Journal of Non-Crystalline Solids 347 (2004) 285–288

Letter to the Editor

How many non-crystalline solids can be made from all the elements of the periodic table?

E.D. Zanotto [a,*], F.A.B. Coutinho [b]

[a] *Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, Via Washington Luiz – Km. 235, UFSCar 13565-905, São Carlos – SP, Brazil*
[b] *School of Medicine, University of São Paulo, USP 01246-903, São Paulo – SP, Brazil*

Received 5 March 2004; received in revised form 17 June 2004
Available online 12 October 2004

Abstract

We estimate that over 200 000 non-crystalline solids (NCS) have already been produced in the last 6000 years of glass history. We then develop an equation to calculate how many NCS can (theoretically) be made from all the 80 useful elements of the periodic table, and conclude that, as we expected, astronomically long times would be required to experimentally synthesize, or simulate and test the properties of the vast number of NCS yet to be made. Nevertheless, because the properties of NCS depend mostly on their chemical nature rather than on their method of fabrication, and in view of today's rapid scientific developments in computer technology and in ab-initio calculations and molecular dynamics simulations, we propose that 'computer-made NCS' may be a solution to probe the structure and properties of a significant fraction of the colossal number of possible compositions. Despite the fact that it would be impossible to prepare all possible compositions, one can anticipate many surprises in the future, with a plethora of new exotic NCS.

We begin by defining NCS – glasses and amorphous solids – outlining a brief history of glass from the standpoint of its chemical compositions, and estimating how many glasses have already been made in the last six thousand years. We then develop an equation and estimate how many possible non-crystalline solids can still be devised. We have chosen to study this class of materials because, contrary to their crystalline counterparts, the structures and resulting properties of NCS are almost independent of the processing or synthesis technique employed in their fabrication, depending, instead, mostly on their chemical composition. Thus, we will focus on how many different glasses or amorphous compositions can (theoretically) be made from the useful elements of the periodic table.

We should begin by clarifying two related but often misleading controversial concepts. Gupta [1] demonstrated that non-crystalline solids could be divided into two distinct classes: glasses and amorphous solids. He argued that they behave differently upon heating and proposed structure-based definitions for glasses and amorphous solids. In short, a NCS is a *glass* if the short-range order, SRO, of solid (below the glass transition temperature, T_g) and melt are the same, i.e., SRO (glass) = SRO (melt). Glasses always exhibit a glass transition upon cooling or heating. These two conditions are always satisfied for NCS obtained by melt cooling because the liquid must undergo a glass transition to vitrify. On the other hand, a NCS is an *amorphous solid* if the SRO (a-solid) ≠ SRO (melt). Amorphous-Si and a-Ge, for instance, are well-known

* Corresponding author. Tel.: +55 16 33518527; fax: +55 16 33615404.
E-mail address: dedz@power.ufscar.br (E.D. Zanotto).
URL: http://www.lamav.ufscar.br.

0022-3093/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2004.07.081

examples of amorphous solids because their co-ordination number in the liquid state is greater than four. Amorphous solids are produced by techniques such as sol–gel, sputtering, mechanical alloying, crystal amorphization by high pressure or bombardment with charged particles, etc. However, some glasses can also be produced by these alternative techniques. In this article, all types of NCS synthesized by any possible route are considered.

It is a matter of dispute whether the first man-made glass was (accidentally) discovered in 4000 B.C. or in 2500 B.C. somewhere in Mesopotamia – where Iraq is today, or in Egypt [2]. In ancient times, glasses were made by melting natural, impure, raw materials such as sand (mostly SiO_2), vegetable ash (that are rich in K_2O and SiO_2), sea shells (mostly CaO and P_2O_5), Natron (Na_2CO_3) and Limestone ($CaCO_3$). Their compositions fluctuated around the soda–potash–lime–silica family and contained five or six main components and several impurities such as Fe_2O_3, MgO, MnO, etc. (Table 1). These traditional glasses constitute the basis of the contemporary window and bottle glass industries, and are a source of myths, such as the (alleged) slow flow of medieval cathedral glasses [3], and sacred colored images, which mysteriously appear on old windows [4].

The chemical industry developed five or six millennia after the discovery of glass, in the early 19th century (thanks to the availability of laboratory glassware), and a variety of purer chemicals such as carbonates, oxides, nitrates and sulfates became available for chemists, physicists and glass researchers. Several other compounds, such as PbO, BaO, SrO, ZnO, Li_2O, B_2O_3, transition metal and rare earth oxides were then introduced in a variety of optical and laboratory glasses. All these glasses derived from mixtures of oxides that were melted above their respective liquidus, which typically ranged from 900 to 1200 °C, and cooled to room temperature at relatively slow rates ($q < 1$ K/s). These traditional compositions are thus classified as good glass formers.

