

# ON CORRELATIONS OF INDEXES OF MELT FRAGILITY IN METALLIC GLASS-FORMERS

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**Abstract.** Indexes of thermodynamic fragility show discrepancies with respect to kinetic ones for metallic glass formers (slope of viscosity at the glass transition,  $m$ , vs. reduced temperatures at which specific entropy values are obtained). On the other hand, the reduced span of the glass transition range scales well with  $m$ .

A correlation, recently reported, between melt strength/fragility and the elastic moduli of glassy materials (namely the ratio of the bulk to shear modulus) is actually not stringent. There is, however, the possibility of distinguishing among various types of glasses, e. g. inorganic, organic, metal-metal and metal-metalloid.

## 1. INTRODUCTION

The concept of melt strength or fragility, developed for inorganic and molecular glass-formers [1], is applied also for metallic alloys: the kinetic fragility is related to the viscous behaviour of the liquid and the thermodynamic fragility to the entropy loss on undercooling [2-6]. A connection between the two quantities has been envisaged, but is still unclear. In the following, the basis for it will be recapped and the related parameters discussed. Such an effort has at least two justifications. It will help in the understanding the features of the glassy state for metals in relation to all glass-formers and, on a practical ground, it could provide indication on properties which are difficult to determine experimentally, such as the temperature dependence of viscosity, using measurements commonly performed in laboratories, e. g. DSC runs.

## 2. VISCOSITY AND KINETIC INDEXES OF FRAGILITY

The non-linear dependence of viscosity on inverse temperature for glass formers is most often described by the VFT equation [1]

$$\eta = A \exp \left[ \frac{B}{(T - T_{0,\eta})} \right], \quad (1)$$

where  $A$  and  $B$  are constants and  $T_{0,\eta}$  is the temperature where the viscosity should diverge, or, alternatively, by the free volume expression [7]

$$\eta = A \exp \left[ \frac{\gamma v^*}{v_f} \right], \quad (2)$$

where  $\gamma v^*$  is a product of free parameters and  $v_f$  is the free volume relative to the atomic (molecular)

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volume of the glass component. If  $v_f$  depends linearly on temperature, Eq. (2) reduces to the form of Eq. (1). A connection between transport and thermodynamic properties is suggested by the Adam-Gibbs equation [8]

$$\eta = A \exp \left[ \frac{C}{TS_c} \right] \quad (3)$$

relating the viscosity to  $S_c$ , the liquid configurational entropy, being  $C$  a constant.  $S_c$  cannot be separated from the vibrational part of entropy in most practical cases. It is usually approximated by the entropy difference between the liquid and the corresponding crystal,  $\Delta S$ , so its reference state becomes the Kauzmann temperature,  $T_K$ , where such difference should vanish. The approximation implies the equality of vibrational entropies in the liquid and the crystal which is certainly strong for metallic glass formers in that such systems do not crystallize in a single crystalline phase but in a phase mixture. The use of the above formula stems from the assumption that both the entire excess liquid entropy and the configurational contribution  $S_c$ , change with temperature proportionally: a change in vibrational entropy of the liquid would cause a corresponding effect in the configurational part [8]. Note that if the specific heat difference,  $\Delta C_p$ , is taken as inversely proportional to temperature in

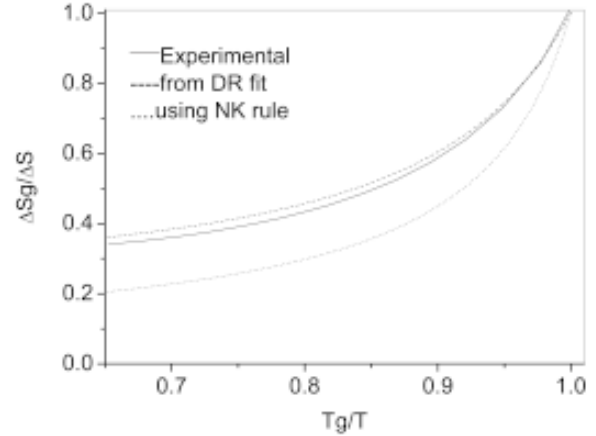
$$S_c = \Delta S = \int_{T_K}^T \Delta C_p d \ln T \quad (4)$$

Eq. (3) reduces to the form of equation (1).

