INTERPRETATION
OF TOOL–NARAYANASWAMY–MOYNIHAN
RELAXATION PARAMETERS

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Differential scanning calorimetry (DSC) measurements were used to study enthalpic structural relaxation in selenide glasses. The examined compositions were, apart from pure Se, the following $Se_{(100-y)}Te_y$ (for y = 0.1, 0.2 and 0.3), $Ge_ySe_{(100-y)}$ (for y = 0.02, 0.04, 0.06, 0.08, 0.10 and 0.15) and $As_ySe_{(100-y)}Te_y$ (for y = 0.02, 0.04, 0.06, 0.08 and 0.10). Based on the results of fitting and non-fitting methods, relaxation behavior of these glasses was described in terms of the Tool–Narayanaswamy–Moynihan (TNM) model. The TNM model parameters as well as their change with respect to both increasing content of dopant in Se matrix within each chalcogenide system and different structural units employed in the respective systems were discussed. A unique conception was suggested, introducing a connection between the values of TNM parameters and respective molecular structures and their changes during structural relaxation. By such qualitative interpretation, the main disadvantage of phenomenological models may be, at least partially, overcome.

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Introduction

Glass formation and structural relaxation processes belong to the greatest "mysteries" in the field of condensed matter physics and material science. Although these phenomena have been known and studied for several hundreds of years (!), their true nature still remains unrecognized. Current state of knowledge regarding this topic is very well summarized, e.g., in Refs [1-5]. Nevertheless, even today the theories and respective models are not capable of reliable finite description of the involved structural changes and relevant physico-chemical background for relaxation processes in amorphous materials. Considering the high importance of stability of basic properties for glassy materials used in high-tech applications, the glass-to-undercooled liquid transformation continues to be of high interest not only to theoretical science but also to the application sphere.

During past decades, a significant effort was put into development of various theoretical models describing the relaxation behavior. Nowadays, it is probably the phenomenological four-parameter Tool–Narayanaswamy–Moynihan (TNM) model [6-8] that has the highest credibility and is used most often. The phenomenological description provided by this model allows a very precise description of experimental data (given by its unconstrained derivation based on rather mathematical approach), while retaining the qualitative ideas representing the basic structural relaxation features: hysteresis, non-linearity, non-exponentiality and thermo-rheological simplicity. On the other hand, the phenomenology of TNM model has also, obviously, one disadvantage, namely that the parameters do not have any physical meaning. Due to this fact, there has always been an intention to, by some means, link the parameters of phenomenological models with particular relaxation features and specific molecular structures of glassy materials in more than very general and vague ways. By succeeding against this challenge, the ability to provide a very accurate description of the experimental data would be then further supported by the structurally meaningful interpretation of the description, which, obviously, would not only greatly enhance the utilization of the particular phenomenological model but might also lead to a better understanding of the glass transition phenomenon itself.

The Tool–Narayanaswamy–Moynihan model is defined by the following equations

$$\Phi(t) = \exp\left[-\left(\int_0^t \frac{dt}{\tau}\right)^\beta\right] \tag{1}$$

$$\tau(T, T_f) = A \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f} \right] \tag{2}$$

where $\Phi(t)$ is the relaxation function of the given property, t is time, τ is the relaxation time, β is the non-exponentiality parameter, A is the preexponential factor, x is the non-linearity parameter, Δh^* is the apparent activation energy of the structural relaxation, R is the universal gas constant, T is temperature and T_f is the fictive temperature, which is defined as the temperature of the undercooled liquid with the same structure as that of the relaxing glass. Certain emphasis will thus be given to an attempt at explanation of relaxation features on the basis of particular values of TNM parameters found for various chosen glassy structures.

Three chalcogenide glassy systems will be discussed within the framework of this article: Se-Te (0-30 at. %), Ge-Se (0-15 at. %) and As-Se (0-10 at. %). These three systems then represent three model systems distinguished according to their differing archetypal structural units. With respect to the particular structural orderings, the following can be stated.

Structure of Se-Te glasses consists of heteropolar twofold coordinated helical chains and rings, where the selenium atoms are being more or less randomly replaced by the tellurium atoms [9-11]. However, several recent results [12-14] suggest that the randomness is only partial and the Se-Te bonds are prioritized over the Te-Te and Se-Se bonds — this was also confirmed by our own preliminary EXAFS measurements for $Se_{70}Te_{30}$ bulk glass. Based on these mea-surements the average interatomic distances were also determined: $R_{Se-Se} = 2.34 \pm 0.01$ Å and $R_{Se-Te} = 2.54 \pm 0.01$ Å. Moreover, if we compare the densities of Se-Te glasses to that of pure amorphous selenium, we can conclude that the structure where Se atoms are replaced by Te atoms is only slightly looser than that of pure Se. In other words, an addition of tellurium atoms into selenium glass does not seem to be accompanied by any significant distortion of molecular structures or change in atomic density due to the difference in atom sizes.

The results for Ge-Se glassy system taken from, e.g., Refs [15-20] indicate the structure consisting of two-coordinated Se atoms and four-coordinated Ge atoms. While the structure of pure glassy selenium contains chains and rings of Se atoms, the addition of germanium into the matrix results in the formation of Ge-Se heteropolar bonds that produce $GeSe_4$ tetrahedra. Increase in the Ge concentration then results in continuous (up to 33.3 at. % corresponding to $GeSe_2$) replacement of Se chain fragments with corner- and edge-shared $GeSe_4$ tetrahedra. Nevertheless, the structural characteristics in the intermediate range beyond the nearest and next-nearest neighbor coordination shells still remain controversial. It is mainly the relative extent of connectivity between the $GeSe_4$ tetrahedra *via* corner- and edge-sharing and formation of Ge-Se-Ge segments that remains unclear. The models proposed in this regard range all the way from the chain-crossing model to the fully clustered or phase-separated model [16,17]. The NMR

analysis performed by Bureau *et al.* [16,17] for $Ge_ySe_{(100-y)}$ system showed only the presence of Se-Se-Se and Ge-Se-Ge segments for $0.11 < y < 0.33$; the absence of Se-Se-Ge segments can then be interpreted in terms of the fully clustered structural model. On the other hand, Gjersing *et al.* [15] in their high-resolution ^{77}Se MAS NMR study observed the presence of all four possible linkages (Se-Se-Se, Se-Se-Ge, corner-shared Ge-Se-Ge and edge-shared Ge-Se-Ge) for $0.10 \leq y \leq 0.23$. The compositional variation of the relative fractions of these Se sites is then in agreement with the statistically random model of connectivity between $GeSe_4$ tetrahedra and selenium chain fragments.

