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Conditions for the formation of glasses by cooling melts of one-component systems

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Well-known conditions for the formation of glass from the melt are sufficiently fast cooling rates and directed bonding between the constituents. These conditions, however, are not specific enough to select promising melts which may form glasses upon cooling. Therefore, the phase transition from a solid to a melt and the accompanying flow and storage of enthalpy and entropy are considered in detail.

The melting entropy is stored in the new configuration of the constituents. Upon cooling a melt, this entropy can only be removed by thermal conduction after it has been reloaded onto the vibrations of crystals. This reloading may be a bottleneck. The smaller the temperature interval where crystallisation is possible, the easier is glass formation. Extrapolating the enthalpy function from the molten state to lower temperatures, that temperature interval (relative to the melting temperature T_m) has been estimated to be $\Delta T_{min}/T_m = \Delta H_m/[T_m(2C_{pl} - C_{ps})] = \Delta S_m/(2C_{pl} - C_{ps}) \approx \Delta S_m/C_{pl}$, wherein ΔH_m and ΔS_m are the molar melting enthalpy and entropy, respectively, and C_{pl} and C_{ps} are the molar specific heat capacities at constant pressure in the molten (index "l") and crystalline (index "s") states. In fact, $\Delta T_{min}/T_m$ is small for all known one-component systems forming glasses by cooling their melts, which seems to characterize their glass forming capability quite well.

Bedingungen zur Glasbildung beim Kühlen der Schmelzen von Einstoff-Systemen

Gläser können durch Kühlen von Schmelzen gebildet werden, wenn die Kühlgeschwindigkeit genügend groß ist und wenn zwischen den Bauelementen gerichtete Bindungen vorhanden sind. Diese Bedingungen sind jedoch nicht spezifisch genug, um vorherzusagen, aus welchen Schmelzen durch Kühlen Gläser gebildet werden. Deshalb werden der Phasenübergang Festkörper/Schmelze und die dabei fließenden Enthalpie- und Entropieströme und ihre Speicherung näher betrachtet.

Infolge des Aufschmelzens nehmen die Bausteine eine neue Konfiguration ein, wodurch die Schmelzentropie gespeichert wird. Bei der Abkühlung kann die so gespeicherte Entropie durch Wärmeleitung aber erst dann abgeleitet werden, wenn sie auf Gitterschwingungen im kristallinen Zustand umgeladen wurde. Diese Umladung kann einen Engpass darstellen. Je kleiner das Temperaturintervall ist, in dem Kristallisation durch Aufbrechen und Umordnen von Bindungen möglich ist, umso leichter ist die Glasbildung. Man kann dieses Temperaturintervall (bezogen auf die Schmelztemperatur T_m) aus der Schmelzenthalpie ΔH_m bzw. -entropie ΔS_m und den spezifischen Wärmekapazitäten C_{pl} und C_{ps} bei konstantem Druck im geschmolzenen (Index „l") und festen (Index „s") Zustand zu $\Delta T_{min}/T_m = \Delta H_m/[T_m(2C_{pl} - C_{ps})] = \Delta S_m/(2C_{pl} - C_{ps}) \approx \Delta S_m/C_{pl}$ abschätzen. Für alle bisher bekannten Einstoff-Systeme, die Gläser durch Abkühlen der Schmelze bilden, ist $\Delta T_{min}/T_m$ in der Tat sehr klein, so daß diese Relation die Neigung zur Glasbildung von Einstoff-Systemen sehr gut beschreibt.

1. Introduction

Vitreous materials can be made by different techniques: In the solid phase by shock waves, irradiation, photolytic and thermal decomposition, powder metallurgy or by electrolysis of the electrode material; in the liquid phase by cooling of melts or from a sol by gelling, drying and heating, and via the vapour phase by applying different deposition techniques. Therefore, glasses are no longer defined by a special production technique, but rather by their structure as solids without periodic arrangement of the constituents on a time average. If one neglects the

time average, in a strict sense any solid at finite temperature will be a glass.

Today, one believes that any compound forming a solid can be brought into a structurally glassy state by sufficiently fast cooling or quenching, not necessarily from the melt but including quench condensation from the vapour phase. Thus, additional criteria must be fulfilled for a composition to readily form a structural glass by cooling its melt. In the following section, several criteria already known will be mentioned and investigated. In the subsequent sections a new criterion based on the enthalpy function will be reviewed and tested with data for the chemical elements and for one-component sys-

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tems. In this case, additional effects of mixing, diffusion and phase separation can be neglected, which may also play a role in glass formation.

2. Selection of known criteria of glass formation

Many researchers have been investigating which conditions have to be fulfilled to favour glass formation by cooling melts. The well-known random network hypothesis of Zachariasen [1] and the crystallite hypothesis of Lebedev [2] are no theories of glass formation but of the arrangement of the constituents of glasses and thus of the structure of glasses.

