides including Cu<sub>2</sub>ZnSnS<sub>4</sub> and other newer examples, halide perovskites containing organic cations as well as pure inorganic halide perovskites. The data are assembled from several sources;<sup>[17-19]</sup> the reader is referred to these and the references therein for more detailed information. The figure shows that the halide perovskites stand out in terms of low voltage losses in the relevant bandgap range. The chalcogenides nearest the appropriate bandgap range (of which there are few) have considerably larger voltage losses with respect to the SQ limit. Part of these voltage losses could simply be due to nonoptimal contacts and interfaces in the solar cell structures used.<sup>[20]</sup> However, unlike the halide perovskites, none of the chalcogenide candidates has shown any other primary indication of high photovoltaic potential, such as a high luminescence

quantum yield that would suggest open-circuit voltage potential near the SQ limit. This points to a widespread problem of low defect tolerance in the wide gap chalcogenide absorber materials that have been examined thus far.

### Review of literature:

Crystalline solid state is characterized by strict order in the position of atoms even at large atomic distances. CGs could be characterized by short-range order (SRO) and partially by intermediate range order (IRO). That means that after changing the crystalline state of a crystal in vitreous or amorphous state, the shortest distance between neighboring atoms is almost the same as in the crystal, may be, only with small distortion, which certainly leads to destroying of the long-range order (LRO). For example, the first atomic coordination in the crystals and glasses of As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub> are almost the same<sup>16</sup>. Of course, this is not characteristic for all materials. The germinate glasses (GexCh1-x, where Ch=Se, Te, S) are a typical example of different SRO in crystals and glasses of the same composition<sup>17,18</sup>. CGs bear some similarity to oxide glasses, since both oxygen and chalcogen belong to group VI in the Periodic Table. A CG can be regarded a kind of ‘soft semiconductor’, soft because its atomic structure is flexible and viscous (due to two-fold coordination of chalcogen atoms) and a semiconductor because it possesses a band gap energy (~2 eV) characteristic of semiconductor materials (1-3 eV). Accordingly, a CG may be characterized as being in between an oxide glass composed of three-dimensional networks and an organic polymer possessing one-dimensional chain structure<sup>19</sup>. Atomic bonding is, therefore, more rigid in CGs than that of organic polymers and more flexible that of oxide glasses (Fig. 3). Atomic structure and related properties in CGs depend upon preparation methods and history after preparation<sup>20,21</sup>.

### Electronic Properties

CGs possess electrical and optical band gaps of 1-3 eV and accordingly they can be regarded as amorphous semiconductors. Gap decreases in the sequence of S, Se and Te, reflecting enhanced metallic character. As a semiconductor, overall property of CGs can be grasped as the vertical sequence (Fig. 3). That is, with the change from organic semiconductors, chalcogenides, hydrogenated amorphous silicon films, to crystalline semiconductors, the electronic mobility becomes higher and a faster response is available. The material also becomes more rigid. Instead, material prices seem to increase with this sequence, which may reflect their typical preparation methods (coating, evaporation, glow discharge, and crystal-growth techniques). Electrically, CGs exhibit smaller

conductivities than the corresponding crystals<sup>20,21</sup>. This is because the electronic mobility is suppressed by band tail and gap states, which are manifestations of disordered structures. Glass can be regarded as a p-type semiconductor or, more exactly, hole conduction is greater than electron conduction<sup>20, 21</sup>. In selenium at room temperature, holes exhibit conventional Gaussian transport with a mobility of  $0.1 \text{ cm}^2 (\text{Vs})^{-1}$ . However, at low temperatures and, in several materials, at room temperature, holes exhibit so-called dispersive transport, and the effective mobility decreases to  $10^{-5} \text{ cm}^2 (\text{Vs})^{-1}$  or even less. Such hole motions are described in terms of multiple trapping with band-tail states or hopping transport in gap states. In general, the position of Fermi energy, which may be located near the center of the band gap, cannot be controlled by impurity doping. However, there are a few exceptions, such as Bi-Ge-Se, Pb-Ge-Se and Pb-In-Se, in which thermo power indicates n-type conduction<sup>22-28</sup>.

