

STRUCTURAL AND OPTICAL EVOLUTION OF ANTIMONY CHALCOGENIDE GLASSES UNDER CONTROLLED ANNEALING

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ABSTRACT

This study follows how controlled isochronal annealing changes the structure and optical response of an antimony-bearing chalcogenide glass, $\text{Ge}_{15}\text{Sb}_{20}\text{Se}_{65}$, prepared by melt quenching and deposited as thin films by thermal evaporation. Films about 600 nm thick were annealed for two hours in argon at 373, 423, 473 and 523 K and compared with the as-deposited state. Differential scanning calorimetry on the parent glass gave a glass transition near 468 K and a crystallization onset near 553 K at 10 K/min, with activation energies close to 190 kJ/mol for both processes. X-ray diffraction showed an amorphous structure up to 473 K and incipient Sb_2Se_3 -type crystallinity (about 12%, crystallite size 18 nm) at 523 K. Raman spectra indicated a steady fall in the proportion of Se–Se homopolar bonding, with the Se–Se to network band ratio dropping from 0.55 to 0.29 at 473 K. Over the same range the refractive index at 1550 nm rose from 2.62 to 2.77, the Tauc gap narrowed from 1.46 to 1.37 eV, and the Urbach energy decreased from 88 to 63 meV. At 523 K the index reached 2.86 and the gap 1.30 eV, but the Urbach energy rose to 82 meV as crystallites introduced disorder and scattering. A single-oscillator analysis showed that the dispersion energy and static index grew together while the oscillator energy fell. The results link network relaxation, bond rearrangement and early crystallization to quantifiable optical tuning, and define a processing window for index adjustment without major loss.

Keywords: *Antimony chalcogenide glass¹; Ge–Sb–Se thin films²; Controlled annealing³; Urbach energy⁴; Refractive index⁵; Optical band gap⁶; Structural relaxation⁷*

1. INTRODUCTION

1.1 Why Antimony-Bearing Chalcogenide Films Matter

Chalcogenide glasses carry light in the near- and mid-infrared with a high refractive index and strong optical nonlinearity, which makes them attractive for compact photonic circuits [1]. Low-loss planar waveguides in As_2S_3 were among the first demonstrations that these glasses could be patterned to the standard needed for signal processing [2], [3]. Interest has since moved toward integrated sensing and mid-infrared photonics on silicon, where chalcogenide waveguides detect gases and liquids through their absorption fingerprints [4], [5]. Antimony enters this picture as a substitute for arsenic in Ge–As–Se and related compositions. It raises polarisability, lowers the band gap, and avoids the toxicity concerns of arsenic. Because Sb is three-fold coordinated, like arsenic, the network topology stays comparable, but bond energies and the tendency to crystallise differ. Understanding how such films behave after heat treatment is not an academic exercise. Any device that is baked, packaged or operated at elevated temperature inherits the changes described below [6].

1.2 Structural Basis of Annealing Effects

The structure of an amorphous chalcogenide is best described as a covalent random network with chalcogen chains cross-linked by Ge and Sb atoms [7]. Constraint counting predicts that a network becomes rigid when the mean coordination number approaches about 2.4 [8], [9]. The composition used here has a mean coordination number of 2.5, close to this threshold, which should make it sensitive to rearrangement while retaining enough rigidity to resist rapid crystallization. A film deposited by evaporation does not reach this ideal. It contains Se–Se homopolar bonds, dangling bonds, and void space that vapour deposition leaves behind. Charged defect pairs in lone-pair semiconductors contribute localised states in the gap [10], and these states broaden the absorption edge. Heating allows atoms to move and the structure to approach a lower-energy configuration, with consequences for the density and electronic structure. The kinetics of this process are tied to the glass transition, which itself depends on heating rate and thermal history [11]. Annealing at chosen temperatures relative to the transition therefore probes distinct structural regimes.

1.3 Objectives of the Present Work

Work on phase-change materials has shown how large an optical contrast can be obtained when an amorphous chalcogenide crystallizes [12]. Recent reports on Sb_2S_3 and Sb_2Se_3 demonstrate low-loss switching suitable for photonic integrated circuits [13], and non-volatile reconfigurable photonics has been demonstrated on this basis [14]. What is less well characterised is the territory before crystallization, where the film is still amorphous but relaxing. The present paper addresses that range with three objectives. The first is to measure how structural indicators from calorimetry, X-ray diffraction and Raman scattering change with annealing temperature. The second is to quantify the associated changes in refractive index, band gap, Urbach energy and dispersion parameters. The third is to test whether the optical changes can be explained by the observed structural ones.

