

STRUCTURAL FORMS, PROPERTIES AND APPLICATIONS OF CHALCOGENIDE MATERIALS: A REVIEW**Neeraj Jaiswal¹, Ashutosh Singh^{2,*}, Yogender Singh² and Abhishek Singh^{3,*}**¹Department of Chemistry, K.S. Saket P.G. College, Ayodhya-224001, India²Department of Chemistry, Government Degree College, B.B. Nagar, Bulandshahr-203402, India³Department of Chemistry, Udai Pratap College, Varanasi-221002, India

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ABSTRACT

Chalcogenide materials, primarily consisting of sulfur (S), selenium (Se), and tellurium (Te), have become a focal point in materials science and engineering due to their distinctive structural diversity, remarkable electronic and optical properties, and broad applications. This comprehensive review delves into an extensive analysis of the structural variations, properties, and applications of chalcogenide materials. The exploration begins by examining the diverse structural arrangements displayed by chalcogenide compounds, ranging from amorphous to crystalline and layered structures. It emphasizes the pivotal role of atomic bonding and coordination in shaping properties such as electrical conductivity, optical transparency, and thermal stability. The review elucidates the electronic properties of chalcogenides, highlighting their adjustability through doping and alloying strategies. These materials are renowned for unique characteristics, including high electrical conductivity in certain phases, excellent photoconductivity, and intrinsic semiconducting behaviour. Their compatibility with emerging technologies like flexible electronics, optoelectronics, and photovoltaics is discussed. Additionally, the review provides insights into the optical properties of chalcogenide materials, explaining their nonlinear optical behaviour. Practical applications span diverse fields such as electronics, photonics, energy storage, and sensing, with examples like phase-change memory devices, chalcogenide-based transistors, photodetectors, and energy-efficient memory storage solutions. Finally, the review addresses challenges and future prospects in the synthesis, processing, and commercialization of chalcogenide materials, emphasizing their immense potential in advancing modern technologies. It calls for continued research efforts to fully harness the capabilities of chalcogenide materials for future applications.

Keywords: Chalcogenide materials, Electronic properties, Optical properties, Topological insulators, Semiconductors, Photodetectors, Energy storage, Applications.

1. INTRODUCTION

Modern electronics are built around silicon-based components has prompted a search for fresh materials [1]. Chalcogenide glasses are one such class of materials that have one or more chalcogens as constituent elements used in many different fields and have fascinating properties [2]. These amorphous semiconductors are used in a variety of modern electronic, optical and optoelectronic devices, such as waveguides, biosensors, planar optics, photonic integrated circuits and Phase Change Memory (PCM), a kind of non-volatile RAM[3].

The term "chalcogenide" originates from the Greek words "chalcos," meaning ore, and "gen," meaning formation [4]. Chalcogens constitute elements in group 16 of the periodic table. While oxygen differs in chemical behaviour, it is often treated separately due to its distinct characteristics. Despite not being a chalcogen, oxygen is essential, found in water and organic molecules, crucial for life. Elements in the chalcogen group share similar chemical traits, particularly in forming compounds with oxygen [5,6]. Though oxide materials are ancient glass-forming systems, they are distinct from more recent chalcogenide compounds [7]. Chalcogenide glasses, a well-known type of inorganic glass, always include one or more chalcogen elements [8,9]. Creating these glasses involves alloying chalcogens with electropositive elements like arsenic, germanium, phosphor, antimony, bismuth, silicon, tin, lead, aluminum, gallium, silver, etc., resulting in fascinating properties [10].

Chalcogenide glasses, a versatile alternative to silicon, offer great promise. Unlike typical glasses made of

silicates and quartz that transmit visible electromagnetic radiation, chalcogenide glasses excel in applications requiring the transmission of infrared radiation up to approximately 2 μm wavelength. Three distinct categories of special glasses cater to these needs: fluoride glasses like zirconium fluoride (ZrF_4) and hafnium fluoride (HfF), chalcogenide glasses (CG) including As-S, As-Se, As-Se-Te, Ge-Se-Te, Ge-As-Se, and heavy metal oxide (HMO) glasses such as $\text{GeO}_2\text{-PbO}$, $\text{TeO}_2\text{-PbO}$. These glasses, with higher refractive indices and lower phonon energies than SiO_2 , transmit in the middle and far infrared ranges. Optical devices rely on properties like refractive index and optical band gap, while memory devices focus on electrical properties. Sensing devices primarily hinge on chemical properties, occasionally incorporating optical properties. In active optical devices, chalcogenide glasses doped with rare-earth elements like Nd, Er, *etc.*, are employed. Chalcogenide and glass fibers find utility in infrared transmission, with applications spanning civil, medical, and military domains. Chalcogenide fibers serve passive roles as conduits for light, facilitating data transmission without altering optical properties. These highly nonlinear glasses play a crucial role in all-optical switching (AOS) [16].

Chalcogenide glasses exhibit sensitivity to electromagnetic radiation absorption, leading to photo-induced effects that are harnessed for creating diffractive, waveguide, and fiber structures [17]. These covalently bonded network glasses play a crucial role in modern optoelectronics, photonics, telecommunications, xerography, and sensor technologies. The following sections of this paper provide an in-depth overview of these promising materials, covering their structural forms (mono-, di- & transition metal, pyrites, and tri & tetra-chalcogenides), as well as their diverse structural, electrical, optical, and thermal properties. The practical applications of chalcogenide materials are explored, followed by a discussion on the challenges and future prospects in the synthesis, processing, and commercialization of these materials.

2. Structural (different) forms of Chalcogenides

The chalcogen elements (S, Se and Te) and one or more electropositive (or electronegative in a few cases) elements are all present in chalcogenides [18]. The periodic table's groups IB (Cu, Ag), IIB (Zn, Cd, Hg), IVA (Si, Ge, Sn), IIIA (In, Tl), IVB (Zr, Hf), IIA (Mg, Ba) and IA (Li, K, Cs) generally contain the electropositive elements [19]. Lanthanide elements like La, Lu and others may also be involved in some circumstances. Chalcogenide compounds are a special class of materials that are infrequently found in other material classes like semiconductors, large gap insulators, superconductors, silicate glasses, metallic alloys, *etc.* because of their extremely diverse compositional space [20]. Chalcogenides are a unique class of materials with a variety of structures and properties due to the formation of various possible chemical bonds between these elements [21].

Transition metal chalcogenides can have a wide range of stoichiometries and structural variations [22]. But the most prevalent and significant chalcogenides technologically are those with straightforward stoichiometries, like 1:1 and 1:2. Extreme examples include chalcogenide-rich materials like Re_2S_7 , which exhibit extensive chalcogen-chalcogen bonding and metal-rich phases (for example, Ta_2S), which exhibit extensive metal-metal bonding [23]. The chalcogenide, which includes S_2 , Se_2 and Te_2 is frequently thought of as a dianion for the purposes of classifying these materials. The semiconducting properties of transition metal chalcogenides actually reveal that they are highly covalent, not ionic. There are numerous structural variations of chalcogenides materials as discussed below:

2.1. Monochalcogenides

The formula ME, where M is a transition metal and E is S, Se or Te, is used to describe metal monochalcogenides [25]. One of two motifs, named after the corresponding zinc sulfide forms, is typically how they crystallize. The sulfide atoms are arranged in a cubic symmetry and take up half of the tetrahedral holes in the zinc blend structure. It produces a diamond-shaped framework. The primary alternative structure for monochalcogenides is the wurtzite structure, which has hexagonal crystal symmetry but similar atom connectivity (tetrahedral) [26]. The nickel arsenide lattice is a third motif for metal monochalcogenides, where the metal and chalcogenide have octahedral and trigonal prismatic coordination, respectively. This motif frequently experiences non-stoichiometry. Some pigments, most notably cadmium sulphide, are monochalcogenides that are significant [27]. Different structural form of monochalcogenides is shown in Fig.1.

