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Thermodynamic and relative approach to compute glass-forming ability of oxides

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Abstract. This study deals with the evaluation of glass-forming ability (GFA) of oxides and is a critical reading of Sun and Rawson thermodynamic approach to quantify this aptitude. Both approaches are adequate but ambiguous regarding the behaviour of some oxides (tendency to amorphization or crystallization). Indeed, ZrO_2 and Al_2O_3 were inappropriately listed by Sun and Rawson to be glassformer oxides while being intermediate ones. We present a non-dimensional approach to value GFA of single oxide by affecting to each one of the coefficients (without measuring units). Obeying to the non-dimensional analysis rules, we introduce a neglected (in all prior thermodynamic models) characteristic: the isobaric heat capacity (C_p) of oxides, and execute a mathematical treatment of oxides thermodynamic data. We note this coefficient as thermodynamical relative glass-forming ability (ThRGFA) and formulate a model to compute it. Computed values of 2nd, 3rd, 4th and 5th period metal oxides reveal a clear differentiation between them. Indeed, all glass former oxides are characterized by ThRGFA values over 1·709. Moreover, the value intervals confirm the oxides classification into three groups (forming, intermediate and modifier) and sorting of the former ones in distinctive strong and fragile oxides.

Keywords. Glass-forming ability; oxides; Sun and Rawson criteria.

1. Introduction

Many criteria (dealing with structural and thermo-kinetic orders) were proposed to explain the oxides glass-forming ability (GFA). They are founded on crystallochemical concepts or refer to the criteria linked to the nature, the chemical bond strength and other characteristics of metal oxides (Goldschmidt 1926; Zachariasen 1932; Dietzel 1941; Stanworth 1946, 1948, 1952; Sun 1947; Smekal 1951; Rawson 1956, 1967; Turnbull 1969; Hrubý and Štourač 1974; Minaev 1978, 1980, 1983, 1991; Štěpánek and Hrubý 1980; Červinka and Hrubý 1982; Inoue *et al* 1990; Lu *et al* 2000; Stoch 2001; Lu and Liu 2003; Rao *et al* 2004). The main purpose is to predict and/or describe how any single oxide (and under what conditions) is able to form glasses. The structural theory of GFA was first proposed by Goldschmidt (1926) and completed by Zachariasen (1932) who studied all the oxides GFA theories and published his crystallochemical theory. This theory placed the understanding of glass structure and its relationship to composition on a chemical basis. Zachariasen (1932) claimed four rules for structure that allow oxides that tend to form glasses: (i) an oxygen atom is linked to not more than two glass-forming atoms, (ii) the coordination number of the glass-forming atoms is small, (iii) the oxygen polyhedra share corners with each other, not edges or faces and (iv) the polyhedra are linked in a three-dimensional network. From these considerations, following oxides are known to be glass formers: B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_3, Sb_2O_5, Sb_2O_3, In_2O_3, Tl_2O_3, SnO_2, PbO_2, P_2O_3, As_2O_5, Nb_2O_5 and Ta_2O_5 while TeO_2, SeO_2, MoO_3, WO_3, Bi_2O_3, Al_2O_3 and V_2O_5 are listed to be ‘conditionally’ glass formers. All other oxides are classified as modifiers (alkali and earth-alkali oxides) or intermediate (transition metal oxides).

Inspired by the atomic field of Dietzel (1941), Stanworth (1946, 1948, 1952) and Smekal (1951) added details of electronegativity and bonding nature between E atoms and oxygen atoms in E_xO_y oxide. Thermodynamical theory of glass formation was proposed as the ‘energy criterion’ by Sun (1947) who attempted to establish a correlation between the bond strengths (between the cation E^{y+} and the anion O^{2-}) and this aptitude. He proposed his own criterion, the ratio $E_B^{Sun} = E_d/I$ (kcal·mole^{-1}), where E_d is the oxide dissociation energy and I the oxide crystal coordination number. Sun’s basic idea is that, when a melt is quenched to form a glass, the stronger the M–O bonds, the more difficult are the structural rearrangements necessary for crystallization and hence, the easier is glass formation. Stoch (2001), correlated this flexibility of structure with GFA in his chemical approach, assessing that the flexibility of the internal structure of solids stems from the free motion of their structural units without discontinuity of the structure as a whole. Lu *et al* (2000) reviewed some simple GFA parameters based on characteristic temperatures and other physical properties of oxides, oxide melts and bulk metallic glasses (BMGs). Among them, the reduced glass transition temperature, T_{rg} (ratio of the glass transition temperature, T_g and the