Finally, since the late 1960s, there has been an explosion of discoveries of new families of both oxygen and oxygen-free glasses and of amorphous solids, such as fluoride, metallic and chalcogenide systems, which contain metallic, semi-metallic and non-metallic elements of the periodic table. Many of these modern glasses must be cooled from the liquid state at much higher rates than their ancestors, typically at $10^0 < q < 10^6$ K/s; otherwise, they crystallize on the cooling path and cannot vitrify. Their uses include not only domestic but also sophisticated applications in medical and dental implants, electronic and electro-optical components, electrochromic and self-cleaning windows, golf clubs, etc.

Table 1
Typical compositions of window glasses (wt%)

	Modern	Medieval
SiO_2	73.2	45–75
Na_2O	13.4	0.1–18
K_2O	0.8	2.0–25
CaO	10.6	1.0–25
Al_2O_3	1.3	0.8–2.0
MgO	0.7	0.8–8.0
Fe_2O_3	0.1	0.3–2.1
MnO	–	0.3–2.3
P_2O_5	–	2.5–10

One can estimate the number of different glasses that have been (published) produced so far by analyzing both scientific and patent literature, and the two most comprehensive glass databases, Interglad [5] and SciGlass [6]. Such analyses reveal that over 200 000 inorganic glass compositions have already been published! (The number of amorphous solids produced so far represents only a small fraction of the number of glasses). Many other glasses have probably been synthesized, but their compositions and properties have been lost or remain hidden away in *logbooks* in universities and industrial laboratories. Since these compositions are largely unknown, some researchers may attempt to synthesize them again! In this article we also consider compositions of organic and polymer (high molecular weight) glasses containing C, H, N, and O, but disregard the fact that, for any given composition, the structures and properties of this special class of NCS are also dependent on the molecular weight. This amazing number of glasses has led some glass researchers to speculate that this field has been almost exhausted and that further innovation in glass technology can only be achieved through new processing methods and coatings rather than through new compositions.

Hence it is of fundamental importance to investigate how many different NCS can still be made. It is empirically known that some compositions, such as the ancient soda–potash–lime–silica glasses, vitrify easily while others, such as most (albeit not all) vitreous metallic alloys so far discovered, are reluctant glass formers that require high cooling rates to vitrify from the liquid state. However, it is now accepted that a glass of *any* desired composition can be synthesized if the cooling rate is sufficiently rapid to prevent crystallization on the cooling path, e.g., Ref. [7]. High cooling rates can be achieved, for instance, with laser melting, melt spinning and similar techniques. In addition, alternative processing methods are becoming increasingly available to produce glasses or amorphous solids, such as: (i) sol–gel methods [8] whereby a chemical solution of the desired elements is heated slowly to a temperature below liquidus, evaporating the solvent but side-stepping crystallization; (ii) containerless melting [9] in which an acoustic or electrostatic field keeps a certain quantity of melt floating in the

atmosphere, free of contact with crucible walls or solid impurities that might otherwise trigger crystallization; (iii) high energy methods, such as mechanical alloying [10] whereby hard spheres are violently impacted against a powder mixture that is 'sintered' without crystallizing; (iv) crystal amorphization by high energy particles or by the slow application of high pressures at temperatures below liquidus [11], etc.

Therefore, we anticipate that many of the possible compositions, such as pure elements or combinations that do not include the typical oxide glass formers (SiO_2, B_2O_3, GeO_2, P_2O_5 and a few others), will be difficult to vitrify and will require very high cooling rates, in the range of 10^4–10^{10} K/s (if produced by melt-quenching). For instance, pure Ni has been vitrified at a cooling rate of 10^{10} K/s [12]. These hyper-quenched glasses will necessarily have small dimensions (thin plates, films, fibers or powders). It should be stressed that the so-called 'principle of maximum confusion' (it has been empirically established that multi-component compositions vitrify more easily than compositions containing only a small number of chemical elements) helps glass formation with combinations of many elements. In addition, thanks to the advent of both new and some as yet undiscovered processing techniques, one can predict that any composition can, in principle, be transformed into a NCS. Obviously, many of these NCS will be unstable and useless, but it is reasonable to assume that countless other, as yet unknown, NCS may have interesting properties.

