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Influence of oxygen traces on physical properties of glassy $GeSe_2$

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The influence of oxygen impurities on some physical properties (optical absorption in the infrared spectral region, slope of short wavelength edge, d.c. conductivity, crystallization) of glassy $GeSe_2$ was studied. It was shown that incorporation of traces of GeO_2 (up to 1000 p.p.m. by weight of oxygen) into the glassy matrix of $GeSe_2$ is connected with an increase of the slope of the exponential absorption edge and also with the shift of this edge to higher energies. D.c. electrical conductivity slightly decreases on doping of $GeSe_2$ with oxygen, which probably reflects the increase of the gap. The crystallization of $GeSe_2$ in the course of differential thermal analysis seems to be suppressed by oxygen. It is supposed that this can be connected to the interaction of GeO_2 with both the homonuclear Se–Se bonds on the surface of the outrigger rafts and the Ge–Ge bonds in ethane-like units, respectively.

1. Introduction

Oxygen is the most common impurity in chalcogenide glasses. The role of oxygen in the physical properties of chalcogenide glasses seems to be not fully clear. In some cases contamination of glasses by oxygen leads to a change in their physical properties. It was shown, e.g. [1], that an addition of oxygen of the order of p.p.m. will decrease electrical resistivity of selenium by up to eight orders and decrease the activation energy of electrical conductivity from 1.2 to 1.3 eV to 0.55 to 0.65 eV. It was suggested by Twaddell *et al.* [1] that SeO_2 molecules bond chemically with existing selenium chain ends and such bonding configuration introduces shallow acceptor levels. Small quantities of oxygen (up to 100 p.p.m.) have a profound influence on the glass transition temperature (T_g) of glassy As_2Se_3 while the change (decrease) of the electrical conductivity and permitivity is only slight [2]. It is supposed that oxygen atoms replace selenium atoms in As–Se bridges. On the other hand, in some more complex glasses (Ge–Se–Bi, Ge–Te–As, In–Ge–Te) the significant influence of oxygen on the physical properties was not observed [3]. For example in glassy $Ge_{15}Te_{81}As_4$ with oxygen contents of 130, 210, 380, 550 p.p.m., no influence of oxygen was observed on T_g, crystallization temperature, d.c. conductivity and switching characteristics of the samples. It seems that the influence of oxygen on the physical properties of chalcogenide glasses is connected with both the chemical composition and/or the structure of glasses and with the content of oxygen, because at some critical concentration (perhaps of the order of 10 p.p.m.) further increase of oxygen content (e.g. up to 10^3 p.p.m.) does not lead to a change in the physical properties [1, 2].

In the present paper a qualitative study of the influence of oxygen, mainly on optical and electrical properties of glassy $GeSe_2$ is reported. The glassy $GeSe_2$ is a prototype of 4 : 2 coordinated chalcogenide glasses and a number of experimental and theoretical works have been devoted to the study of properties of this glass. However, to our knowledge no systematic study of the influence of oxygen on its physical properties has been performed.

2. Experimental procedure

There are several possible sources of oxygen contamination of $GeSe_2$: (i) the inner surface of quartz ampoules used for synthesis, (ii) the residual atmosphere in the evacuated ampoules, (iii) the interaction of germanium with the inner walls of the ampoules at high temperatures (iv) oxygen contamination of selenium (it is known that semiconductive-purity germanium is not responsible for oxygen contamination of glasses [4]). To suppress oxygen contamination of $GeSe_2$ we have used the following synthesis technique. The chemically cleaned quartz ampoules (QUARC Nemours) for synthesis were heated for 4 h at 1000° C under vacuum ($p \sim 10^{-3}$ Pa) and then cooled to room temperature without breaking the vacuum. The ampoules were then filled with dry argon. Germanium (99.999% purity) and selenium (Boliden, 99.999%) deoxidized by heating for 2 h at 200° C and $p \sim 10^{-3}$ Pa, were inserted into ampoules under argon. Because there are losses of selenium during deoxidation, we have used, on the

