Native metastability in chalcogenide glasses described within configuration-coordinate model

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Abstract. It was created configuration-coordinate model for describing of native metastability in chalcogenide glasses. It was shown that potential should be at least triple-well. System of differential equations for describing transitions between the atomic states was made and solved within present configuration-coordinate model.

1. Introduction
Chalcogenide glasses (ChG) obtained as alloys of chemical elements from IV and V group of Periodic Table with chalcogens (S, Se and Te, but not O) are the perspective materials for optoelectronics [1-3]. Their semiconducting properties were firstly discovered by B.T. Kolomiets and N.O. Goryunova in 1960th [4]. However, the wide application of ChG is limited by their structural metastability – the common feature of all disordered materials. The reason for metastability is connected with technological routes of ChG preparation – quenching of the melt. Owing to such synthesis procedure it is obvious that vitreous state should remain some peculiarities of liquid [5]. As a result, thermo-induced ageing phenomenon is character for ChG. It means that long-term isothermal annealing leads to the approaching of ChG enthalpy to the thermodynamic equilibrium of supercooled liquid [6].

The changes of the ChG properties can be native or induced. Effects of short- and long-term ageing are determined by native metastability. Sufficiently these processes can be described by configuration-coordinate model (CCM).

2. The basics of configuration-coordinate modelling
Within the frameworks of configuration-coordinate modeling, all possible atomic states and system of transitions should be correctly described for determination of real (physically observed) patterns of corresponding physical processes [7,8].

Atomic states in CCM are representing as parabola or its closely related modification. In the elementary case (that is ideal in respect to possible additional perturbations) energetic characteristic of the atomic state $E$ is describing by parabolic dependence from the generalized configuration coordinate $q$ (analogically to the harmonic motion of atoms near their equilibrium position) [9]:

$$E = \frac{1}{2}kq^2.$$  (1)
The ground state is undermost, all higher states are metastable. Metastable states are time- and thermo-unstable. Physicochemical properties of ChG are changed with gradually relaxing of metastable states to the ground state. The rate and effectiveness of such relaxation processes are determined by the parameters of responsible atomic states such as energy barriers with ground state (or first energetically lower state) [10].

In fact, atomic state modifies due to additional perturbations (formation of quasistable atomic groups or molecular complexes, wrong chemical bonds, etc.). It leads to the displacement of equilibrium position of parabola, change of parabola branches curvature and parabola splitting in the some quasiparabolas. As result it is accompanied by forming of so-called many-well potentials [9-11]. Such potentials are typical for all topologically-disordered solids (including ChG) obtained from the high-temperature defect liquid state.

Transitions between the atomic states are able in CCM. They could be both vertical (that is without change of configuration coordinate) and horizontal (that is accompanied by configuration coordinate of atomic complex change). Horizontal transition could be as tunneling through the barrier (at the low temperatures) or thermoactivated skip over the energy barrier (at temperatures over 10 K) [9].

3. Describing of native metastability within CCM
Our created CCM describing native metastability in ChG is shown on Fig. 1. Within this CCM it is assumed that potential, which corresponds to structural fragments, is many-well (at least triple-well). Every potential barrier between the metastable states is characterized by barrier height $\Delta E$ and asymmetry of the potential. The transitions from the more high states to the more energetically favorable lower states are conformed to the ageing effects.

\[
\begin{align*}
\frac{dN_X}{dt} &= \frac{N_Y}{\tau_Y} \\
\frac{dN_Y}{dt} &= \frac{N_Z - N_Y}{\tau_Z - \tau_Y}
\end{align*}
\]

which could be transferred into the
\[
\begin{align*}
\frac{dN_X}{dt} &= \frac{N_Y}{\tau_Y} \\
\frac{dN_Y}{dt} &= \frac{N - N_X - N_Y}{\tau_Z} - \frac{N_Y}{\tau_Y} \\
\end{align*}
\]

(3)

where \(N_X, N_Y\) and \(N_Z\) are the number of structural fragments in the ground (X) and metastable (Y i Z) states correspondingly;

\(N\) – total number of all structural fragments (\(N = N_X + N_Y + N_Z\));

\(\tau_Y\) and \(\tau_Z\) – lifetime of the structural fragments in metastable states Y and Z correspondingly.

On the normal conditions value of \(\tau\) is determined by the thermal skips of the structural fragments into the lower state over the corresponding energy barrier. It is characterized by exponential dependence on the temperature:

\[
\tau^{-1} = \nu \exp\left(\frac{\Delta E}{kT}\right),
\]

(4)

where \(\Delta E\) – height of the energy barrier for metastable state;
\(\nu\) – “attempt” frequency which is of the order of the frequency of vibrations in the well.

Solution of the differential system (3) could be written as follow:

\[
\begin{align*}
N_X &= N + \frac{\tau_Y N_X(0) - \tau_Y N - \tau_Z N_Y(0)}{\tau_Y - \tau_Z} \exp\left(-\frac{t}{\tau_Y}\right) + \frac{\tau_Z N_Y(0) - N_X(0) + N}{\tau_Y - \tau_Z} \exp\left(-\frac{t}{\tau_Z}\right) \\
N_Y &= \frac{\tau_Y N_Y(0) - \tau_Y N - \tau_Z N_Y(0)}{\tau_Y - \tau_Z} \exp\left(-\frac{t}{\tau_Y}\right) + \frac{\tau_Z N_Y(0) - N_X(0) + N}{\tau_Y - \tau_Z} \exp\left(-\frac{t}{\tau_Z}\right)
\end{align*}
\]

(5)

where \(N_X(0)\) and \(N_Y(0)\) are the number of structural fragments at the moment of time \(t = 0\) in the states X and Y correspondingly.

In our CCM it is considered that higher states characterized by smaller potential barriers. Accordingly, structural fragments of higher states have the less relaxation time. Thus, within our CCM it could be concluded that transitions between more high states corresponds for short-term physical ageing, while transitions between low states corresponds for long-term physical ageing.

4. Conclusions
Native metastability in chalcogenide glasses is described within configuration-coordinate model. Atomic state is shown as triple-well potential. The kinetic of transition between the states is characterized by exponential rule.

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