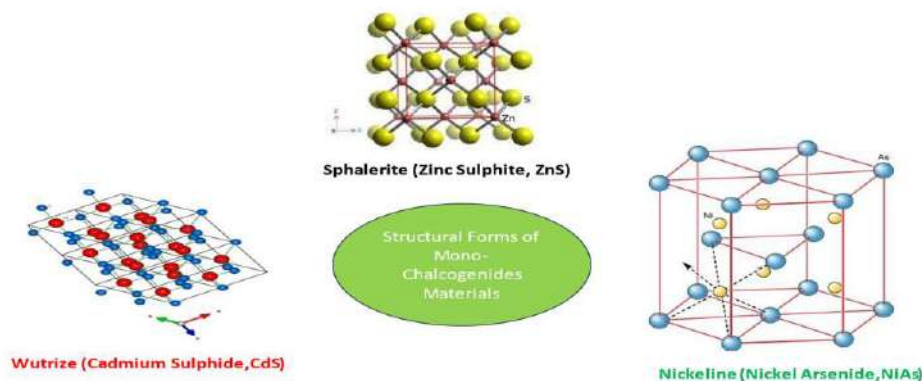


Fig.1. Different structural form of Monochalcogenides Materials

2.2. Dichalcogenides and Transition metals dichalcogenides

The most prevalent metal dichalcogenide, MoS_2 , has a layered structure. The formula for metal dichalcogenides is ME_2 , where M is a transition metal and E is one of S, Se or Te [28]. The sulfides are the group's most significant members. They have semiconducting properties, are always dark diamagnetic solids and are insoluble in all solvents. Superconductors are among them [29].

These compounds are typically thought of as derivatives of M^{4+} , where $\text{M}^{4+} = \text{Ti}^{4+}$ (d^0 configuration), V^{4+} (d^1 configuration) and Mo^{4+} (d^2 configuration). Utilizing titanium disulfide's capacity to reversibly undergo intercalation by lithium, it was studied in prototype cathodes for secondary batteries [30]. The primary ore of molybdenum, known as molybdenite, is molybdenum disulfide. It serves as a catalyst for hydrodesulfurization and a solid lubricant. TiSe_2 , MoSe_2 and WSe_2 are a few examples of the corresponding di-selenides and even ditellurides that are known [31].

Typically, transition metal dichalcogenides adopt either molybdenum disulfide or cadmium diiodide structures [32]. The metals show octahedral structures in the CdI_2 motif. The metals show trigonal prismatic structures in the MoS_2 motif, which is not observed in dihalides [33]. The weak chalcogenide-chalcogenide bonding between the layers contrasts with the strong bonding between the metal and chalcogenide ligands. Due to the different bond strengths, alkali metals intercalate in these materials [34]. Charge transfer occurs concurrently with the intercalation process, converting the M(IV) centres to M(III) . In comparison to a typical 3D semiconductor, the attraction between electrons and holes in 2D tungsten di-selenide is hundreds of times stronger [36]. Fig.2 displays the structural form of dichalcogenides and transition metals dichalcogenides materials.

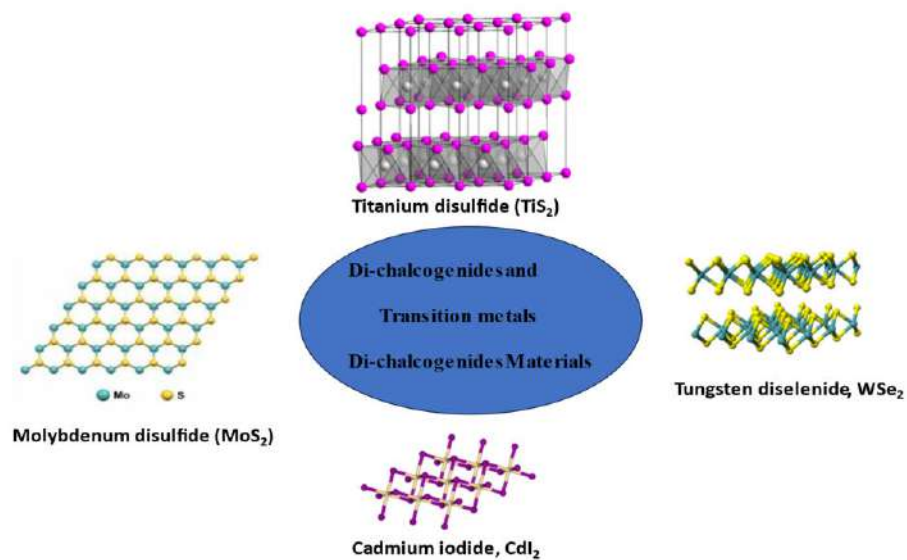


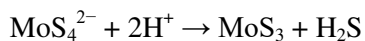
Fig.2. Various structural form of dichalcogenides and transition metals dichalcogenides materials

2.3. Pyrite and related disulfides

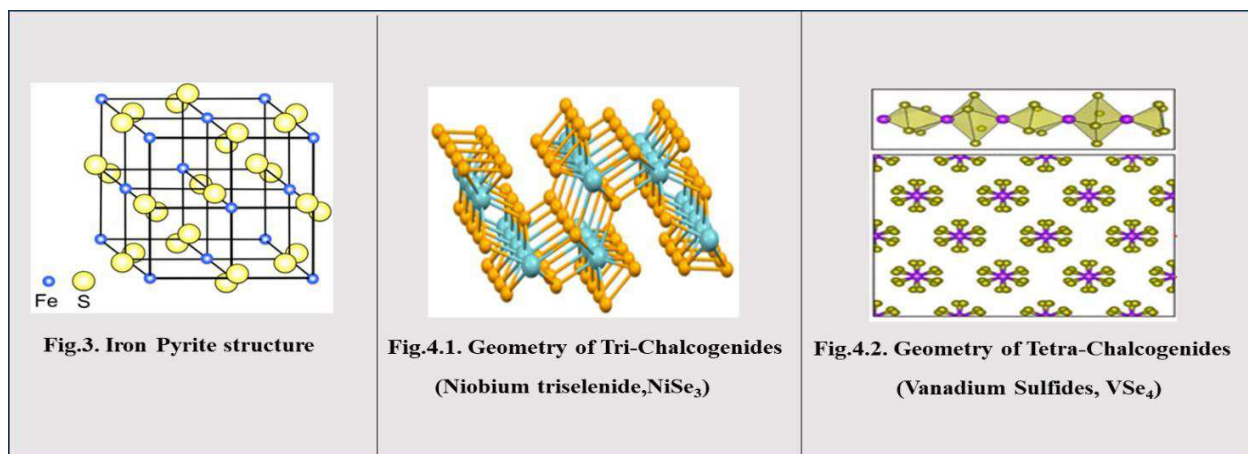
Iron pyrite (Fig.3), a common mineral, is typically described as consisting of Fe^{2+} and the persulfido anion S_{22} , in contrast to classical metal dichalcogenides. A brief S-S bond holds the sulphur atoms in the di-sulfido dianion together. In contrast to early metals (V, Ti, Mo, W), which adopt 4+ oxidation states with two chalcogenide dianions, ‘late’ transition metal disulfides (Mn, Fe, Co and Ni) almost always adopt the pyrite or the related marcasite motif [37].