Among the simple criteria to be fulfilled are the ratio of the ionic radii of the constituents (Goldschmidt in 1926 [3]), the strength of the single bonds (Sun in 1947 [4]), the mixed bonding rule (Smekal in 1949 [5]), the electronegativity rule (Stanworth in 1948 [6 and 7]), the ionic field strength criterion (Dietzel in 1942 [8]), the ratio of the bonding strength to the melting temperature (Rawson in 1956 [9 and 10]), the p-electron criterion (Winter in 1957 [11]; it is interesting to note that this term is used by Rawson [10]; Winter does not use this term but considers just the results for the different chemical groups in her experimental study for glass formation), and the topological constraint hypothesis (Phillips in 1979 [12]).

Most of these criteria apply rather to the formation of glasses with special compositions, such as the oxide glasses or chalcogenide glasses. On the same premises, however, each rule fails to explain simultaneously the occurrence of single-element glasses, metallic glasses, heavy metal fluoride glasses, chalcogenide and TEX glasses. Rawson [10], Zarzicky [13] and Scholze [14] already summed up in some detail glass compositions obeying and contradicting these rules. Obviously, each of these rules is valid in a limited range of special compositions and components. These rules do not contradict or exclude each other necessarily, however, each of them seems to represent a subset of a more general rule. It seems that all of these criteria are fortuitously synonymous to the presence of elements or − more generally − constituents with an appropriate number and strength of directed bonds. The p-electron criterion of Winter [11] implicitly points at this necessity of directed bonds. Obviously, the covalent bonds between different atoms necessarily possess an asymmetry of the local probability distribution of the binding electrons, since their electrical potential for the binding electrons is asymmetric. Thus, the mixed bonding rule of Smekal [5] is a simple consequence of covalent bonding between different atoms and of covalent contributions between the atoms of metals with uncompleted inner electronic shells.

The strength of the bonds alone cannot be a general criterion either, since the disordered structure cannot be maintained upon cooling a melt if the bonding is due to spherical bonding forces around the constituents, such as for the alkali halides. Also, the metals with completed inner shells do not form glasses upon cooling of the melt, since the ions in the Fermi-sea are able to rearrange at temperatures much lower than the melting temperature to form a regular packing.

In particular, the so-called network formers according to the field strength criterion of Dietzel [8] fulfil the criterion for directed bonds, as can be seen from table 1. In this table, taken from [8], an additional column with the electron configuration of the outer shells of the respective element is included. It is easy to see that the network formers are elements with their outer sub-shell of s-orbitals completed and the corresponding sub-shell of p-orbitals partially filled. Such a configuration favours (with or without hybridization with other s-, d-, and f-orbitals) strong directed bonds, whereas the network modifiers possess essentially occupied outer s-orbitals and completed p-, d- or f-orbitals, which − as a consequence of the completion − do not contribute to the bonding.

The field strength at the position of the O^{2-} ions adjacent to the cations obviously does not have the values defined by Dietzel. The first reason is that the presumed ions, including the O^{2-} ions, generally do not exist in a solid; instead, the orbitals represent the probability to find an electron in a given volume element, since the electrons cannot be localized. Secondly, the charge (e.g. 4+ of the silicon in the SiO_2 network) of the constituents is defined by equating the oxidation number with the corresponding charge, which is not justified. In this respect it has to be pointed out that in Dietzel's field strength criterion the presumed charge of the anions (from 1+ of the alkalis to 5+ of phosphorus and even to 8+ (!) for sulphur [14]) defined in this way contributes most to the large difference in the field strength, but not the ionic radii.

3. New criterion of the glass formation from one-component melts

The presence of constituents with directed bonds seems to be a necessary but not a sufficient condition for glass formation from the melt, since the pure element silicon, e.g., with strong directed bonds does not form a glass by normal cooling but rather by deposition from the vapour phase, which is a low-temperature deposition process as compared with the melting temperature. Therefore, besides directed bonds between the constituents and sufficiently fast cooling rates an additional criterion seems to be necessary [15], which is to be discussed in the present section. For this purpose, the phase transition from solid to melt and vice versa shall be considered. In the following, molar quantities are used, since processes with a constant number of particles of

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Table 1. Properties and field strength of different elements according to Dietzel [8]

element	electron configuration of the outer shells	valence Z	ionic radius r in 10^{-10} m for coordination number = 6	most frequent coordination number	ionic distance for oxides a in 10^{-10} m	field strength at distance of O^{2-} ions Z/a^2	function in glass structure
K	$4s^1$	1	1.33	8	2.77	0.13	
Na	$3s^1$	1	0.98	6	2.30	0.19	
Li	$2s^1$	1	0.78	6	2.10	0.23	
Ba	$6s^2$	2	1.43	8	2.86	0.24	network
Pb	$6s^26p^2$	2	1.32	8	2.74	0.27	modifiers
Sr	$5s^2$	2	1.27	8	2.69	0.28	$Z/a^2 \approx 0.1 \ldots 0.4$
Ca	$4s^2$	2	1.06	8	2.48	0.33	
Mn	$3d^54s^2$	2	0.91	6	2.23	0.40	
Fe	$3d^64s^2$	2	0.83	6	2.15	0.43	
Mn	$3d^54s^2$	2	0.83	4	2.03	0.49	
Mg	$3s^2$	2	0.78	6	2.10	0.45	
			–	4	1.96	0.53	
Zr	$4d^25s^2$	4	0.87	8	2.28	0.77	
Be	$2s^2$	2	0.34	4	1.53	0.86	intermediates
Fe	$3d^64s^2$	3	0.67	6	1.99	0.76	$Z/a^2 \approx 0.5 \ldots 1.0$
			–	4	1.88	0.85	
Al	$3s^23p^1$	3	0.57	6	1.89	0.84	
			–	4	1.77	0.96	
Ti	$3d^24s^2$	4	0.64	6	1.96	1.04	
B	$2s^22p^1$	3	0.20	4	1.50	1.34	
				3	1.36	1.63	network
Ge	$4s^24p^2$	4	0.44	4	1.66	1.45	formers
Si	$3s^23p^2$	4	0.39	4	1.60	1.57	$Z/a^2 \approx 1.5 \ldots 2.0$
P	$3s^23p^3$	5	0.34	4	1.55	2.10	