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basis of a blank test, 5 wt % overstoichiometry of selenium. After filling the ampoules were evacuated ($p \sim 10^{-3}$ Pa) and sealed. Synthesis was carried out in a rotary furnace; the ampoule was first heated for 3 h at 550° C, and then the temperature was increased to 900° C and the ampoule was heated for 15 h. Before quenching in ice–water the melt was mixed rigorously for at least 5 min. The prepared $GeSe_2$ was doped with GeO_2 in amounts corresponding to 100, 500 and 1000 p.p.m. by weight of oxygen. The mixture of $GeSe_2$ and GeO_2 was inserted into ampoules purified in the way described above. Alloying of $GeSe_2$ and GeO_2 was carried out under the same conditions as the synthesis of $GeSe_2$. In all cases the total weight of materials used was 2 g, the ampoules used were 10 cm long and 0.8 cm diameter, wall thickness 0.1 cm. From the used overstoichiometry of selenium (to compensate for losses of selenium due to deoxidation) and the results of the blank test, the estimated actual composition of the prepared glasses is:

"pure" $GeSe_2$	$Ge_{32.59}Se_{67.41}$
100 p.p.m. wt O_2	$Ge_{32.59}Se_{67.36}O_{0.05}$
500 p.p.m. wt O_2	$Ge_{32.59}Se_{67.17}O_{0.24}$
1000 p.p.m. wt O_2	$Ge_{32.44}Se_{67.08}O_{0.48}$

From the prepared bulk plan parallel samples of thicknesses varying between 0.01 and 0.11 cm were made for optical measurements (polishing was always done with a suspension of Al_2O_3 powder in water-free ethanol) and for electrical measurements.

Infra-red transmission measurements between 4000 and 200 cm^{-1} were made using a Perkin-Elmer 684 spectrophotometer. The short wavelength absorption edge was measured on three different thicknesses using a Specord UV VIS Carl Zeiss Jena spectrophotometer. Reflectivity in the short wavelength absorption edge was measured using a single-beam spectrophotometer [5]. The d.c. conductivity was measured in a sandwich arrangement using a Keithley 610 C electrometer. Aquadac contacts were used. DTA thermograms were obtained using a Du Pont 990 Thermal Analyser, the bulk samples (~20 mg) being placed in an open quartz pan. The reference material was Al_2O_3. During the measurements the sample chamber was continuously flushed with dry argon.

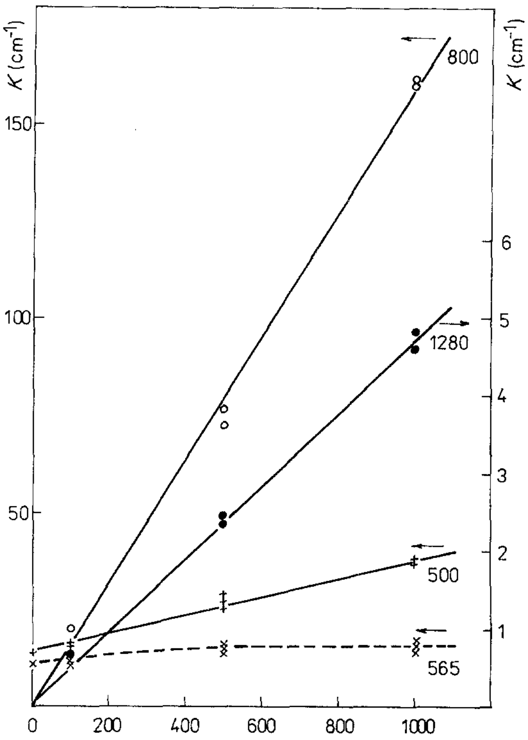

Figure 2 Absorption coefficient of glassy $GeSe_2$ at 500, 565, 800 and 1280 cm^{-1} plotted against concentration of oxygen.

