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Preparation and characterization of telluride glasses

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Abstract

Chalcogenide bulk glasses $Ge_{20}Se_{80-x}Te_x$ for $x \in (0, 10)$ have been prepared by systematic replacement of Se by Te. Selected glasses have been doped with Er and Pr, and all systems have been characterized by transmission spectroscopy, measurements of dc electrical conductivity and low-temperature photoluminescence. Absorption coefficient has been derived from measured transmittance and estimated reflectance. Both absorption and low-temperature photoluminescence spectra reveal shifts of absorption edge and/or dominant luminescence band to longer wavelength due to Te → Se substitution. Arrhenius plots of dc electrical conductivity, in the temperature range 300–450 K, are characterized by activation energies roughly equal to the half of the optical gap. Arrhenius plots for temperatures below 300 K yield much lower activation energies. The dominant low-temperature luminescence band centered at about half the band gap energy starts to quench above 200 K and a new band appears at 900 nm. The band at 900 nm, due to band to band transitions, overwhelms the spectra at room temperature. Systems doped with Er exhibit a strong luminescence due to $^4I_{13/2} \rightarrow I_{15/2}$ transition of Er^{3+} ion at 1539 nm, and Pr doped samples exhibit a relatively weak luminescence peak at 1590 nm, which we tentatively assign to $^3F_3 \rightarrow {}^3H_4$ transition of Pr^{3+} ion.

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1. Introduction

Chalcogenide glasses possess a number of interesting optical properties with various potential applications as it has been recently reviewed in, for example, [1,2]. They are promising materials for telecommunication applications, integrated optics, biomedicine and thermal imaging because they are transparent over a wide range of wavelengths in the infrared region, they possess high refraction index and low phonon energies.

There are differences between sulphide, selenide and telluride glasses in glass forming region, glass forming ability, thermal stability and in the positions of short and long wavelength cut off. In general the sulphide and selenide glasses are more stable as compared to telluride glasses. Glasses containing tellurium have worse glass forming ability, smaller glass forming region, lower transmission, higher refraction index and the transmission is shifted to longer wavelengths (up to 20 μm). They also have higher tendency to crystallization and phase separation.

It should be noted that applications in optoelectronics demand high chemical and physical purity of glass materials. The chemical purity is determined by the concentration of chemical impurities (metals, hydrides, oxides, carbon, carbonates); the physical purity is defined by the concentration of physical defects as heterogeneous particles, microcrystalline phase separation, cracks and in-homogeneities. To achieve values of optical losses that approach the theoretical ones, the concentration of impurities should be approximately 10^{-5} mol% for hydrides, 10^{-6} mol% for oxides, 5×10^{-5} mol% for silicon and carbon and

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the concentration of physical defects should be about 10^2–10^3 cm^{-3}. For this reason new progressive purification and preparation procedures were developed [3–6]. When doped with rare-earth (RE) elements, these glasses, by virtue of their low phonon energy and high refractive index, open up the possibility of new 4f–4f transitions and significantly may increase pumping efficiencies.

The attention in this paper is focused on the preparation of $Ge_{20}Se_{80-x}Te_x$ glass systems for $x \in (0, 10)$ and on the investigation of their optical and electrical properties. Multi-component telluride glasses on the base of Ge have been prepared by systematic substitution of Se with Te. Selected systems have been doped with Er and/or Pr and inner shell 4f–4f transitions of RE^{3+} ions have been investigated. Er and Pr have been chosen because of their importance for optoelectronic applications and the fact that our low-temperature PL spectrometer enables to measure in the spectral range 400–1700 nm, i.e. the range of relevant 4f–4f transitions of these RE^{3+} ions.

2. Experimental

Glasses were prepared by direct synthesis from pure starting elements. Chalcogenide glasses belong to substances which have an incongruent melting point, exhibit a high partial vapour pressure during melting and therefore the synthesis must be carried out in sealed evacuated quartz ampoule. The synthesis conditions are widely varied – they depend on the glass composition, glass forming region and glass forming ability.