In the As-Se chalcogenide system according to, e.g., Refs [21-25] As-Se pyramids are dominating. In the case of Se-rich glasses, the structure consists of a mixture of $AsSe_3$ pyramidal structural units and Se chains/rings, where the pyramids incorporate into the chains and interconnect them. At a higher As content (20-40 at. %), the pyramidal units start to be packed into ribbon-like structures, essentially forming wavy layers. For the As_2Se_3 glass then the structure is theoretically formed only by the $AsSe_3$ bi-pyramids; the further addition of As atoms then leads to a continuous replacement of Se in the pyramidal structure (resulting in As_2Se_2 or As_3Se structures). Bureau *et al.* [21] in their MAS NMR study found that, based on the relative representation of the Se-Se-Se, As-Se-Se and As-Se-As lines, the structure in the As-Se system is organized in terms of the so-called "chain crossing model" (chemical ordering of homogeneously distributed $AsSe_3$ pyramids). Identification of small deviations from the chain crossing model behavior were later reported by the same authors [22].

Applied Evaluation Methods

The determination of the Tool–Narayanaswamy–Moynihan relaxation parameters was done in terms of various evaluation techniques. The curve-fitting was taken as a standard/reference method . The computer programme designed for this task was based on the following equations [26]

$$T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{ 1 - \exp\left[-\left(\sum_{k=j}^{n} \frac{\Delta T_k}{q_k \tau_k} \right)^{\beta} \right] \right\} \tag{3}$$

$$T_{f,n} = T_0 + \sum_{j=1}^{n_A} \Delta T_j \left\{ 1 - \exp\left[-\left(\sum_{k=n_A}^{n} \frac{\Delta t_{e,k}}{\tau_k} \right)^{\beta} \right] \right\} \tag{4}$$

where T_0 is the initial equilibrium temperature and t_e is the annealing time. This means that the continuous cooling or heating is replaced by a sequence of n temperature jumps ΔT followed by isothermal holds with duration determined by the cooling and heating rates $\Delta t = \Delta T/q$. Each isothermal step was divided into 500 sub-intervals, elementary non-isothermal intervals, over which relaxation time and fictive temperature were recalculated, were set to be 0.1 K. A further reduction of these intervals had no effect on curve-fitting or simulation results. The input data were in the form of normalized heat capacity C_p^N, where the corresponding limiting states (glass and undercooled liquid) were set to: $c_{pg} = 0$ and $c_{pl} = 1$. Usually sets of the so-called "classic cycles" were taken for curve-fitting — this term (and corresponding thermal history) will be explained in Experimental part.

In addition to the curve-fitting, several other non-fitting methods based on a simple transformation of experimental data were used. The utilization of these evaluation techniques subsisted either in a verification of the curve-fitting results (in the case of the curve-fitting being very consistent, with no diverging fits) or as a provision of estimates of input values for the fitting procedure.

Probably the most important TNM parameter is the apparent activation energy Δh^*. This parameter is usually evaluated according to one of the following two equations

$$-\frac{\Delta h^*}{R} = \frac{\mathrm{d}\ln|q^-|}{\mathrm{d}(1/T_f)} \tag{5}$$

$$-\frac{\Delta h^*}{R} = \left[\frac{\mathrm{d}\ln|q^+|}{\mathrm{d}(1/T_p)}\right]_{q^-/q^+ = \text{const.}} \tag{6}$$

where T_f is a fictive temperature determined by the equal area method [8,27] and T_p is the temperature corresponding to the maximum of the relaxation peak. The dependence of T_g on the cooling rate [8,27] (Eq. (5)) is evaluated from the so-called classic cycles; for the determination of Δh^* by means of the peak-shift method [28,29] (Eq. (6)), the so-called intrinsic cycles are used (corresponding thermal histories will be explained in Experimental part. Based on our previous findings [30-35], the evaluation according to Eq. (5) often provides unreasonably high activation energies (inconsistent with any acceptable experimental or simula-ted curves). Therefore, in the case of the glasses studied within the framework of this article, the evaluation according to Eq. (6) was used for the estimation/verification of Δh^*.

Another applied evaluation technique was the original peak-shift method [36-38]. This method serves for estimation of the TNM non-linearity parameter x from the so-called annealing experiments

$$x^{-1} - 1 = \Delta C_p \left(\frac{\partial T_p}{\partial \delta_H} \right)_{q^-, q^+} \tag{7}$$

where δ_H stands for the total excess enthalpy. Peak-shift method was derived for limiting conditions of a well-stabilized glass, i.e., of a glass that was annealed for a long time. During the evaluation, the so-called "upper peaks" [29] (corresponding to the poorly stabilized glass at shorter annealing times) need to be thoroughly distinguished from the main annealing peaks, otherwise the parameter x incorrectly shifts towards higher values. This unfortunately limits the outcome of this method. In the case of certain materials, not even the relaxation periods measured up to ~ 1500 minutes (which is already barely manageable with respect to maintaining constant conditions in the DSC cell) are not sufficient to provide a reliable and consistent slope in the T_p vs. δ_H plot. Hence the error of x determination is high in such case. Alternatively, a set of samples may be measured outside DSC in an annealing furnace; however, in such case the errors associated with δ_H greatly increase due to dissimilar samples being measured under dissimilar conditions (e.g., differences in positioning of crucible in the cell, positioning of sample in the crucible, *etc.*).

Lastly, the so-called simulation methods are used for the estimation of the TNM parameters. Hutchinson and Ruddy [29] developed a method for the estimation of the non-exponentiality parameter β and/or non-linearity parameter x from classic cycles (standardly, parameter x should be estimated using the peak-shift method, parameter β is then unambiguously determined). If the heating scan curves are normalized in order for C_p to rise from zero (glassy state) to unity (undercooled liquid state), then the C_p value of the maximum of the endothermic peak (may be denoted C_p^{max}) is characteristic for given TNM parameters and $|q^-|/q^+$ ratio. This method is then in fact based on the comparison of the experimental and theoretically simulated data for the height of the relaxation peaks C_p^{max}. A disadvantage of this method lies in the fact that activation energy Δh^* and pre-exponential factor A (and optionally also parameter x) need to be determined in advance.

