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Review on Chalcogenide glass

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Abstract

This paper describes the overall review of Chalcogenide glass. The synthesis of Chalcogenide glass by different method is described in details. This paper also discuss the different apparatus which is used to characterized the Chalcogenide glasses for example XRD, UV-visible spectrophotometer, EDAX analysis, Photoluminescence spectroscopy, dielectric properties Field Emission Scanning Electron Microscope (FE-SEM), Differential scanning calorimetry.

Keywords: Chalcogenide glass, Synthesis, Characterization, XRD, EDAX, FE-SEM.

1. Introduction

The term "chalcogen" means "ore former," derived from the Greek words chalcos "ore" and gen "formation" (Jensen et al.1997). Chalcogenide glasses contain one or more of the chalcogen elements: S, Se and Te, but not O. These elements have pronounced tendency to link together to form long chains. They can be regarded as a 'soft semiconductor' due to flexible and viscous of their atomic structure and semiconductors because of band gap energy (~2eV) characteristics of semiconductor materials (1–3eV) (Elliott et al.1991). Chalcogenide glasses can be prepared by different methods, like melt quenching, vacuum deposition and other less common methods such as microwave irradiation (Lezal et al. 2003).Chalcogenide glasses are characterized by short range order (Zallen et al. 1983). The atomic bonding structure of chalcogenide glasses is more rigid than that of organic polymers and more flexible than that of oxide glasses. Chalcogenide glasses composed of heavier elements (S, Se, and Te) are denser than polymers and oxide glasses. The mechanical strength and thermal stability of chalcogenide glasses are much lower than oxide glasses and the thermal expansion, temperature coefficient of refractive index and relative photo elastic coefficient are much higher than oxide glasses (Hilton et al. 1966). Chalcogenide glasses are covalent where as oxide glasses are ionic. Chalcogenide glass appears to possess intermediate properties between a crystalline material and polymers (Ovshinsky et al. 1976), (Fritzsche et al.1976). Ovshinsky and his co-workers discovered that some chalcogenide glasses exhibited memory and switching effects (Stocker et al.1969). After this discovery it becomes clear that the electric pulses could be switch the phases in chalcogenides glasses back and forth between amorphous and crystalline state. Amorphous chalcogenide glasses posses the semiconductor properties (Goryunova et al. 1955) and there band gap depends on the existence of short-range order rather than on the long-range order of the lattice (Ioffe et al. 1960).The concept of localization of electronic states to explain the hopping conduction in crystalline semiconductors to show the electronic wave function has finite value in limited space and zero elsewhere (Anderson et al. 1958).The geometric disorder of the material forms a short range of localized states at the band edges while the neutral dangling bonds give rise a well-separated narrow band of localized states, at the center of the gap where the Fermi level (EF) lies (Davis et al.1970). Interactions between lone pair electrons on different atoms and interaction with their local environment result in localized states in the gap of chalcogenide glasses is suggested by (Ovshinsky et al. 1974).Chalcogenide glasses as a p-type semiconductor (Elliot et al.1991); Feltz et al. 1993). Chalcogenide glasses exhibit smaller conductivity due to band tail and gap states, which are manifestations of disordered structures than the corresponding crystals (Elliot et al. 1991; Feltz et al. 1993).

