# Dielectric and structural characterisation of chalcogenide glasses via terahertz time-domain spectroscopy

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## ARTICLE INFO

## ABSTRACT

Terahertz time-domain spectroscopy (THz TDS) was used to investigate a series of chalcogenide glasses. In particular, the dielectric properties at terahertz frequencies were determined and correlated with the glass composition. The experimental results showed a strong relationship between the dielectric properties and the polarizability of the glasses studied. A new explanation based on the coordination number of the metallic cations was proposed to understand these observations.

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## 1. Introduction

Chalcogenide glasses are amorphous materials consisting of chalcogen anions and one or more electropositive cations. Chalcogen anions include all the elements of the group XVI of the periodic table. However, the term is generally used only for S, Se and Te, restricting oxide materials to a separate category. The cations commonly used to form chalcogenide glasses belong to the p-block of the periodic table, with some exceptions such as La and Na [1].

The elements forming chalcogenide glasses are generally covalently bonded due to the small difference in electronegativity between cations and anions. As a result, the strength of the bonding is lower than in oxide materials, making glass formation feasible over a large variety of compositions. Indeed, both heteronuclear (e.g., La-S) and homonuclear (Se-Se) bonds can be formed, leading to the formation of non-stoichiometric compounds [1]. Lanthanum and sodium based glasses tend to have a more ionic character due to the weaker electronegativity of these metals [2]. For these glasses, a narrower range of glass-forming composition is found due to the strong tendency to crystallise [3].

The nature of the bonding in chalcogenide glasses gives rise to their unique optical and dielectric properties, such as high refractive index, low phonon energy, photosensitivity and chemical-mechanical durability [1,4,5]. Due to their low phonon energy, chalcogenide glasses are widely employed in infrared optics and photonics for a variety of active and passive applications such as light delivery, supercontinuum generation, fibre lasers, imaging and sensing [6,7].

Previous studies on terahertz properties of glasses were focused on sodosilicate and borosilicate glasses, and on chalcogenide glasses such as GaLaS, AsSe and GeGaSe [8—11]. In this work we report the absorption coefficients and refractive indices in the THz range for 3 compositions of GaLaS glass, for two compositions of the GaLaSSe glass and for 2 compositions of commercial GeSe-based glass, namely IG5 ($Ge_{28}Sb_{12}Se_{60}$) and IG2 ($Ge_{33}As_{12}Se_{55}$). The data was correlated to the mean polarizability of the materials and the impact of charge distribution on the absorption loss was examined. The aim of the study was to develop a deeper understanding of these glassy compounds and to exploit terahertz time-domain spectroscopy (THz TDS) as a useful tool for characterisation of amorphous materials.

## 2. Experimental

GaLaS and GaLaSSe glasses were prepared using the melt-quenching process as previously reported [12]. Mixtures of $La_2S_3$, $Ga_2S_3$ and $Ga_2Se_3$ were prepared in a dry-nitrogen purged glovebox, avoiding exposure to atmospheric oxygen. The mixtures were

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homogenised with the aid of a roller mixer for 1 h to enhance the homogenisation of the glasses. Vitreous carbon crucibles were used to contain the precursors during the melting and quenching steps. The crucibles were placed in a silica tube purged with Ar and a split-tube furnace was used to melt the mixtures. The glasses produced by this process were subsequently annealed at 490 °C for 48 h to release internal stresses in the glassy network. Samples for THz measurements were fabricated by cutting the glasses into flats whose faces were lapped and polished to optical finish. Samples of IG2 and IG5 were purchased from Vitron GmbH. The compositions of all glasses are listed in Table 1.

THz optical properties of the glasses were measured by a laboratory-built THz TDS using a standard configuration incorporating a Ti:Sapphire femtosecond laser, four off-axis parabolic mirrors, a biased GaAs emitter, and electro-optic detection with a ZnTe crystal and balanced Si photodiodes [13]. The measurement bandwidth was limited by the dynamic range of the system and sample absorption, and therefore was smaller in more strongly absorbing materials [14].

## 3. Results and discussion

The absorption coefficients and refractive indices of the investigated chalcogenide glasses are shown in Figs. 1 and 2 respectively, and their values at 0.8 THz are listed in Table 1. The refractive index found for Sample 3 is in good agreement with a previous study which reports a value of ~3.6 at 1 THz [11].

As seen in Table 1, the THz refractive indices of all glasses are much higher than they are in the visible. This is explained by the fact that at THz frequencies the polarizability of polar dielectric materials combines contributions from both electronic and ionic polarizabilities [17]. The electronic component is due to the distortion of the electron charge cloud of the compound by an applied oscillating electric field. Since electrons can respond on short timescales ($10^{14}$–$10^{15}$ Hz), electronic polarizability operates at frequencies up to the optical regime; this is the mean molecular polarizability quoted in the literature. In contrast, ionic polarizability arises when an applied oscillating field causes vibrational movement of anions and cations with respect to each other, i.e. when it excites optical phonons. Because ionic relaxation times are much slower than electronic, ionic polarizability occurs at lower frequencies; in glasses this is in the THz band. Since ionic polarizability leads to optical phonon excitations, it is also associated with absorption losses.