2.4. Tri- and tetrachalcogenides

Trichalcogenides are also formed by a number of metals, primarily the early metals (Ti, V, Cr and Mn groups) [37]. Typically, these substances are referred to as $\text{M}^{4+} (\text{E}_{22}) (\text{E}_2)$ (where E is S, Se or Te). Niobium triselenide (Fig.4.1) is an illustrative example [38]. Acid is used to process tetrathiomolybdate to develop amorphous MoS_3 :



A metal tetra chalcogenide is a mineral with the chemical formula VS_4 (Fig.4.2) called patrónite [39]



2. Properties of chalcogenides Materials

An intensive property of a material or a physical characteristic that is independent of the amount of the material, is called a material property. These quantitative characteristics can be used as a yardstick to compare the advantages of various materials, assisting in the choice of materials. Anisotropy is the term for the tendency of a material's properties to vary to some extent depending on the direction of the material in which they are measured. When used within a certain operating range, materials properties that relate to various physical phenomena frequently behave linearly (or roughly so). Similar to other materials, chalcogenides have unique material characteristics that can be divided into structural or physical, thermal, electrical, optical, *etc.* and are discussed below:

3.1. STRUCTURAL PROPERTIES

Even at great atomic distances, there is order in the position of the atoms in crystalline solid states. Short range order (SRO) and partially intermediate-range order (IRO) are characteristics of chalcogenides. This indicates that the shortest distance between adjacent atoms in a crystal after switching between its crystalline and non-crystalline states is nearly the same, perhaps with a minor distortion that results in the destruction of the long range order (LRO) [40].

Since chalcogen and oxygen both falls under group VI of the periodic table, chalcogenides resemble oxide glasses in some ways [41]. Because of its flexible and viscous atomic structure and band gap energy (2 eV) characteristics of semiconductor materials, a chalcogenide can be thought of as a type of "soft semiconductor" (1-3 eV). A chalcogenides is therefore defined as a material that lies between an organic polymer with a one-dimensional chain structure and an oxide glass composed of three-dimensional networks [42]. Chalcogen elements S, Se and Te are combined with network-forming elements like Ge, As, P and S-band Si to form chalcogenide glasses. The resulting glass displays several characteristics resembling those of an amorphous semiconductor [43]. Unlike other glasses, which have ionic bonds between their molecules, the glass structure is made up of covalently bonded molecules, which are then weakly bound together by a combination of covalent and Van der Waals-like attraction. Numerous different compositions of chalcogenide glasses are possible because both heteropolar and homopolar bonds are capable of forming. The atomic ratio of arsenic to sulphur in the As-S glass system can range from 1.5 to 9. As a result, specific properties can be tuned by varying the chalcogenide glasses' chemical makeup [44]. The average bond strength decreases for a given chalcogenide glass system as the relative atomic mass of the chalcogen or its proportion in the glass increases. Chalcogenide glasses are typically less durable than oxide glasses due to their weaker bonds. For instance, they have higher thermal expansion coefficients, lower softening temperatures and harder materials [45].

3.2. ELECTRONIC PROPERTIES

Because of their 1-3 eV electrical and optical band gaps, chalcogenides are classified as amorphous semiconductors [46]. Gaps get smaller in the order of S, Se and Te, indicating a more prominent metallic quality. That is, electronic mobility increases and a faster response is available when switching from organic semiconductors, chalcogenides and hydrogenated amorphous Si films to crystalline semiconductors [47].

Chalcogenide glasses can be classified as covalent, metallic, or ionic in different ways. The so-called 8-N rule applies to the coordination number of the constituent atoms in covalent chalcogenide glasses like Se and As_2S_3 , for example, the coordination number of chalcogens is typically 2 because the total number of valence electrons is $N = 6$ [48]. The band gap increases in the series Te Se S, with a range of 1-3 eV depending on the composition. In many chalcogenide glasses, holes control electrical conduction. These glasses can therefore be thought of as amorphous semiconductors [49]. The band gap narrows (by about 1 eV) and the glass becomes more metallic in a glass with a lot of Te, though. The discovery of sharp, reversible transitions in electrical resistance in the amorphous chalcogenide $Te_{48}As_{30}Si_{12}Ge_{10}$ above a threshold voltage led to the development of electrical switching in chalcogenide semiconductors in the 1960s [50]. It would appear that quick, purely electronic processes started the switching mechanism. The non-crystalline material heats up and transforms into crystalline form if the current is allowed to continue [51]. An instantaneous, intense pulse of heat can melt a crystalline region. The melted region is then sent back through the glass transition by subsequent rapid cooling. A more

prolonged, lower-intensity heat pulse, on the other hand, will cause an amorphous region to crystallize [52].

Phase-change random-access memory is built on attempts to electrically cause chalcogenides to transform into glassy crystals (PC-RAM). The commercial application of this new technology is just around the corner [53]. An electric current provides the heat pulse during write operations. The relatively significant difference in electrical resistance between the glassy and crystalline states is used to perform the reading process at sub-threshold voltages. Amorphous chalcogenides can have significant ionic conductivities, but contributions from ions were not taken into account, despite the electronic structural transitions being strongly featured that are relevant to both optical discs and PC-RAM [54]. In a solid chalcogenide electrolyte, it is demonstrated that ionic transport can also be helpful for data storage. This electrolyte is composed of crystalline metallic silver selenide islands (Ag_2Se) dispersed in an amorphous semiconducting matrix of germanium selenide at the nanoscale (Ge_2Se_3) [55].

3.3. OPTICAL PROPERTIES

Chalcogenide materials, which include compounds containing tellurium, sulphur, selenium, and other related elements, have a variety of optical properties that may be adjusted, which makes them very appealing for a variety of uses. Because of its transparency in the infrared spectrum, chalcogenide glasses are used in infrared optics and communication systems, as one prominent example. For example, the exceptional transparency of arsenic sulphide (As_2S_3) glass has been explored extensively for its potential in fibre optics for communication and sensing [56]. Chalcogenides also exhibit nonlinear optical characteristics that are useful in signal processing and frequency conversion, such as fourth-wave mixing and second-harmonic generation (SHG). One chalcogenide with intriguing nonlinear optical behaviour is bismuth selenide (Bi_2Se_3), whose SHG features have been studied in anticipation of possible use in nonlinear optical systems.[57]. A photonic bandgap is exhibited by some chalcogenides, which makes it possible to manipulate light propagation and makes the creation of photonic devices easier. Electro-optic characteristics enable the application of an electric field to modulate optical signals, a feature that is employed in devices such as electro-optic modulators. Lead sulphide (PbS) nanoparticles, for example, show the electro-optic properties of chalcogenides by changing their optical characteristics when an electric field is applied. This characteristic is important for the advancement of modulators that use light [58]. Photodetectors use chalcogenides with clearly defined absorption edges. Light-emitting diodes, phosphors, and sensors all use luminescence, including fluorescence and phosphorescence. Materials like cadmium selenide (CdSe) nanoparticles, which are widely employed in optoelectronic devices like light-emitting diodes (LEDs) and biological imaging applications, are prime examples of chalcogenides' luminous characteristics [59]. The applications of chalcogenides in devices such liquid crystal displays, thermal imaging instruments, and photodetectors are further enhanced by their photoconductivity, birefringence, and thermal optical properties. Thus, due to their desirable optical characteristics, such as their high refractive index, high photosensitivity and significant optical nonlinearity, chalcogenides are widely used for photonic applications [60] which are discussed below:

3.3.1. Photo-Induced Effects

Only amorphous chalcogenides can undergo a variety of physical changes caused by various photo-induced phenomena; crystalline chalcogenides rarely undergo such changes [61]. Sulfide glasses have a wide range of useful applications thanks to their powerful photo effects. In amorphous chalcogenides, this is possible through at least seven different mechanisms, which can lead to materials with different properties after optical irradiation [62]. Thus, photo crystallization, photopolymerization, photodecomposition, photo-induced morphological changes (*i.e.*, photo-contraction), photo-vaporization, photo-dissolution of metals and light-induced changes in local atomic configuration can all occur when samples of a suitable geometry are exposed to light. These modifications are accompanied by adjustments to the material's optical constants, particularly the location of the optical band gap. Depending on whether the band gap shifts to a longer or shorter wavelength, this phenomenon is referred to as photo-darkening or photo-bleaching. Applications for the numerous methods by which optical changes in chalcogenides can be induced include diffraction gratings, integrated waveguide circuits and surface and potential volume data storage [63]. Both reversible and irreversible components can be found in photoinduced

alterations, depending on the sample's composition, preparation method, illumination conditions, and history. If the film is properly annealed at a temperature close to the glass transition temperature, the exposure-induced structural and optical changes ought to be reversible. The photogenerated stress (or strain) is shifted to an illuminated surface by the photoinduced fluidity. As a result, with a thick film, the photo-expansion is delayed by the PD. The predicted atomic density is between 0.5 and 1 percent, in line with the usual displacements. In Fig. 5., the schematic diagram is displayed [64].

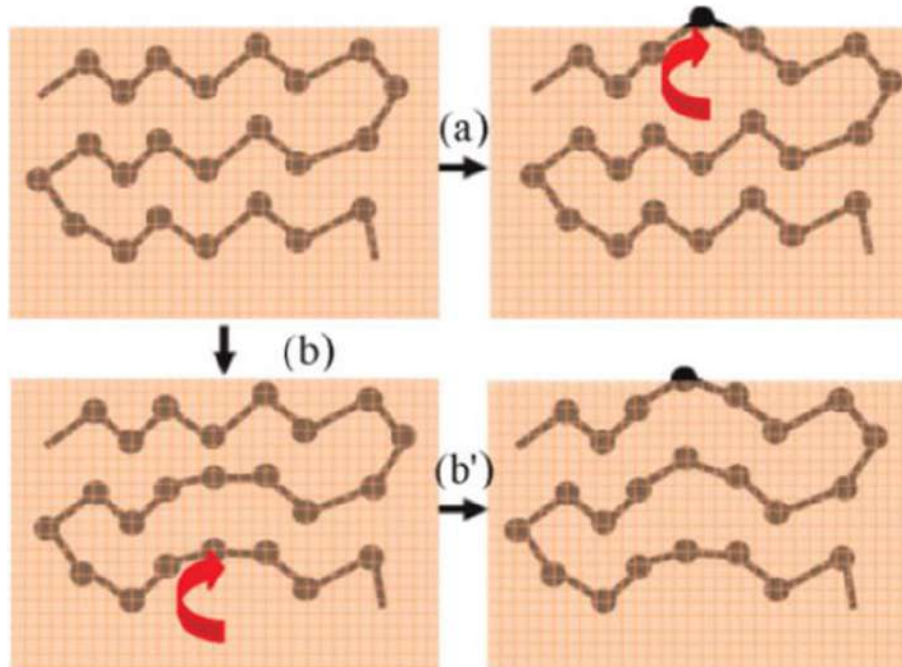


Fig.5. Diagrammatic representation of photoexpansion in both thick and thin samples. Viscosity transfer causes these films to twist both on the outside and inside [64].

3.3.2. Photo-crystallization

Photocrystallization is a phenomena when an amorphous material undergoes a transition into a crystalline state upon exposure to light. Under optical irradiation, a chalcogenide sheet crystallises due to a heating action. Low glass transition temperature chalcogenides, which are mostly found [65]. The development of rewritable optical storage systems, where chalcogenide materials are frequently used, especially in the context of phase-change materials, makes this property more important. When exposed to external stimuli like heat or light, phase-change materials can undergo reversible transitions between amorphous and crystalline forms. Ge₂Sb₂Te₅ (GST) is a well-known example of a chalcogenide material that exhibits photocrystallization [66]. Because GST can quickly transition between crystalline and amorphous forms in response to laser pulses, it is frequently utilised in phase-change memory systems. A high-resistance state (logical "0") is associated with the amorphous state, and a low-resistance state is associated with the crystalline state (logical "1"). This characteristic makes it possible for GST-based devices to efficiently store and retrieve data [67]. Chalcogenide materials are appropriate for high-speed, non-volatile memory applications since they also show rapid and reversible photocrystallization. Fast read and write operations are made possible by the transition, which can happen in nanosecond timeframes [68]. Applications for photocrystallization in chalcogenide materials include optical data storage devices. Data encoding is made possible by the ability to create particular crystalline patterns by varying the intensity and duration of light exposure [69, 70].

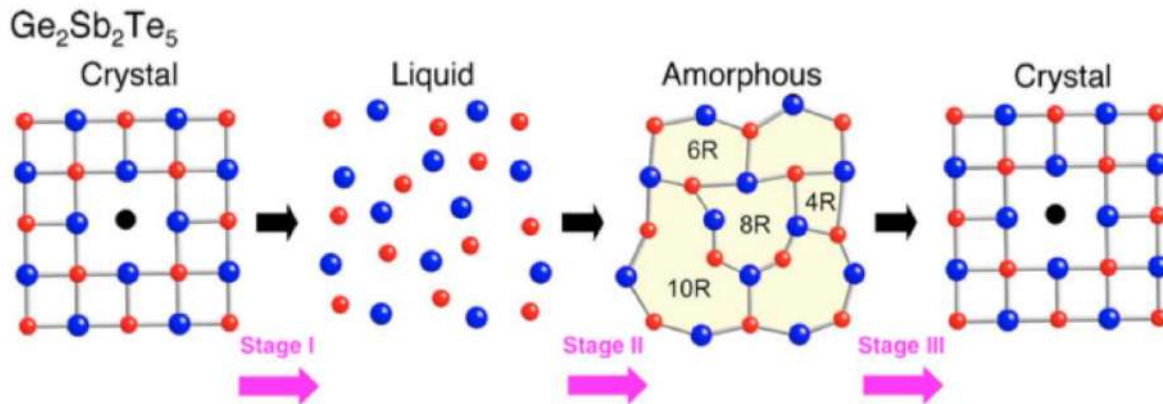


Fig.6. Transformation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from amorphous to crystalline state [66]

3.3.3. Photo-polymerization

In general, photo-polymerization refers to a process in which light stimulates and starts the synthesis of polymer chains from monomer molecules. This idea is more commonly related to organic polymers than inorganic chalcogenide substances [71]. The process of polymerization involves the joining of two or more molecules to create a more intricate, continuously-bonding molecule [72]. In some chalcogenides, these processes can be thermally and photochemically induced. Nonetheless, chalcogenide materials—especially some chalcogenide glasses—can occasionally experience structural changes brought on by light, though not always as a result of following a traditional polymerization procedure. Light exposure, usually in the visible or near-infrared spectrum, can cause photodarkening or photo-induced structural alterations in chalcogenide glasses. These alterations are frequently linked to adjustments in the chalcogen atoms' configuration inside the glass matrix. For instance, exposure to light in certain chalcogenide glasses can result in the creation of photo-induced defects, modifications to bond configurations, or even localised crystallisation. The technique involves an optical feature that changes the material's absorption and transmission characteristics as it comes into contact with light. According to a polymerization model, after thermal annealing at the glass transition temperature, arsenic sulfide (As_4S_4) polymers are produced in the arsenic tri-sulfide glass [73]. The reversible structural changes that chalcogenide glasses, as those in the As-S-Se system, can undergo in response to light have been investigated [74, 75]. Chalcogenide glass is a dynamic and adjustable material for a variety of applications, such as optical switching devices, holographic storage, and integrated photonics. Changes in the glass's structure can modify its optical properties [76]. Under some circumstances, the material may be able to revert to its initial state as a result of these light-induced changes (e.g., thermal annealing). The alterations in chalcogenide glasses caused by light may find use in integrated photonics, holographic storage, and optical switching. These alterations are appealing for dynamic and tunable optical devices because they are reversible [77,78].