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*Author for correspondence (amkroula@univ-jijel.dz) liquidus temperature, T_l), proposed by Turnbull (1969) with an assumption that the nucleation frequency and crystal growth of melt scales are inversely proportional to viscosity of the liquid. T_{rg} indicator was developed for only monoatomic systems. Later on, Lu and Liu (2003) confirmed that T_{rg} computed by T_l/T_g shows a better correlation with GFA than that given by T_g/T_m for different multicomponent alloy systems (T_m is the melting point). Inoue *et al* (1990) proposed a new GFA indicator, called the supercooled liquid region, ΔT_{xg} (the temperature difference between the onset crystallization temperature, T_x and the glass transition temperature, T_g) based on the considerations of supercooled liquid stability against crystallization. Both ΔT_{xg} and T_g/T_l ratios are commonly used as GFA indicators for BMGs. Hrubý and coworkers (Hrubý and Štourač 1974; Štěpánek and Hrubý 1980; Červinka and Hrubý 1982) used DTA data analysis technique to value GFA of materials (that was for the approaching chalcogenide glasses and BMGs) in Ge–Si–S system. Sun criterion was enriched by Rawson (1956, 1967) and finally described as the 'kinetic theory of glass formation' by Turnbull (1969). Studying the oxides GFA, Rawson introduced the oxide melting temperature (T_m) as a necessary parameter to link with its bond strength. He proposed the ratio $E_B^{\mathrm{Rawson}} = E_B^{\mathrm{Sun}}/T_m = E_d/(I \cdot T_m)$ (kcal·mole^{-1}·K^{-1}) that is considered to be the thermal bond strength. Its value is high for all oxide formers. The lower the value, the harder the amorphization will be. Minaev (1978, 1980, 1983, 1991) partially agreed with Rawson and suggested a theoretical model to compute the oxide bond strength.

2. A relative approach to GFA

Focusing on single oxides GFA, literature analysis showed that all the aforementioned criteria appeared to be useful for the general understanding of GFA but (except Rao *et al* (2004)) have found no use for direct comparative estimation of this phenomenon. The non-dimensional method for experimental data analysis permitted Rao *et al* (2004) to study the glass formation tendency (GFT) of a wide range of materials. Author proposed the criterion G, linked with bonding (bond energy and ionicity), structure (constraints and size asymmetry) and viscosity (configurational entropy) factors and assessed '...G is a product function for simple materials and is intended to be like a figure of merit' (Rao *et al* 2004). Rao ranked the most used oxides as following: B_2O_3, SiO_2, P_2O_5, GeO_2, MoO_3, TeO_2, V_2O_5, WO_3, PbO_2, SnO, PbO, Al_2O_3, AS_2O_3, Li_2O, MgO, Na_2O and CaO.

From a unique thermodynamical point of view, Sun criterion, $E_B^{\mathrm{Sun}} = E_d/I$, is unable to sort oxides as formers on the one hand and intermediate and modifiers on the other. Indeed, the obtained values are $E_B^{\mathrm{Sun}} > 79\,\mathrm{kcal \cdot mole^{-1}}$, (60–79) kcal·mole^{-1} and $E_B^{\mathrm{Sun}} < 63\,\mathrm{kcal{\cdot}mole^{-1}}$ for glass former, intermediate and modifier oxides, respectively. The obtained values for this criterion are ambiguous because they do not lead to the three oxide groups (sorted by their own distinctive interval values). Al_2O_3 is a real intermediate oxide that may be a former one, when considered with a coordination number $I = 4$ ($79 < E_B^{\mathrm{Sun}} < 101$ kcal·mole^{-1}), while being a modifier, if $I = 5$ ($63 < E_B^{\mathrm{Sun}} < 73$ kcal·mole^{-1}) or intermediate, if $I = 6$ ($53 < E_B^{\mathrm{Sun}} < 67$ kcal·mole^{-1}). That is why it never forms glass by itself but contributes to any form of melting of other oxide formers. Rawson criterion ($F_b = F_L/T_m$) is more suitable for the definitive sorting between the former and the other (modifiers and intermediate) oxides. A real oxide former as SiO_2 ($F_L = 106$ kcal·mole^{-1}·K^{-1}) is definitively separated from an intermediate one such as zirconium dioxide ($F_L = 81$ kcal·mole^{-1}·K^{-1}). Because of its higher melting point, ZrO_2 possesses a low Rawson criterion value and consequently to Rawson's considerations cannot form glasses. In contrast, Rawson criterion value of B_2O_3 is very high and thus, this oxide never crystallizes.

Minaev confirmed this criterion and enriched the model to compute the bond strength of oxides and their melts. Moreover, researchers have often faced contradictions. Indeed, according to Stanworth (1946) electronegativity criterion, Si, Ge, Sn and Sb possess an electronegativity of 1·8. However, oxides of the first two elements are good glass formers, while Sb_2O_3 forms glasses only at very high cooling rates and SnO_2 never form glasses (Červinka and Hrubý 1982).