3. Results and discussion

Infrared spectra of the prepared glasses are shown in Fig. 1. The main features are: (i) in "pure" $GeSe_2$, a weak absorption band at 750 cm^{-1} and two absorption bands at 565 and 500 cm^{-1}, (ii) in GeO_2-doped glasses, new weak absorption band at 1280 cm^{-1}, strong absorption band at 800 cm^{-1} and both bands at 565 and 500 cm^{-1}, respectively, remain. However, with increasing oxygen content the absorption band at 565 cm^{-1} seems to be a shoulder of the band at 500 cm^{-1}. It has been proposed [6] that in the region of 400 to 600 cm^{-1} there are two-phonon absorption processes in $GeSe_2$ and thus we assume that the observed bands at 500 and 565 cm^{-1} in "pure" $GeSe_2$ can be connected with these processes. As the fundamental stretching in $GeSe_2$ seems to be at 263 cm^{-1} [7], the weak absorption at 750 cm^{-1} can probably be assigned to the intrinsic three-phonon process. Fig. 2 shows the dependence of the absorption coefficient on

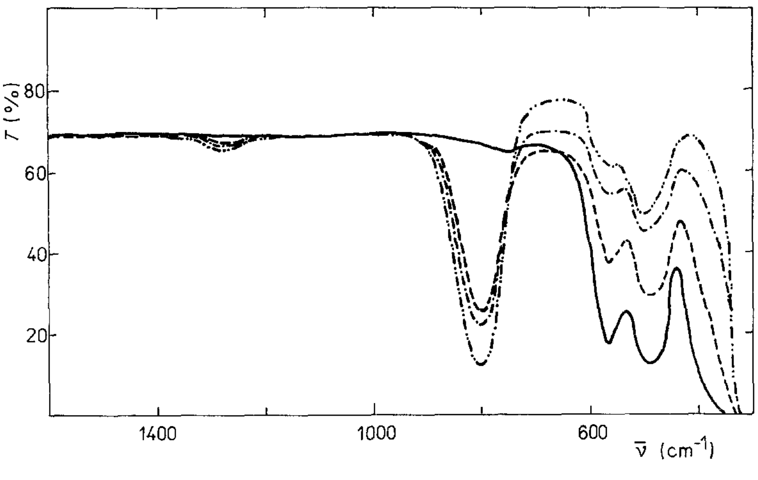

Figure 1 Infrared spectra of glassy "pure" $GeSe_2$ and $GeSe_2$ doped with various amounts of GeO_2 (with sample thicknesses given in parentheses): (——) < 1 p.p.m. wt O_2 (1.160 mm), (– – –) 100 p.p.m. wt O_2 (0.450 mm), (–·–) 500 p.p.m. wt O_2 (0.145 mm), (–··–) 1000 p.p.m. wt O_2 (0.103 mm).

the oxygen content in the glasses studied. The absorption coefficient (K) was calculated according to relation:

$$K = d^{-1}\ln(\{(1 - R)^2 + [(1 - R)^4 + 4R^2T^2]^{1/2}\}/2T) \quad (1)$$

where T is transmission and d sample thickness. The reflectivity (R) was calculated from the apparent transmission (T_0) in the region $\sim 1100\,\text{cm}^{-1}$ according to relation:

$$R = (1 - T_0)/(1 + T_0) \quad (2)$$

As is evident from Fig. 2, with increasing oxygen content the absorption of 500, 800 and $1280\,\text{cm}^{-1}$, significantly increases, while absorption at $565\,\text{cm}^{-1}$ seems to be almost independent of oxygen content. It is clear that these bands are connected to the doping of $GeSe_2$ with oxygen. It is well known that in germanium chalcogenide glasses the oxygen is preferentially bonded to germanium atoms. In principle, oxygen can be bonded to the forming GeO_2 or it can be incorporated into the Ge–Se matrix forming, e.g. $Se_{3-x}O_x$–Ge–O–Ge–O_xSe_{3-x} entities. In the former case, one would expect the existence of the strong absorption bands at $\sim 870\,\text{cm}^{-1}$ and at 600 to $700\,\text{cm}^{-1}$ because at these frequencies the most intensive features of infrared spectra of vitreous GeO_2 appear [8].