3.3.4. Photo-dissolution of Metals

Nonetheless, chalcogenide materials—especially chalcogenide glasses—can experience a range of photo-induced transformations, such as phenomena resembling photodissolution. A layer of metal in contact with the chalcogenide can be forced to melt into it by exposing it to light with an energy comparable to the chalcogenide's band gap. It is challenging to undo this process [79]. Certain chalcogenide glasses may experience a dissolution-like process wherein the material undergoes structural or compositional changes upon exposure to particular light wavelengths. This may entail bonds being broken or rearranged in reaction to light. Additionally, exposure to light can affect the way chalcogen atoms are arranged, which can change the material's optical absorption, transmission, and even solubility properties [74,75].

3.3.5. Photo-contraction

Photocontraction, if it refers to a contraction or change in dimensions induced by light exposure, might be associated with photo-induced structural changes in chalcogenide materials. One characteristic that sets chalcogenide materials apart is the presence of massive structural flaws brought about by the rapid melt-freezing process. The sensitivity of chalcogenide materials to light exposure is an intriguing characteristic. When exposed to light, the aforementioned materials exhibit a range of light-induced phenomena. Kuzukawa *et al.* [80] have observed that some thin films like $a\text{As}_2\text{S}_3$ - As_2Se_3 are expanded and other thin films like $a\text{-GeS}_2$, $a\text{-GeSe}_2$ are shrunk (Fig.7) [80].

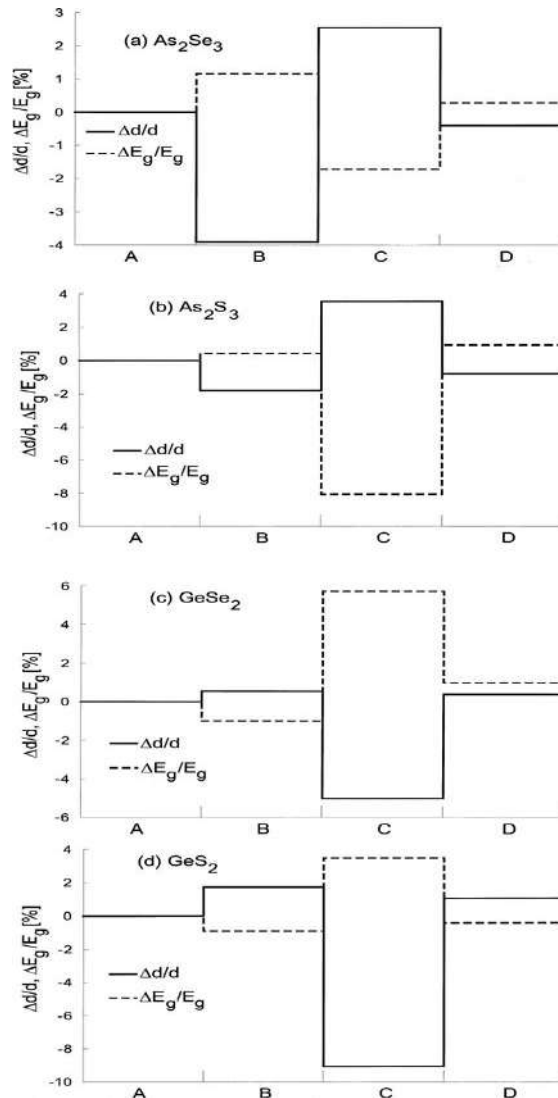


Fig.7. Relative variations in optical band gap and thickness. The variations in thickness and the optical band gap are shown by the solid and dotted lines, respectively. [80].

The formation of VAPs describes the configurationally disorder that has been seen by several workers in the vicinity of the excitation, together with alterations in atomic coordination [81, 82]. The development of new inter chain bonds has been proposed as a possible explanation for the observed results in $a\text{-Se}$ and related alloys [81]. According to Zhang *et al.*, bond creation and breaking are essential for the production of photoinduced effects [82,83]. Chalcogenide glasses, such as those in the As-S-Se system, have been studied for their ability to undergo

reversible changes in structure when exposed to light leads to light -induces structural changes. These changes can include modifications in the arrangement of chalcogen atoms, which may result in alterations in the material's physical properties [84].

3.3.6. Photo-darkening

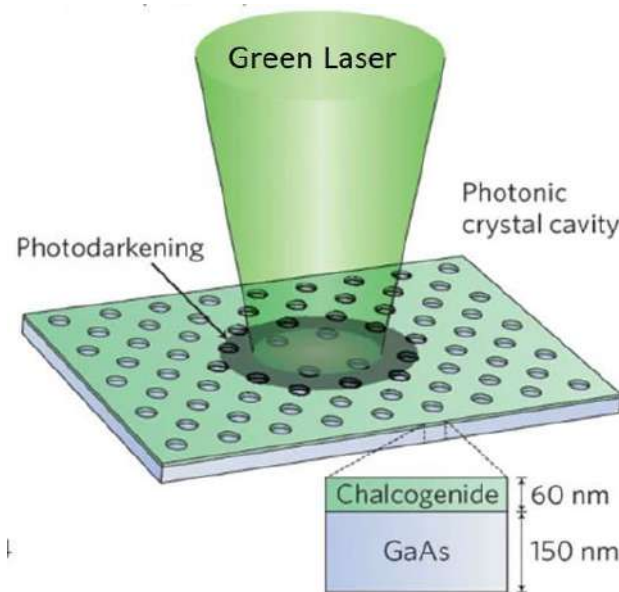


Fig.8. Photodarkening Phenomenon by Chalcogenide glass [86]

Chalcogenides are among the optical materials in which photodarkening is a phenomenon. Compounds containing elements from the periodic table's chalcogen group, such as tellurium, selenium, or sulphur, are known as chalcogenides. The development of infrared optics and photonics applications frequently makes use of these materials [85]. The term "photodarkening" describes how a material becomes darker or more coloured when exposed to light, usually intense light like laser radiation. When it comes to chalcogenides, this phenomena is frequently seen in fibres and glasses [86,87]. Amorphous selenium is one chalcogenide material that displays photodarkening. One type of chalcogenide semiconductor used in photoreceptors and X-ray detectors is amorphous selenium. Amorphous selenium can experience photodarkening in response to strong optical or X-ray radiation, which modifies the material's optical characteristics. Although the precise processes causing photodarkening in chalcogenides can differ, flaws or contaminants in the material are frequently linked to it. High-intensity light exposure can cause structural alterations or charge transfer processes that cause the material to discolour [88]. The optical absorption of the chalcogenide increases at a particular wavelength after irradiation, in part from a shift in the Urbach edge to lesser energies. The effect is major at low temperatures even as at higher temperatures, close to the glass transition; the effect is not calculated since the glass is annealed as fast as the change is induced. Photo-darkening is sometimes associated with other structural alterations in the chalcogenide [89].