One can thus calculate the number of possible *candidate compositions* with any desired combination of elements from the periodic table, varying each element in certain increments (Δ). One can, for instance, choose a very small increment to simulate NCS with compositions as complex as those of the human body: $H_{2\,00\,000}O_{77\,000}C_{38\,000}N_{1900}Ca_{760}P_{460}S_{120}Na_{120}K_{100}Cl_{80}Mg_{20}Si_{20}F_4Fe_2Zn_1$ plus 40 trace elements [13], or to exemplify the sensitivity of the material's optical and electronic properties to chemical compositions (Δ = 0.1 mol%), or to its chemical and rheological properties (Δ = 1 mol%). Whatever one's purposes, the formula derived below can be used to calculate the number of NCS for any desired incremental compositional change.

Let us now describe how one can calculate the number of glasses, N_g, which can be made with N elements of the periodic table. To begin with, let us assume one wants all the glasses with p elements, say $X_1, X_2, \ldots X_p$, in such a way that the percentage of each element in the glass is a multiple of a percentage Δ. Let $n_1\Delta$ be the percentage of the element X_1 in the glass, $n_2\Delta$ the percentage of the element X_2 in the glass, and so on. Therefore, one must have

$$n_1\Delta + n_2\Delta + \ldots + n_p\Delta = 100, \tag{1}$$

or

$$n_1 + n_2 + \ldots + n_p = 100/\Delta. \tag{2}$$

The number of possible compositions is, therefore, given by $(p-1)$ combinations of $(100/\Delta) - 1$ distinct numbers, that is 1,2,. . . . $(100/\Delta) - 1$

$$C((100/\Delta) - 1, p-1) = \frac{((100/\Delta) - 1)!}{(p-1)!((100/\Delta) - 1 - (p-1))!}. \tag{3}$$

This equation makes sense only if $(100/\Delta)$ is an integer. Let us give an example to clarify Eq. (3). Suppose one takes Δ = 1 and p = 5. Then, one possible combination in the set of C (99,4) combinations is, for example, 3, 15, 29, 37. Hence, the NCS will have the following composition: (3–0)% of the element X_1, (15–3)% of the element X_2, (29–15)% of the element X_3, (37–29)% of the element X_4 and (100–37)% of the element X_5.

It is now clear that the total number of glasses that can be formed by mixing p elements from the total of N is

$$C(N,p)C((100/\Delta) - 1, p-1) \tag{4}$$

Therefore, the total number of glasses, N_g, is given by

$$N_g = \sum_{p=2}^{N} C(N,p) \cdot C((100/\Delta) - 1, p-1) \tag{5}$$

Finally, one must add N to Eq. (5) to allow for NCS that are constituted of single elements.

Fig. 1 shows the results obtained with Eq. (5). Taking, for instance, combinations of 10 or 60 elements, in 1.0 mol% increments, which are typical for contemporary chalcogenide and metallic glasses, one has 4.2×10^{12} and 2.3×10^{44} different compositions, respectively. Now taking the 80 most useful elements of the periodic table (which are not inert gases, artificial or strongly radioactive, and neglecting the fact that several elements have different valence states) and combining them in 1.0 mol% results in $N_g = 1.3 \times 10^{52}$

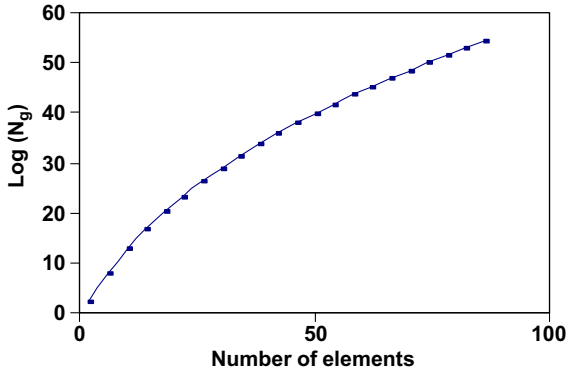

Fig. 1. Logarithm of the number of possible glass compositions, N_g, as a function of the number of chemical elements used in their formulation, in such way that the amount of each element is a multiple of 1 mol%.

compositions. For combinations of these 80 elements in 0.1% increments $N_g > 10^{300}$! These astronomical numbers are vastly higher than the number of compositions published so far in the 6000 years of glass history.

Similar calculations can be made for any class of materials, e.g., semiconductors, crystalline alloys, fully or partially crystallized ceramics and glass–ceramics, single crystals, etc. However, it should be stressed that the molecular/nano/micro or macro structures and resulting properties of crystalline materials strongly depend on the processing technique used in their fabrication. Hence, the calculations presented here, which take only the chemical composition as a variable, are valid for NCS, but give a lower bound for crystalline materials.