Regarding the simulation methods, in our recent work a new comparative simulation method was proposed [35]. This method is in the fact a modification of the method based on the comparison of experimental C_p^{max} evaluated from a set of classic cycle experiments with theoretical simulated values. In the case of our new proposed methodology, the overall course of experimental and theoretical curves is compared for the set of classic cycles. Thermal history needs to be exactly the same for experimental and theoretically simulated data in such case. Advantage of such approach lies in the fact that several new aspects are considered during the examination. The amount of necessary theoretical data is, therefore, rather extensive, which is why it is extremely useful to know at least one of the

parameters in advance. For obvious reasons (certainty of its determination in comparison to other TNM parameters), the apparent activation energy Δh^* should be taken as fixed (pre-exponential factor A can then be only quickly estimated for the whole set of simulated curves during a "preliminary fit" of any experimental data). In terms of the proposed methodology, certain aspects can be newly considered for the given sets of curves (contrary to the original simulation method [29], where only the height of the experimental and theoretical peaks was compared). The following aspects belong among the most prominent ones: the shift of the overall onset peak edge towards higher temperatures for increasing x; the sharpness of the peak onset increasing with β; the existence (magnitude, position) of the undershoot — the so-called relaxation pre-peak; the height of the peaks (increasing with increasing β and decreasing x); or the decreasing overall width of the relaxation effect with increasing β. Most these effects seem to be only slightly influenced by distortions of the peak shape (tested for bad thermal contact, higher masses of the sample or dissimilar c_{pg}-T and c_{pl}-T dependences). By considering the above mentioned aspects, the parameters β and x can relatively accurately be determined.

Experimental

The three chalcogenide systems studied were represented in this study by the following compositions: Se, $Se_{90}Te_{10}$, $Se_{80}Te_{20}$, $Se_{70}Te_{30}$, Ge_2Se_{98}, Ge_4Se_{96}, Ge_6Se_{94}, Ge_8Se_{92}, $Ge_{10}Se_{90}$, $Ge_{15}Se_{85}$, As_2Se_{98}, As_4Se_{96}, As_6Se_{94}, As_8Se_{92}, $As_{10}Se_{90}$. All the glasses were prepared from pure elements (5N, Sigma Aldrich) by the classical melt-quenching technique — fused silica ampoule with proper amounts of elements was first degassed and sealed. Then it was placed in the rocking furnace and held there for 24 hours at a temperature high enough for the mixture of components to react and homogenize. The glasses were then prepared from their melts by quenching the ampoules in water. An amorphous nature of each glass was checked by X-ray diffraction; the homogeneity of the glasses was verified from the position of the relaxation peak which was measured under defined thermal history for samples taken randomly from the bulk glass.

The enthalpy relaxation of the prepared glasses was studied by a conventional DSC 822^e (Mettler, Toledo) equipped with a cooling accessory EK90 Haake. Dry nitrogen was used as the purge gas at the rate of 20 cm^3 min^{-1}. The DSC was calibrated by employing the melting temperatures of In, Zn and Ga. The baseline was periodically checked. Each prepared glass was ground to powder with particle size in the range of 125-180 μm and, consequently, thin layer of the powder was spread on the bottom of aluminum pan to improve thermal contact. The masses of the samples ranged between 8-10 mg.

In the case of the compositions studied, three types of enthalpic relaxation

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experiments were performed — the so-called "classic" and "intrinsic" cycles and annealing experiments. In the case of the cyclic experiments, the sample was first annealed at a temperature well above T_g to erase any previous thermal history, then it was cooled through T_g to temperature $T < T_g$ at a defined cooling rate q^-, which varied within one set of the cycles usually from 0.5 to 30 K min^{-1}; lastly the sample was heated over T_g to the initial temperature. A necessary condition for the cyclic experiments was reaching of steady/true glassy and undercooled liquid states at the respective temperature boundaries. The difference between the two types of cyclic experiments lay in the fact that during the classic cycles the heating steps were always performed at the same rate (10 K min^{-1}), while during the intrinsic cycles the heating rates varied — their magnitude was always similar (except for the sign) to that of the previous cooling rate. The third type of thermal history was the annealing experiments. During these measurements, the sample was again first annealed at some temperature above T_g for a sufficiently long time (typically 30-60 minutes) to get to equilibrium. Then it was rapidly (at a controlled rate of approximately 40 K min^{-1}) cooled to a selected temperature below T_g, where the sample was annealed for certain time t_a. The annealing step was immediately followed by heating the sample well above T_g again. The applied annealing times were: 0, 0.1, 0.5, 1, 3, 5, 10, 15, 20, 30, 50, 100, 200, 300, 400, 600, 800, 1100 and 1400 minutes.

Each set of measurements (either a set of classic cycles, intrinsic cycles or annealing experiments) was performed using the same sample, which was not removed from the measuring DSC cell for the whole duration of the given set. This was done in order to reduce the experimental error resulting from slightly different positioning of the sample pan in the cell. The baseline was checked before and after each set of measurements.

Results

The enthalpic Tool–Narayanaswamy–Moynihan parameters for the studied chalcogenide glasses were determined using various methodologies; always the most reliable evaluation technique was chosen while the alternative ones served as confirmation of formerly obtained results. In the case of amorphous selenium, curve-fitting was found to provide very precise and consistent results, which were further confirmed also by dilatometric and viscosity measurements [30,39]. Similarly, also for Se-Te glasses the curve-fitting resulted in narrow and consistent intervals of TNM parameters values. In this case, evaluation according to Eq. (6), the peak-shift method and the original β/x simulation method were used to confirm the fitting results [40].