Five tables present the data, and the argument built from them is carried through the abstract, discussion and conclusion.

2. SURVEY OF RELATED WORK

Optical and structural changes on annealing have been reviewed extensively for chalcogenide glasses, with the general conclusion that thermal treatment alters the optical gap, refractive index and absorption edge through structural relaxation, crystallization or both [15]. The metastable behaviour of these glasses, including reversible and irreversible changes, was synthesised by Shimakawa and colleagues [16], who emphasised that changes occur because the as-prepared network is far from its lowest-energy configuration. Applications reviews for electronics and optoelectronics stress that these shifts can be exploited, but also that they limit stability [17].

Interest in Sb_2Se_3 has come from two directions. Photovoltaic studies on crystalline films with oriented one-dimensional ribbons showed that grain orientation controls carrier transport [18], and vapour transport deposition produced devices with efficiencies near 7.6% [19]. In these works annealing is a processing step used to build crystalline order, and optical constants are of interest mainly for absorption. Photonic studies on Sb_2Se_3 revealed a large change in refractive index and band gap between amorphous and crystalline states and showed that the wide gap keeps absorption low into the visible [20]. Delaney and colleagues extended this to Sb_2Se_3 and framed both materials as a family of low-loss phase-change media [13].

Methodological papers set the tools used to read the data. The Tauc relation [21] and its Davis–Mott extension [22] provide ways to extract an optical gap from the absorption edge of an amorphous solid. Wood and Tauc described weak absorption tails and how they relate to disorder [23], and the exponential edge was first described by Urbach [24]. The envelope method of Swanepoel gives refractive index and thickness from interference fringes in transmission spectra [25], and the Wemple–DiDomenico model describes dispersion through an oscillator energy and a dispersion energy [26]. Thermal analysis relies on the Kissinger method for activation energies of crystallization [27], and on the heating-rate dependence of the glass transition [11].

Gaps in this body of knowledge motivate the present work. Phase-change studies emphasise the endpoints, amorphous versus fully crystalline, and rarely follow the continuous evolution through relaxation. Photovoltaic studies concentrate on crystalline films. Glass studies often report a single anneal. Few papers combine thermal, structural and optical measurements on the same set of films at several temperatures with a consistent analysis. In addition, the relationship between Se–Se bonding and band-edge behaviour is often asserted but seldom quantified. The data below attempt to fill this gap for a single well-defined composition, which removes the confounding effect of compositional variation that complicates cross-study comparison.

3. METHODOLOGY

Bulk glass of nominal composition $\text{Ge}_{15}\text{Sb}_{20}\text{Se}_{65}$ was prepared from high-purity elements sealed in an evacuated quartz ampoule (about 10^{-4} Pa), heated stepwise to 1223 K, held for 24 h with periodic rocking to ensure

homogeneity, and quenched in ice water. Thin films about 600 nm thick were deposited on cleaned glass substrates by thermal evaporation from powdered glass at a base pressure near 10^{-4} Pa and a rate of roughly 1 nm/s, with thickness monitored by a quartz crystal. Composition was checked by energy-dispersive spectroscopy and found to lie within about ± 1 at.% of nominal. Films were annealed in a tube furnace under flowing high-purity argon for two hours at 373, 423, 473 and 523 K, with a heating ramp of 5 K/min and slow cooling inside the furnace. An as-deposited set was kept as reference. Each condition was prepared in triplicate.

Thermal characterisation used differential scanning calorimetry on powdered bulk glass at heating rates of 5, 10, 15 and 20 K/min under nitrogen. The glass transition temperature, crystallization onset and peak temperature were read from each curve. Activation energy of crystallization was obtained from the Kissinger relation [27], plotting $\ln(\beta/T_p^2)$ against $1/T_p$, and the activation energy for the glass transition from the heating-rate dependence of T_g [11]. Structural characterisation used X-ray diffraction with Cu K α radiation over 2θ from 10° to 70° at 0.02° steps. Crystallite size followed from the Scherrer equation [28] with a shape factor of 0.9, and crystalline fraction from the ratio of crystalline peak area to total scattered area after background subtraction. Raman spectra were recorded with a 785 nm laser at low power to avoid photo-induced changes, and band intensities were obtained by fitting Gaussian components to the $150\text{--}300\text{ cm}^{-1}$ region.

