



Glass Formation In Oxides -- Zachariasen's Rules

In 1932 W.H. Zachariasen published a paper, "The Atomic Arrangement in Glass", which described the ability of various oxides to form glass and had great impact on material scientists of the period. Zachariasen's work placed the understanding of glass structure and its relationship to composition on a chemical basis for the first time.

Zachariasen considered the relative glass-forming ability of oxides and concluded that the ultimate condition for glass formation is that a substance can form extended three-dimensional networks lacking periodicity but with energy content comparable with that of the corresponding crystal network. From this condition he derived four rules for oxide structure that allow selection of those oxides that tend to form glasses. The rules are the following:

- An oxygen atom is linked to not more than two glass-forming atoms.
- The coordination number of the glass-forming atoms is small.
- The oxygen polyhedra share corners with each other, not edges or faces.
- The polyhedra are linked in a three-dimensional network.

Oxides A_2O or AO , where A is a metal atom, do not satisfy any of the rules. Oxides A_2O_3 satisfy the rules if the oxygen atoms form triangles around each A atom, and AO_2 or A_2O_5 satisfy these rules if the oxygen atoms form tetrahedra around each A. From these considerations Zachariasen concluded that the following oxides should be glass formers:

B_2O_3 , **SiO_2** , **GeO_2** , **P_2O_5** , **As_2O_3** , Sb_2O_3 , V_2O_5 , Sb_2O_5 , P_2O_3 , As_2O_5 , Nb_2O_5 , and Ta_2O_5 .

At the time of Zachariasen's research, only the first five oxides above [in bold] had been made into glasses, but since then glasses of two other oxides [underlined] in the list have been prepared. Five others on his list have never been successfully prepared as glasses. On the other hand, five oxides [the last five in the first line below, italics] not cited by Zachariasen have been made into glasses, as well as nine other oxides that have "conditionally" been prepared as glasses. Overall, in spite of Zachariasen's mediocre prediction record, he has received great recognition in terms of being the first to systematically address the relationship between atomic structure and glass forming ability.

Oxides formed as glasses:

B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , As_2O_3 , Sb_2O_3 , *In_2O_3* , *Tl_2O_3* , *SnO_2* , *PbO_2* , *SeO_2*

Oxides "Conditionally" Formed as Glass

TeO_2 , SeO_2 , MoO_3 , WO_3 , Bi_2O_3 , Al_2O_3 , Ba_2O_3 , V_2O_5 , SO_3