An opposite case was the Ge-Se glasses [35], where in the case of higher Ge

Table I Tool–Narayanaswamy–Moynihan parameters obtained for studied Se-Te, Ge-Se and As-Se glasses

	$\Delta h^*/R$ kK	$\ln A$ s	x -	β -
Se [30]	42.8 ± 0.2	-133 ± 0.5	0.52 ± 0.05	0.65 ± 0.05
$Se_{90}Te_{10}$	38 ± 1	-113 ± 2	0.50 ± 0.04	0.83 ± 0.03
$Se_{80}Te_{20}$	36 ± 1	-106 ± 3	0.45 ± 0.05	0.81 ± 0.05
$Se_{70}Te_{30}$	34.5 ± 1	-100 ± 3	0.43 ± 0.03	0.73 ± 0.02
Ge_2Se_{98}	50 ± 2	-152 ± 5	0.48 ± 0.05	0.62 ± 0.05
Ge_4Se_{96}	42.5 ± 2	-127 ± 2	$\in (0.4; 0.45)$	$\in (0.45; 0.5)$
Ge_6Se_{94}	33 ± 1	-91 ± 2	$\in (0.4; 0.45)$	$\in (0.4; 0.45)$
Ge_8Se_{92}	31.5 ± 1	-85 ± 2	~ 0.3	~ 0.4
$Ge_{10}Se_{90}$	29 ± 1	-74 ± 2	~ 0.3	~ 0.4
$Ge_{15}Se_{85}$	25.5 ± 4	-	~ 0.3	~ 0.2
As_2Se_{98}	52 ± 1	-158 ± 3	0.45 ± 0.05	0.63 ± 0.05
As_4Se_{96}	52 ± 1	-162 ± 4	0.45 ± 0.03	0.63 ± 0.04
As_6Se_{94}	53 ± 2	-152 ± 2	0.47 ± 0.06	0.65 ± 0.03
As_8Se_{92}	53 ± 2	-149 ± 2	0.43 ± 0.05	0.58 ± 0.05
$As_{10}Se_{90}$	43 ± 1	-116 ± 3	~ 0.4	~ 0.6

concentrations the DSC signal corresponding to the relaxation response started to be distorted due to the increasing continuous change in the underlying C_p-T dependence. Moreover, the relaxation overshoot decreased and widened with an addition of Ge, so even slight inaccuracy in the subtraction of the thermo-kinetic background would result in a significant distortion of the peak shape (in addition, widened low-rise peaks also make the T_p determination difficult and inaccurate). For this reason, the curve-fitting in the case of the glasses with "higher" germanium content was applied only to verify approximate validity of Δh^* determined according to Eq. (6) and to estimate the corresponding pre-exponential factor A.

The As-Se chalcogenide glassy system then represents a somewhat intermediate case, where the curve-fitting provides reasonable results, which however, seem to show dependence on thermal history; i.e., the course of underlying C_p-T dependence and its change seem to be significant — even if not so pronounced as in case of Ge-Se glasses. For this reason, the curve-fitting outputs needed to be made more precise by a reiterative procedure. At the same time, the new comparative simulation method introduced in [35] was consulted, so that the

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looking for the *RSS* minimum was directed correctly and local minima were avoided.

Apart from the above given cause of the inaccuracy of curve-fitting in the case of certain glasses, one more explanation may be suggested. Namely, that for certain combinations of relaxation parameters the unideality of heat propagation in the sample results in characteristically widened relaxation peaks, which consequently cannot be correctly fitted by the TNM model. In addition, assuming validity of this conception, this effect would have to be scalable and non-linearly proportional to the deviation of the considered TNM parameters from (their) certain threshold values. The introduced conception will be further treated in the Discussion section.

The resulting values of TNM parameters for all the studied glasses are listed in Table I. The evolution of the parameters with compositional changes in particular glassy structures is going to be discussed in the next section.

Discussion

In the first part of the Discussion, the three studied chalcogenide systems will be described separately with respect to the evolution of TNM parameters with changing composition. Afterwards, the respective compositional dependencies are going to be compared and discussed with respect to the involved structural units.

Se-Te System

It can be seen from Table I and Fig. 1 that apparent activation energy of the structural relaxation Δh^* continually decreases with an increasing Te content for all studied Se-Te glasses. As the incorporation of Te atoms into the selenium chains consists of a simple replacement of selenium atoms preserving the same twofold coordination, the fraction of crosslinked chains (where the occasional crosslinking is caused by rarely occurring defective C_3 bonding states) probably remains similar to that in pure Se. Anyway, the important fact is that no new "set" of structural units (as, e.g., the $GeSe_4$ tetrahedra in Ge-Se glasses), that would cause the structure to become heavily crosslinked or interconnected, are being formed. Therefore, no initial rapid increase in activation energies with an increasing Te content has to be expected. The factual decrease in Δh^* is probably related to the lower energy of Se-Te bonds [41,42]. The process of structural relaxation involves many different subprocesses (as, e.g., translation of atoms, molecules or even larger structural units, distortion of bonding angles and lengths, destruction of old bonds and formation of new ones, *etc.* — the exact nature of these subprocesses is, of course, dependent on the specific structure of each glass), where each of them

contributes to the total (macroscopic) apparent activation energy of relaxation. We believe that in the case of Se-Te glasses, it is the increasing number of weaker Te-Se bonds that significantly lowers the apparent activation energy with an increasing tellurium content in the glass. It was further shown by several authors [43,44] that with addition of tellurium into a glassy selenium matrix the intra-chain forces decrease, while interchain forces increase. The decreasing apparent activation energy with increasing Te content thus implies that primary processes involved in structural relaxation of the polymeric Se matrix are based on local destruction and re-formation of interatomic bonds rather than large changes in chain conformations with only insignificant fraction of breaking bonds (which would, on the contrary, result in an increase in Δh^* due to the need for interruption of larger number of stronger van der Waals inter-chain bonds). In addition, another possible influence affecting the value of the activation energy may be associated with the steric changes caused by the substitution of Se atoms by the tellurium ones. However, we consider this influence of rather minor importance.
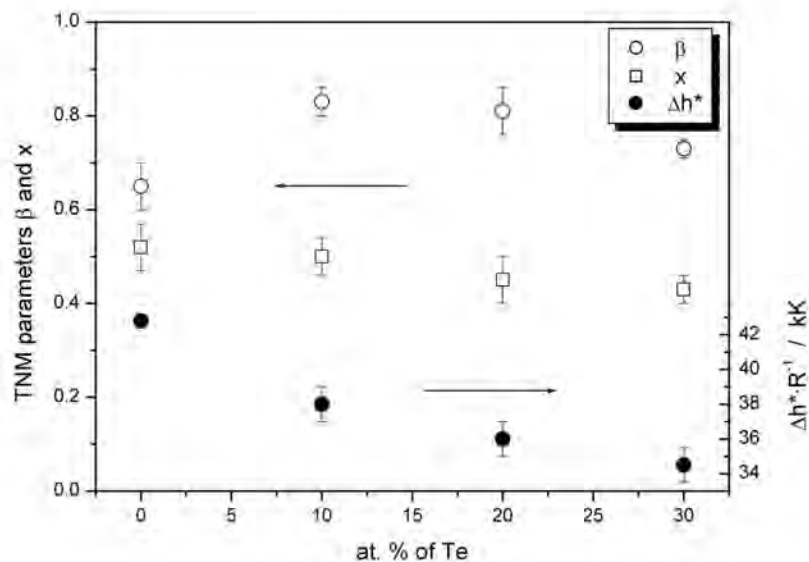

