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Study of Chalcogenide Glass and their Physical Properties and Applications

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Introduction : Chalcogenide glasses are based on the chalcogen elements S, Se, and Te. These glasses are formed by the addition of other elements such as Ge, As, Sb, Ga, etc. They are low-phonon-energy materials and are generally transparent from the visible up to the infrared. Chalcogenide glasses can be doped by rare- earth elements, such as Er, Nd, Pr, etc., and hence numerous applications of active optical devices have been proposed. Since chalcogenide-glass fibers transmit in the IR, there are numerous potential applications in the civil, medical, and military areas. Passive applications utilize chalcogenide fibers as a light conduit from one location to another point without changing the optical properties, other than those due to scattering, absorption, and reflection.

These glasses are optically highly nonlinear and could therefore be use- ful for all-optical switching (AOS). Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photoinduced effects as a result of illumination. Various models have been put forward to explain these effects, which can be used to fabricate diffractive, waveguide and fiber structures.

Key Words : Chalcogenide, Glasses, AOS,

Structure of Chalcogenide Glasses

Solids are a particular state of condensed matter characterized by strong inter- actions between the constituent particles (atoms, molecules). Solids can be found or prepared either in an ordered (crystalline) state or in a disordered (non crystalline) state.

A few structural forms, a disordered material is neither unique nor clearly defined. An ideal crystal corresponds to a regular arrangement of atoms in a lattice with well-defined

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symmetry, and a structural unit called the unit cell can be defined. Translation of the unit cell along the three coordinate axes reproduces the whole assembly of atoms.

Chalcogenide glasses form an important class of materials. Chalcogenide glasses are disordered non crystalline materials which have pronounced tendency their atoms to link together to form link chain. These glasses are a recognized group of materials always containing one or more of the chalcogen elements such as Se, Te or S,. Chalcogenide glasses can be obtained by mixing the chalcogen elements, viz, S, Se and Te with elements in the periodic table such as Si, Ge, Ga, As, Sb In, Sn, and Bi, Ag, Cd, Zn, lanthanides and Na etc. Chalcogenide glasses can also contain halogen elements, and include the TeX (X = halogen) gIasses[65] In these glasses, short-range inter-atomic forces are predominantly covalent: strong in magnitude and highly directional, whereas weak van der Waals' forces contribute significantly to the medium-range order. The atomic bonding structure is, in general more rigid than that of organic polymers and more flexible than that of oxide glasses. Chalcogenide glasses are generally less robust, more weakly bonded materials than oxide glasses. Both heteropolar(eg. Ge-Se) and homopolar (eg. Se-Se, Ge-Ge) bonds can form in them. Thus a glass contains a non-stoichiometric amount of chalcogens, and excess chalcogen atoms, if any can form chains. The chemical bonding of the matrix is usually directional and covalent. Some metallic element containing chalcogenide glasses behave as (super) ionic conductors. These glasses also behave as semiconductors or, more strictly, they are a kind of amorphous semi-conductors with band gap energies of 1±3eV (Fritzsche, 1971). Commonly, chalcogenide glasses have much lower mechanical strength and thermal stability as compared to existing oxide glasses, but they have higher thermal expansion, refractive index, larger range of infrared transparency and higher order of optical non-linearity.

Properties:

- ***Chemical structure properties :*** Chalcogenide glasses are based on the chalcogen elements S, Se and Te combined with network-forming elements, such as Ge, As, P, Sband Si. The resulting glass exhibits a number of amorphous semiconductors like properties. The glass structure consists of covalently bonded molecules, as opposed to the ionic bonding of other glasses and these are weakly bound together via a combination of covalent and Van der Waals-like attraction. Chalcogenide glasses may form with a wide

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range of compositions as both hetropolar and homopolar bonds may form. In the case of the As-S glass system, the atomic ratio of arsenic to sulfur can be varied between 1.5 and 9. As a result, the composition of the chalcogenide glasses can be adjusted to tune particular properties. For a given chalcogenide glass system, increasing the relative atomic mass of the chalcogen or its proportion in the glass reduces the average bond strength. The weaker bonds of chalcogenide glasses contribute to them being generally less robust than oxide glasses. For example they have lower softening temperatures and hardness, and higher thermal expansion coefficients.

