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Insights of Chalcogenide Glasses for Innovation in Applied Science

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Abstract: Chalcogenides are low-phonon-energy materials and are generally transparent from the visible up to the infrared. Interest in chalcogenide glasses has, over the past few years, increased significantly as glasses, crystals and alloys find new life in a wide range of photonic devices. Chalcogenide glasses have many unique properties that allow them to be used in a variety of optical applications. Chalcogenide glass fibers transmit in the infrared red region, hence they have potential applications in the civil, medical, and military areas. Infrared transparency also allows them to be used in sensors for molecules that have "fingerprints" in the 2 to 25 μm range. The application in optics, photonic, optoelectronics increased the demand in glasses, which can transmit a radiation in infrared range up to the wavelength ~2 μm. Chalcogenide glasses represent one of the major categories of amorphous semiconductors because of their physical properties such as the switching and memory effects and for their IR transmittance.

Keywords: Chalcogenide glasses, infrared region, applications

1. Introduction

Awareness towards conserving the environment has driven the focus of researchers to develop sustainable and renewable green materials. Chalcogenide glass is a glass containing one or more chalcogens containing Se, Te and S. The classical chalcogenide glasses (mainly sulfur-based ones such as As-S or Ge-S) are strong glass-formers and possess glasses within large concentration regions. Glass-forming abilities decrease with increasing molar weight of constituent elements, i.e., S > Se > Te. Most stable binary chalcogenide glasses are compounds of a chalcogen and a group 14 or 15 element and may be formed in a wide range of atomic ratios. Ternary glasses[1] are also known. All chalcogenide compositions do not exist in glassy form, though it is possible to find materials with which these non-glass-forming compositions can be alloyed in order to form a glass, viz. gallium sulphide-based glasses. In the last few years owing to their interesting properties and technological applications these materials are used in optical and photonic devices. The first chalcogenide glass to be commercially developed was As_2S_3, produced for passive, bulk optical components for the mid-IR in the 1950s. The modern technological applications of chalcogenide glasses are widespread. Goryunova and Kolomiets[2] showed that amorphous chalcogenide glasses are semiconducto-rs. Anderson introduced the concept of localization[3] whereas Ioffe and Regel[4] realized that band gap depends on existence of short range order of lattice. Mott and Twose[5] showed chalcogenide glasses have been studied intensively owing to their interesting properties. These materials are used in optical and photonic devices as they have good electro-optic, thermo-optic, magneto-optic, acousto-optic properties, high refractive index and I R transparency[6-9]. Amorphous chalcogenide materials can be broadly classed by the type of atoms to which they bond to form amorphous systems. Table 1 lists the chalcogenide classifications and gives some examples of the type of chalcogenide which falls into each category.

Table 1 Amorphous chalcogenide systems

S.No.	**Class**	**Examples**
1.	Pure chalcogenide	S, Se, Te, $SxSe_1$-x
2.	Pnictogen-chalcogen	(V-VI) As_2S_3, P_2Se
3.	Tetragen-chalcogen	(IV-VI) $SiSe_2$, GeS_2 (III-VI) B_2S_2, In_xSe_{1-x}
4.	Metal chalcogenide	MoS_3,WS_3, Ag_2S-GeS_2
5.	Halogen-chalcogenide,	As-Se-I,Ge-S-Br,Te-Cl

Chalcogenide glasses material heat to melt is the form of a liquid and at some instant freeze the position of every atom by quenching. Even in this freezed position they retain short range order and the position of the nearest neighbor remains nearly the same. These glasses are useful in the preparation of passive devices like lenses, windows, fibers etc active devices like laser fiber amplifiers[10] and non-linear components[11-13]. The application in optics, photonic, optoelectronics increased the demand in glasses, which can transmit a radiation in infrared range up to the wavelength ~2 μm. Chemical and physical properties of so-called special glasses (figure 1) will complete the ones of silicate glasses. Special glasses can be divided into three groups: Fluoride glasses based on ZrF_4 or HfF_4, chalcogenide glasses based on chalcogens (S, Se, Te) and Heavy metal oxide (HMO) glasses such as GeO_2PbO, TeO_2-PbO, etc.