The major sources of hydride, oxide and carbon related impurities seem to be starting elements (Ge, Se, Te) and therefore re-purification of these elements must be carried out. The sublimation under vacuum and the reactive atmosphere proved to be very effective for Se and melting under vacuum showed similar effects for Ge. The technological procedures involving the distillation, synthesis of undoped and RE doped glasses and the preparation of preforms for fibres drawing were carried out in one special quartz ampoule [3]. For the removal of oxide impurities a gettering was used by exploiting aluminium (Al) in the amount of 100 wt. ppm as the gettering agent. This procedure lowers the possibility of contamination during preparation steps. The melting temperature of glasses depends on their composition; for glasses containing Ge it is about 850–950 °C. The melting time was 15–20 h and then the ampoule with glass melt was cooled to room temperature. Preforms of 10 mm in diameter and 50–80 mm in length were obtained. Glasses doped with Pr^{3+} and Er^{3+} ions are homogenous up to the RE concentration 1500–2000 wt. ppm.

Prepared glasses have been examined by absorption spectroscopy, light scattering, low temperature photo-luminescence (PL) spectroscopy and temperature dependent dc current–voltage (*I–V*) characteristics. The difference in the batch composition and that of the prepared glass was less than 6% on average. The composition has been monitored via quantitative Electron Diffraction X-ray analysis using Philips XL 30 CP Scanning Electron Microscope equipped with EDX system.

Transmission spectra in the visible range have been measured by using Helios Beta of Thermo Electron Corporation and in the near infrared region by Matson Galaxy 3000. Photoluminescence (PL) spectra were taken at various temperatures and various levels of excitation by He–Ne and Ar ion lasers in an optical He closed cycle cryostat enabling measurements in the range 3.5–300 K. The 1 m focal length monochromator with the cooled high purity Ge detector and/or cooled GaAs photo-multiplier enables sensitive and high resolution measurement in the spectral range 400–1800 nm by using the lock-in technique and the computer controlled data collection. Typical spectral resolution in reported experiments was in the range 0.04–0.08 nm and 20 measurements were collected for each wavelength of the spectrum. The *I–V* characteristics were measured manually step-by-step by KEITHLEY 236 Source-Measure Unit in the range from 1 V to 110 V on samples placed in the temperature controlled liquid nitrogen cryostat AIR LIQUIDE TR7. The temperature was adjusted manually and controlled by LAKE SHORE 330 Autotuning Temperature Controller. The random and systematic errors were estimated by repeated measurements of *I–V* characteristics and they were displayed by symbol sizes on the data in the figures.

3. Results

3.1. Electrical characterization

The *I–V* characteristics were measured on circular wafers with the diameter of about 10 mm and the widths about 1.5 mm. For the measurements down to 200 K the width of the wafers was reduced by polishing to about 0.2 mm, in order to achieve higher electric fields. The wafers were furnished with metal contacts on both sides by coating with colloidal silver paint. The *I–V* characteristics were measured manually at temperatures in the range from 210 K to 430 K with the interval 10 K. The voltage was varied step-by-step from 1 V to 110 V. The measured current settled down slowly at each voltage step. Sufficient time was awaited at each step before the current was settled down. Currents above 0.5 pA were observable above the noise. The measured conductivity of samples $Ge_{20}Se_{73}Te_7$ and $Ge_{20}Se_{72}Te_8$ is shown in Figs. 1 and 2, respectively. Glasses with Te content $x = 7$ having much smaller conductivity than the ones with Te content $x = 8$ could be measured above the room temperature only. Strong dependence of conductivity on the Te content can be understood when compared with the dependence of the band gap on the Te content. The measured temperature dependence of *I–V* characteristics for sample with Te content $x = 8$ is shown in Fig. 3 in log-log scale.