We would like to emphasize that although it is not a particularly unexpected fact that the number of NCS that could be synthesized from all the useful elements is exceptionally large, some authors believe that the development of new NCS compositions is an almost exhausted field. We are therefore convinced that the present calculations are important to catalyze further thinking on the subject.

It should be stressed, however, that it would be impossible to experimentally synthesize all the NCS. A reasonable estimate for the number of atoms in the universe is 10^{79}, e.g., Ref. [14]. Thus, in principle, if we were to make cumulatively, say, a mole of each possible NCS ($=10^{24}$ atoms $\times 10^{52}$ compositions) we would have to use 10^{76} atoms to prepare and *store* each sample. So the universe would become a glass! This only means that, if the limited number of atoms were the only circumstance preventing us from preparing all the possible NCS, we would not be able to make them all at the *same time*. If, however, one plans to prepare these specimens by recycling all the elements of each NCS made before making another one, then one would need only a relatively small, limited amount of each of the 80 elements (but this strategy would also be prohibitively expensive and time consuming!). Of course, one way or the other, we would have no time to prepare all the NCS, so the lack of atoms is not the sole objection. The example below, given by an anonymous reviewer, illustrates the problem: '*...assuming that each of one billion people could prepare (say computationally) one billion glasses per second, this would make less than* 10^{26} *glasses per year. The time required would be fantastically longer than the age of the universe and our sun would have collapsed well before the task was completed.*' However, this practical impossibility does not mean that the present calculations are incorrect.

It is clear, therefore, that an infinite amount of time (and an incalculable amount of money) would be required to experimentally synthesize and test the properties resulting from some astronomical number of NCS yet to be made. It is thus obvious that appropriate statistical planning (linked to a solid knowledge about glass science) must be devised to efficiently probe a significant *fraction* of the *most promising* compositions. The fact that the properties of NCS depend mostly on their chemical nature, and due to scientific developments regarding ab initio and molecular dynamics calculations, as well as the increasing availability of powerful software and hardware, indicates that computer simulations may offer the only viable solution to probe the structure and properties of a myriad candidate compositions. However, even in this case, the time needed to simulate all these compositions would be impracticably long. Nevertheless, it is clear that the field is far from being exhausted, and one can thus anticipate many surprises in the future, with a plethora of new exotic non-crystalline solids!

Acknowledgments

To CNPq, Pronex and Fapesp (Brazil) for funding this research.

References

[1] P.K Gupta, J. Non-Cryst. Solids 195 (1-2) (1996) 158.
[2] J.M.F. Navarro, El vidrio, CSIC, Madrid, Spain, 1991, p. 3.
[3] E.D. Zanotto, P.K. Gupta, Am. J. Phys. 67 (3) (1999) 260.
[4] E.D. Zanotto. The saint in the window. Yet another myth of glass. Pesquisa Fapesp, vol. 79, 2002, p. 10. Electronic version at: www.revistapesquisa.fapesp.br:2222/transform.php?xml=3/0/20020903/20020979/en/SEC23_2.xml&xsl=xsl/en/article.xsl & transf=normal&id=SEC23_2&lang=en&issue=20020979.
[5] Interglad- International glass database, version 5.0: Interglad site: www7.big.or.jp/~cgi19786/ngf/interglad5/index_e.html.
[6] Sciglass database – Science Vision, version 3.5- www.esm-software.com/sciglass/.
[7] A.A. Cabral, A.A.D. Cardoso, E.D. Zanotto, J. Non-Cryst. Solids 320 (1–3) (2003) 1.
[8] M.A. Aegerter, M. Jafellici Jr., D.P. Souza, E.D. Zanotto, Sol–gel Science and Technology, World Scientific, London, 1989, p. 505.
[9] NSF News: Containerless melting of glass- www.nsf.gov/od/lpa/news/03/pr03113.htm.
[10] L.C. Zhang, Z.Q. Shen, J. Xu, J. Mater. Res. 18 (9) (2003) 2141.
[11] G.N. Greaves, F. Meneau, A. Sapelkin, L.M. Colyer, I.A.P. Gwyin, S. Wade, G. Sankar, Nature Mater. 9 (2003) 571.
[12] R. Elliot, in: R. Hartnoll (Ed.), Eutectic Solidification Processing, Crystalline and Glassy Alloys, Bodmin, Cornwall, 1983, p. 38.
[13] R.A. Freitas Jr. The chemical composition of the human body- www.foresight.org/Nanomedicine/Ch03_1.html.
[14] Sunspot Astronomy and Visitor Center Home Page – How many atoms there are in the universe? www.sunspot.noao.edu/sunspot/pr/answerbook/universe.html#q70.