The relationship between polarizability and refractive index is represented by the Lorentz-Lorenz equation in the form [17–19].

$$\frac{n(f)^2 - 1}{n(f)^2 + 2} = \frac{4\pi}{3} N p(f) \tag{1}$$

where $n(f)$ is the frequency-dependent refractive index, $p(f)$ is the frequency-dependent polarizability of the material, and $N$ is the
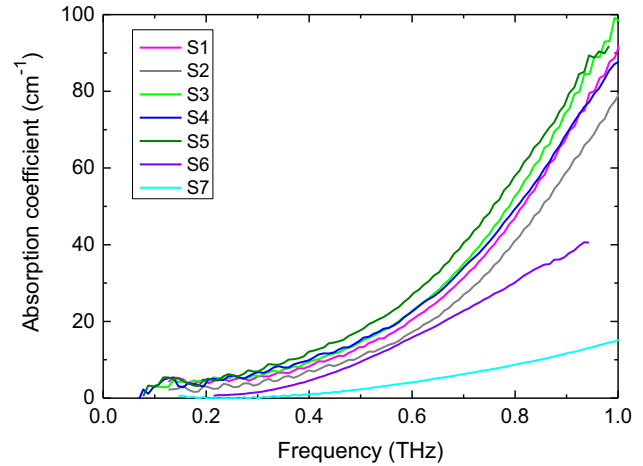


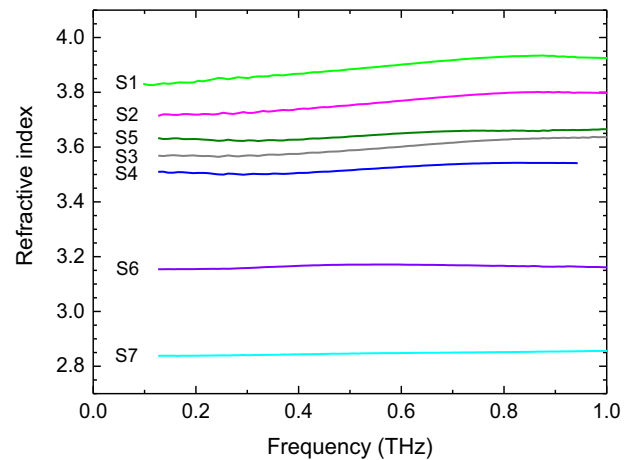**Fig. 1.** Absorption coefficients of the glasses studied.



**Fig. 2.** Refractive indices of the glasses studied.

number of molecules per unit of volume. It is important to note that the value of $N$ can vary significantly among different glasses, and can be calculated from the glass composition using the formula [18].

$$N = \frac{\rho}{MW} N_A \tag{2}$$

where $\rho$ is the density of the material in g·m$^{-3}$, $MW$ is the molecular weight of the composition in g·mol$^{-1}$ and $N_A$ is the Avogadro's number. The difference between the refractive indices of a material at THz and optical frequencies therefore represents the contribution of its ionic polarizability.

**Table 1**
Composition of the investigated glasses and their density, optical refractive index, and refractive index and absorption coefficient at 0.8 THz.

| Sample number | Composition | Density (g/cm) | Optical refractive index @ 1.5 μm | Refractive index @ 0.8 THz | Absorption coefficient @ 0.8 THz (cm$^{-1}$) |
|---|---|---|---|---|---|
| 1 | $La_{20}Ga_{20}S_{60}$ | 4.27 | 2.37 ± 0.04[a] | 3.93 ± 0.01 | 52 ± 2 |
| 2 | $La_{16}Ga_{24}S_{60}$ | 4.48 | 2.38 ± 0.04[a] | 3.80 ± 0.01 | 46 ± 2 |
| 3 | $La_{12}Ga_{28}S_{60}$ | 4.11 | 2.37 ± 0.04[a] | 3.63 ± 0.01 | 40 ± 2 |
| 4 | $La_{12}Ga_{28}S_{48}Se_{12}$ | 3.99 | 2.31 ± 0.04 [12] | 3.54 ± 0.01 | 51 ± 2 |
| 5 | $La_{12}Ga_{28}S_{39}Se_{21}$ | 4.21 | 2.37 ± 0.04 [12] | 3.66 ± 0.01 | 60 ± 3 |
| 6 | $Ge_{28}Sb_{12}Se_{60}$ (IG5) | 4.41 | 2.60 [15] | 3.17 ± 0.01 | 31 ± 1 |
| 7 | $Ge_{33}As_{12}Se_{55}$ (IG2) | 4.66 | 2.73 [16] | 2.85 ± 0.01 | 9 ± 0.5 |

[a] Measured using ellipsometry.