Chalcogenide glasses can be used in solid state batteries and micro batteries in environmental monitoring, in IR, chemical and ionic sensors, X-ray and diagnostically sensors, as surgical lasers, eye safe radars etc. (Frumar et al. 2003; Schubert et al 2001; Boolchand et al. 2001). The refractive index of first and second order is high in chalcogenide materials are very useful for optical switching in IR spectral region (Sanghera et al. 1999; Asobe et al. 1997; Zakery et al. 2003). Narayanan and his co-workers have reported the large switching fields in metal containing chalcogenide glasses based on chemical disordering (Narayanan et al. 2001). Aggarwal and Sanghera have discussed the development and application of chalcogenide glass for optical fibers in near scanning field microscopy/spectroscopy (Aggarwal et al. 2002). Selenium and Se-based alloys/compounds in the glassy form, so called chalcogenide glasses, still remain a curiosity for scientific researchers due to their unusual and interesting properties, of importance not only for practical applications but also for gaining further understanding of physical phenomena in chalcogenide glasses (Reddy et al. 1992); (Ovshinsky et al. 1968); (Taback et al. 1973); (Gerlach et al. 1979); (Philips et al. 1985). Amorphous selenium rich semiconducting alloys exhibit an interesting property of reversible phase change transformation and this property makes it very useful in optical memory devices. But in the pure state it has the disadvantages of short lifetime and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms. It has been found that substitution of Te by Se in Se–Te glasses breaks up the Se8 ring structure and slightly increases the chain fraction but reduces the chain length (Sharma et al. 2008).Glassy alloys of Se–Te system based on Se have become materials of considerable commercial, scientific, and technological importance. They are widely used in many fields as optical recording media because of their excellent laser writer sensitivity, xerography, and electrographic applications such as photoreceptors in photocopying and laser printing, infrared spectroscopy and laser fiber techniques (Tripathy et al. 2005); (Akiyama et al. 2001). Se–Te alloys have greater hardness, higher crystallization temperature, and lower ageing effect as compared to amorphous Se (Shimakawa et al. 1982). Se–Te based alloy films are thought to be one of the most promising media, which make use of phase change between an amorphous state and crystalline state. Amorphous selenium binary alloys with tellurium, due to their electro photographic applications such as photoreceptors in photocopying and laser printing, have been widely studied in both vacuum deposited amorphous film and vitreous bulk form in the past as reported and reviewed by a number of authors (Borisova et al. 1981); (Kotkata et al. 1981); (Abkowitz et al. 1982); (Abkowitz et al. 1987); (Vaezi-Nejad et al. 1987); (Springett et al. 1988, 1994); (Kasap et al. 1991); (Onozuka et al. 1988). Hanmei et al. has pointed out that the reduction in the band gap on the addition of Te is attributed to the lesser energy of Se–Te bonds as compared to that of Se–Se bonds (Hanmei et al. 1986). Kasap et al. have studied. They found that the as-prepared samples has short range order and does not have medium range order or layer structure.

2. Bulk and Nano Chalcogenide

Chalcogenide nanoscience is the study and application of nanoscience to chalcogenide-nanoparticle matrices, where nanoparticles are those with at least one dimension of less than 100 nm. The transition from micro to nanoparticles is lead to change in its physical as well as chemical properties. Two of the major factors in this are the increase in the ratio of the surface area to volume, and the size of the particle. The increase in surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over that of those interior of the particle. This affects the properties of the particles when they are reacting with other particles. Because of the higher surface area of the nanoparticles, the interaction with the other particles within the mixture is more and this increases the strength, heat resistance, etc. and many factors to change for the mixture.

3. Preparation techniques

3.1 Chalcogenide bulk glass preparation

In the present work, melt quenching method has been adopted to prepare chalcogenide bulk alloys. One of the most important features of the melt quenching technique is the high flexibility of geometry and composition and the advantage of obtaining materials of large size in comparison to other methods. The doping or codoping of active ions or transition metals is quiet easy using this method. This method can be used for the preparation of silicate, borate, phosphate, oxide, or non oxide systems .One of the main disadvantages of this method is the lack of ultra high purity as compared to other chemical methods. In order to avoid contamination, the crucibles made of noble metals can be used. Melt quenching method applied for chalcogenide glass preparation is based on the fusion of raw materials in to a viscous solid, followed by forming in to a shape and quenching to a glass. The exact amount of electronic grade (5N purity) constituent elements (Te, Se, Cd, and Hg) of raw materials were weighed in proportion to their atomic weight percentages using an electronic balance with the least count of a 10^{-4} gram and then placing into ultra-cleaned quartz ampoules (length ≈ 5 cm and internal diameter ≈ 10 mm).The ampoules were evacuated and sealed under a vacuum of 10^{-3} Torr with an oxygen-indane flame torch using rotary pumps to avoid reaction of alloying elements with oxygen at a higher temperature. The sealed ampoules were heated in a furnace at the rate of 4^0C/min. The temperature was raised up to 1000^0 C and was maintained for 10 hours. During the heating process, the ampoules were constantly rocked by a ceramic rod to ensure the homogeneity of the alloying materials. The ampoules with molten materials were rapidly quenched into the ice-cooled water to allow glass formation and to avoid crystallisation. The ingots of chalcogenide materials were taken out from ampoules by breaking them. The obtained melt was ground into powder form and filtered to obtain homogeneous alloy.