3.3.7. Photo-bleaching

When a substance is exposed to light, it might lose its colour or become less absorbent, a process known as photobleaching occurs. Photobleaching is defined by a fading or loss of colour, whereas photodarkening entails darkening or coloration. Under some conditions, photobleaching in the context of chalcogenide materials can be observed. Chalcogenide glasses are renowned for their distinct optical characteristics. These glasses can contain elements such as tellurium, selenium, or sulphur. Numerous products, such as photonic devices, sensors, and infrared optics, use these glasses. When chalcogenide glasses are subjected to strong light, usually in the form of laser radiation, photobleaching may happen [90]. When chalcogenide glasses are subjected to intense light, their

molecular bonds may change or break, which is one possible process for photobleaching. This mechanism results in a fading or bleaching effect because it reduces the absorption of specific wavelengths. During photo-bleaching, the optical absorption edge moves to shorter wavelengths. It is a common effect in chalcogenide films and has been observed in Ga: La: S films. As with photo-darkening, bleaching is the outcome of a structural alteration in the glass network [91].

3.3.8. Photo-induced Anisotropy

When exposure to light causes a directional dependency in the optical characteristics of the material, photo-induced anisotropy in chalcogenide materials can be seen [92]. Chalcogenide glasses' photoinduced variations in birefringence are one such example [93]. The ability of a substance to display distinct refractive indices along various axes is known as birefringence. The potential of chalcogenide glasses in optical data storage applications—where photo-induced anisotropy is critical—has been investigated. In this case, the recording medium is a particular kind of chalcogenide glass that is frequently based on elements like tellurium, arsenic, and selenium [94]. A common reason for this photo-induced anisotropy is alterations in the molecular structure of the chalcogenide glass. The glass network's local order and symmetry can change as a result of bonds breaking or forming when exposed to light. Consequently, this leads to directional dependencies in optical characteristics like birefringence or refractive index [95].

Printing with chalcogenide glass involves exposing it to intense laser light, which alters its structure. Comparing the irradiated and non-irradiated regions, the former show different molecular structures or bonding patterns. Anisotropy is introduced into the material's optical characteristics by this modification. In optical data storage, where stored information may be read out depending on the anisotropic optical response of the material, the ability to induce and control anisotropy in chalcogenide glasses has useful uses. This application makes use of the photo-induced modifications' reversibility to enable several write-read cycles. Reconfigurable photonic devices, integrated optics, data storage, and other advanced optical devices are made possible by our ability to comprehend and manage photo-induced anisotropy in chalcogenide materials.[96].

3.3.9. Photomechanical Effect

The photomechanical effect is the outcome of a material's interaction with light, which causes the substance to alter mechanically. Numerous mechanisms, such as variations in temperature, tension, or phase transitions brought on by light absorption, might cause this effect [97]. Chalcogenides are recognised for their capacity to go through reversible transitions between amorphous and crystalline phases. This is especially true of phase-change materials. Light exposure, such as laser pulses, can start the phase-change process. This characteristic has been thoroughly investigated for potential uses in rewritable optical storage (like DVDs and Blu-ray discs). Significant structural reorganisations occur at the atomic level during this shift. Variations in the crystalline structure of a material can lead to modifications in its mechanical properties, such as variations in stress or volume [98]. In this case, the material changing physically (e.g., expanding or contracting) as a result of the phase transition brought on by exposure to light is the manifestation of the photomechanical effect.

M. Stuchlik *et al.* [99] made the initial discovery of the optomechanical effect in amorphous chalcogenide films deposited on clamped STM cantilevers. When incident on the chalcogenide film, band gap light that is linearly polarised either parallel or perpendicular to the axis of the cantilever causes a contraction or an expansion of the chalcogenide layer. As a result, the free end of the clamped cantilever is dislocated optically, demonstrating a photomechanical effect [99]

3.4. THERMAL AND THERMAL -ELECTRIC PROPERTIES

The glass transition temperature, T_g , which is correlated with the strength of cohesive forces in the network, is one temperature characteristic that describes the thermal properties of Chalcogenides. These signify the crucial factors that must be taken into account when developing CG applications. Differential thermal analysis (DTA) is used to determine the appropriate values for these parameters. The importance of the softening point, where the glass has a viscosity of 107.6 poise, has already been reported through a DTA trace. This temperature or higher

allows the glass to be drawn into fiber. In comparison to other chalcogenide and halide glasses, the thermal properties of Ga-La-S-based glasses are typically characterized by high transition temperatures, given that these materials have superior environmental strength [100].

Another thermal characteristic of chalcogenides that provides information about material expansion as a function of temperature is the expansion coefficient. Compared to oxide glasses, chalcogenide glasses have a very high thermal expansion coefficient [101]. The relationship between the expansion coefficient and the curve's gradient is linear. Another crucial characteristic of chalcogenides is specific heat, which is the quantity of heat needed to raise a material's temperature by 1° per unit mass [102]. It was found that Tellurium-based chalcogenides have a specific heat between 373 and 600 K. As temperature rises, specific heat values rise as well. The ability of a material to conduct heat completely through its body is measured by its thermal conductivity [103].

Chalcogenides are a class of materials that contain elements like tellurium, selenium, and sulphur from group 16 of the periodic table. These compounds have interesting thermoelectric properties. Applications requiring the transformation of thermal energy into electrical energy and vice versa depend heavily on these characteristics [104]. Temperature, doping, crystal structure, and the particular elements involved all affect chalcogenides' thermoelectric performance. The voltage produced in a material per unit temperature differential is measured by the Seebeck coefficient, also known as thermopower. It is an important criterion for evaluating the thermoelectric performance of a material. For thermoelectric conversion to be efficient, higher Seebeck coefficients are preferred. High electrical conductivity is a common feature of efficient thermoelectric materials, which helps charge carriers flow (electrons or holes). Chalcogenides can exhibit different levels of electrical conductivity depending on their composition and structure. Low thermal conductivity is desirable for thermoelectric materials to enhance their efficiency. Chalcogenides can have varying thermal conductivities based on their specific composition and crystal structure. The carrier concentration (number of charge carriers) and mobility (how easily charge carriers can move) are critical factors affecting electrical conductivity. Doping, which involves introducing impurities, can be used to manipulate these properties. The electronic band structure of a material plays a significant role in determining its thermoelectric properties. Chalcogenides with suitable band structures may exhibit enhanced thermoelectric performance. Thermoelectric properties are often temperature-dependent. Some materials may perform better at higher temperatures, while others are optimized for lower temperatures. The overall thermoelectric performance of a material is often characterized by the dimensionless figure of merit (ZT). A high ZT indicates a more efficient thermoelectric material. Optimizing ZT involves balancing the conflicting requirements of high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. The thermoelectric properties of chalcogenides materials can be beneficial in various applications, particularly in the field of energy conversion and waste heat recovery [105]. One notable example is the use of tellurium-based chalcogenides, such as and lead telluride (PbTe), in thermoelectric generators. These materials exhibit a high Seebeck coefficient, meaning they generate a substantial voltage in response to a temperature gradient [106]. Additionally, they possess relatively high electrical conductivity, allowing efficient movement of charge carriers. The combination of these properties is advantageous for converting waste heat from industrial processes or other sources into electrical power. For instance, in thermoelectric power generators, a temperature difference is applied across the material, causing electrons to move from the hot side to the cold side, generating an electric current. This principle is exploited in applications like automotive thermoelectric generators to improve fuel efficiency by converting excess heat from the engine into electricity [107]. Another example is the use of chalcogenide thermoelectric materials in portable devices, where they can convert heat from the human body into electrical power to supplement or replace traditional batteries. This has the potential to extend the operational life of wearable devices or medical implants [108]. Furthermore, chalcogenides are explored for applications in solid-state cooling systems, where they can absorb heat from a certain area, carry it away, and release it in another area when an electric current is applied. This solid-state cooling technology can be more environmentally friendly and energy-efficient compared to traditional refrigeration methods [109].