### Optical Properties

Extensive studies have been made on photoinduced phenomena in CGs<sup>29,30</sup>. At least seven distinct photo-induced phenomena are observed in amorphous chalcogenides but not usually in crystalline chalcogenides. Photo-induced phenomena observed in CGs can be classified into two groups (Fig. 4): i) It includes heat-mode phenomena, in which the heat generated through non-radiative recombination of photo-excited carriers triggers atomic structural changes; and ii) Photon-mode, which can further be divided into the phenomena observed under illumination and after illumination. The best-known heat-mode phenomenon may be the optical phase change, or the optical Ovonic effect<sup>29</sup>. This phenomenon appears in tellurium compounds, which undergo thermal crystallization. A light pulse heats the film sample above crystallization temperature, resulting transformation from amorphous to crystalline phases. In some materials, this change is reversible. That is, a more intense light pulse heats the sample above melting temperature, and a successive temperature quenching can reproduce original amorphous structure. As for the photon-mode phenomena, reversible photo-darkening and related changes have been extensively studied<sup>29,30</sup>. Here, light illumination induces a red shift of the optical absorption edge, so that the sample becomes darker, while the red shift can be reversed with annealing at the glass-transition temperature. Refractive index in transparent wavelength regions increases with the red shift, which is consistent with the expectation obtained from the Kramers-Kronig relation. Sample volume, elastic, and chemical properties also change with illumination and recover with annealing. As for the

light, band gap illumination ( $h\nu = E_g$ ) has been assumed to be effective. However, sub-gap light with photon energy lying in Urbach-tail region also produces some changes, which can be more prominent than those induced by band gap light<sup>29</sup>. phenomenon, which is characteristic of CG. That is, it does not appear in the corresponding crystal. Some structural studies have demonstrated that the amorphous structure becomes more disordered with illumination. However, it is difficult to identify explicitly the structural change in amorphous phases, and the mechanism is not yet elucidated. An example of photo-thermal bulk phenomena is the photo-induced anisotropy originally discovered by Fritzsche<sup>29</sup>. Macroscopically, untreated glasses are generally isotropic, while illumination with linearly polarized light can add some anisotropy such as dichroism, birefringence, and axial strains. Even unpolarized light can induce anisotropy if the light irradiates a side surface of a sample<sup>29</sup>. Photo-doping is a famous photo-thermal chemical reaction<sup>29</sup>. Consider a bilayer structure consisting of silver and As<sub>2</sub>S<sub>3</sub> films. When this bilayer is exposed to light, the silver film dissolves rapidly into the As<sub>2</sub>S<sub>3</sub>. For instance, if the silver film is 10 nm in thickness, and the exposure is provided from the semitransparent silver side using a 100 W ultrahigh-pressure mercury lamp, the silver film will dissolve within few minutes. Since the reaction becomes slower if the sample is illuminated at lower temperatures, this can be regarded as a photo-thermal phenomenon. However, it should be mentioned that temperature rise induced by illumination is not essential. There are also several irreversible and transitory changes. Examples are photo-polymerization and photo-induced fluidity<sup>29</sup>. Not only photons but also other excitations such as electrons can give rise to a variety of structural changes<sup>31</sup>. Some of these are similar to, but others are dissimilar from, the corresponding photon effects. For instance, electron beams can enhance silver doping into chalcogenide films like photons<sup>31</sup>, while the beam can suppress crystallization of Se, in contrast to the photocrystallization phenomenon. Studies using scanning tunneling microscopes etc. demonstrate nanometer scale structural changes in CGs.

### Conclusion:

Chalcogenides such as sulfide, selenide, and telluride based-chalcogenides are abundant materials. Their derivatives such as binary, ternary, and quaternary chalcogenide materials are applicable in many areas such as photovoltaic, photocatalyst, sensor, fuel cell, and battery. Chalcogenide compounds also can be prepared with many methods such as hydrothermal, solvothermal, one-pot, microwave-assisted, sonochemical, and

electrochemical methods. The morphology of chalcogenide materials are also affected by the composition of raw materials, methods of synthesis and treatment. Sulfide, selenide, and telluride-based chalcogenides have their own unique characteristics, structure, and physical as well as chemical properties making them one of the most studied nanostuctures. There are numerous chalcogenides that have been studied extensively over the years where future of chalcogenides-related fields can be expected.