In this paper, using IUPAC and NIST data (Pauling 1970; Burdett 1995; Lide 2009) and obeying to the main rules of the mathematical non-dimensional analysis, we suggest to take into account of an omitted thermodynamical characteristic: the isobaric heat capacity (C_p) valued at the melting temperature (it is defined to be an extended value that allows measuring the faculty of all chemical components to absorb/restore the energy during all transformations with a temperature variation). This was the objective of Rawson (1956, 1967) who confounded between temperature and heat. At the melting temperature, the available heat depends on C_p according to the following: $C_p^{E_xO_y} = a + b \cdot 10^{-3} \cdot T_m$ (kcal·mole^{-1}·K^{-1}), where a and b are constants (Pauling 1970). We propose to add C_p computed at T_m temperature to Rawson's formula denominator, which makes it non-dimensional. The mathematical non-dimensional analysis permits to describe any physical phenomenon with a single non-dimensional equation (with no measurement units, as atoms of electronegativity). It gives the number of non-dimensional equations E as the difference $P - U$, where P is the number of the studied properties and U, the number of measurement units (S.I.). In our considerations, GFA is the studied phenomenon, while $P = 4$ (E_d; I; T_m; C_p) and $U = 3$ (cal; mole; K). Thus $E = P - U = 4 - 3 = 1$; that means that oxides GFA can be described using one and only one equation (that is consequently a non-dimensional one). Considering any oxide E_xO_y, its thermodynamical relative GFA will be:

$$\mathrm{ThRGFA}^{E_xO_y} = E_B^{\mathrm{Rawson}}/C_p = E_B^{\mathrm{Sun}}/\left(T_m \cdot C_p\right).$$

3. Results and discussion

Table 1 reports the needed physicochemical data of selected oxides. Sun and Rawson GFA criteria values are given and

Table 1. Parameters and GFA criteria values of some oxides.

E_xO_y	I	E_d (kJ/mole)	T_m (K)	C_p (kJ/mole·K)	Criteria			Group
					Sun (kJ/mole)	Rawson (kJ/mole·K)	ThRGFA $\times10^3$	
As_2O_5	4	1458·82	388	144·386	364·705	0·939961	6·510020	Glassformer oxides
PbO_2	4	970·7	563	73·377	242·675	0·431039	5·874252	
SeO_2	4	950·5	613	72·065	237·625	0·387642	5·379057	
MoO_3	4	2307·36	1073	108·164	576·84	0·537595	4·970183	
B_2O_3	4	1488·08	723	109·806	372·02	0·514550	4·68595	
GeO_2	4	1801·58	1389	82·615	450·395	0·324258	3·924898	
TeO_2	4	1136·96	1006	79·834	284·24	0·282544	3·539136	
Sb_2O_5	4	1417·02	798	138·351	354·255	0·443928	3·208692	
SiO_2	4	1772·32	1999	69·844	443·08	0·221650	3·173493	
SnO_2	4	1162·04	1902	52·599	290·51	0·152739	2·903800	
V_2O_5	4	1876·82	943	181·238	469·205	0·497566	2·745363	
P_2O_5	4	1847·56	853	213·368	461·89	0·541488	2·537814	
WO_3	6	2583·24	1745	115·866	430·54	0·246727	2·129415	
Ta_2O_5	4	2429	2173	135·082	607·25	0·279452	2·068749	
Tl_2O_3	4	1172	1107	139·322	293	0·264679	1·899759	
Bi_2O_3	4	969	1040	135·491	242·25	0·232932	1·719172	
Nb_2O_5	4	2298·5	1783	188·578	574·625	0·322279	1·709000	
TiO_2	6	1820	2236	86·448	303·333	0·135658	1·569241	Intermediate oxides
BeO	4	1046	2853	70·715	261·5	0·091656	1·296154	
Al_2O_3	4	1504·8	2327	141·131	376·2	0·161667	1·145512	
ZrO_2	6	2027·3	2983	99·063	337·883	0·113269	1·143402	
ZnO	4	601·92	2248	61·723	150·48	0·066939	1·084502	
CuO	8	794·3	1599	60·472	99·287	0·062093	1·026800	
PdO	8	498	1143	53·347	62·25	0·054461	1·0208	
Ag_2O	12	424·5	503	72·848	35·375	0·070328	0·96540	
FeO	8	933·5	1651	74·405	116·687	0·070676	0·94988	
PtO	8	1500	1895	104·9	187·5	0·098944	0·943227	
NiO	8	919·6	2228	56·127	114·95	0·051593	0·91921	
Cr_2O_3	4	1340·35	2673	150·963	335·087	0·125360	0·830397	
MnO	8	894	2148	63·919	111·75	0·052025	0·81391	
CoO	8	911·3	2078	67·480	113·912	0·054818	0·812362	
CaO	8	1074·26	2888	62·50	134·282	0·046496	0·74394	Modifier oxides
Li_2O	4	603	1974	104·642	150·75	0·076367	0·729800	
SrO	8	1070·08	2733	67·333	133·76	0·048942	0·726872	
BaO	8	1087	2191	87·843	135·875	0·062015	0·705974	
CdO	8	497·42	1774	53·524	62·177	0·035049	0·654825	
Ga_2O_3	6	1107·76	2068	144·807	184·626	0·089277	0·616526	
MgO	8	928·8	3099	61·177	116·1	0·037463	0·612380	
HgO	8	284·24	1098	62·734	35·53	0·032358	0·515809	
Na_2O	6	502	1405	117·398	83·667	0·059549	0·507240	
K_2O	8	480·7	1050	115·437	60·087	0·057226	0·495735	