3. APPLICATIONS OF CHALCOGENIDE GLASSES:

Some of promising applications of chalcogenides glasses are:

4.1. Phase change memory applications

PCM technology stores binary data in the anatomy of the alloy using a thermally activated, reversible, rapid switch. Two different phases of the material, each of which requires no energy to maintain in either structural state, are used to represent binary information. Amorphous and polycrystalline states are the two structural states of chalcogenide alloys that are stable. Similar to metal, the polycrystalline state shows a significant increase in free electron density. Changes in reflectivity and resistivity are caused by the excess free electron density. For rewriteable CDs and DVDs, the material is heated using a laser to transition between stable states. By directing a low power laser beam and identifying the variation in reflectivity between the two phases, the state of the memory can be read.

A promising technology for non-volatile mass storage applications is phase-change memory (PCM). Hard disc drives are currently taking the place of NAND flash memories in small-capacity memory applications. The main drawbacks of block erasing and read-write restrictions are present in flash memory, which is the industry standard for non-volatile memory and is designed using Si fabrication techniques. As a result, a memory that has quick read, write and erase cycles, low cost, low power, high endurance, scalability and the ability to store multiple bits in a single cell is needed today. NAND memory cell scaling limitations, however, cause NAND flash memories to have lower storage capacities than hard disc drives [110]. Utilizing 3D (three-dimensional) NAND flash memories, this issue can be solved [111].

Ge₂Sb₂Te₅ amorphous thin films produced by metal oxide chemical vapour highly dense three-dimensional phase-change memories can be produced by increasing deposition below the temperature at which metal-organic precursors begin to decompose. The high resistive "reset state" of the film is changed to a low resistive "set state" by application of the current pulse. About 0.5 V is the set voltage. When current pulses are applied continuously while increasing the pulse height, the set state is reset at about 1.5 V. It can be used as a phase change memory cell because the set-reset resistivity ratio is high enough. We can achieve a speed and voltage that is suitable for highly dense memories [112]. GeSbTe systems are utilised for optical storage media, such as Blu-ray Discs and rewritable digital versatile discs (DVDs) [113].

The PCM's multilevel cell technology uses intermediate resistance states to provide a higher storage density. It is observed that the resistivity of chalcogenide glass [114-117].

4.2. Pollutant Monitoring in Underground Water

Water monitoring can also be done by using chalcogenide materials. Chemical sensors made of chalcogenide glass are successfully used in biological, medical and food applications. The FEWS (fiber evanescent wave spectroscopy) method aids in locating volatile organic pollutants in groundwater. In this case, a fibre is used to transmit IR beams from the spectrometer to the sample while inserting a portion of the fibre into the stud environment. The measurement is based on the evanescent wave that forms around the fibre as light enters the fibre. Te₂As₃Se₅ has recently been used by researchers to create fibres because it has good thermomechanical properties and large transmission windows from 4000 to 9000 cm⁻¹. They tested the fibre in a real-world setting to detect the addition of trichloroethylene, tetrachloroethylene and dichlorobenzene as pollutants while wearing proper Teflon protection. [118].

4.3. Reverse Ridge/Slot Waveguides

Mid-IR sensors and nonlinear photonic devices that can be integrated into a chip are now possible thanks to chalcogenide glasses used as waveguides [119,120]. As₂S₃ is employed to create a reverse ridge/slot hybrid chalcogenide glass waveguide. It has two silicon dioxide slots that are vertical. When creating chalcogenide-based photonic devices, proper consideration must be given to the dispersion design. These devices are capable of operating in quasi-TE mode in three ZDWs with a very flat dispersion profile [121]. Mid-IR optical devices can be materialized using chalcogenide glasses. Phase mismatch of the degenerate four wave mixing (FWM) process

is measured by reverse ridge waveguides. A new wavelength is created by the interaction of 2 or 3 different wavelength signals in FWM. Using nonlinear optical devices, the efficiency of the system can be measured as a function of the phase mismatch in the signals. Thermal evaporation, sputtering, or the micro-trench filling method could all be used to deposit As_2S_3 film on the substrate while utilizing As_2S_3 glass that has undergone solution processing. The narrow bandwidths of conventional ridges have been optimized to achieve near-zero IR dispersion [122].

4.4. Photonic Crystal Waveguides

Designing photonic integrated devices can benefit from using photonic crystal waveguides (PCWs). A photonic crystal strip with a uniform cross-section makes up the majority of it. These strips' cross-sectional variations enable lossless light transmission through Bloch modes. By utilizing slow light effects and small cross-sectional modalities, these waveguides enhance nonlinearity effects. Chalcogenide glass properties guarantee the creation of integrated optical devices.

Both two-photon absorption and high optical Kerr nonlinearity are present. The nonlinearity has a response time of less than one picosecond and is non-resonant. When illuminated by a light source close to the bandgap, chalcogenide glasses display a number of photo-induced phenomena. Chalcogenides can thus be used to create waveguides and gratings and to post-tune PCWs. [123].

Ag-doped As_2S_3 glass-made PCWs have higher Kerr nonlinearity than As_2S_3 -made PCWs. These materials have very little material absorption loss in the infrared spectrum. E-beam lithography and the Inductively Coupled Plasma (ICP) etching process can be used to create PCWs. The advantages of Chalcogenide-based PCWs can be formed and processed at low temperatures when compared to Silicon (Si). On the other hand, since chalcogenides are softer than Si, it can be challenging to achieve vertical sidewalls of air holes and clean facets for effective optical coupling to waveguides. [124].

4.5. Photo-sensing

Amorphous semiconductors called chalcogenide thin films are sensitive to electromagnetic radiation and can be used as photosensors. Different optoelectronic applications benefit from the chalcogenides' electronic and optical characteristics. An essential semiconducting component in solar cells, supercapacitors, gas sensors and related applications is copper sulphur (CuS) chalcogenide [125]. Covellite (CuS) in the sulfur-rich region, anilite ($\text{Cu}_{1.75}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$), djurleite ($\text{Cu}_{1.95}\text{S}$) and chalcocite (Cu_2S) in the copper-rich region are reported as the five stable phases of CuS at room temperature. Due to its important characteristics, such as good electrical conductivity, charge-transfer mechanism and nearly ideal solar control characteristics, CuS (covellite) is preferred for photosensitive devices. CuS thin films were made using the chemical bath deposition method, which is an easy and affordable process. Large-scale deposition and processing at low temperatures are also made possible by this technique [126].