The available viscosity data for metallic glass forming melts have been plotted in various instances versus  $T_g/T$  (Angell plot) showing a positive curvature with different slopes for various alloys [2-6]. The increase in the slope of the Angell plot at  $T_g$  roughly scales with that of the cooling rate needed for glass production. The slope of the plot at  $T_g$  provides the fragility parameter  $m$  defined as

$$m = \left[ \frac{d \log(\eta)}{d \left( \frac{T_g}{T} \right)} \right]_{T=T_g} \quad (5)$$

Observing that the viscosity of glass formers can span about 17 orders of magnitude from above the melting point ( $\log \eta = -5$ ) to the glass transition



**Fig. 1.** Plots of  $\Delta S_g/\Delta S$  versus  $T_g/T$  for the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy. Original data are taken from [9].

( $\log \eta = 12$ ), Angell [1] has introduced a kinetic fragility index defined as

$$F_{kin,1/2} = \frac{2T_g}{T_{1/2}} - 1, \quad (6)$$

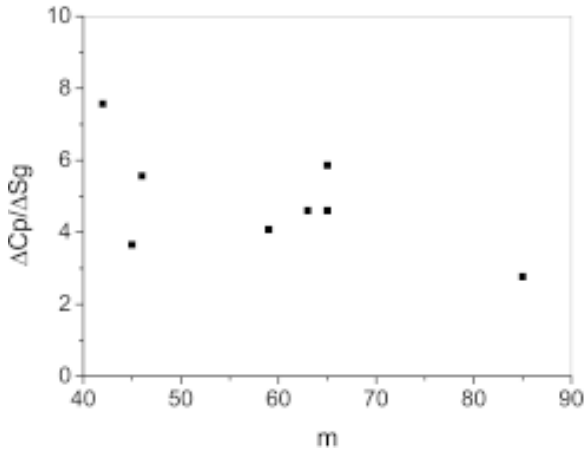
where  $T_{1/2}$  is the temperature at which  $\log \eta$  is half way the above range ( $\log \eta = 3.5$ ). The  $F_{kin,1/2}$  parameter scales with the  $m$  index for metallic glass-formers [3].

### 3. ENTROPY AND THERMODYNAMIC INDEXES OF FRAGILITY

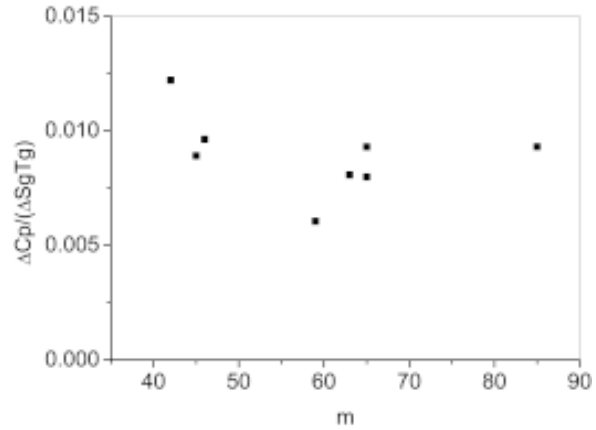
The thermodynamic evidence of liquid fragility is given by the rate of entropy loss as a function of temperature. Taking  $T_m$  as reference temperature where the excess entropy of the liquid with respect to the crystal,  $\Delta S_m$ , is known, the difference in entropy is then

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p d \ln T. \quad (7)$$

Data for metallic glass formers were used to compute  $\Delta S_g/\Delta S$  to be plotted versus  $T_g/T$  [3,4].  $\Delta S_g$  is the entropy difference at  $T_g$  taken as a reference state. An example is reported in Fig. 1 for the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy where the trend of the entropy curves is actually reminiscent of that of  $\log \eta$ . In case  $\Delta C_p$  is not known in the entire temperature range, it is shown that the Dubey-Ramachandrarao formula [10] containing two ad-



**Fig. 2.** Plot of  $\Delta C_{p,g}/\Delta S_g$  (slope of  $\Delta S_g/\Delta S$  versus  $T_g/T$  computed at  $T_g$ ) versus  $m$  for various metallic glasses. The values for individual alloys are listed in Table 1. Sources of data are compiled in [3-5].