Fig. 1 Evolution of TNM parameters in Se-Te glassy system with increasing tellurium content. Apparent activation energy of structural relaxation is displayed in its reduced form $\Delta h^*/R$ on separate (right-hand) axis

Looking at the development of the non-exponentiality (β) in the Se-Te system, the first interesting thing to state is that the course of this dependence is not monotonic, showing a relatively large increase in β between the 0 and 10 % of tellurium content. One possible explanation for this fact might lie in a gradual initial (with respect to the increasing Te content) saturation of a number of weaker bonds engaged in the relaxation process. In other words, the lowered activation enthalpy per relaxing cluster due to the increased number of weaker Te-Se bonds may also imply a decreased degree of cooperativity (high β) and lower number of chain segments involved in the relaxation process. The suggested idea of saturation

then reflects the fact that for chain-like materials the bond-breaking processes represent only a part of the relaxation event, and there is a limited number of bonds that actually break and/or are being formed again during the relaxation process. However, the ongoing replacement of stronger Se-Se bonds by weaker Te-Se bonds alone would not explain the decrease in the β parameter after the assumed saturation. Therefore, we believe that in fact there are two overlapping influences, where the second one outweighs the former after the tellurium content in the Te-Se glass is high enough to saturate the number of broken bonds during the relaxation event. True physical nature of this second effect remains, however, unclear. Among possible explanations might count a distortion of the original selenium structure due to the integration of tellurium atoms resulting in a larger spatial heterogeneity caused by the accumulation of Te atoms in certain chains, or a slowly increasing cooperativity due to the larger fraction of chains being interconnected by the van der Waals bonds [43,44].

If one looks at the development of parameter x (Table I and Fig. 1), one can see that with a rising Te content in the Se-Te glasses the importance of temperature for the very relaxation processes decreases while the importance of actual glassy structure increases. One possible explanation might again be related to the idea of the apparent activation energy of the structural relaxation decreasing with a larger amount of weaker Te-Se bonds. As the TNM model only takes into account a single averaged value of the activation energy with respect to all involved subprocesses (macroscopic representation of the relaxation process), the interpretation of Δh^* decreasing primarily due to the thermodynamic structural aspects naturally implies an increase in the relative importance of the relaxation dynamics — which is reflected in the decreasing nonlinearity parameter.

Ge-Se System

Figure 2 and Table I show the evolution of TNM parameters for the Ge-Se system. Considering first the Δh^* parameter, the first addition of germanium into the selenium matrix causes a sharp increase in the activation energy of the structural relaxation. The probable explanation for this fact is that creation of the first small amount of $GeSe_4$ tetrahedra interconnects the polymeric selenium chains, strongly decreasing their mobility. As the number of tetrahedra is small indeed, the structure (selenium matrix) still relaxes in terms of movement of particular linear Se chains. Hence, the added motion restriction represented by the localization of a certain part of the chain would result in an increased activation energy for the movement (relaxation) process. As a consequence of continuously increasing degree of cross-linking (with further addition of Ge atoms), larger numbers of shorter segments need to change their position by a smaller amount for the glass structure to occupy new, a more compact conformation. This then perfectly corresponds to the later

observed decrease in the activation energy of the structural relaxation. Furthermore, the continuous slow-down of Δh^* decrease observed for a higher germanium content corresponds to constantly decreasing relative contribution of added Ge atoms to the factual increase in the structure interconnection (due to the certain portion of surplus germanium being used up in the corner-shared $\rightarrow$ edge-shared tetrahedra transformation [15]).
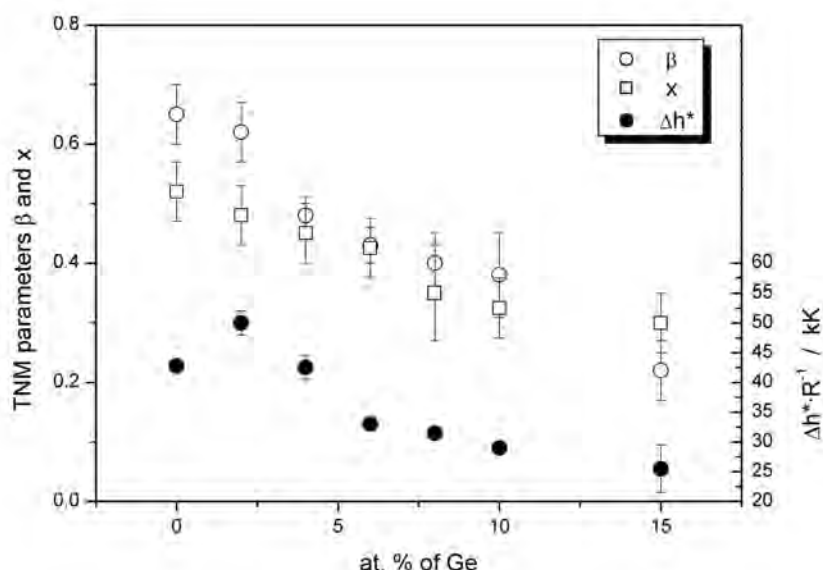

Fig. 2   Evolution of TNM parameters in Ge-Se glassy system with increasing germanium content. Apparent activation energy of structural relaxation is displayed in its reduced form $\Delta h^*/R$ on separate (right-hand) axis

The evolution of β in the case of Ge-Se glasses can be explained in terms of the segmental cooperativity concept. Decreasing β corresponds to a wider distribution of relaxation times, i.e., higher spatial heterogeneity. As the number of $GeSe_4$ tetrahedra increases, connecting the original matrix of Se chains into a 3D-network, the number of independently relaxing clusters increases on account of their magnitude and relative importance for the overall relaxation process. Hence the decreasing segmental cooperativity — the phrase is used in terms of individuality of particular involved processes. In addition, with regard to the experimental data, the heterogeneity of structure/relaxation times can be recognized in widening relaxation peaks. Interestingly, in the case of the Ge-Se glasses the parameter β can also be understood in terms of deviation from the uniformly relaxing ideal $GeSe_2$ theoretical structure composed entirely of CS tetrahedra (for which β would be expected to be close to unity).