one mole are considered. This is important for comparison of different materials.

Melting a crystalline solid is a first-order phase transition. Thus, there are two molar enthalpy functions H_s and H_l, which are defined for temperatures below and above the melting temperature, T_m. Between both functions is a discontinuity due to the melting enthalpy per mole, ΔH_m ("molar heat of fusion"). An example is represented in figure 1 for silicon. The ordinate represents also the average enthalpy per particle, if the numbers of the molar enthalpy function are divided by the numbers of constituents in the chemical formula and by Avogadro's number. The shape of the curves remains the same, just the units of the ordinate change. The same is true for the slope of the molar enthalpy, which is the specific molar heat capacity or specific molar enthalpy capacity in the liquid or solid state, $C_{pl}(T)$ or $C_{ps}(T)$.

For the temperature to increase, entropy has to flow into the system and fill the entropy capacity. One can understand entropy as the quantity flowing due to a temperature difference without concomitant flow of particles. In an insulating crystalline solid, the entropy is stored essentially in the lattice vibrations (or phonons) and to a lesser degree in the creation of defects and elec-
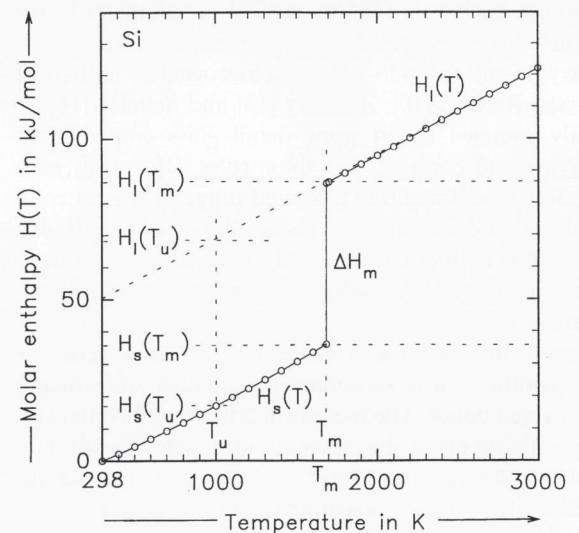
Figure 1. Molar enthalpy of silicon below and above the melting temperature T_m; data from [18].

tron-hole pairs (transitions of electrons from bonding into anti-bonding states) and their excitations. The same

is also true for the storage of entropy in the melt. However, the density of the frequency spectrum of the phonons in the molten state differs from that in the solid state, since bonds are broken and consequently the restoring forces are different. This may also include the diffusive movement of particles corresponding to the limit of vibrations at zero frequency, if restoring forces are less effective due to relaxation in the melt. Thus, increasing the entropy in a material fills the entropy capacity and increases its temperature both in the solid and in the molten state.

At the melting temperature, T_m, the entropy per mole flowing into the crystalline material,

$$\Delta S_m = \Delta H_m / T_m , \tag{1}$$

is not causing a temperature increase, however; thus, the entropy capacity becomes infinite and one has the problem to explain where the entropy is stored. It is stored partially in a changing configuration of unbound moving particles due to the melting, which includes the creation of defects. This corresponds to a disordered configuration or arrangement of the constituents, which in addition varies in a melt with time. The directed entropy flow (because of the temperature gradient) is loaded during melting onto the atoms and ions, which move away from their places in the ordered solid changing its configuration. Furthermore, the vibration spectrum changes upon melting. The long-wavelength vibrations become soft, since the broken bonds decrease the restoring forces of the oscillators, as has been mentioned already. Thus, the average vibration frequency decreases and more phonons are excited at a given temperature corresponding to a larger molar entropy capacity. Hence, it is obvious why the entropy must be increased during the melting process. Simultaneously, the enthalpy or the energy of the material is increased, since the energy flow is necessarily coupled to the entropy flow. The energy is needed to break the bonds so that the atoms or ions can move and accept a new configuration and to fill the larger enthalpy capacity. It is useless to ask which quantity, either the entropy or the energy, is primary. Both quantities are coupled by the melting temperature, T_m, according to equation (1). Thus, one can even claim that both quantities adjust T_m in order to provide simultaneously both the necessary energy (enthalpy) for breaking the bonds and for delivering the correct entropy needed for the new state or (time-dependent) configuration. If the phase transformation is completed, further entropy is obviously stored by increasing the temperature of the material. Very often, the specific heat capacity is larger in the molten state than in the solid state. This can be understood by a further demand of enthalpy to break additional bonds or the excitation of rotational vibrations, e.g.