**Fig. 3.** Plot of  $\Delta C_{p,g}/(\Delta S_g T_g)$  (slope of  $\Delta S_g/\Delta S$  versus  $T$  computed at  $T_g$ ) versus  $m$  for various metallic glasses. The values for individual alloys are listed in Table 1. Sources of data are compiled in [3-5].

justable parameters,  $\Delta C_p^m$ , the specific heat difference between liquid and crystal at the melting point,  $T_m$ , and the dimensionless quantity  $\alpha$ ,

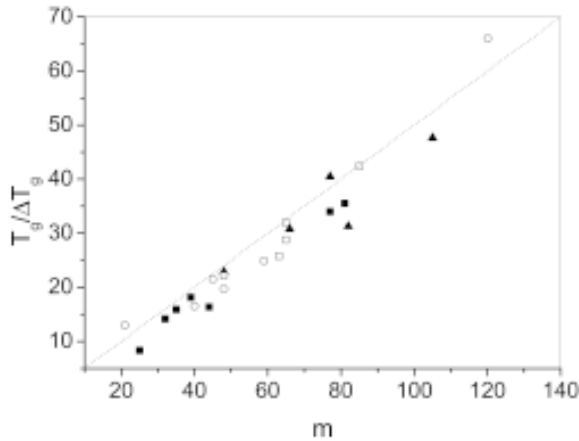
$$\Delta C_p = \Delta C_p^m \left( \frac{T_m}{T} \right)^2 \exp \left[ -\alpha \left( \frac{T_m}{T} - 1 \right) \right] \quad (8)$$

provides a very good approximation to  $\Delta C_p$ . Proper integration provides equations for  $\Delta S$  and  $\Delta H$  between liquid and crystal phases. The latter quantity can be obtained with experiments at the melting and crystallization temperatures of the alloy. Moreover,  $\Delta C_p$  can be measured at  $T_g$  so that the free parameters can be determined.

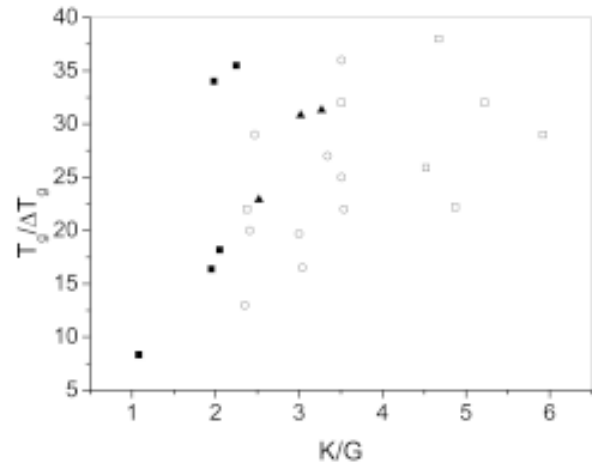
The experimental specific heat of the crystal phases of this alloy deviates from the Neumann-Kopp (NK) behaviour, additive of the components specific heat. Instead, should the NK rule be used to eliminate mixing contributions in the crystal state which are not relevant for the liquid properties, the  $\Delta S$  curve would shift considerably (Fig. 1) towards more fragile behaviour. This clearly indicates that these plots are very sensitive to the quality of data and the choice of reference states. It is no surprise, therefore, that the fragility index  $F_{ld,1/2}$  suggested by Angell [8], having analogous meaning as  $F_{kin,1/2}$ , displays a correlation only with some of the  $F_{kin,1/2}$  points [3]. Therefore, at the moment, the link between kinetic and thermodynamic fragility in metallic melts is likely, but not proven. There are multiple reasons for the poor correlation: there are

uncertainties in some thermodynamic data, namely entropy of fusion (because of the occurrence of metastable crystalline phases and because the melting interval of alloys can be ill defined), liquid specific heat (because in most cases the data need to be interpolated from the high to the low temperature ranges and because of the inherent scatter of data); also measurements of the crystal specific heat can be difficult because of the reactivity of alloy components. Moreover, the approximation of the configurational liquid entropy described above may fail because of different contributions to the vibrational part of entropy in various alloys [6].