Optical transmission and reflection spectra were measured from 400 to 2500 nm. Refractive index and thickness were derived from interference extrema by the envelope method [25]. The absorption coefficient was computed from transmission corrected for reflection, and the optical gap taken from Tauc plots with an exponent for indirect allowed transitions [21], [22], fitted over a fixed window of the linear region for all samples so that differences were not caused by fit selection. The Urbach energy was obtained from the inverse slope of $\ln \alpha$ against photon energy in the exponential tail [23], [24]. The dispersion of refractive index was fitted with the single-oscillator model [26] to obtain the oscillator energy E_0 and dispersion energy E_d . Quoted values are means over three films, with typical uncertainties of ± 0.01 in refractive index, ± 0.02 eV in gap, and ± 3 meV in Urbach energy.

4. DATA COLLECTION AND ANALYSIS

The data are presented in five tables, each tied to a step in the argument. The thermal data establish where the annealing temperatures sit relative to the glass transition. The structural data show what changes in the network. The optical data show the consequences and the dispersion analysis tests whether they form a coherent picture.

Table 1: DSC characteristic temperatures of bulk $\text{Ge}_{15}\text{Sb}_{20}\text{Se}_{65}$ glass at different heating rates

Heating rate β (K/min)	T_g (K)	T_x onset (K)	T_p (K)	$\Delta T = T_x - T_g$ (K)
5	462	541	562	79
10	468	553	571	85
15	472	560	577	88
20	475	565	581	90

Table 1 fixes the thermal landscape. All characteristic temperatures rise with heating rate, as expected for kinetic processes. At 10 K/min the glass transition is 468 K and crystallization starts near 553 K, leaving a supercooled-liquid window of 85 K, which indicates reasonable stability against devitrification. The Kissinger plot gives an activation energy for crystallization of about 189 kJ/mol, and the heating-rate dependence of T_g gives about 195 kJ/mol for the glass transition. The similarity of the two values suggests that structural rearrangement near the transition and the onset of crystal growth involve comparable bond-breaking steps. The annealing temperatures of 373, 423 and 473 K therefore span sub-transition and near-transition regimes, while 523 K lies inside the supercooled-liquid region, 30 K below the crystallization onset at 10 K/min but long enough in duration to allow nucleation.

Table 2: XRD results for as-deposited and annealed films

Condition	XRD pattern	Halo centre (2θ , °)	Halo FWHM (°)	Crystallite size (nm)	Crystalline fraction (%)
As-deposited	Amorphous halo	28.6	8.4	–	0
373 K	Amorphous halo	28.7	8.1	–	0
423 K	Amorphous halo	28.9	7.6	–	0
473 K	Amorphous halo	29.1	7.0	–	<2
523 K	Halo + weak Sb_2Se_3 -type peaks	29.2	6.5	18	12

The diffraction data show that the films remain amorphous through 473 K but change in subtle ways. The halo moves to slightly higher angle and narrows, from 8.4° to 7.0° , which is consistent with a modest contraction of average interatomic distances and increased medium-range order. This agrees with the roughly 5% thickness decrease found from the optical analysis, from 612 nm in the as-deposited film to 581 nm at 523 K. At 523 K weak crystalline reflections appear, indexed to an Sb_2Se_3 -type phase, with a Scherrer crystallite size of 18 nm and a crystalline fraction near 12%. The film is thus a composite of amorphous matrix and nanocrystals, and not fully crystalline.

Table 3: Raman band intensity ratios

Condition	$I(215)/I(195)$, edge- to corner-sharing units	$I(250)/I(195)$, Se–Se chains to network
As-deposited	0.42	0.55
373 K	0.40	0.47
423 K	0.38	0.38
473 K	0.37	0.29
523 K	0.45	0.22

Table 3 supplies the structural mechanism. The ratio of the Se–Se chain band near 250 cm^{-1} to the network band near 195 cm^{-1} falls steadily with annealing, from 0.55 to 0.29 at 473 K and 0.22 at 523 K, a drop of roughly 47% by 473 K. This is the signature of homopolar Se–Se bonds converting into heteropolar Ge–Se and Sb–Se bonds as the network cross-links. The edge-sharing to corner-sharing ratio declines slightly up to 473 K and then rises at 523 K, which fits the growth of edge-sharing-like units associated with the nascent crystalline

phase. Together with the diffraction data, the Raman results indicate that relaxation dominates up to 473 K and that crystallization begins at 523 K.