3.2 Thin film preparation

Thin film preparation can be prepared by physical deposition or chemical deposition method. Depositions due to chemical reaction are; Chemical Vapour Deposition (CVD),Electro deposition,Epitaxy,Thermal oxidation etc. and Depositions due to physical reaction are; Physical Vapour Deposition,Evaporation, Sputtering and Casting etc. The vapour deposition methods such as thermal evaporation, sputtering and chemical vapour deposition methods can yield amorphous thin films deposited on a substrate (Frey et al. 2011), (A. Goswami et al. 1996).

3.3 Thermal evaporation technique

In chalcogenide glass system, the deposition of the film at the oblique incidence may result to structural in homogeneity which may lead to formation of columnar growth morphology for the films (H.E.Atyia 2008).The making of an amorphous chalcogenide thin film by thermal evaporation in vacuum coating unit is done in the following way. The unit used for coating is Hind High Vacuum coating unit (model 12A4D). Firstly, bulk sample is loaded in tungsten boat in the system. After that the bell jar is closed and the system pumped down to around $2*10^{-5}$ torr through a diffusion pump. At this level of air pressure, the entire environment inside the deposition chamber is free of impurities and the sample is ready for deposition. With the shutter in the closed position, the temperature of the substrate is set to the desired level heated till the sample loaded starts to evaporate. The heating element in the system is conal sheated nichrome having a power rating of 500 watts, 120 V to 140V. Once the evaporation rate is stabilized and the substrate reaches its desired temperature, the vapour is allowed to come into contact with the substrate. The rate of evaporation is maintained to be $10A^0$/s. The evaporation rate as well as the film thickness can be controlled using a quartz crystal in Digital thickness Monitor Model-CTM-200 attached to the bell jar. When the desired thickness is reached, the shutter is closed. The amorphous film is maintained at the substrate temperature until the boat and the chamber cooled down to a level suitable for the film to be removed from the system.

4. Experimental tool and techniques used for characterization of Chalcogenide glass

In this section the structural, compositional, optical, thermal and dielectric characterization and the tools used for characterizing chalcogenide based materials are included.

4.1 X -Ray diffraction (XRD)

It is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. Structural characterization of the grown crystals for bulk solids and thin films has been done using X-ray powder diffraction technique. X-ray diffraction (XRD) is a non-destructive experimental technique that has been used to addressing the crystal structure of the solids, lattice constants, geometry, preferred orientation of polycrystals, identification of unknown materials, orientation of single crystals, defects, stresses, etc. of the bulk solids and thin films. In XRD, when a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 A^0 is incident on a specimen, diffraction of these rays by the crystalline phases in the specimen occurs according to Bragg's law: $n\lambda = 2d \sin\theta$ where, n = order of diffraction, λ = wavelength of monochromatic X-rays , d = inter planer distances, θ = glancing angle. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. Diffraction peak positions are accurately measured with XRD and its pattern compared with JCPDS (Joint Committee on Powder diffraction standards) database cards or any other reported work which makes it the best method for characterizing homogeneous and inhomogeneous system. Inhomogeneous system is varying from crystallite to crystallite or within a single crystallite and this cause a broadening of the diffraction peaks that increase with sinθ.. X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizeable amount of powder. This technique is very useful in characterizing nanoparticles. XRD is more sensitive to high– Z materials, and for low Z-materials, neutron or electron diffraction is more suitable. Thus compound is identified and the phases are known.