4.6. Temperature Sensors

In chalcogenide glass, the covalent glass network has a typical rigid structure. Below the glass transition region, the optical absorption edges of these materials exhibit temperature dependence and exhibit quasi-linear behaviour. This attribute serves as the foundation for the sense of temperature. Extremely pure selenium and As_2Se_3 glass were used to create the $\text{Ge}_{18}\text{As}_{18}\text{Se}_{64}$ samples and the absorption edge changes as the temperature of the experimental setup changes. The long wave shift of the transmission spectrum has been seen to rise with temperature [123]. $\text{Ge}_{18}\text{As}_{18}\text{Se}_{64}$ is a promising composition for temperature sensing, according to experimental results, because it has good linearity and stability of optical properties in the temperature range of 180-200 °C. [127].

4.7. Optical Waveguides for biosensing

The important characteristics of chalcogenide glasses are based on their composition, large refractive indices and wide transmission windows, which enable extremely high light concentration outside the core material. Chalcogenides can thus delicately detect changes in the environment or in the clinical setting. Optical biosensors

are applied using optical waveguides based on chalcogenides. The Te-As-Se (TAS) glass used in chalcogenide biosensors, which are essentially optical fibre sensors, has a high refractive index, a sizable transmission window and good thermo-mechanical properties. This glass has been used to gather immediate information on changes in the metabolism of rat brains [128].

4.8. Brain Computing

The important characteristics of chalcogenide glasses are based on their composition, large refractive indices and wide transmission windows, which enable extremely high light concentration outside the core material. Chalcogenides can thus delicately detect changes in the environment or in the clinical setting. Optical biosensors are applied using optical waveguides based on chalcogenides. The Te-As-Se (TAS) glass used in chalcogenide biosensors, which are essentially optical fibre sensors, has a high refractive index, a sizable transmission window and good thermo-mechanical properties. This glass has been used to gather immediate information on changes in the metabolism of rat brains [129]. In order to replicate this, photonic axons and synapses transmit data as optical pulses move along the fibre. Through photo-darkening brought on by exposure at sub-bandgap wavelengths, the transmission is altered. Excitatory or inhibitory action potentials are produced by photomodulation [130]. This exploration done by researchers at The Photonics Institute (TPI), gives rise to an all-optical implementation of a number of intraneuronal and intraneuronal communication protocols that underlie learning and cognition in the brain.

Gallium lanthanum oxysulphide (GLSO) is used to create the photonic axon and synapse. From a pre-melted polished glass preform, GLSO microfibers with the chemical compositions Ga_2S_3 and La_2O_3 were produced using conventional fabrication methods on a fibre drawing tower that had been specially modified. Under sub-bandgap green illumination, they can be identified for their photo-darkening properties. Multichannel neuromorphic modules and systems are realized in visible to mid-infrared wavelengths by amorphous metal-sulfide microfiber. Chalcogenides' photo-induced properties enable the creation of real neuromorphic devices with fast operation, wide bandwidth and small thermal footprint.

5. Challenges and Future Prospects in the Synthesis, Processing and Commercialization of Chalcogenide Materials:

5.1. Challenges:

- **Synthesis Complexity:** Chalcogenide materials often exhibit complex atomic arrangements and stoichiometries, making their synthesis challenging. Developing scalable, reproducible and cost-effective synthesis methods for a wide range of chalcogenides remains a significant challenge.
- **Phase Control:** Achieving precise control over the phase and crystallinity of chalcogenide materials is essential for tailoring their properties. Controlling phase transitions and avoiding unwanted crystalline phases during synthesis is a key challenge.
- **Chemical Stability:** Many chalcogenide materials are sensitive to moisture and oxygen, which limits their shelf-life and long-term stability. Developing strategies to enhance their chemical stability without compromising their properties is crucial.
- **Material Purity:** Impurities and defects can significantly impact the properties of chalcogenide materials. Ensuring high material purity and minimizing defects in large-scale production is a persistent challenge.
- **Scalability:** Transitioning from laboratory-scale synthesis to scalable, industrial production methods is a critical hurdle. It requires optimizing processes for high-throughput production while maintaining material quality and consistency.
- **Environmental Concerns:** The extraction and processing of some chalcogenide raw materials may have environmental impacts. Developing sustainable and eco-friendly production methods is a growing concern.

- **Safety Hazards:** Some chalcogenides, such as certain tellurides, can be toxic and pose safety hazards during synthesis and handling. Safe manufacturing and disposal procedures must be developed and adhered to.

5.2. Future Prospects:

- **Advanced Synthesis Techniques:** Emerging synthesis techniques, such as chemical vapor deposition (CVD), solvothermal methods and molecular beam epitaxy (MBE), offer greater control over chalcogenide materials' properties. Continued advancements in these methods will enable the production of tailored materials with improved properties.
- **Nanomaterials and Nanostructuring:** Nanoscale engineering of chalcogenide materials can unlock novel properties and applications. Future research will likely focus on designing and fabricating chalcogenide nanostructures with enhanced performance.
- **Computational Design:** Computational materials science and machine learning can aid in predicting and designing chalcogenide materials with desired properties. This approach will accelerate the discovery of new materials for specific applications.
- **Environmental Sustainability:** Efforts to develop environmentally friendly synthesis routes and recycling methods for chalcogenide materials will gain prominence. Green chemistry principles will be applied to minimize the environmental footprint of production processes.
- **Integration in Emerging Technologies:** Chalcogenide materials will continue to find applications in emerging technologies such as quantum computing, neuromorphic computing and advanced energy storage systems. Their unique properties make them promising candidates for these cutting-edge applications.
- **Standardization and Quality Control:** As chalcogenide materials move toward commercialization, standardization and quality control measures will become increasingly important to ensure consistency and reliability in their performance.
- **Collaborative Research:** Collaboration between academia, industry and government agencies will be crucial for addressing challenges and accelerating the development and commercialization of chalcogenide materials. Public-private partnerships can facilitate research and development efforts.

Thus, chalcogenide materials present exciting opportunities for various applications, overcoming synthesis, processing and commercialization challenges is essential for realizing their full potential. Future prospects involve advanced synthesis techniques, sustainable practices and integration into emerging technologies, positioning chalcogenides as critical materials in the 21st century.

6. CONCLUSION

Most chalcogenide glasses are based on the chalcogen elements S, Se and Te along with more electropositive elements. Other elements like Ge, As, Sb, Ga, *etc.* are added to create these glasses. These low-phonon energy materials make glasses that are typically transparent from the visible to the infrared range. Since rare-earth elements like Er, Nd and Pr can be doped into chalcogenide glasses, many applications for active optical devices have been suggested. These glasses are helpful for switching entirely optically. The following are the results of the survey. Due to the fact that the vast majority of molecular species vibrate in the infrared spectrum, chalcogenide fibres are ideal for chemical sensing applications. There are numerous chalcogenide glass applications in contemporary technology. The main benefit of these materials is that they transmit across a broad range of the infrared electromagnetic spectrum. Examples include infrared detectors, moldable infrared optics such as lenses and infrared optical fibres. Optical switching applications may benefit from their high optical nonlinearity. The following are the results of the survey. Due to the fact that the vast majority of molecular species vibrate in the infrared spectrum, chalcogenide fibres are ideal for chemical sensing applications. There are numerous chalcogenide glass applications in contemporary technology. Examples include infrared detectors, bendable infrared optics like lenses and infrared optical fibres. The outcomes of the studies mentioned above

make it clear that there is a possibility that chalcogenide glasses will be used in more applications. The foundation for the creation of potential applications and devices is outlined in this effort. It would be beneficial to conduct additional research to fine-tune the properties for particular applications by adjusting the stoichiometric combinations and preparation techniques

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