Table 4: Optical parameters of as-deposited and annealed films

Condition	Thickness (nm)	n at 1550 nm	Δn (%)	Eg Tauc (eV)	ΔE_g (eV)	Urbach energy Eu (meV)
As-deposited	612	2.62	–	1.46	–	88
373 K	606	2.66	+1.5	1.43	–0.03	79
423 K	598	2.71	+3.4	1.40	–0.06	70
473 K	590	2.77	+5.7	1.37	–0.09	63
523 K	581	2.86	+9.2	1.30	–0.16	82

Table 4 contains the main result of the paper. Between the as-deposited state and 473 K, the refractive index climbs from 2.62 to 2.77, the gap narrows from 1.46 to 1.37 eV, and the Urbach energy declines from 88 to 63 meV. All three changes point to a film that is denser, more fully bonded and less disordered. At 523 K the index and gap continue their trends, reaching 2.86 and 1.30 eV, but the Urbach energy reverses to 82 meV. This reversal marks the point where nanocrystals and the associated structural inhomogeneity add disorder and scattering to the tail. The Urbach energy is thus the clearest single indicator of the transition from relaxation to crystallization. Across the entire series, the change in index of 0.24, or 9.2%, is accompanied by a gap shift of 0.16 eV.

Table 5: Single-oscillator dispersion parameters

Condition	E_0 (eV)	E_d (eV)	n_0 (static)	E_0/E_g
As-deposited	3.00	16.3	2.54	2.05
373 K	2.95	16.6	2.57	2.06
423 K	2.90	17.0	2.62	2.07
473 K	2.85	17.5	2.67	2.08
523 K	2.70	17.7	2.75	2.08

Table 5 checks that the refractive-index data form a coherent dispersion picture. The oscillator energy E_0 falls from 3.00 to 2.70 eV, tracking the band gap, while the dispersion energy E_d rises from 16.3 to 17.7 eV, which reflects increased bond density and coordination in the denser film. The static index n_0 climbs from 2.54 to 2.75. The ratio E_0/E_g stays close to 2 across the series, indicating that the oscillator moves with the gap and that the change in index is driven by both effects, a lower oscillator energy and a larger dispersion energy. The consistency of this analysis with the Tauc-derived gaps supports the reliability of both.

5. DISCUSSION

The five tables describe one connected sequence. Table 1 shows that 473 K lies just above the glass transition, and the data in Tables 2 to 4 show that this is where the film's relaxation is nearly complete, with the largest reduction in tail width. Annealing at 373 and 423 K, well below T_g , still produces measurable change, which confirms that the as-deposited film is far enough from equilibrium to relax even when atomic mobility is low.

The thickness decrease of about 5% from 612 to 581 nm quantifies this densification and accounts for part of the index rise, since a denser film has more polarisable bonds per unit volume.

The link between structure and optical gap is supported, with caveats. Across the five conditions the Se–Se band ratio and the Tauc gap are strongly correlated (Pearson $r \approx 0.97$), consistent with the idea that Se–Se chains contribute states at the top of the valence band, so that their loss lowers the gap through network cross-linking and band broadening. Yet this is a correlation across five points, in which temperature drives everything simultaneously. It cannot separate the contribution of bond conversion from that of density change or incipient crystallization. A fair reading is that the data are consistent with the proposed mechanism and do not prove it.

The Urbach energy tells a more discriminating story than the gap does. Its decrease up to 473 K shows that disorder decreases as the network relaxes. Its increase at 523 K, even as the gap continues to narrow, shows that the late-stage gap change has a different origin. Here the 12% crystalline fraction and the small crystallite size, 18 nm, produce a heterogeneous film in which the tail is broadened by interfaces and strain. A reader who looked at the gap alone would conclude that annealing at 523 K continues the same improvement, when the tail and scattering losses show otherwise. For device purposes, this indicates that the useful tuning window ends near 473 K for this composition.

The relationship between index and gap does not follow a simple rule. The product $n^4 E_g$, which is constant in the Moss relation [30], rises from about 69 eV in the as-deposited film to about 87 eV at 523 K. The index increases faster than the gap decreases, so the gap cannot serve as a predictor of index in this system. The single-oscillator parameters explain why, since E_d increases alongside the fall in E_0 , so density and bonding contribute independently of the gap.

Limitations deserve statement. Thermal data come from bulk powder while the optical data come from films, so the T_g used to place the annealing temperatures relative to the transition is an approximation. A single composition and a single hold time were examined, so neither the composition dependence nor the time dependence of relaxation was tested, and the equivalence of time and temperature is untested. The crystalline fraction at 523 K comes from a weak diffraction signal and carries a large relative uncertainty. Finally, Raman ratios from Gaussian fitting depend on the fitting model, so the absolute values matter less than the trend. Despite these limitations, the internal consistency of five independent measurement types gives confidence in the qualitative conclusions.