Cooling the melt requires the removal of entropy and energy (enthalpy). Above T_m, this is easily possible for the directed entropy flow driven by the temperature gradient to the surface. For the removal of the entropy coupled to the atomic or ionic configuration of the melt, a temperature gradient cannot be a driving force. The entropy must first be loaded from the diffusing particles in the melt to bound constituents in order to be transported by a directed flow (of phonons in a solid, e.g.) driven by a temperature gradient. This reloading occurs necessarily with the bonding of the atoms or ions and results in many cases in ordered crystalline solids. Because of the bonding, the entropy and the energy (enthalpy) is loaded from the carriers "unbound moving particles" and "vibrations of the disordered constituents" to "vibrations of ordered constituents". This reloading from one carrier to another requires some time and may be the bottleneck for crystallization during cooling of the melt. The energy released due to the bonding of a particle below T_m can increase the temperature in the vicinity towards and beyond T_m causing local remelting and rearrangement of the constituents of the material. For spherical atoms without directed bonds like the alkalis and alkaline earth metals with s electrons and substances with completed outer shells, only little energy is needed to shift an atom or ion on the surface of a co-atom or -ion, whereas in the case of directed bonds a sufficient amount of energy (which may be larger than the melting enthalpy per particle) is necessary. On the other hand, just that energy is released on an average by the addition of an atom or ion at the interface between the crystallite and the melt. As a consequence, neighbouring bonds can be reopened in the vicinity, since sufficient energy is available by the bonding of new particles.

During the cooling of the melt below T_m in the example of figure 1, the enthalpy per mole of the melt follows the dashed extrapolated portion of $H_l(T)$ into the temperature range of undercooling (hypercooling). If bonding occurs, the energy $H_l(T_u) - H_s(T_u)$ per particle is released at temperatures $T_u < T_m$, which can drive the neighbourhood of the bound particle under consideration along $H_l(T)$ to temperatures $T \approx T_m$. This, however, is possible only as long as the difference between both enthalpy curves obeys

$$H_l(T_u) - H_s(T_u) \geq H_l(T_m) - H_l(T_u). \tag{2}$$

The sign of equality defines the minimum temperature difference of undercooling $(T_m - T_{u\,min})$, for which local remelting is just not expected to occur upon binding of particles to crystallites. From this equation one can calculate $T_{u\,min}$. To simplify the evaluation, however, the data of the enthalpy functions near the melting temperature are linearly extrapolated to lower temperatures with the slopes C_{pl} and C_{ps} near T_m. This seems to be justified, since the formation of glass occurs rather close to the melting temperature, where this approximation is sufficiently precise. In the limit of this linear approximation and extrapolation of the molar enthalpy functions, $H_l(T)$ and $H_s(T)$, this statement is equivalent to the condition
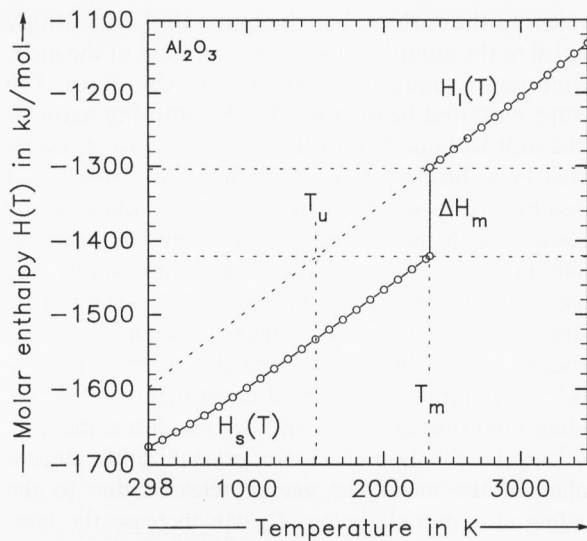
Figure 2. Molar enthalpy of Al_2O_3 below and above the melting temperature T_m; data from [17].
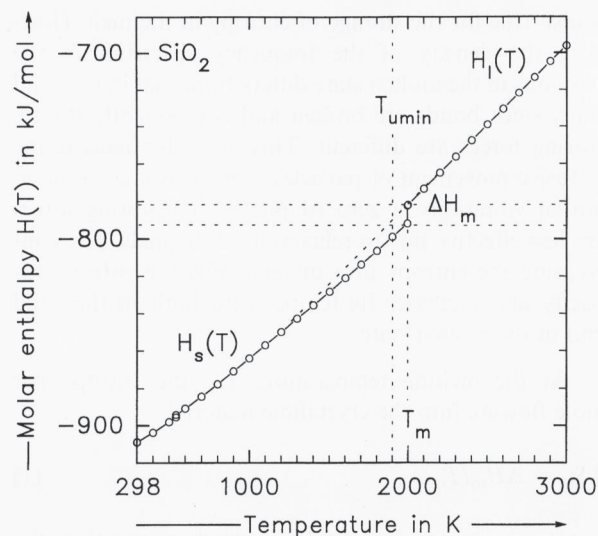