Looking at the non-linearity parameter, x, a mild decrease can be observed with a rising Ge content. Hence, with a rising Ge content in the Ge-Se glass, the importance of temperature for the very relaxation processes decreases while the importance of actual glassy structure increases. A possible explanation might be related to the idea of the apparent activation energy of the structural relaxation

decreasing with interconnectivity of the structure. The interpretation of the Δh^* decreasing primarily due to the thermodynamic structural aspects naturally implies an increase in the relative importance of the actual structural state itself, which is reflected in the decreasing nonlinearity parameter.

As-Se System

Lastly, the parameters for the As-Se chalcogenide system are displayed in Fig. 3 and Table I. By comparison of results for the Ge-Se and As-Se systems, it can be deduced that the evolution of relaxation behavior for the As-Se glasses is similar to that of Ge-Se glasses, only more expanded with respect to the atomic percentage of the element added into the Se matrix. This is in agreement with the lower (and more slowly increasing) degree of crosslinking in the case of the As-Se structure — each $AsSe_3$ pyramid causes only a single link to a neighboring Se chain (with the As atom being incorporated in one chain and the neighboring chain being terminated in the last corner of the pyramid), while the $GeSe_4$ tetrahedron interconnects the chains by means of their true crossing. Following this idea, we can explain the evolution of As-Se TNM parameters similarly as that of the Ge-Se ones.
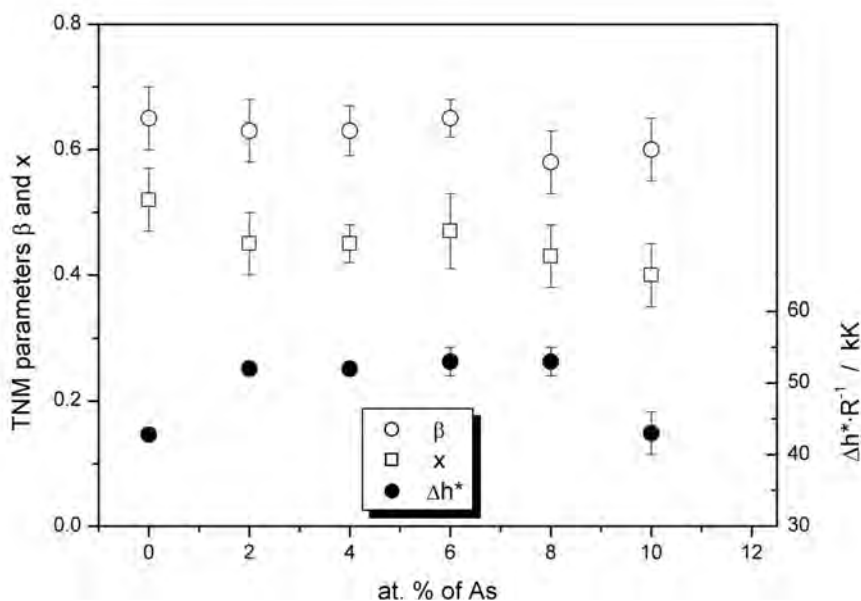

Fig. 3 Evolution of TNM parameters in As-Se glassy system with increasing arsenic content. Apparent activation energy of structural relaxation is displayed in its reduced form Δh^*/R on separate (right-hand) axis

Due to the first additions of As atoms into the Se matrix, the interconnection of polymeric chains strongly decreases their mobility. The low-As-structure still relaxes in terms of chain movements, hence the increased Δh^*. The factual degree of crosslinking increases only slowly with an addition of As atoms; therefore, the relaxation in terms of chain movements predominates over the relatively high As

content (~10 at. %). The consequent slow decrease in Δh^* corresponds to the changing relaxation mechanism, where larger numbers of shorter segments need to change their position by a smaller amount for the glass structure to occupy new, more compact conformation. The almost indefinable decrease in the β and x parameters then again corresponds to the increasing number of independently relaxing clusters, their decreasing magnitude and also decreasing relative importance of the clusters for the overall relaxation process.

TNM Parameters vs. Structural Units

The comparison of the respective TNM parameters with an increasing Te/Ge/As content is shown in Figs 4-6. In the case of the apparent activation energy of the structural relaxation, two different trends are observable with respect to varying application of structural units. For the Se-Te system the Δh^* decrease is rather monotonic, as a consequence of the Te atoms being randomly incorporated into the Se chains, representing the "weak spots" (lower strength of the Se-Te bond), where the chains are disrupted during the secondary relaxation process. Thus, the disruption of Se-Te chains seems to significantly contribute to the relaxation, in addition to the main process represented by chain movements. In the case of Ge-Se and As-Se glasses, the situation is completely different. Both Ge-Se and As-Se bonds are relatively strong; therefore, the chain movements here represent a major
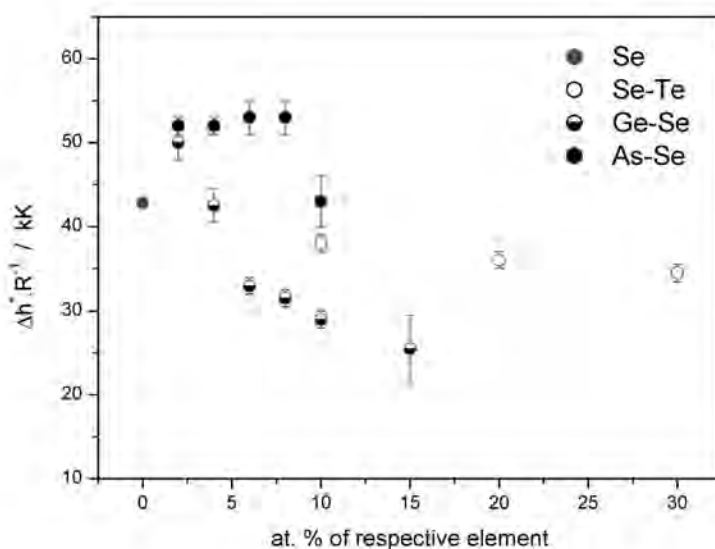