The position of the most intensive absorption band in our glasses doped with GeO_2 is at $800\,\text{cm}^{-1}$. We assume that this band is connected with the incorporation of oxygen into the glassy matrix in the form of the entities mentioned above with $0 < x < 3$. In such a case the $870\,\text{cm}^{-1}$ band corresponding to the antisymmetric stretching motion of oxygen in the intertetrahedral position [8] in GeO_2 can be shifted to the lower frequency because of the mixed coordination of germanium atoms. This seems to be a reasonable explanation because a similar influence of the mixed coordination (of the central atom) was observed in the Si(F) amorphous system for Si–F stretching [9] and also in the case of photo-oxidized and/or hydrolysed $Ge_{30}S_{70}$ layers for Ge–O stretching vibration [10]. Perhaps for the same reason the absorption band at $500\,\text{cm}^{-1}$ is caused by the shift of that broad band between 500 and $600\,\text{cm}^{-1}$ of pure GeO_2. In such a case an increase of the absorption coefficient at $500\,\text{cm}^{-1}$ can be a result of the superposition of the intrinsic two-phonon process of "pure" $GeSe_2$ with the extrinsic Ge–O vibration shifted to $500\,\text{cm}^{-1}$, because of the mixed coordination of the germanium. The small, but detectable, absorption band in glasses doped with GeO_2 at $1280\,\text{cm}^{-1}$ could be assigned to the combination of Ge–O bands at 800 and $500\,\text{cm}^{-1}$. Supposed assignments of observed infrared features in the glasses studied are summarized in Table I.

The spectral dependences of the short wavelength edges in log K against $\hbar\omega$ coordinates are shown in Fig. 3. All dependences can be described using the relation $K \sim \exp(\hbar\omega/\Delta)$ where Δ is the slope of the edge. In the insert of Fig. 3 the course of Δ in $Ge_{1-x}Se_x$ is shown, for $(0 \leqslant x \leqslant 0.4)$ taken from [11]. The horizontal lines mark our values of Δ for "pure" $GeSe_2$ and $GeSe_2$ doped with 100, 500 and 1000 p.p.m. oxygen. It is evident from this figure that the observed changes of the values of Δ cannot, most probably, be due to the change of the ratio Ge:Se of prepared samples. Because our samples have the same thermal history, we suppose that the changes of Δ in glasses studied could be connected with the incorporation of oxygen into the glassy matrix. It follows from the infrared spectra that the oxygen is most probably incorporated into the glassy matrix in the form of Ge–O–Ge bridges. Then, in principle, the chemical disorder in these glasses increases with oxygen content. In such a case the slope of the exponential edge also increases because it is sensitive to the disorder [12].

The influence of oxygen on electrical conductivity is shown in Fig. 4. The temperature dependence of the electrical conductivity (σ) can be described using the common relation $\sigma = \sigma_0 \exp(-\Delta E/k_B T)$ where σ_0 is the pre-exponential factor and ΔE is the activation energy. The small traces of oxygen, up to 100 p.p.m., lead to a decrease in conductivity. This could be due to (i) the shift of the Fermi level higher into the band gap; (ii) the decrease of the density of localized states near the valence band (we assume p-type conductivity); or simply due to the increase of the gap. In principle, oxygen can form singly coordinated charged defect states, O_1^-, which can be compensated by positive valence alternation states somewhere in the solid [13]. In such a case, new sets of Street–Mott levels are introduced into the gap and the equilibrium of the charged defect states is changed. This process may lead, depending on the relative values of the average carrier excitation energy, to an increase of the Fermi level and a decrease of the electrical conductivity. If such new Street–Mott gap states are introduced as proposed in [13], these states lie rather below the corresponding levels of the other valence alternation pair centres (due to the higher electronegativity of

TABLE I Intrinsic and impurity infrared absorption bands in $GeSe_2$ glass

Sample	cm^{-1}	μm	Possible assignment
"Pure" $GeSe_2$	500	20.0	Intrinsic two-phonon processes Ge–Se
	565	17.7	
	750	13.3	Intrinsic three-phonon processes Ge–Se
$GeSe_2$ doped with GeO_2 at a level of 1000 p.p.m. oxygen	500	20.0	Superposition of intrinsic two-phonon processes Ge–Se + extrinsic Ge–O
	565	17.7	Intrinsic two-phonon Ge–Se
	800	12.5	Extrinsic Ge–O
	1280	7.8	Extrinsic Ge–O, combination of 500 + 800