Figure 3. Molar enthalpy of SiO_2 (cristobalite) below and above the melting temperature T_m; data from [18].

$$H_l(T_m) - [H_l(T_m) - C_{pl}(T_m - T_{u\,min})] = \quad (3)$$

$$= H_l(T_m) - C_{pl}(T_m - T_{u\,min}) - [H_s(T_m)$$

$$- C_{ps}(T_m - T_{u\,min})],$$

which yields

$$(T_m - T_{u\,min}) = \Delta T_{min} = \Delta H_m/(2C_{pl} - C_{ps}) \quad (4)$$

or the minimum relative temperature difference of undercooling

$$\Delta T_{min}/T_m = \quad (5)$$

$$= \Delta H_m/[T_m(2C_{pl} - C_{ps})] = \Delta S_m/(2C_{pl} - C_{ps}).$$

The larger $(T_m - T_{u\,min})$ or $\Delta T_{min}/T_m$, the more difficult it is to avoid crystallization during cooling. Using the linear extrapolation one estimates from figure 1 that silicon has to be undercooled theoretically to temperatures far below 300 K in order to yield a stable glass. To avoid crystallisation, one needs very fast cooling rates, since the crystallization can proceed in a self-catalysing process due to the large energy released once it started during the cooling.

For pure Al_2O_3 the necessary $(T_m - T_{u\,min})$ is about 800 K, which is also rather large (figure 2). Hence one can understand why Al_2O_3 is not produced in the glassy state for technical reasons. As examples for easy glass formation the enthalpy functions of SiO_2 (cristobalite) are shown in figure 3 and of BeF_2 in figure 4. Here, one can see that the range of minimum undercooling is only about 100 K.
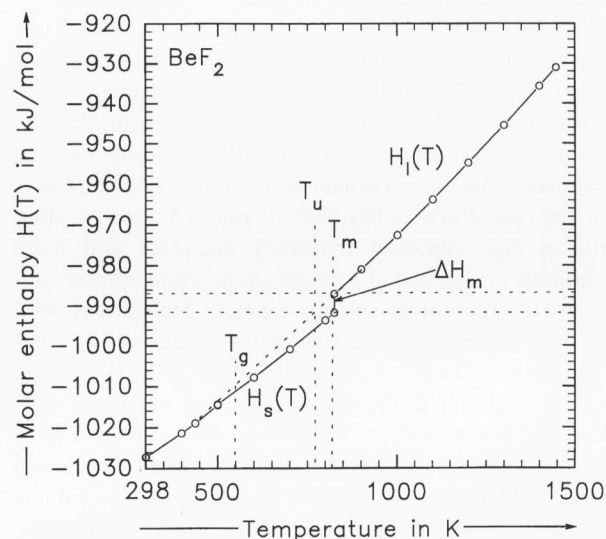

Figure 4. Molar enthalpy of BeF_2 below and above the melting temperature T_m; data from [17].