6. COMPARISON WITH PAST WORK

The thermal results fit the established behaviour of Ge–Sb–Se glasses. A transition near 468 K at 10 K/min and a supercooled-liquid window of 85 K sit within the broad range that has been reported for chalcogen-rich compositions near a mean coordination number of 2.5, in line with constraint-based expectations [8], [9]. The heating-rate dependence of T_g follows the pattern described in the classical analysis [11], and the similarity of

the transition and crystallization activation energies, around 190 kJ/mol, is of the order commonly reported for chalcogenide glasses analysed by the Kissinger method [27]. Absolute values vary widely across the literature with composition and method, so the agreement is one of magnitude, not of precise numbers.

The sub-transition trends match the general picture in reviews of metastability in amorphous chalcogenides, where annealing of as-deposited films lowers the gap and raises the index as the network relaxes [15], [16]. Our contribution is to attach numbers to each stage on a single composition and to show that the tail-width reduction accompanies those changes. The decrease in Urbach energy is in keeping with the interpretation of the exponential edge as a measure of disorder [23], [24]. Some reports on sulfur-rich films describe a widening gap after air annealing, which is opposite to our result. The present films were annealed in argon, and the difference is consistent with oxidation or loss of volatile species in those cases, although this study did not test the point directly.

The crystallization-related changes agree in direction with phase-change work on Sb_2S_3 and Sb_2Se_3 , where crystallization raises the refractive index and lowers the gap [13], [20]. Reported index contrasts in the near-infrared between fully amorphous and fully crystalline states are of the order of several tenths, larger than the 0.24 observed here. The difference is expected, since the present film at 523 K is only about 12% crystalline and still carries a large amorphous fraction. The 523 K data therefore represent a snapshot early on the route to the full contrast, and the large contrasts measured on those binary compounds are not contradicted. The gap of 1.30 eV at 523 K lies between the amorphous value of the film and the lower gaps typically quoted for crystalline Sb_2Se_3 in photovoltaic studies [18], [19], which fits a partially crystallized composite. Because the Ge-containing glass matrix keeps a wider gap than pure Sb_2Se_3 , full crystallization of this composition would not be expected to reach the pure-compound values.

A further point of comparison concerns loss. Phase-change studies highlight that wide-gap Sb_2S_3 and Sb_2Se_3 retain low absorption after switching [13], [20], in contrast to the Ge–Sb–Te alloys that dominated earlier work [12]. The increase in Urbach energy at 523 K in our films is a reminder that partially crystallized composites can show added tail absorption and scattering even when the bulk compounds are low-loss, because grain boundaries and strain matter at the nanoscale. This suggests that photonic devices using partial crystallization for fine index trimming would need to manage the loss that accompanies it, whereas those using sub-transition relaxation avoid it.

Compared with earlier work, the main differences are in design. Many studies report one temperature or compare the extremes of amorphous and crystalline states, whereas the present series covers relaxation, near-transition behaviour and incipient crystallization on one composition with the same analysis applied throughout. The coherence of the dispersion analysis [26], with E_0 tracking the gap and E_d rising with densification, provides a consistency check that single-quantity studies cannot offer. The weaknesses identified in earlier work, namely unspecified atmospheres, inconsistent gap fits and absent replicates, were addressed here by using

inert gas, a fixed fitting window and triplicate films, but the limitations of single composition and single hold time remain.

7. CONCLUSION

Controlled annealing changes the optical constants of $\text{Ge}_{15}\text{Sb}_{20}\text{Se}_{65}$ films in a graded and measurable way. Up to 473 K, just above the glass transition at 468 K, the films stay amorphous while the refractive index at 1550 nm rises from 2.62 to 2.77, the Tauc gap narrows from 1.46 to 1.37 eV, and the Urbach energy falls from 88 to 63 meV. Raman data show that these changes accompany a decrease of nearly half in the Se–Se chain contribution, and X-ray diffraction shows a narrowing halo and a thickness reduction of about 5%, so the picture is one of densification and bond conversion. At 523 K, early crystallization produces about 12% Sb_2Se_3 -type crystallites of 18 nm, the index reaches 2.86 and the gap falls to 1.30 eV, but the Urbach energy rises to 82 meV as disorder and scattering enter.

Two practical conclusions follow. First, for this composition the window for low-loss index tuning lies below roughly 473 K, where a 5.7% index change is available without added tail absorption. Second, the Urbach energy, not the band gap, is the most sensitive indicator of when relaxation gives way to crystallization. The single-oscillator analysis confirms that the index change arises from both a lower oscillator energy and a higher dispersion energy, which is why the gap alone cannot predict it.

Several limits qualify these findings. Only one composition and one hold time were studied, and thermal data from bulk powder were used to interpret film behaviour. Future work should vary composition and time, follow the optical constants in situ during heating, and test the stability of the annealed state over time and under illumination. Such data would turn the trends reported here into calibrated design rules for thin-film chalcogenide photonics.

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