STRUCTURE-PHASES IN THE SILICATE GLASS SYSTEM: $CaO \cdot Na_2O \cdot SiO_2$[1,2]

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Abstract

When the data for the total and species densities of soda-lime-silica glasses are plotted as functions of the ratios of sodium and calcium atoms to oxygen, they are found to fall on a three-dimensional diagram whose surface is made up of planes. The planes are bounded by straight lines which join rational compositions called "structure-phases." The data are interpretable as indicating that the structure-phases are those compositions in which the ratios of silicon to oxygen atoms are those for crystalline silicate structural types such as mica, amphibole, and pyroxene.

Introduction

The writer has pointed out elsewhere (2) that plots of the density of atomic species in silicate glasses as a function of the ratio of the metal atoms to oxygen atoms are essentially phase diagrams inasmuch as they reveal compositional regions in which the density follows well-defined laws and which are bounded by rational compositions. Since these compositions are not phases in the generally accepted physical chemical sense, it was proposed to call them "structure-phases," a term which implies the influence of the structure of the silicon-oxygen framework on the rate of change of the density. Huggins (1), who first investigated the variation of density with the ratio of metal to oxygen atoms, pointed out that the data could be represented by straight lines with changes in slope at the specific ratios of silicon to oxygen atoms that characterize crystalline silicate structural types. From Huggins' work and that of the writer (2), the structural control of the positions of the boundaries seems well established.

The early work of Huggins was concerned with the variation in the volume per gram atom of oxygen with the ratios of sodium and silicon atoms to oxygen. The writer showed that, not only are the computations much simplified, but also a great deal more information may be obtained if the densities of the atomic species are considered. It was found, for

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[1] Sponsored by the Owens-Illinois Glass Company.

[2] From an address, "The Application of Crystal Chemical Principles to the Problem of Glass Structure," read before *The Crystallographic Society of America*, Annapolis, Maryland, March 19, 1947.

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instance, that the packing laws of the sodium atoms differ from those of the silicon-oxygen framework. Whereas the rate of change of the density of sodium shows discontinuities at all of the ratios representing crystalline types, as well as one for which no crystalline analogue is known, that of the framework shows only the last named discontinuity. It was suggested that this discontinuity represents saturation of the essentially cristobalite-like structure of the framework with sodium atoms.

That the data on density—and a number of other physical properties, as well—can be represented for a two-component system by a series of straight lines with discontinuities at points which have structural signifi-
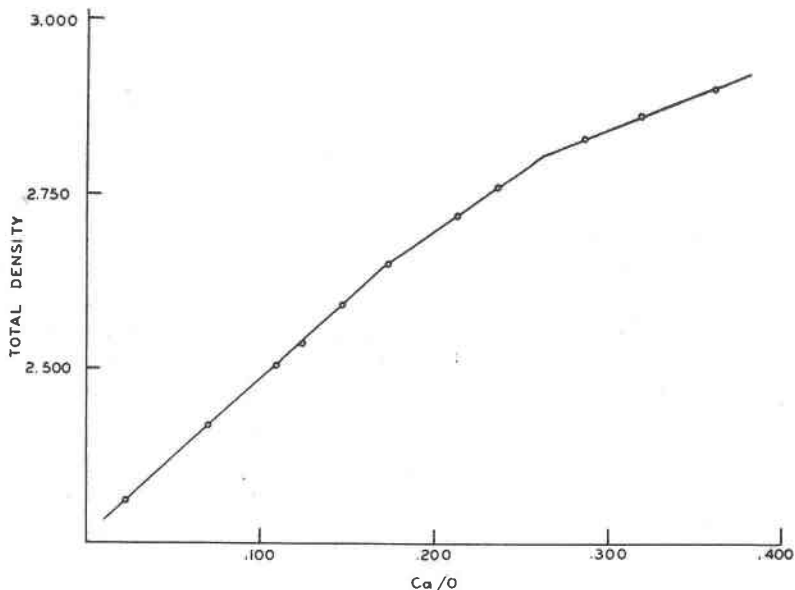