It is worth mentioning that the criterion (5) occurs also in the literature on hypercooling of metal melts [16]. Cooling melts of metals below $T_m - \Delta T_{min}$ is known as hypercooling, where the melt solidifies under nonequilibrium conditions. The hypercooling temperature $\Delta T_{hyp} = \Delta H_m/C_{pl} \approx \Delta T_{min}$ corresponds to equation (5), since $C_{pl} \approx C_{ps}$. However, it has not yet been applied to glass formation before, but to discriminate between equilibrium and nonequilibrium conditions of crystallization.
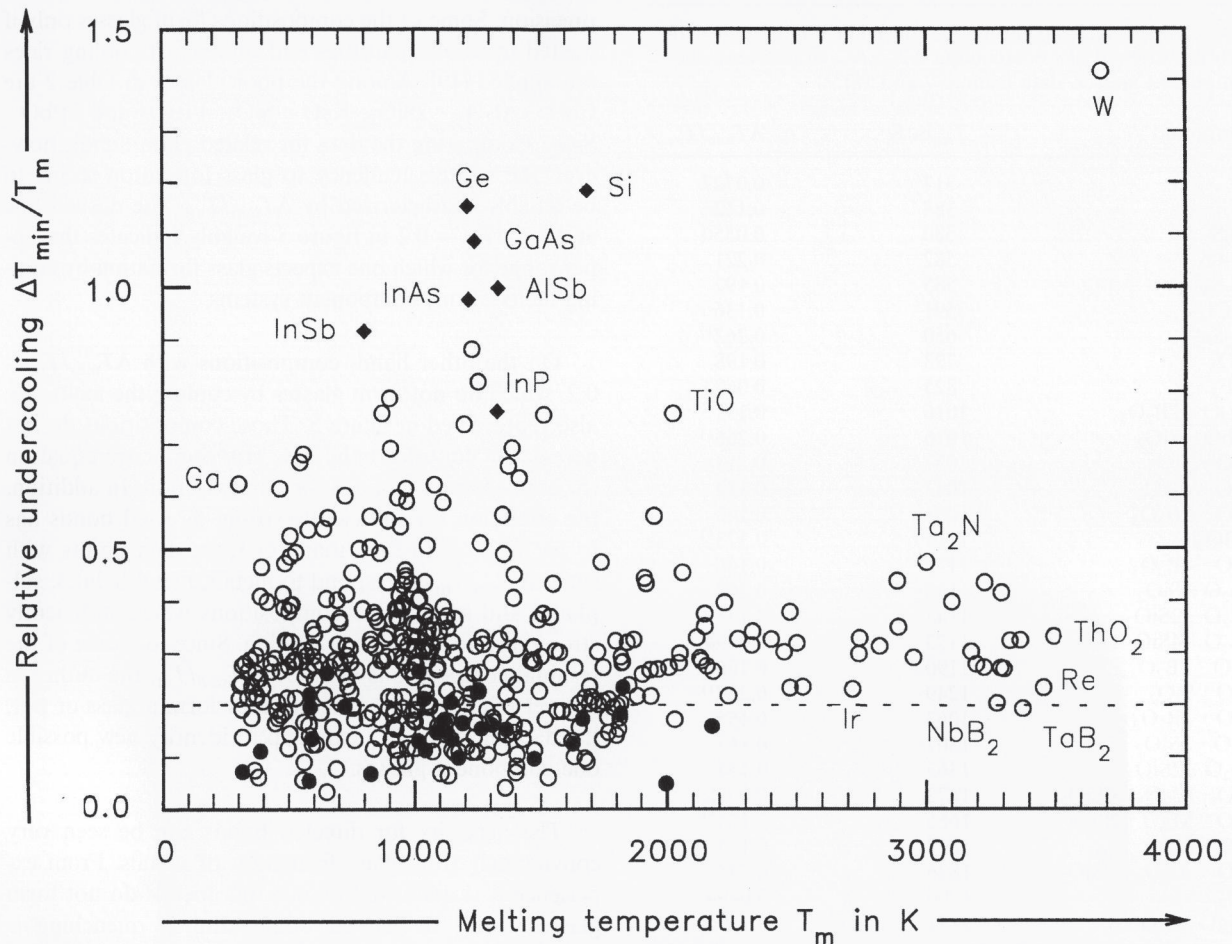
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Figure 5. Minimum undercooling interval relative to the melting temperature $\Delta T_{min}/T_m$ according to equation (5) as a function of the melting temperature T_m for different elements and one-component systems; data from [17 and 18]. Filled diamonds represent several semiconductors. Full circles represent known glasses, listed in table 2.

4. Application to elements and one-component systems

The simple criterion (5) of glass formation, which has been derived on the basis of the melting enthalpy and melting entropy, has been applied to about 450 different one-component systems using the data given in [17 and 18]. Figure 5 shows the relative temperature interval of undercooling, $\Delta T_{min}/T_m$, as a function of the respective melting temperature, T_m. Because of lack of space the compositions could not be included in that figure except for some special cases. For the interested reader, however, the coordinates of the data points together with the respective compositions are available from the author.

To calculate $\Delta T_{min}/T_m$, the specific molar heat capacities near T_m have been used for the extrapolation. Therefore, $\Delta T_{min}/T_m > 1$ can occur, which should not be interpreted as an undercooling below absolute zero, since the linear extrapolation is not applicable in this case. Instead, it means that the actual necessary undercooling to inhibit crystalliztion is very large. The val-

ues $\Delta T_{min}/T_m < 0.5$ are expected to be sufficiently precise with a quantitative meaning. On the other hand, one cannot expect that ΔT_{min} is the exact interval of minimum undercooling. Because of thermal fluctuations, spontaneous thermal crystallization is also possible below $T_{u\,min}$. Crystallization may be observed even in the range of undercooling about 2 or at most 3 times as large, if $\Delta T_{min}/T_m$ is small.

Layers of the elements and of compounds can be deposited by evaporation, sputtering and other vacuum techniques at low temperatures. In order to re-crystallize these layers, they have to be heated at least to about 2/3 of T_m as a rule of thumb. It seems that condition (5) is a better estimate for most individual cases, whereas $2T_m/3$ seems to be close to the average of the data presented in figure 5.

Since the relative temperature interval of undercooling, $\Delta T_{min}/T_m$, is considered, one does not observe in figure 5 a special dependence with respect to T_m, which is in agreement to the expectations. Large values of