The slope of the  $\Delta S_g/\Delta S$  versus  $T_g/T$  computed at  $T_g$  is related to  $\Delta C_{p,g}/\Delta S_g$ , being  $\Delta C_{p,g}$  the specific heat difference between undercooled liquid and crystal at  $T_g$  approximating the specific heat difference between undercooled liquid and glass. The above ratio should scale with the  $m$  parameter. The correlation is shown in Fig. 2. It is again mediocre. However, before drawing conclusions one should note that the number of precisely measured data is limited and relaxation effects due to different quenching rates can add uncertainty to the values especially of the height of the specific heat jump at  $T_g$ . In general, caution is taken also because only metallic glasses are considered here for which the span of fragility indexes is narrow whereas various classes of glass formers were used for previous analyses. At variance, the derivative of  $\Delta S_g/\Delta S$  ver-



**Fig. 4.** The inverse reduced width of the glass transition range,  $T_g/\Delta T_g$  versus  $m$  for various glasses: black squares: inorganic glasses; black triangles: organic glasses; open squares: metal-metal glasses; open circles: metal-metalloid glasses. The line gives  $T_g/\Delta T_g = m/2$ . Data for glasses other than metallic are from refs. [3,8,14].



**Fig. 5.** Correlation between the fragility index  $T_g/\Delta T_g$  and the ratio of bulk to shear modulus,  $K/G$ , in various types of glasses. Symbols as in Fig. 1. Data as in [3] with the addition of values for  $Gd_{40}Y_{16}Al_{24}Co_{20}$  [15] and  $Ni_{60}Nb_{37}Sn_3$  [16].

sus  $T$  computed at  $T_g$  is related to  $\Delta C_{p,g}/(\Delta S_g)$ . The latter quantity is plotted versus  $m$  in Fig. 3 resulting roughly constant for melts of varying strength.

There is clearly need for a larger number of accurate data to confirm the existence of the correlation indicated by Figs. 2 and 3 which could confirm the connection between transport and thermodynamic properties of metallic, glass-forming melts. Note that the  $m$  values used in the present work are obtained exclusively from viscosity data according to Eq. (5). Parameters obtained by means of other techniques (e. g. the relaxation time at the glass transition obtained by DSC experiments at various rates [12,13]) have not been used to avoid considering a further experimental uncertainty and, therefore, to simplify the check for correlations.

#### 4. THE TEMPERATURE RANGE OF THE GLASS TRANSITION AND FRAGILITY

A thermal index of fragility, the reduced width of the glass transition range,  $\Delta T_g/T_g$ , [3,13] has predictive character. The use of this quantity which is easily determined in differential scanning calorimetry experiments, is suggested by the consideration that the viscosity changes in the temperature range

from the onset,  $T_g'$ , to the end,  $T_g''$ , of the glass transition ( $\Delta T_g = T_g' - T_g''$ ) of about two orders of magnitude:

$$\ln \frac{\eta_{onset}}{\eta_{finish}} \cong B \frac{\Delta T_g}{(T_g - T_{0,1})^2} \cong 2. \quad (9)$$

Using the VFT equation to derive  $m$  from Eq. (5), it is obtained:

$$\frac{\Delta T_g}{T_g} \cong \frac{2}{m}. \quad (10)$$

In principles,  $\Delta T_g$  values must be collected for the same heating rate and for samples cooled at the same rate. The above equation implies that the more fragile the liquid, the narrower the glass transition range. The correlation is noticeable as shown in Fig. 4 which contains data deduced from the literature on various glasses.

#### 5. MELT FRAGILITY AND ELASTIC CONSTANTS OF THE GLASS

The glass transition occurs when the glass does not resist shear stress, therefore, the shear modulus of the glass,  $G$ , should reflect this when compared to the bulk modulus,  $K$ . The dimensionless parameter  $K/G$  has been taken as a measure of

**Table 1.** Indexes expressing the strength/fragility of melts either kinetic ( $m$ ,  $T_g/\Delta T_g$ ) or thermodynamic ( $\Delta C_p/\Delta S_g$ ,  $\Delta C_p/(\Delta S_g T_g)$ ), and data on the ratio of bulk ( $K$ ) to shear ( $G$ ) moduli for glass forming metallic alloys. The sources of data are references [3-5].