Fig. 1. Section through the structure-phase diagram of the total density in the system: CaO · Na₂O · SiO₂. Ratio Na/O constant.

cance is of particular value since the positions of the discontinuities are independent of the metallic species present and represent changes in the linkage of the tetrahedrons of silicon and oxygen atoms. In studying a two-component system for the effect of the addition of a constant amount of a third component, one need only determine the slopes of the lines and their positions along the vertical scale. In the work previously referred to (2), it was suggested that the structure-phase diagram of a three-component system should be characterized by surfaces made up of planes. It is the purpose of this communication to consider this possibility in the three-component system CaO · Na₂O · SiO₂. Unfortunately, available published data are not particularly well adapted to this work and, although

the general theory appears to have been confirmed, many of the con-
clusions must be considered tentative.

<div align="center">EXPERIMENTAL</div>

The data for a series of sodium calcium silicate glasses prepared by
Morey and Merwin (3) have been plotted as functions of the two vari-
ables, Na/O and Ca/O, expressed as numbers of atoms. This results in a
three-dimensional graph which, according to theory, should have a sur-
face consisting of planes. Both the total density and the species density
of the silicon-oxygen framework have been so treated. To test whether
the surface is actually made up of planes, one may pass a section through
the graph and plot any observed densities which fall along the line of the
section. The observed values should, of course, lie along one or more
straight lines. That this is the case is shown in Fig. 1, which is the plot
of the densities which lie along a section of constant Na/O content in the
structure-phase diagram constructed from the total density. Other sec-
tions, crossing the graphs in various directions, confirm the planar nature
of the surfaces.

In order to determine the locations of the intersections of the planes,
a number of sections have been constructed and the positions of the dis-
continuities plotted. Because the compositions of the glasses were not
chosen for this purpose, it is only coincidental that a number of observed
data happen to fall along a straight line. In order to collect enough data
on the positions of the discontinuities so as to locate the boundaries, it
was necessary to include points somewhat off the lines of the sections.
Inclusion of such points makes the precise location of the discontinuity
in any one section uncertain. However, in those cases in which a number
of observed discontinuities fall along a straight line, it may be assumed
that the boundary is accurately located.

Since the data do not permit accurate location of all of the boundaries
by sectioning, it is necessary to consider other methods. One of these is
to contour the surface. If the surface of the structure-phase diagram is
made up of planes, the contours should be straight lines, with changes in
direction at the boundaries. Contours drawn through points of equal
density are, indeed, straight lines in the areas outlined by sectioning.
The directions of the lines are the same within an area and slightly dif-
ferent in adjacent areas. The positions of the changes in direction may
be taken as additional boundaries. Both the total density and the frame-
work density can be well represented by straight line contours.

Information obtained from the sections and contours have been com-
bined into consistent patterns of planes intersecting in straight lines.
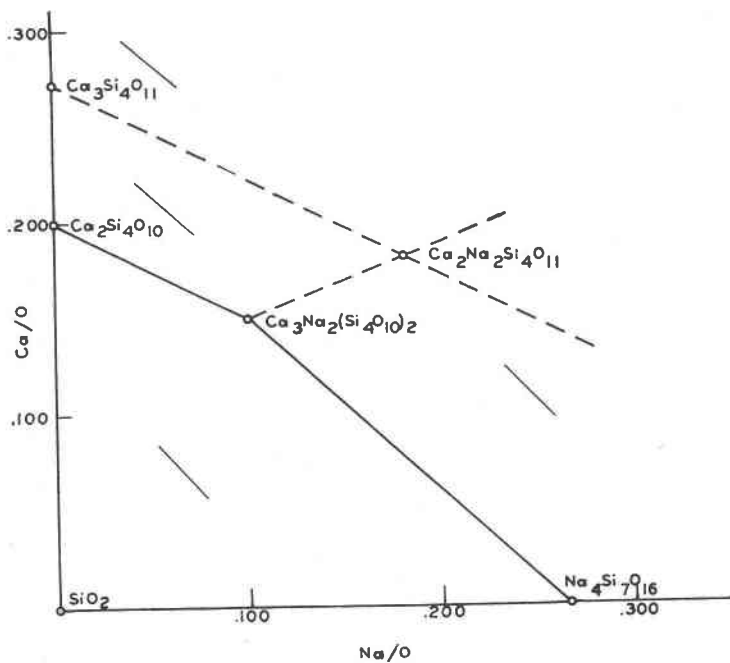These are shown in Figs. 2 and 3, which are the plan views of the three-