- ***Refractive index and dispersion :*** Chalcogenide glasses possess relatively large refractive indices between 2 to greater than 3. The refractive index increases as sulfur is replaced by the more polarizable selenium and tellurium. The high refractive index is advantageous for strong optical field confinement which allows small waveguide bend radii and enhanced optical intensities. In addition, the large index contrast relative to air can potentially provide a complete band-gap for photonic crystals. The zero dispersion wavelengths for chalcogenide glasses lie well in the mid IR. At communication wavelengths around 1.55 μm these materials exhibit strong normal dispersion. This is not necessarily detrimental to performance as typical device lengths are short, of the order of centimetres and the dispersion sign ensures that possibility of using waveguide dispersion to engineer the chromatic dispersion, similar to what has been achieved in silicon.

- ***Linear loss mechanisms :*** For chalcogenide glasses the long wavelength cut-off lies in the mid infrared due to large atomic masses and relatively weak bond strengths resulting in low phonon energies. As a rule of thumb, the transparency edge is 12 μm for sulfide based glasses, 15 μm for selenide glasses and 20 μm for telluride glasses. In the absence of extrinsic attenuation mechanisms, Rayleigh scattering defines the minimum attenuation of the glass within the electronic and multiphoton absorption window. Free carrier absorption is generally negligible in Chalcogenide glasses. While most chalcogenide glasses have small band gaps, they also exhibit low carrier mobility. As the magnitude of the free carriers in solids in the low mobility case is proportional to the

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carrier mobility, free carrier absorption is not important in chalcogenide glasses. However chemical impurities, particularly oxygen can result in a drastic reduction in infrared transmission. Typically ultra pure chemicals must be further purified, for example by hydrogen distillation, before being melted either under vacuum or within a nitrogen environment to create bulk glasses.

- ***Photo-induced phenomena*** Chalcogenide glasses exhibit several types of photo-induced phenomena including: photocrystallisation, photo-polymerization, photodecomposition, photo-contraction, photovaporisation, photo-dissolution of metals and light-induced changes in local atomic configuration. These changes are accompanied by changes in the optical band gap and thus optical constants. Chalcogenide glasses exhibit strong photo-induced properties because of their inherent structural flexibility. The usually double covalent bonded chalcogen atom possesses a lone pair of non-binding electrons that under illumination can alter the bond number. These photo induced effects have been used for the formation of various components including waveguides and surface grating

Applications :

The first chalcogenide glass to be commercially developed was A2S3, produced for passive, bulk optical components for the mid-IR in the 1950s. The modern technological applications of chalcogenide glasses are widespread.

The physical properties of chalcogenide glasses (high refractive index, low phonon energy, high nonlinearity) also make them ideal for incorporation into lasers, planar optics, photonic integrated circuits, and other active devices especially if doped with rare earth ions.

Many chalcogenide glasses exhibit several non-linear optical effects such as photon-induced refraction, and electron-induced permittivity modification.

Some chalcogenide materials experience thermally driven amorphous crystalline phase changes. This makes them useful for encoding binary information on thin films of chalcogenides and forms the basis of rewritable optical discs and non-volatile memory devices such as PC-RAM.

Applications of infrared optics include energy management, thermal fault detection, electronic circuit detection, temperature monitoring and night vision

Infrared detectors, mouldable infrared optics such as lenses, and infrared optical fibers, with the main advantage being that these materials transmit across a wide range of the infrared

Chalcogenide fibers are well-suited for chemical-sensing applications, since most molecular species vibrate in the infrared region. Chalcogenide fibers can be used in fiber-optic chemical-sensor systems for quantitative remote detection and identification, as well as detecting chemicals in mixtures. Different sensing techniques including attenuated total reflectance (ATR), diffuse reflectance, and absorption spectroscopy have been introduced. 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.

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