Alloy composition	$m$	$\Delta C_p/\Delta S_g$	$\Delta C_p/(\Delta S_g T_g) \cdot 10^3$	$T_g/\Delta T_g$	$K/G$
Au <sub>77</sub> Ge <sub>13.6</sub> Si <sub>9.4</sub>	85	2.76	9.31	42.4	
Au <sub>53.2</sub> Pb <sub>27.6</sub> Sb <sub>19.2</sub>	120			66	
Ce <sub>70</sub> Al <sub>10</sub> Cu <sub>10</sub> Ni <sub>10</sub>	21			13	2.35
Cu <sub>47</sub> Zr <sub>34</sub> Ti <sub>11</sub> Ni <sub>8</sub>	59	4.07	6.06	24.9	
Fe <sub>50</sub> Mn <sub>10</sub> Mo <sub>14</sub> Cr <sub>4</sub> C <sub>16</sub> B <sub>6</sub>				22	2.375
Fe <sub>29</sub> Ni <sub>49</sub> P <sub>14</sub> B <sub>6</sub> Si <sub>2</sub>				32	3.51
Fe <sub>80</sub> P <sub>13</sub> C <sub>7</sub>				38	4.67
Gd <sub>40</sub> Y <sub>16</sub> Al <sub>24</sub> Co <sub>20</sub>				29	2.47
Mg <sub>65</sub> Cu <sub>25</sub> Y <sub>10</sub>	45	3.65	8.91	21.5	2.28*
Ni <sub>60</sub> Nb <sub>37</sub> Sn <sub>3</sub>				36	3.51
Pd <sub>77.5</sub> Cu <sub>6</sub> Si <sub>16.5</sub>	65	5.86	9.30	32	5.22
Pd <sub>43</sub> Cu <sub>27</sub> Ni <sub>10</sub> P <sub>20</sub>	65	4.60	7.99	28.8	
Pd <sub>40</sub> Cu <sub>30</sub> Ni <sub>10</sub> P <sub>20</sub>	63	4.60	8.08	25.9	4.53
Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub>	46	5.57	9.63	22.2	4.87
Pt <sub>57.5</sub> Cu <sub>14.7</sub> Ni <sub>5.3</sub> P <sub>22.5</sub>				29	5.97
Ti <sub>50</sub> Be <sub>40</sub> Zr <sub>10</sub>				20	2.41
Zr <sub>55</sub> Al <sub>10</sub> Cu <sub>30</sub> Ni <sub>5</sub>				22	3.54
Zr <sub>50</sub> Cu <sub>50</sub>				27]	3.34
Zr <sub>48</sub> Nb <sub>8</sub> Cu <sub>14</sub> Ni <sub>12</sub> Be <sub>18</sub>				25	3.51
Zr <sub>41.2</sub> Ti <sub>13.8</sub> Cu <sub>12.5</sub> Ni <sub>10</sub> Be <sub>22.5</sub>	48	7.57	12.2	19.7	3.01
Zr <sub>46.75</sub> Ti <sub>8.25</sub> Cu <sub>7.5</sub> Ni <sub>10</sub> Be <sub>27.5</sub>	40			16.5	3.04

\*value taken as for Mg<sub>65</sub>Cu<sub>25</sub>Tb<sub>10</sub>.

such resistance. Further, it has been supposed that the resistance to shear in the glassy state corresponds to the analogous property of the melt, i.e. its strength [14]. Therefore  $K/G$  should scale with it. The relationship between the parameter  $m$  relative to the molten state and the ratio  $K/G$  for the solid glass claimed for some inorganic and organic glass-formers [14] is now considered also for metallic glasses. Elastic constants have been collected from the literature for several alloys and reported in [3]. The  $\Delta T_g/T_g$  index, shown above to scale with  $m$ , for which data are more abundant than for  $m$ , is plotted versus  $K/G$  in Fig. 5 for various glasses. The correlation does not appear stringent as already pointed out, not only for metallic systems but also for the ensemble of inorganic and organic glasses [3,18]. More than a general correlation, the plot seems to suggest the dependence of the indexes on the type of material: inorganic, organic, metal-metal and metal-metalloid glasses. In fact,

the areas of the plot pertaining to the categories of glassy materials are rather clearly singled out. Among amorphous alloys the higher values of  $K/G$  belong to metal-metalloid systems containing noble and transition metals and phosphorus. Metal-metal alloys cluster at lower values of the ratio of elastic constants.