Fig. 4 Evolution of apparent activation energy of structural relaxation $\Delta h^*/R$ for increasing content of dopants in selenium matrix. Data for all three studied chalcogenide systems are displayed

contribution to the relaxation process. The crosslinking of the structures due to the formation of $GeSe_4$ tetrahedra and $AsSe_3$ pyramids then partially restricts these movements, implying an increased Δh^*. This increase is then later eliminated by

high degree of interconnection, which results in larger numbers of shorter segments needing to change their position by a smaller amount, thus decreasing the activation energy. The content of the doping element (Ge, As), at which the activation energy starts to decrease, then corresponds to the respective degree of crosslinking.

If we consider the evolution of the non-exponentiality parameter β (see Fig. 5), we may employ the concept of segmental cooperativity in the explanation. Again, it is the influence of the respective structural units that differentiates the relaxation behavior of the particular chalcogenide glasses. In the case of the Ge-Se and As-Se systems, the increasing crosslinking essentially leads to a formation of independently relaxing clusters (this corresponds to the starting decrease in the activation energy). This is the reason why in the case of Ge-Se system the parameter β decreases already at a low Ge content, while in the case of less crosslinked As-Se (considering the same content of dopant), the non-exponentiality parameter changes only insignificantly — the degree of interconnection needed for the formation of independent clusters was not reached here yet. The relaxation in the Se-Te system is then characterized by a different mechanism involving breaking of Se-Te bonds, which in the combination with the contending effect of a larger fraction of chains being interconnected by the van der Waals bonds for increased Te content results in the non-monotonic dependence of β.
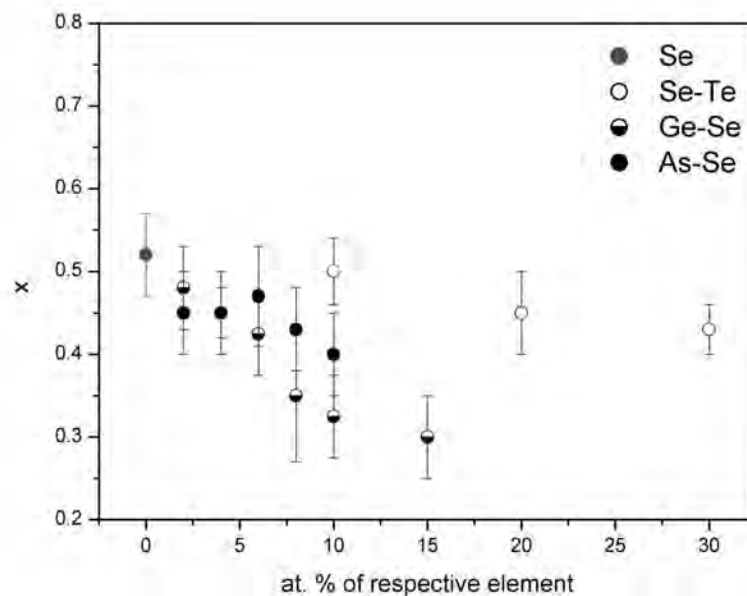

Fig. 5   Evolution of non-exponentiality parameter β for increasing content of dopants in selenium matrix. Data for all three studied chalcogenide systems are displayed

The decreasing non-linearity parameter x (Fig. 6) can then be possibly related to the course of the apparent activation energy. As the TNM model only takes into account the single averaged value of activation energy with respect to all involved subprocesses (macroscopic representation of the relaxation process), the

interpretation of Δh^* decreasing primarily due to the thermodynamic structural aspects implies an increase in the relative importance of the current state of the relaxing structure — which is reflected in the decreasing nonlinearity parameter.
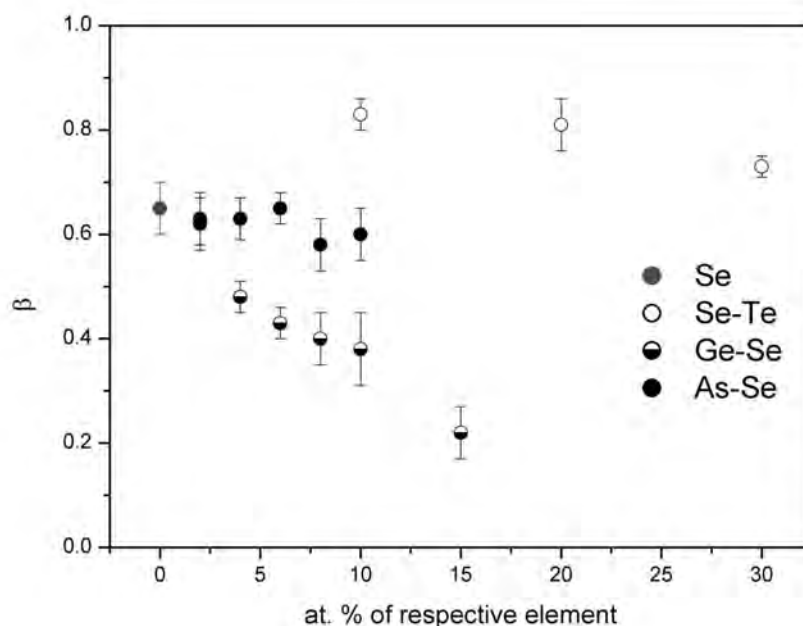

Fig. 6 Evolution of non-linearity parameter x for increasing content of dopant in selenium matrix. Data for all three studied chalcogenide systems are displayed

Conclusion

The enthalpic structural relaxation in selenium based glasses was studied by the differential scanning calorimetry. The chalcogenide systems involved in this work were: Se-Te, Ge-Se, As-Se and pure Se. The description of relaxation behavior for the studied glasses was realized in terms of the phenomenological Tool–Narayanaswamy–Moynihan model. Both, curve-fitting and non-fitting methods were employed in evaluations of the TNM parameters. The evolution of the respective TNM parameters (Δh^*, β and x) was discussed in the dependence on both changing dopant content within each composition and involved structural units, which are characteristic for each studied system. The qualitative description of relaxation features in the studied glassy systems was based on specific molecular structures and their changes during relaxation. This conceptual description then appears to represent a unique connection between various molecular structures and parameters of the phenomenological TNM model — an interpretation that was intensively looked for during past decades. The validity of the introduced concept may be supported by its possible general applicability — three chalcogenide glassy systems, each containing different characteristic structural units, were described within the presented conception.