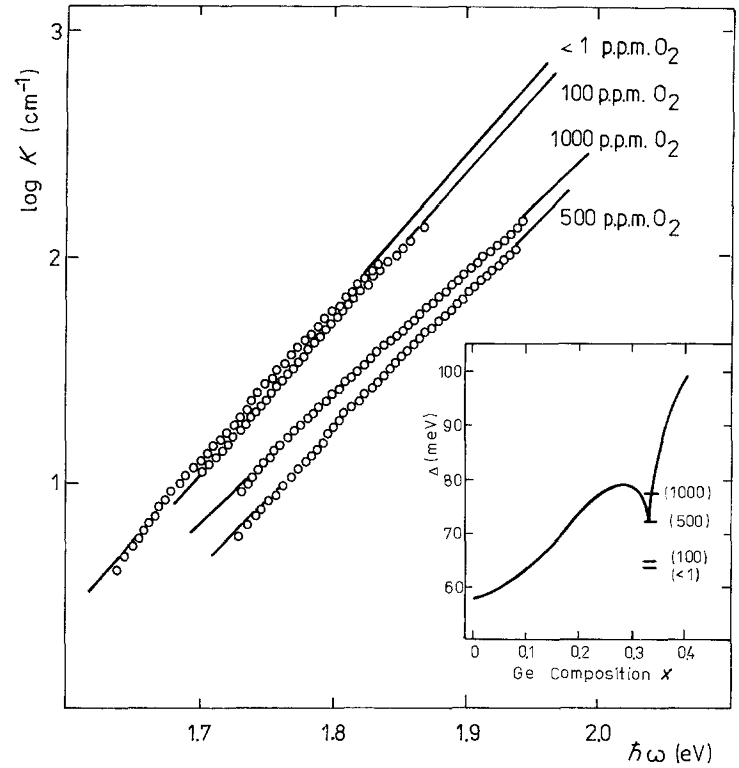

Figure 3 Spectral dependences of absorption coefficient of glassy "pure" GeSe$_2$ and GeSe$_2$ doped with various amounts of GeO$_2$ in the region of the short wavelength edge. The insert shows the compositional dependence of the slope of the Urbach tail Δ in Ge$_x$Se$_{1-x}$ compounds measured at 293 K taken from [11]. The horizontal lines mark the present experimental values.

oxygen), and consequently an increase in the density of localized states could be achieved. In such a case the slope of the exponential edge should rather increase, as we observe, because the disorder increases.

A less intricate and reasonable qualitative explanation of the increase in activation energy of the electrical conductivity can be made by assuming that due to the incorporation of oxygen into the glassy matrix of GeSe$_2$ the gap increases and consequently ΔE also increases. Some indications of the increasing gap are seen in the small shift of the exponential edge to higher energies with increasing oxygen content, see Fig. 3.

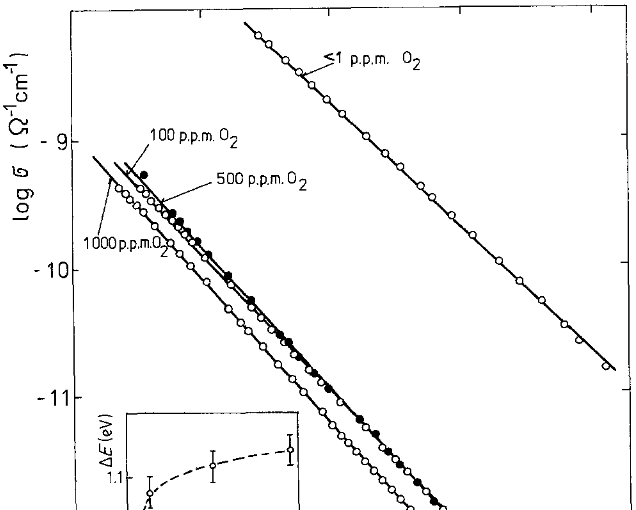

Figure 4 Temperature dependences of d.c. conductivity of glassy "pure" GeSe$_2$ and GeSe$_2$ doped with various amounts of GeO$_2$. The insert shows the activation energy of d.c. conductivity plotted against the concentration of oxygen.