## 6. CONCLUSIVE REMARKS

The non-linear increase in viscosity and the loss of entropy on melt undercooling has been amply demonstrated for glass forming metallic alloys. The temperature dependence of entropy is due to the substantial values of the excess specific heat in the liquid state. A connection between transport and thermodynamic properties of melts stems from the Adam-Gibbs model of viscosity. The correlations described above, although rough, can be explained by assuming that both the entire excess liquid entropy and the configurational contribution  $S_c$ ,

change with temperature proportionally: a change in vibrational entropy of the liquid would cause a corresponding effect in the configurational part, i.e. in the accessibility of configurational states [8]. This has been recently questioned on the ground that different anharmonic contributions to the excess entropy occurring in various glasses will impair the above assumption [6]. Actually, the large variation of the  $K/G$  ratio among the various families of glasses and within the same family, which stems from the ratio of longitudinal to transverse sound velocities, can be an indication of the varying degree of anharmonicity.

Finally, uncertainties can arise from liquid specific heat values which need to be interpolated from the high to the low temperature range and because of the considerable scatter of most data; also it can be difficult to determine precisely the crystal specific heat because of the reactivity of alloy components.

The relationship between strength in the melt and elastic constants in the glassy state is shown to be lousy, at variance to the general correlation inferred previously when the plot contained only some inorganic and organic glass formers [14]. Considering the different families of glass formers separately, a slight correlation between  $m$  and  $K/G$  can still be envisaged.  $m$  is inversely proportional to the resistance to shear stress in the undercooled liquid. The  $K/G$  ratio provides a measure of the relative resistance to dilatation and shear stress in the glassy solid. Since the glass retains features of the atomic short range order existing in the liquid a correspondence between the two quantities could exist in a given family of materials. As an example, for metal-metal glasses, it is expected that the bonding has no or little directional character in comparison to metal-metalloid systems, therefore, the  $K/G$  ratio should approach the average of the constituent elements and be closer to the ideal value, i.e.  $8/3$  when the Poisson ratio is  $\nu = 1/3$ .

A large value of  $K/G$  has been reported for the most ductile metallic glass known to date,  $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$  arguing that the weakness in elastic shear response can help in extending the tip of a shear band instead of causing initiation of a crack [17]. High  $K/G$  values should, therefore, indicate enhanced ductility. From the collection of data displayed in Figs. 4 and 5, it is expected that

ductile bulk metallic glasses will mostly be found among metal-metalloid systems.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] C. A. Angell // *Science* **267** (1995) 1924.
- [2] R. Busch // *JOM* **52** (2000) 39.
- [3] L. Battezzati // *Materials Transactions* **46** (2005) 2915.
- [4] L. Battezzati, A. Castellero and P. Rizzi // *Journal of Non-Crystalline Solids* **353** (2007) 3318.
- [5] L. Battezzati // *Mater. Sci. Eng. A* **375** (2004) 60.
- [6] G. J. Fan, E. J. Lavernia, R. K. Wunderlich and H.-J. Fecht // *Philos. Mag.* **84** (2004) 2471.
- [7] A. van der Beukel and J. Sietsma // *Acta Metall. Mater.* **38** (1990) 383.
- [8] L.-M. Martinez and C. A. Angell // *Nature* **410** (2001) 663.
- [9] R. Busch, Y. J. Kim and W. L. Johnson // *J. Appl. Phys.* **77** (1995) 4039.
- [10] K. S. Dubey and P. Ramachandrarao // *Acta metall.* **32** (1984) 91.
- [11] D. N. Perera and A. P. Tsai // *J. of Phys. D - Appl. Phys.* **33** (200) 1937.
- [12] L. Shadovspeaker and R. Busch // *Appl. Phys. Lett.* **85** (2004) 2508.
- [13] C. T. Moynihan // *J. Am. Ceram. Soc.* **76** (1993) 1081.
- [14] V. N. Novikov and A. P. Sokolov // *Nature* **431** (2004) 961.
- [15] S. Li, X. K. Xi, Y. X. Wei, Q. Luo, Y. T. Wang, M. B. Tang, B. Zhang, Z. F. Zhao, R. J. Wang, M. Z. Pan, D. Q. Zhao and W. H. Wang // *Sci. Tech. Adv. Mater.* **6** (2005) 823.
- [16] H. Choi-Yim, D. Xu, M. L. Lind, J. Loeffler and W. L. Johnson // *Scripta Mater.* **54** (2006) 187.
- [17] J. Schroers and W. L. Johnson // *Phys. Rev. Lett.* **93** (2004) 255506.
- [18] S. N. Yannopoulos and G. P. Johari // *Nature* **444** (7118) (2006) E8.