Table 2. Melting temperature T_m and relative minimum temperature interval of undercooling $\Delta T_{min}/T_m$ of different one-component glasses, data from: [17 and 18]

compound	T_m in K	$\Delta T_{min}/T_m$
P	317	0.0727
S	388	0.112
As_2S_2	580	0.0556
As_2O_3	582	0.221
As_2S_3	585	0.197
$ZnCl_2$	591	0.136
As_2Se_3	650	0.262[1]
B_2O_3	723	0.198
BeF_2	825	0.0683
$Na_2O \cdot 2B_2O_3$	1016	0.131
$2PbO \cdot SiO_2$	1016	0.266[1]
$PbO \cdot SiO_2$	1037	0.213
$K_2O \cdot 4SiO_2$	1043	0.114
$K_2O \cdot 2B_2O_3$	1088	0.148
$LiBO_2$	1117	0.173[1]
$K_2O \cdot 4B_2O_3$	1130	0.146
$Rb_2O \cdot SiO_2$	1143	0.207
$Na_2O \cdot 2SiO_2$	1147	0.135
$Rb_2O \cdot 4SiO_2$	1173	0.0994
$Li_2O \cdot 2B_2O_3$	1190	0.166
$K_2O \cdot SiO_2$	1249	0.227[1]
$CaO \cdot 2B_2O_3$	1263	0.155
$Li_2O \cdot 2SiO_2$	1307	0.163
$Rb_2O \cdot 2SiO_2$	1363	0.154
$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	1473	0.0978
$CaO \cdot MgO \cdot 2SiO_2$	1665	0.174[1]
$CaO \cdot SiO_2$	1817	0.184
$CaO \cdot Al_2O_3 \cdot 2SiO_2$	1826	0.235[1]
SiO_2	1996	0.0494
$2MgO \cdot SiO_2$	2171	0.159[2]

[1] Poor glass or borderline.
[2] Glass by splat cooling.

$\Delta T_{min}/T_m$, however, are seen for some elemental and III-V-semiconductors represented by the filled diamonds. These data are in surprising agreement with the fact that these materials crystallize very easily and perfectly by cooling from the melt, since the enthalpy of the crystal is much lower than that of the disordered solid driving the melt to nearly perfect crystals with very low defect concentrations. Otherwise, such materials would be disadvantageous for semiconductor and opto-electronic devices, since glass formation would prohibit these very low concentrations of intrinsic defects and the high mobility of the charge carriers required in electronics.

Known one-component glasses are marked in figure 5 by the full circles. To facilitate the association with the data points in figure 5, the compositions are listed in table 2 in the order of increasing melting temperature, T_m, together with the corresponding relative undercooling temperatures (equation (5)) using the data from [17 and 18]. In fact, the relative undercooling is rather small for glasses, which confirms the ideas presented in section 3. Unfortunately, the cooling rates for practical glass formation are not quantified in the literature with sufficient

precision. Some of the compositions form glasses only if melted in small quantities and rather fast cooling rates are applied [19]. Among the poor glasses in table 2 are $CaO \cdot Al_2O_3 \cdot 2SiO_2$, $K_2O \cdot SiO_2$, $LiBO_2$ and $2PbO \cdot SiO_2$. Comparing the data for related compounds, however, the relative tendency to glass formation seems to be reliably characterized by $\Delta T_{min}/T_m$. The dashed line at $\Delta T_{min}/T_m = 0.2$ in figure 5 roughly indicates the upper range for which one expects glass formation by cooling melts of one-component systems.

On the other hand, compositions with $\Delta T_{min}/T_m < 0.2$, which do not form glasses by cooling the melts, are also represented in figure 5. Those compositions do not necessarily contradict the new criterion, since equation (5) is a necessary, not a sufficient condition. In addition, the condition for sufficiently strong directed bonds has to be fulfilled. In fact, many of these data points with small $\Delta T_{min}/T_m$ correspond to metals, metal halides, sulphates and some other compositions where sufficiently strong directed bonds are missing. Since for some of the residual compositions with low $\Delta T_{min}/T_m$, the author is not yet reliably aware whether they form a glass or not, the data on $\Delta T_{min}/T_m$ can help to identify new possible one-component glasses.

The necessity for directed bonds can be seen very convincingly from glass formation of metals. From experience it is quite well known that metals do not form glasses easily. In general, some kind of quenching is necessary to transform a melt into a stable glass. This can be understood if directed bonds are weak or lacking as has been pointed out in section 2 already. However, metals with partially filled p- and d-shells (especially filled by about one half) may show sufficiently strong directed bonds. Crystals made of these elements are often brittle, which confirms the presence of directed bonds. Since the directed bonds are effective in addition to the simple metallic bond by free s-electrons, the melting temperature is in this case higher as compared to the other elements. On the other hand, bonds due to free electrons from spherical orbitals, like the alkalis, favour ductility. Then, the bonding does not depend on a special section on the surface of the constituents. Therefore, an adjacent constituent can be shifted easily on that surface without breaking a bond, which would require some energy. This shift is possible also at much lower temperatures than $T_{u\,min}$ given by equation (4) until an optimum nearest-neighbour ordering has been attained. Thus, in order to form a metallic glass, sufficient constituents with strong directed bonds are necessary. In fact, metallic glasses are made by quenching from the melt using compositions containing a sufficient amount of elements with directed bonds due to p- and d-orbitals or hybrids, like Al, Ga, Ti, V, Y, Zr, Nb, In, Sn, and elements, which form brittle crystals [20], like B, C, Si, Ge, P, S, Se, Te, As, Sb, Cr, Mn, Fe, Co, Zn, Mo, Os, Ir, and Bi. For a survey of different compositions of glassy metals see [21 to 23].