Finally, the results of the differential thermal analysis of the glasses studied are shown in Fig. 5. In "pure" GeSe$_2$ there are two exophenomena corresponding to the crystallization at T_{c1} = 505 and T_{c2} = 530° C and small endophenomena at T = 573° C. The origin of the endophenomena is not at all clear; however, as mentioned by Ross and Bourgon [14], it is observed near the GeSe$_2$ composition only. Two crystallization phenomena can perhaps be due to the two mutually independent nucleation-growth processes. In the first the surface nucleation can be dominant, while the bulk nucleation is perhaps dominant in the second.

The most important feature of our DTA results is the absence of the crystallization exotherm in glasses doped by GeO$_2$. It seems that incorporation of oxygen into the glassy matrix suppresses the crystallization (at least it suppresses crystallization under the conditions of DTA measurements, heating rate 10 K min^{-1}). This seems to be possible because it was mentioned [15] that traces of oxygen impurity assist glass formation in the Ge–Se system.

The qualitative explanation of the influence of the

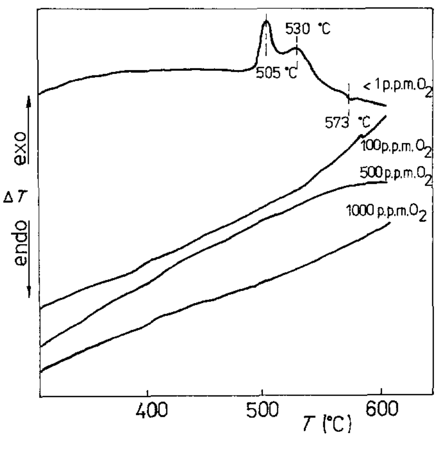

Figure 5 DTA curves of the bulk samples of glassy "pure" GeSe$_2$ and GeSe$_2$ doped with various amounts of GeO$_2$.

oxygen on the crystallization of studied glasses can be based on the fact that glassy $GeSe_2$ is a mixture (on the molecular level) of small germanium-rich ethane-like units and of large selenium-rich outrigger rafts [16]. In the process of nucleation the interaction of these units can lead, perhaps by breaking of the Se–Se bonds of outrigger rafts, Ge–Ge bonds of ethane-like units and subsequent connection of these units by Ge–Se bonds, to the formation of a nucleus of critical dimensions and crystallization can follow. Perhaps due to the solubility of GeO_2 in $GeSe_2$ the oxygen is incorporated into the Ge–Se matrix forming the $Se_{3-x}O_xGe–O–GeO_xSe_{3-x}$ $(x < 3)$ entities. We suppose that these entities are formed by interaction of GeO_2 with broken Ge–Ge and Se–Se bonds. In such a case the density of these bonds decreases and the probability of connection of outrigger rafts and/or ethane-like units into a nucleus of critical dimensions is suppressed in such a way that in the course of DTA (under our experimental conditions), the crystallization was not detected.

4. Conclusion

Oxygen, the most common impurity of the chalcogenide glasses, significantly influences the optical and electrical properties of $GeSe_2$ and also the process of the crystallization of $GeSe_2$. Our main results can be briefly summarized as follows.

1. Except for the well known influence of the traces of oxygen on the extrinsic optical absorption, especially around $800\,cm^{-1}$, the slope of the exponential edge also seems to depend on the oxygen content. An increase of the slope of the exponential edge and the shift of the edge to higher energies probably reflects an increase of the disorder and an increase of the optical gap with increasing oxygen content.

2. The increase of the gap can also be responsible for a decrease of the electrical conductivity, although the new defect states in the gap induced by incorporation of oxygen into the glassy matrix, can also affect the d.c. conductivity.

3. Perhaps because of the incorporation of oxygen into the glassy matrix, the induced subtle changes in the structure and chemical composition of the surface of the basic structural entities of $GeSe_2$ are responsible for suppression of the crystallization of $GeSe_2$ in the course of DTA.

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