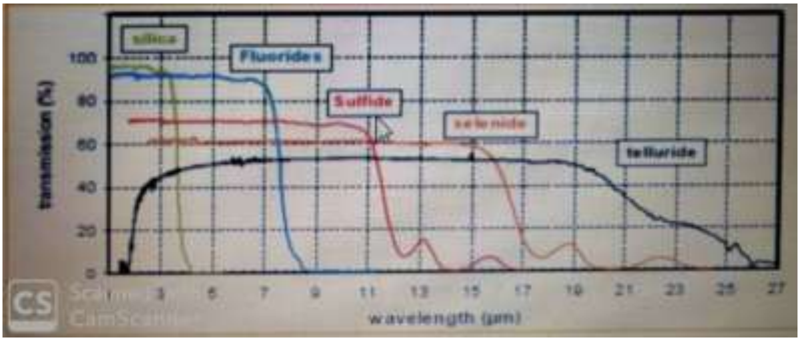

Figure1. Optical Transmission of Chalcogenide Glasses compared to silica and Fluoride glass

Chalcogenide glasses or amorphous semiconductors are applicable materials in modern optoelectronics. Although first studied over fifty years ago, interest in chalcogenide glasses has over the past few years, increased significantly as glasses, crystals and alloys find new life in a wide range of photonic devices. Chalcogenides come in a variety of colours that depend on their chemical constituents, ranging from partially transparent to completely opaque. Chalcogenides are also photosensitive, which, although a potential disadvantage for some applications, is a significant advantage for writing structures into fibres. In addition, they are glassy semiconductors, which gives them interesting electrical properties.

2. Preparation Techniques of Chalcogenide Glasses

Thermal Evaporation Technique: In this technique chalcogenide materia-ls are made amorphous in the form of films by creating vacuum in the bell jar through a diffusion pump and heating the material by passing electricity, where the entire environment inside the deposition chamber is free of impurities and the sample is ready for deposition.

Flash Evaporation Technique: In this technique material is dropped on the pre-heated filament. A magnetic field is established to produce vibrations in the magnetic strip containing material in addition to the coating unit.

Quenching Technique: In this technique, sealed quartz ampoules containing weighed amount of chalcogenide materials is kept in a furnace and rocked for about twelve hours to make a homogenous melt. Quenching is done by dropping the quartz ampoules suddenly in ice-cold water or liquid nitrogen as per requirement.

Sputtering Technique: Sputtering is a well-known vacuum deposition process that has been widely used for the fabrication of high-quality films[14]. Advantages of sputtering include good thickness and compositional uniformity, the capacity to coat large and non-planar surfaces, the capability of depositing multi component materials with a film composition similar to that of the target. Franz et. al.[15] first reported the deposition of thin films of Ga-La-S glass by RF magnetron sputtering. Films ranging in thickness from 0.15 to 3.8 µm were fabricated. They were glassy, uniform in composition. It can be used to create very thin, uniform and the most cost-effective films possible. It can be also used to apply both conductive and insulating materials to any type of substrate, including heat sensitive plastics (sputtering is a cold momentum transfer technique), which is useful for optical disks.

Glow Discharge Decomposition Technique: In this technique, chemical composition of the gas takes place so that solid film is deposited on the substrate kept in the plasma. The films deposited depends upon gas pressure, flow rate, substrate temperature and chamber geometry. This method is similar to sputtering, but instead of ions from the plasma ejecting the material from the target, a chemical reaction is initiated in the gas phase by creating a radio frequency glow discharge of the reactant gas, leading to the deposition of the solid form on a substrate placed inside a chamber. The discharge can be produced either in the pure reactant gas or in a mixture of reactant gas and a carrier gas like argon. By using a combination of reactant gases, films of different materials can be made.

Chemical Vapor Deposition Technique: The chemical vapor deposition technique is widely used in the semiconductor industry to produce thin films. In this process films of materials are deposited from the vapor phase by the decomposition of chemicals on the surface of a substrate. The deposition of the film is controlled by a chemical reaction. The method is hence more versatile than many traditional methods. This technique depends upon the thermal energy for the decomposition and the applied r. f. field serves to heat up the substrate upon which the vapor decomposes.

3. Physical Properties of Chalcogenide Glasses

Structural Properties: In chalcogenide glasses the covalent bonded atoms are arranged in an open network with order extending up to the third or fourth nearest neighbours. The chemical bonding between atoms, result in the short-range order which is responsible for most of the properties of amorphous materials. The semiconducting property chalcogenide glasses is a direct consequence of the covalent bonding existing in these materials.