oxides are sorted according to the decrease of their corresponding computed ThRGFA (see also in figure 1). The new model allows the ranking of oxides in three groups (formers, intermediates and modifiers) according to their specific values: ThRGFA $\geq 1{\cdot}709\times10^3$, $1{\cdot}569\times10^3 \geq$ ThRGFA $\geq 0{\cdot}812\times10^3$ and ThRGFA $\leq 0{\cdot}743\times10^3$, respectively. In the first (oxide former) group, B_2O_3 reappears while being absent in this group according to Sun and/or Rawson criteria. According to the aforementioned classification, ZrO_2 and Al_2O_3 were inadequately supposed to be former oxides regarding their high T_m. The introduction of C_p (as unavoidable characteristic) in the new model permits to reclass it in the adequate (intermediate) group of oxides according to their respective (1·15 and 1·14) ThRGFA values. Thus, ambiguities of Sun and Rawson classification are definitively raised. The confusion regarding B_2O_3 and (Al_2O_3, ZrO_2) classification is resolved: the first one is a real former oxide while alumina and zircon are intermediates. Moreover, the intermediate value of oxides ThRGFA $[6{\cdot}51–1{\cdot}70]\times10^3$ is in accordance with Angell's idea that sorted glass former oxides as strong and fragile ones (Bohmer *et al* 1993; Angell 2008, 2010). The obtained results are in agreement with the

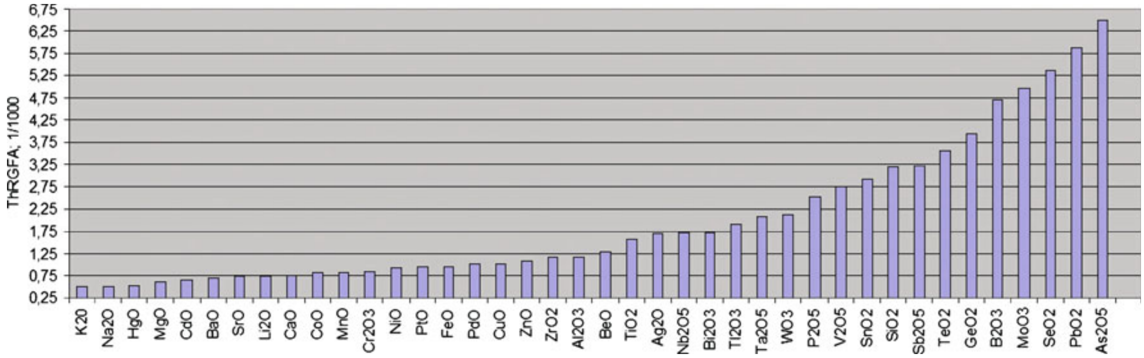

Figure 1. Computed ThRGFA values of some oxides.

mixed approach of Rao *et al* (2004) observation that brillantly ranked the most used oxides as following: B_2O_3, SiO_2, P_2O_5, GeO_2, MoO_3, TeO_2, V_2O_5, WO_3, PbO_2, SnO, PbO, Al_2O_3, AS_2O_3, Li_2O, MgO, Na_2O and CaO (few differences are because of considering only thermodynamic parameters).

4. Conclusions

According to Sun and Rawson, the thermodynamical aspects of oxides GFA led to dimensional values and were linked with the bond strength and associated to their melting points. None of these criteria completely sorted the oxides in the consensually approved three groups; indeed, alumina and zircon were incorrectly listed as former oxides. All the computed non-dimensional ThRGFA values reflect a real ability; such a word is devoted to non-dimensional characterization (as elements electronegativity does). Using the latest thermodynamical data and methods to compute them, ThRGFA model definitively agreed between theoretical and technological considerations. All prior GFA criteria were appropriate, but the misunderstandings that appeared were related to the chosen data (all omitted the isobaric heat capacity), their values and mathematical analysis.

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