Fig. 2. Plan view of the tentative structure-phase diagram of the framework density in the system: $CaO \cdot Na_2O \cdot SiO_2$. Short lines in each field indicate directions of straight line contours of equal density.
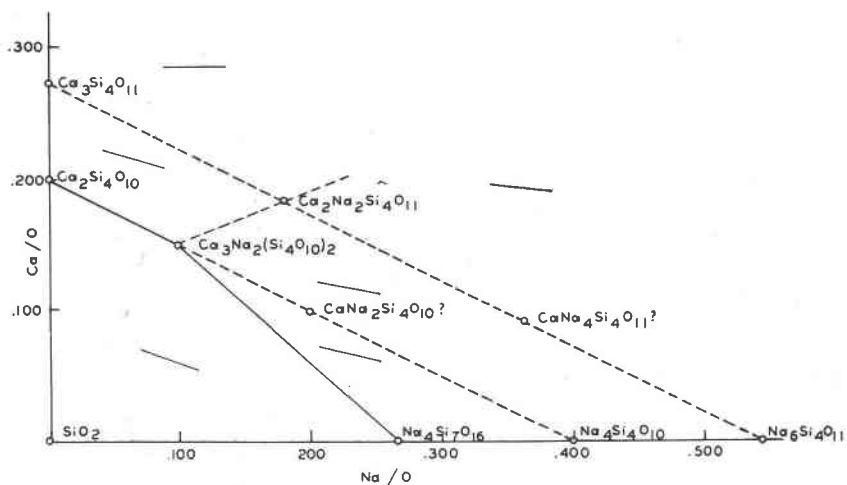

Fig. 3. Plan view of the tentative structure-phase diagram of the total density in the system: $CaO \cdot Na_2O \cdot SiO_2$. Short lines in each field indicate directions of straight line contours of equal density.

dimensional diagrams in which the density is the vertical axis normal to the plane of the paper. Directions of the contours are indicated. Solid lines represent boundaries which appear to have been located with some certainty; dotted lines are either less well determined or, in some cases, inferred. It must be emphasized that the conclusions reached in the present work are based on incomplete data and cannot be considered as final.

DISCUSSION

The Structure-Phase Diagram of the Silicon-Oxygen Framework Density: In the structure-phase diagram of the framework of pure sodium silicate glass, only one discontinuity appears and this is at the ratio $Na/O = .268$. In the three-component system, $CaO \cdot Na_2O \cdot SiO_2$, the axis, $Ca/O = 0$, is, therefore, divided into two fields which join at one structure-phase. In the earlier work (2), it was suggested that the existence of this phase, which does not have a crystal structure analogue, could be explained as representing saturation of the cristobalite-like structure of the framework with sodium atoms. A unit cell of cristobalite contains void space sufficient to house four sodium atoms and, since there are sixteen oxygen atoms in a unit cell of cristobalite, the sodium to oxygen ratio of the saturated structure would be 4/16 or .250, which is close to the observed value of .268. The rational composition is $Na_4Si_7O_{16}$.