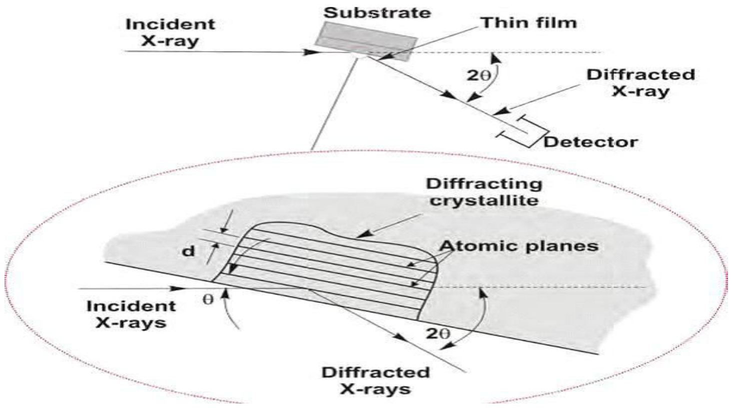

Fig.1. Schematic diagram of the operation of XRD

4.2 EDAX analysis

Energy Dispersive Analysis of X rays or the Energy dispersive spectroscopy (EDS) is an analytical technique used with FESEM for the elemental analysis or chemical characterization of the material.EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. The EDAX provides quantitative calculations for the bulk samples as well as thin films of grown crystals for measuring line intensities for each element in the sample for the same elements in calibration standards of known composition. The EDAX analysis confirms the proper composition of the grown crystals.

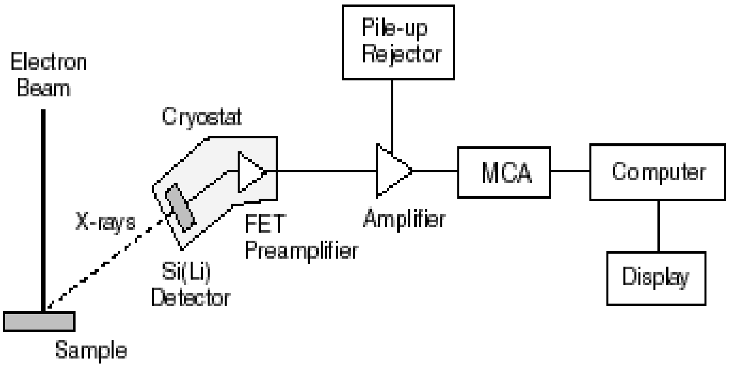

Fig.2.Schematic diagram of the operation of EDS

4.3 Field Emission Scanning Electron Microscope (FE-SEM)

A FESEM is microscope with high vacuum instrument that works with electrons instead of light these electrons are liberated by a field emission source. The vacuum allows electron movement along the column without scattering and helps prevent discharges inside the gun zone. Field Emission Scanning Electron Microscope (FE-SEM) uses strong Field Emission Gun producing a cleaner image, less electrostatic distortions and spatial resolution with smaller beam size than a typical SEM. The function of the electron gun is to provide a large and stable current in a small beam**.** The object is scanned by electrons according to a zigzag pattern for visualize very small topographic details on the surface or fractioned objects. FE-SEM at Labs-Services is capable of performing high resolution imaging with very low accelerating voltages. With these advantages, observations of super fine features, electron beam sensitive materials, as well as non-conductive materials can be easily achieved.

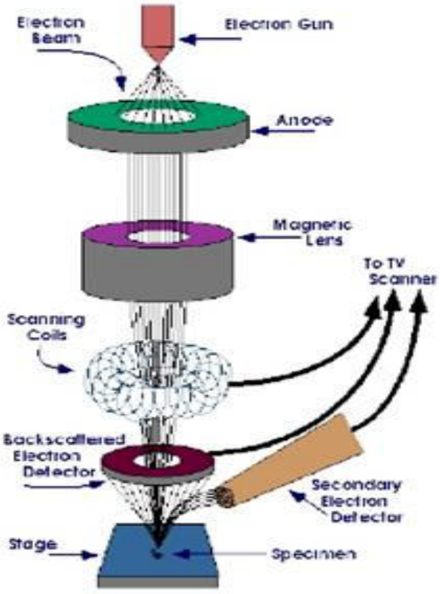

Fig.3. Schematic diagram of the image formation by the FESEM

5. Optical characterization

5.1 UV-visible spectroscopy

Ultraviolet/Visible/Infrared (UV/VIS/NIR) spectroscopy is a technique used to quantify the light that is absorbed and scattered by a sample. When a sample is placed between a light source and a photo detector the intensity of a beam of light is measured before and after passing through the sample are compared at each wavelength to quantify the sample’s wavelength dependent extinction spectrum. The data is typically plotted as extinction as a function of wavelength. UV-Visible spectroscopy can be used as a simple and reliable method for monitoring the stability of nanoparticle solutions. Nanoparticles often posses unexpected optical particle and have a greater surface area per weight than larger particles which causes them to be more reactive to other molecules produces quantum effects that are sensitive to size, shape, concentration, agglomeration state, and refractive index near the nanoparticle surface, which makes UV/VIS/IR spectroscopy a valuable tool for identifying, characterizing, and studying the materials.

