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Crystals in glassy matrix: Transparent Chalcogenide glass-ceramics

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ABSTRACT

Glass-ceramics are a new type of material. It can be fabricated by the incorporation of crystals into the glassy matrix. Glass-ceramics are a mixture of both amorphous and crystalline states. Chalcogenide glass-ceramics are of great interest due to their unique and enhanced optical and mechanical properties for multiple applications. The present paper enlightens about the Chalcogenide glass-ceramics concerning their synthesis, composition, optical properties and mechanical properties.

KEYWORD: *Glass-ceramics, Chalcogenide glass, Amorphous states, Crystalline states.*

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INTRODUCTION

The chalcogenide glasses contain at least one chalcogen element: S, Se or Tewhich have a large transmission range extending from the visible to the mid-infrared region depending on the chalcogen element. The chalcogenides have applications in different fields such as chemical sensing, optical switching, IR sources and lasers [1] and thermal imaging. The chalcogenide glass-ceramics appear promising and more efficient materials for numerous applications in various fields. Chalcogenides have a wide transmission range but poor chemical bonds and inferior thermo-mechanical properties in comparison to oxide glasses. But the thermo-mechanical properties of chalcogenides can be improved by fabricating chalcogenide glass-ceramics. Glass-ceramics are composite materials consisting of crystals in a glassy matrix. They are the combination of two states such as amorphous and crystalline which make them to have unique and enhanced properties. The first glass-ceramic was discovered as Alumina-silicate glasses [2]. Annealing at high temperatures shows the fast growth of crystals but reduces the transparency of the material in the infrared region.

A transparent glass-ceramics from 2 to 15 micrometre having low fractions of crystals can be produced with the nucleation combined with crystal growth temperature slightly higher than the glass transition temperature. Covalent and ionic compounds present in the GeS_2-Sb_2-S_3-CsCl ternary system create controlled crystallisation [3]. Due to low phonon energy, chalcogenide glasses with rare-earth ions are attractive materials for optical applications. Nd^{3+} with glassy matrix Ge-Ga-Sb-S-CsCl can generate nanocrystals [4]**.** Glass-ceramics have a much more intense emission of this ion than glass of the same composition.

SYNTHESIS OF CHALCOGENIDE GLASS-CERAMICS

The Glass-ceramics can be produced with the help of progressive crystallisation of the melt bath during the quenching. When the cooling rate is low crystalline part surrounded by a glassy matrix can be observed. Homogeneous crystallisation with uniform crystal in a glassy matrix is difficult to obtain.Chalcogenide glass-ceramics are mostly prepared using one crystallisation step. Glassy samples are heated at a temperature slightly above glass transition temperature in a furnace and then slowly cooled to room temperature. The temperature near glass transition is low enough to avoid rapid crystallisation of the whole glassy matrix. There are methods to determine the optimal temperature and time of nucleation in Chalcogenide glass-ceramics [5]. It is necessary to differentiate between nucleation and growth steps for the production of glass-ceramics with controlled crystal size and its fraction [6].

Photoinduced crystallisation can be used to prepare Chalcogenide glass-ceramics. The crystallisation of $GeSe_2$ nanoparticles can be seen in irradiated $GeSe_2$ thin films with the help of Raman spectroscopy [7]**.**The crystallisation can be obtained with both athermal and thermal processes. In the athermal crystallisation process, Se-Se lone pair of electrons excited by photons are responsible for crystallisation. In the thermal process, crystallisation occurs due to electron excitation. The absorption of light increases the crystallisation rate [8].

Transparent chalcogenide glass-ceramics can be produced with an innovative approach that combines amorphization by mechanical milling and densification by spark plasma sintering (SPS) [9]. This synthesis can be done even at room temperature. Fast precision molding of infrared optics can be achieved with spark plasma sintering. Controlled crystallisation of nanoparticles can be occurred by increasing the duration of spark plasma sintering.

GLASS CERAMICS SYSTEMS

Systems of transparent infrared glass-ceramics germanium-based glasses with ionic compounds such as alkali halide are reproducible and controllable glass-ceramics. The caesium chloride with the 62.5 GeS_2 - 12.5 Sb_2S_3-25 CsCl glass composition has been shown as the best candidate to make controllable glass-ceramics [10]. Various systems with controlled crystals are the primary choice for glass composition mixing with alkali halide within the glassy matrix. Various alkali halides such as CsBr, RbI can be added in the glassy matrices containing antimony, gallium or indium with sulphur or selenium. Alkali halide decreases the rigidity of glass and lowers mechanical properties such as hardness. Various stable glass-ceramics can be obtained from several glass compositions having Ge-Ga-S/Se systems.

OPTICAL PROPERTIES

Transparency of glass-ceramics in infrared depends on the particle size of the crystal in a glassy matrix. The Second-order nonlinear effects appear in chalcogenide glasses due to their broad transparency in the infrared range. Glasses and glass-ceramics have the efficiency to produce permanent second harmonic generation (SHG) phenomena. Homogeneous crystallisation of $AgGaGeS_4$ is an efficient glass-ceramic for inducing second-order optical non-linearity [11]. $90GeS_2$–$10Ga_2S_3$ chalcogenide glass-ceramics possessing β-GeS_2 shows nonlinear optics [12].Glasses with rare-earth doping have low phonon energy which is appropriate for fetching high quantum efficiency for wavelength transformation. The structuration of emission peaks appears after crystallisation with the incorporation of Er^{+3} with Ga_2S_3 nanoparticles. Doping of Nd^{+3} in the Ge-Ga-S-CsCl glassy matrix increases the luminescence efficiency immensely [13]. Selenium-based Glass-ceramics can be used to fabricate new laser sources[14].

MECHANICAL PROPERTIES

The resistance to fracture, hardness and thermal expansion coefficients are used to measure the strength of the chalcogenide glass-ceramics. The resistance to fracture strongly depends upon the crystallization rate of the glass-ceramics. The amount of crystals in glass ceramics can influence its hardness. High thermal conductivity and low thermal expansion coefficient favour high resistant materials to thermal shocks. Low thermal expansion coefficient of the chalcogenide glass-ceramics is a sign of its resistance to thermal shocks.Shaping of the chalcogenide glass-ceramics can be done dueto its molding ability and etching ability.

CONCLUSION

Chalcogenide glass-ceramics have permanent second-order nonlinear phenomena in the infrared range. The incorporation of rare earth within the crystalline phases significantly increases the luminescence efficiency. Infrared chalcogenide glass-ceramics have enriched optical properties and have many applications. Hence, they are crucial for fabricating optical devices. Chalcogenide glass-ceramics have enhanced properties in comparison to its base glasses and are of great interest for further research. More efforts for their synthesis, composition and analysis is needed to increase their commercial applications.

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