Thermal Properties: Chalcogenide glasses are associated with thermal properties viz., glass transition, crystallization and melting temperatures, along with the coefficient of thermal expansion, thermal diffusivity etc. The glass transition temperature of chalcogenide glasses is related to the magnitude of cohesive forces within the network and these forces must be overcomed to allow atom movement. Thermal conductivity, of a material results from transport of energy via electrons or phonons. Thermal conductivity is related to phonon mean free path which in chalcogenide glasses is considerably shorter and correspondingly thermal conductivity is less. It has been pointed out that there is a strong correlation between the thermal diffusivity and the switching behavior of chalcogenide glasses. Chalcogenide glasses with low thermal diffusivity are likely to exhibit memory behaviour and those with higher values of thermal diffusivity may show threshold-type switching. Properties that are time dependent can be obtained from enthalpy-temperature diagram as shown in figure 2.

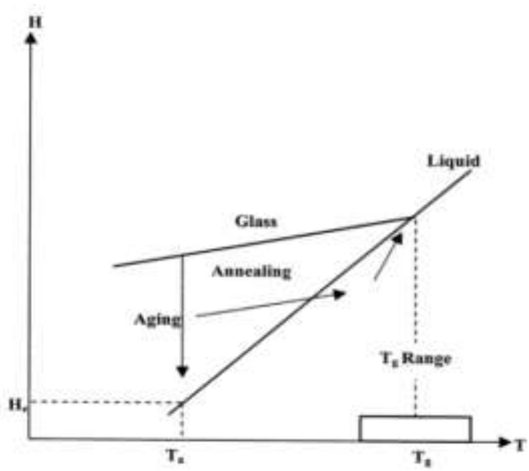

Figure 2. A plot of enthalpy against temperature for chalcogenide glasses

Electronic Properties: The optical and electrical properties of chalcogenide glasses are generally much less sensitive to non-stoichiometry. Ionic conduction arises from the movement of anions or cations when an electric field is applied across an ionic material. Cations are effectively placed in gaps within a glassy structure. The gaps[16] allow the ions an extent of freedom to move under the influence of an electric field.

Chalcogenide glasses can be considered as semiconductors with an energy gap up to 3eV. On the whole chalcogenide materials obey the 8N bonding rule whereby all electrons are taken up in bonds so that the electrical conductivity is not sensitive to small changes in composition or the addition of elements such as Ge or Si with four (or more) outer electrons. Adding elements to the glass with less than four outer s and p electrons often has a major effect[17] on the conductivity. Kolomeits[18] found that the addition of Cu, Ag, In, and Te to As_3Se_2 and As_3S_2 causes a significant increase in conductivity.

Optical Properties: Chalcogenide optical fibers have been important technologically for several decades. These fibers can potentially transmit in the 2-12 µm wavelength region, beyond the transmission window of conventional optical fiber and can therefore enable numerous infrared applications. Optical fibers drawn from chalcogenide-based glasses were first investigated in the 1970’s when fibers from glasses based on arsenic or germanium selenides and tellurites rapidly found application for transmission of carbon dioxide laser wavelengths around 10 microns. Extensive studies[19] have been made on photo-induced phenomena of chalcogenide glasses.

4. Potential Applications of Chalcogenide Glass

Chalcogenide glasses has numerous potential applications in various fields as shown in figure 3. thin films are used in optical data storage and in the manufacturing of highly efficient solar cells. Chalcogenide fibres were studied as waveguides for delivering CO_2 laser light at wavelengths of 10 µm, with the discovery of new lasers, various chalcogenide compositions were developed to address individual wavelengths. Addition of tellurium to the glass tends to increase transmission at infrared wavelengths, whereas sulphur aids transmission at visible wavelengths. Chalcogenides are also useful for medical applications such as laser surgery, which requires a wavelength of around 3 µm. Gallium lanthanum sulphide fibres transmit well at this wavelength, and their non-toxic components and high melting temperature suit minimally invasive surgery.