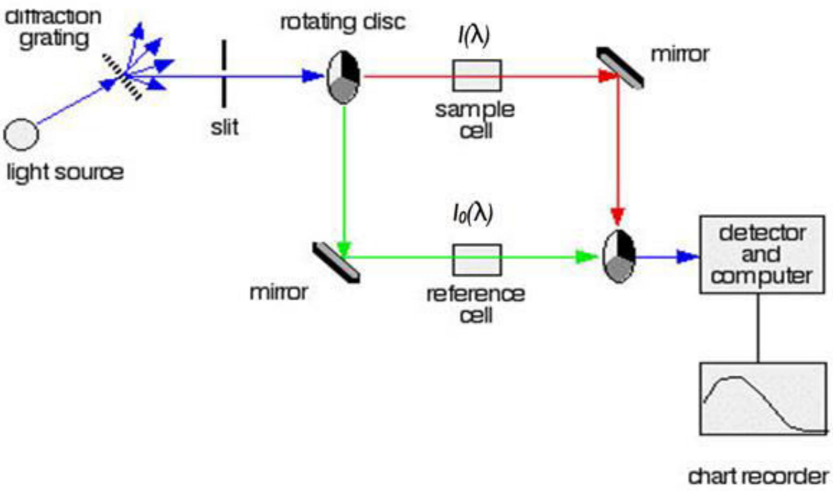

Fig.4. Schematic diagram of the operation of UV/VIS/NIR spectroscopy

As the particles destabilize, the first extinction peak can decrease in intensity attributable to the depletion of stable nano particles, and sometimes the height can broaden or a secondary peak can type at longer wavelengths attributable to the formation of aggregates. UV/VIS/NIR computerized spectrophotometer can be used for measuring the optical absorption, transmission and reflectance spectra of the bulk and thin films measured as a function of wavelength between 200-2700 nm. With the help of these measurements, optical constants like absorption coefficient, optical band gap, absorption constant, and refractive index can be calculated.

5.2 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a powerful technique for extracting information about the electronic structure of the material from any form of matter after the absorption of photons. At room temperature (RT) electron-hole pairs can recombine to emit photons over a range of energies, producing a broad band rather than a sharp peak. Donor, acceptor and defects states are generally fully ionized at room temperature and do not contribute significantly to the observed spectrum. The most basic use of low temperature PL spectra is as an indicator of overall crystal quality. The crystal quality is indicated by two factors: first the ratio of excitonic luminescence to donor-acceptor and deep level luminescence, second the sharpness of the spectrum i.e. the extent to which adjacent lines can be resolved. Apart from indicating overall crystal quality, the low temperature PL can sometimes be helpful in identifying specific impurities as well as quantification of the amount of disorder present in a system (Sheng Guo et al.2010).

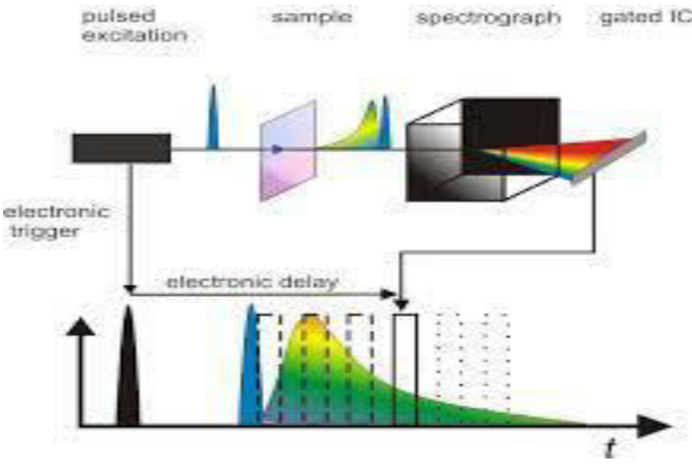

Fig.5. The Schematic diagram of the Photoluminescence spectrophotometer.