5. Discussion and summary

The simple criterion (5) of glass formation has been derived for one-component glasses only. In the case of multi-component melts, the entropy and enthalpy of mixing must be considered and diffusion and transport processes have to be taken into account, which until now seems to prohibit a simple and clear description of the melting and of the glass transition for such systems. For eutectic multi-component systems, however, definite melting enthalpies and temperatures exist. Then, equation (5) can also be applied advantageously, in order to estimate glass formation from the melt of eutectics, if the thermodynamic data are available.

Criterion (5) is based on the melting enthalpy and melting entropy, whereas the kinetic problems of nucleation and crystal growth in the crystallization process have not been considered, since an overwhelming number of publications is already available from the literature. Thus, glass formation and the structural properties of the glasses obviously cannot be based on energetic and entropic principles alone; instead, one has to consider also the kinetics of cooling. All three conditions, a) the necessary cooling rate, b) the presence of directed bonds and c) the sufficiently small undercooling interval depend on each other and have to be considered in glass formation simultaneously. The newly developed criterion (5), however, characterizes which composition is worthwhile testing for glass formation for moderate cooling rates, if sufficiently directed bonds are present.

Both molar enthalpy functions, $H_1(T)$ and $H_s(T)$, increase monotonously with the temperature, T. Using the linear extrapolation of the enthalpy function $H_1(T)$ into the range of undercooling, one may underestimate the minimum temperature difference to avoid local reordering. Once $H_1(T_u) - H_s(T_u) < H_1(T_m) - H_1(T_u)$ is attained, the disordered state seems to be thermally stable or at least metastable. This, however, is valid for the average values, only. Because of thermal fluctuations bonds can still be broken and the local configuration may change, especially due to a rearrangement of the bonds with lower energy. Taking this into account, the range of undercooling in which crystallization can occur may be 2 or even 3 times as large as given by equation (5). With decreasing temperature, however, this rearrangement becomes less probable.

One has to point out that especially in the case of strong directed bonds more than the average melting enthalpy per particle is needed to break bonds and to allow the constituents of the solid to rearrange. For atoms or ions with spherical bonding capability (i.e., bonding is possible at any location of their surfaces) much less energy is needed to shift them as add-ons to a regular position of a crystallite. This seems to be true for the surface of atoms or ions with closed outer electronic shells and s-orbitals. Hence, one can understand why directed bonds are necessary to form glasses.
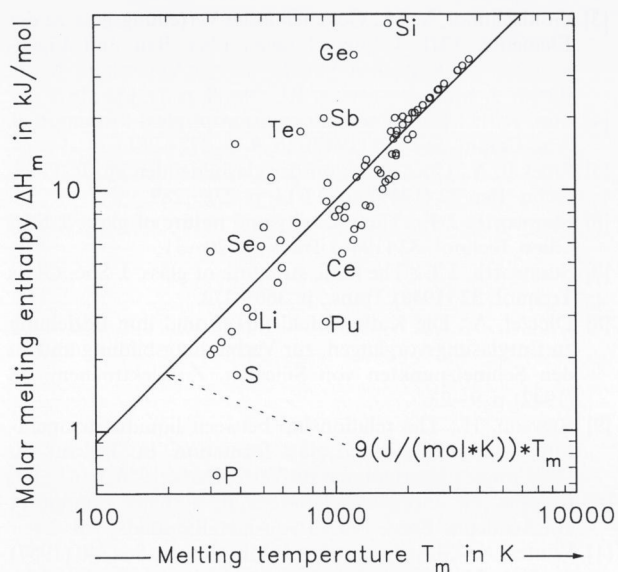

Figure 6. Molar melting enthalpies ΔH_m of chemical elements as a function of the melting temperature T_m; data from [17 and 18].

A very important parameter to quantify the glass forming capability is the molar melting enthalpy according to equations (4) and (5). The molar melting enthalpy of many chemical elements is shown as a function of the corresponding melting temperature in figure 6. The solid diagonal line corresponds to

$$\Delta H_m = 9\,(\mathrm{J/(mol \cdot K)})T_m . \qquad (6)$$

Thus, the average molar melting entropy of the elements is about $9\,(\mathrm{J/(mol \cdot K)}) \approx 1 \cdot R$ (molar gas constant) corresponding to $1 \cdot k_B$ (Boltzmann's constant), if one considers one atom. This is known in the literature as Crompton's rule [24]. Since the specific heat capacity per particle of many melts is about 3 to 5 times k_B, the relative temperature difference (5) to be bridged to form a glass by undercooling without crystallization is necessarily at least between 0.2 and 0.33. For many one-component systems it is difficult to bridge such a large temperature interval of undercooling experimentally. Therefore, most one-component systems do not form a glass by cooling their melts. To form a glass from the melt easily, $\Delta T_{min}/T_m = \Delta H_m/[T_m(2C_{pl} - C_{ps})] = \Delta S_m/(2C_{pl} - C_{ps})$ should be less than about 0.2, preferentially less than 0.1, if one considers table 2. Thus, it seems worthwhile testing the predictive power of relation (5) for new systems and compositions, which includes also metallic glasses.

6. References

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