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Acknowledgement

References

[1] Debenedetti P.G., Stillinger F.H.: Nature **410**, 259 (2001).

[2] McKenna G.B.: *Glass Formation and Glassy Behavior, in: Comprehensive Polymer Science 2*, Pergamon, Oxford, 1989.

[3] Scherer G.W.: *Relaxation in Glass and Composites*, Wiley, New York, 1986.

[4] Scherer G.W.: *Glass Formation and Relaxation, in: Materials Science and Technology 9*, VCH, Weinheim, 1991.

[5] Hutchinson J.M.: *Relaxation processes and physical aging, in: The physics of glassy polymers*, Chapman and Hall, London, 1997.

[6] Tool A.Q.: J. Am. Ceram. Soc. **29**, 240 (1946).

[7] Narayanaswamy O.S.: J. Am. Ceram. Soc. **54**, 491 (1971).

[8] Moynihan C.T., Easteal A.J., DeBolt M.A., Tucker J.: J. Am. Ceram. Soc. **59**, 12 (1976).

[9] Venugopal R.K., Bhatnagar A.K.: J. Phys. D: Appl. Phys. **25**, 1810 (1992).

[10] El-Korashy A., El-Zahed H., Radwan M., Abdalla A.M.: Thin Solid Films **261**, 328 (1995).

[11] Shimakawa K., Nitta S.: Phys. Rev. B **17**, 3950 (1978).

[12] Afify N., Gaber A., Abdalla I., Talaat H.: Physica B **229**, 167 (1997).

[13] Majid M., Benazeth S., Souleau C., Purans J.: Phys. Rev. B **58**, 6104 (1998).

[14] Tsuzuki T., Yao M., Endo H.: J. Phys. Soc. Jpn. **64**, 485 (1995).

[15] Gjersing E.L., Sen S., Aitken B.G.: J. Phys. Chem. C **114**, 8601 (2010).

[16] Bureau B., Troles J., Le Floch M., Guénot P., Smektala F., Lucas J.: J. Non-Cryst. Sol. **319**, 145 (2003).

[17] Bureau B., Troles J., Le Floch M., Smektala F., Lucas J.: J. Non-Cryst. Sol. **326-327**, 58 (2003).

[18] Bychkov E., Benmore C.J., Price D.L.: Phys. Rev. B **72**, 172107 (2005).

[19] Petri I., Salmon P.S., Fischer H.E.: Phys. Rev. Lett. **84**, 2413 (2000).

[20] Edwards T.G., Sen S.: J. Phys. Chem. B **115**, 4307 (2011).

[21] Bureau B., Troles J., LeFloch M., Smektala F., Silly G., Lucas J.: Solid State Sci. **5**, 219 (2003).

[22] Deschamps M., Roiland C., Bureau B., Yang G., Le Polles L., Massiot D.: Solid State Nucl. Magn. Reson. **40**, 72 (2011).

[23] Pangavhane S.D., Němec P., Wágner T., Janča J., Havel J.: Rapid Commun. Mass Spectrom. **24**, 2000 (2010).

[24] Koyzukhin S.A., Kupriyanova T.A., Vargunin A.I.: Inorg. Mat. **43**, 897

(2007).

[25] Rosenhahn C., Hayes S.E., Rosenhahn B., Eckert H.: J. Non-Cryst. Sol. **284**, 1 (2001).

[26] Hodge I.M., Berens A.R.: Macromolecules **15**, 762 (1982).

[27] DeBolt M.A., Easteal A.J., Macedo P.B., Moynihan C.T.: J. Am. Ceram. Soc. **59**, 16 (1976).

[28] Moynihan C.T., Easteal A.J., Wilder J.: J. Phys. Chem. **78**, 2673 (1974).

[29] Hutchinson J.M., Ruddy M.: J. Polym. Sci. B **28**, 2127 (1990).

[30] Svoboda R., Pustková P., Málek J.: J. Phys. Chem. Sol. **68**, 850 (2007).

[31] Svoboda R., Pustková P., Málek J.: Polymer **49**, 3176 (2008).

[32] Svoboda R., Honcová P., Málek J.: J. Non-Cryst. Sol. **356**, 447 (2010).

[33] Svoboda R., Honcová P., Málek J.: J. Non-Cryst. Sol. **356**, 165 (2010).

[34] Svoboda R., Honcová P., Málek J.: J. Non-Cryst. Sol. **358**, 804 (2012).

[35] Svoboda R., Málek J.: J. Therm. Anal. Cal. - submitted.

[36] Hutchinson J.M., Kovacs A.J.: Polym. Eng. Sci. **24**, 1087 (1984).

[37] Hutchinson J.M., Ruddy M.: J. Polym. Sci. B **26**, 2341 (1988).

[38] Ramos A.R., Hutchinson J.M., Kovacs A.J.: J. Polym. Sci. B **22**, 1655 (1984).

[39] Málek J., Svoboda R., Pustková P., Čičmanec P.: J. Non-Cryst. Sol. **355**, 264 (2009).

[40] Svoboda R., Honcová P., Málek J.: J. Non-Cryst. Sol. **357**, 2163 (2011).

[41] Nesheva D., Kotsalas I.P., Raptis C., Arsova D.: J. Appl. Phys. **86**, 4964 (1999).

[42] Kasap S.O., Juhasz C.: J. Mat. Sci. **21**, 1329 (1986).

[43] Ionov R., Dudev T.: Appl. Phys. A **55**, 203 (1992).

[44] Martin R.M., Lucovsky G., Helliwell K.: Phys. Rev. B **13**, 1383 (1976).