6. Differential scanning calorimetric

The thermoanalytical techniques of differential scanning calorimetric (DSC) has, however, offered the promise of obtaining useful data with simple methods.DSC measurements are very useful in obtaining the kinetic parameters related to the glass crystallization process especially in non-isothermal method due to the rapidity of this thermoanalytical technique (Saad M. et al. 1987, K.V.Acharya et al.1999, Pierre Lucas et al.2009).Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_g. DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased.

These transitions seem as a step within the baseline of the recorded DSC signal. This can be owing to the sample undergoing a amendment in heat capacity; no formal state change happens. Because the temperature will increase, an amorphous solid can recede viscous. At some purpose the molecules might acquire enough freedom of motion to ad lib organize themselves into a crystalline type. This can be referred to as the crystallization temperature (Tc). This transition from amorphous solid to crystalline solid is the heat-releasing (energy produced) method, and ends up in a peak within the DSC signal. Because the temperature will increase the sample eventually reaches its melting temperature (Tm). The melting method ends up in the heat-absorbing (energy absorbed) peak within the DSC curve. The flexibility to see transition temperatures and enthalpies makes DSC a valuable tool in manufacturing section diagrams for numerous chemical systems.

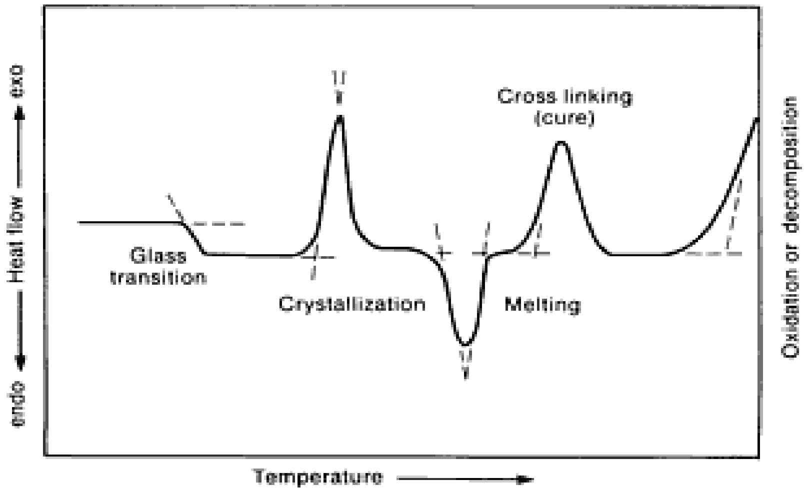

Fig.6. DSC Thermogram for heat flow of the sample

7. Dielectric spectroscopy

Dielectric spectroscopy or impedance spectroscopy measures the dielectric properties of a material and provides the information about molecular structure and mechanisms of molecular process (B.T. Kolomieto 1964). If the molecular structure change, the dielectric properties of the material also changes. The dielectric properties of a material are represented by a complex quantity known as permittivity is one of the factors that determine how a material interacts with an applied electromagnetic field. The real part of permittivity is a measure of the electric energy stored (capacitive nature) called the dielectric constant and the imaginary part of permittivity is a measure of the electric energy loss (conductive nature) called the loss factor or dielectric loss. Dielectric parameter like dielectric constant, dielectric loss, dissipation factor, and conductivity etc. is temperature and frequency dependent due to semiconductor nature of materials (Stuart.O.Nelson 2010).Their magnitudes and dependence on frequency and temperatures are most important for fundamental and applied consideration. The properties of dielectric parameter enter in an important way into the physics underlying the optical, transport and lattice-dynamical properties of semiconductors and they are also important in consideration of defect and impurity states. Dielectrics are also important for explaining various phenomenons in electronics, optics, and solid state physics.

8. Conclusion

The chalcogenide glasses are the low-phonon-energy substances and are typically clear from visible to the infrared. Doping chalcogenide glasses by the rare-earth components has displayed the varied applications of active optical devices. Due to their giant nonlinearities, the chalcogenide glasses are promising materials for all optical switching (AOS) applications. Doping chalcogenide glasses with rare-earth components has allowed the likelihood of victimization these glasses for active applications like amplifiers and lasers. There are various useful applications within the medical, civil and military areas as the chalcogenide glass fibers transmit within the IR. The Chalcogenide fibers are well-suited for chemical-sensor applications i.e., fiber-optic chemical detector systems for the quantitative remote detection and identification further as detection chemicals in the mixtures.

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