### References

- [1]. Lezal D & Macko P, Non-Crystalline Semiconductors (ALFA, Bratislava) 1989.
- [2]. Poulain M, Fluoride Glass Fiber Optics (Academic Press. Inc., Boston) 1991.
- [3]. Goryunova N A & Kolomiets B T, New vitreous semiconductors, Zhurn Techn Fiz, 25 (1955) 984-1015.
- [4]. Ioffe A F & Regel A R, Non-crystalline, amorphous and liquid electronic semiconductors, Progr Semiconductors, 4 (1960) 237-291.
- [5]. Anderson P W, Absence of diffusion in certain random lattices, Phys Rev, 109 (1958) 1492-1505.
- [6]. Mott N F & Twose W D, The theory of impurity conduction, Adv Phys, 10 (1961) 107-163.
- [7]. Cohen M H, Fritzsche H & Ovshinsky S R, Simple band model for amorphous semiconducting alloys, Phys Rev Lett, 22 (1969) 1065.
- [8]. Davis E A & Mott N F, Conduction in non-crystalline systems, Phil Mag, 22 (1970) 903-927.
- [9]. Street R A & Mott N F, States in the gap in glassy semiconductors, Phys Rev Lett, 35 (1975) 1293-1296.
- [10]. Ovshinsky S R, An introduction to ovonic research, J NonCryst Solids, 2 (1970) 99-106.
- [11]. Ovshinsky S R, in Physical Properties of Amorphous Materials, edited by D Adler, B B Schwartz & M C Steele (Institute of Amorphous Studies Series, Plenum Press, N Y) 1985, 105.
- [12]. Ovshinsky S R & Klose P H, Imaging in amorphous materials by structural alteration, J Non-Cryst Solids, 8-10 (1972) 892-898.
- [13]. Tanaka K, Reversible photostructural change: Mechanisms, properties and applications, J Non-Cryst Solids, 35-36 (1980) 1023-1034.
- [14]. Mott N F & Davis E A, Electron Processes in NonCrystalline Materials (Clarendon Press, Oxford) 1979.
- [15]. Lezal D, Pedilkova J, Zavadil J, Kostka P & Poulain M, Preparation and characterization of sulfide, selenide and telluride glasses, J Non-Cryst Solids, 326 & 327 (2003) 47- 52.
- [16]. Lucovsky G, Optic modes in amorphous As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub>, Physical Rev B, 6 (1972) 1480-1489.
- [17]. Fisher G B & Tauc Y, Proc 5th Int Conf Amorphous and Liquid Semiconductors, edited by I Stuke & W Brenig (Taylor & Francis, London) 1974, 1259.
- [18]. Popescu M, Stotzel H & Vescan L, Proc Int Conf Amorp Semicond'80, 1, 44, Chisinau, 1980.
- [19]. Zallen R, The Physics of Amorphous Solids (John Willey & Sons, New York) 1983.
- [20]. Elliot S R, in Chalcogenide Glasses, edited by J Zarzycki (Materials Science and Technology, VCH, New York) 1991.
- [21]. Feltz A, Amorphous Inorganic Materials and Glasses (VCH, Weinheim, Germany) 1993.
- [22]. Morigaki K, Physics of Amorphous Semiconductors (Imperial College Press, London) 1999.
- [23]. Tohge N, Minami T & Tanaka M, Electrical transport in ntype semiconducting Ge<sub>120</sub>Bi<sub>x</sub>Se<sub>70-x</sub>Te<sub>10</sub> glasses, J Non-Cryst Solids, 37 (1980) 23-30. 2
- [24]. Nagel P, Ticha H, Tichy L & Triska A, Electrical properties of glasses in the Ge-Bi-Sb-Se and Ge-Bi-S systems, J Non-Cryst Solids, 59-60 (1983) 1015-1018.
- [25]. Tohge N, Matsuo H & Minami T, Electrical properties of n-type semiconducting chalcogenide glasses in the system Pb-Ge-Se, J Non-Cryst Solids, 95-96 (1987) 809-816.
- [26]. Bhatia K L, Parthasarathy G, Gopal E S R & Sharma A K, Study of effects of dopants on structure of vitreous semiconductors (GeSe<sub>3.5</sub>)<sub>100-x</sub>M<sub>x</sub> (M=Bi, Sb) using high pressure techniques, Solid State Commun, 51 (1984) 739-742.
- [27]. Bhatia K L, Parthasarathy G, Gosain D P & Gopal E S R, Role of dopants in pressure-induced effects in glassy GeSe<sub>3.5</sub> containing Bi and Sb, Phil Mag B, 51 (1985) L63-L68.
- [28]. Kohli S, Sachdeva V K, Mehra R M & Mathur P C, High pressure studies on n-type Se-In-Pb chalcogenide glasses, Phys Stat Sol (b), 209 (1998) 389-394.

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