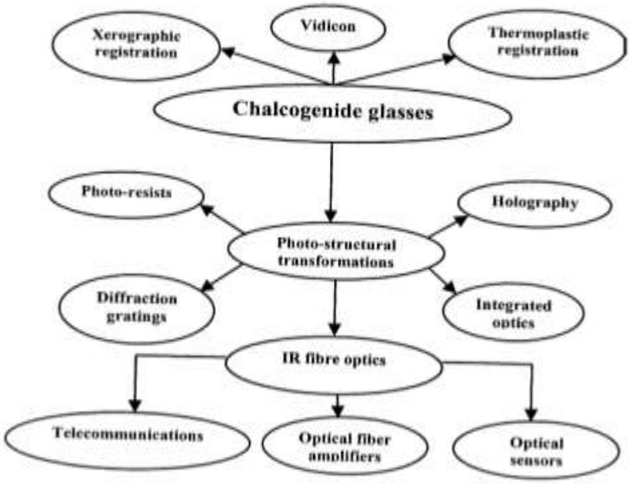

Figure 3. Potential applications of chalcogenide glasses in various fields

Chalcogenide fibers are well-suited for chemical-sensing applications, since most molecular species vibrate in the infrared region. They can be used in fiber-optic chemical-sensor systems for quantitative remote detection and identification, as well as detecting chemicals in mixtures. Numerous systems have been studied which include oil, freon, soap, paints, polymer-curing reactions, glucose-water, benzene and derivatives, chlorinated hydrocarbons, alcohols, carboxylic acids, aqueous acids, perfumes, and pharmaceutical products. Several publications summarize[20-25] the methods for deposition of thin-film absorbers from basic material formulation to device processing techniques. Most of the reviews focus on either chalcopyrite-type or kesterite-type materials[26], and very few reviews have been found on the progress of solution-processed Cu-chalcogenide-based thin-film solar cells. One application of growing interest is the use of chalcogenide fibers to deliver laser power delivery for medical purposes. Laser surgery offers the potential for less painful, minimally invasive treatment for a variety of applications including dentistry, surgery, and dermatology. Chalcogenides have been chosen as a memory material primarily because they can be switched between phases relatively easily and are also thermally stable. Chalcogenide materials have found importance in optical data storage devices. CD-RW and DVD-RW optical discs take advantage of the phase change nature of chalcogenide materials. The active layer of the CD-RW consists of a mix of silver, indium, antimony and telluride 8Ag:13In: 48Sb:30Te. When the layer is heated to above its crystallization temperature and slowly cooled it becomes crystalline, if it is heated a bit higher to the melting temperature it becomes amorphous.

Table 2 Widely known commercial chalcogenide glasses

S.No.	Composition	Common Name	Manufacturer	Website
1.	Ge-As-Se	Black Diamond	Light path technology	www.lightpath.com
2.	As-S	AMTIR-6	Amorphous material Inc.	www.amorphousmaterials.com
3.	Ge-As-Se	AMTIR-1	Texas USA	_
4.	As-Se-Te	C1	_	_
5.	Ge-As-Se	GASIR	The Umicore Group	www.umicore.com
6.	Ge-Sb-Se	GASIR-2	Belgium	_
7.	Ge-As-Se-Te	Vitron IG3	Vitron Spezialwerkstuffe GmB Germany	www.vitron.de
8.	Ga-La-S	Ga-La-S	ChG Southampton Ltd	www.chgsouthampton.com
9.	Ga-La-S-O	Ga-La-S-O	United Kingdom	_
10.	Ge-S	GES	_	_
11.	Ge-Sb-Te	GST	Mitsubishi Materials Corp, Japan	www.mmc.co.jp

Schweitzer et. al.[27] achieved the laser operation in a rare-earth doped chalcogenide glass. A thick glass disk of 1.42 mm with the composition $70Ga_2S_3$:$28.5La_2S_3$:$1.5Nd_2S_3$ was placed in a hemispherical laser cavity and pumped with a Ti : sapphire laser at 890 nm at room temperature. The threshold power[28] is low but the rollover of the output power indicates strong thermal problems in the laser material. Solution-based approaches for the deposition of Cu-chalcogenide thin-film absorbers suggests that methods viz. spin coating, spray pyrolysis, doctor blading etc. hold promise for achieving performances comparable to vacuum-deposition routes as revealed in the recent literature[29-31]. Some commercial chalcogenide glasses have been summarized in table 2. To obtain the solution processed thin-film chalcogenides, there are lots of challenges to be overcome.

5. Conclusion

Chalcogenide glasses are attracting significant attention due to their mid-infrared transparency and highly nonlinear properties. The use of chalcogenide materials has evolved over the last two or three decades from a simple infrared transmitting bulk glass into a multifunctional optoelectronic material for the future. The diversity of both the properties of chalcogenide glasses and the geometries into which they can be formed have ensured current and future interest in the application of these emerging optoelectronic family of materials. Bulk optics and optical fibers were the intial drivers for chalcogenide glass research and development. Interest continues strongly in both these areas but today many promising new applications, for example on chalcogenide films, from nanometer to millimeter thicknesses are being studied. Other applications are exploiting microspheres, nanoparticles and nanowires formed from these incredibly versatile glasses.

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