If it may be assumed that the calcium atom, which is approximately the same diameter as the sodium atom, enters the structure in the same, or a similar, manner to sodium, the phase representing saturation would be expected to follow the straight line $Na/O + Ca/O = .250$. Examination of Fig. 2 reveals that the boundary starting at $Na/O = .268$, $Ca/O = 0$, does actually follow the predicted line. This boundary is the one for which the most data are available and may be considered to be the most accurately located of all the boundaries on the structure-phase diagram. The observed boundary does not, however, appear to follow the theoretical line the entire distance to $Na/O = 0$, $Ca/O = .250$. This is understandable, since the doubly charged calcium atom need not necessarily behave in the same manner as the singly charged sodium atom.

Data on the two-component system, $CaO \cdot SiO_2$, are insufficient to permit the construction of its structure-phase diagram. However, the observed boundaries in the three-component system can be extrapolated to $Na/O = 0$. The extrapolation must be guided by theoretical considerations since the boundaries are not clearly defined by either sections or contours. The known influence of the specific compositions of crystalline silicates in other two-component systems suggests that, by analogy, structure-phases may be expected at the same compositions in the cal-

cium silicate system. Actually, the observed data can be extrapolated to points close to $Ca/O = .200$ and $.273$. These ratios represent the compositions $Ca_2Si_4O_{10}$ and $Ca_3Si_4O_{11}$, respectively, which are the mica and amphibole structural types. What data exist for the pure calcium silicate system are compatible with straight lines having changes in slope at these points.

If the influence of the structural type, $Ca_2Si_4O_{10}$, is admitted and if a line is drawn representing the composition, $Ca_xNa_ySi_4O_{10}$, an intersection is found with the previously located saturation boundary at the point, $Ca/O = .150$, $Na/O = .100$. The observed data from sections are consistent with such a line. The composition at the intersection is a rational one, being $Ca_3Na_2(Si_4O_{10})_2$. This represents the replacement of one quarter of the calcium atoms of $Ca_2Si_4O_{10}$ by an electrostatically equivalent number of sodium atoms. It also represents the composition at which the framework becomes saturated with metal atoms.

Following the same reasoning as in the previous case, one may draw a line representing the composition $Ca_xNa_ySi_4O_{11}$. The discontinuities observed in sections through this region are consistent with such a line, but the agreement is not convincing. Data, particularly that obtained from contours, indicate that this line is intersected by one from the composition $Ca_3Na_2(Si_4O_{10})_2$ near the point, $Ca/O = .182$, $Na/O = .182$. This is again a rational composition and represents the replacement of one half of the calcium atoms by the electrostatic equivalent of sodium. The composition is, therefore, $Ca_2Na_2Si_4O_{11}$.

The remainder of the diagram has been constructed mainly from inference and it will not be discussed. The observed species densities can, however, be represented by straight line contours in the various fields.

The Structure-Phase Diagram of the Total Density: Since the total density of the sodium silicate system shows discontinuities at the Na/O ratios of $.268$, $.400$, $.545$, and $.667$, there are boundaries starting at all of these points in the three-component system. With the exception of that starting at $.268$, these boundaries can logically be expected to follow rational compositions. For those at $.400$ and $.545$, respectively, the compositions are $Ca_xNa_ySi_4O_{10}$ and $Ca_xNa_ySi_4O_{11}$. (No data are available to show the existence of a boundary starting at $.667$ and following the line $Ca_xNa_ySiO_3$, although such a boundary might well be expected.) The boundary starting at $.268$ follows the saturation line until it intersects with that representing $Ca_xNa_ySi_4O_{10}$, as in the case of the framework density. The structure-phase diagram of the total density, while tentative, is consistent with observed data, which can be represented by straight line contours in the various fields. It is of interest to note that the contours in the region above $Ca/O = .273$ and between $Na/O = 0$ and

about .200 are parallel to the sodium axis. This means that, for constant Ca/O, the addition of sodium to the glass has no effect on the total density.

Structure-Phases Deduced from the Diagrams: On the basis of Figs. 2 and 3, one may conclude, tentatively, that the rational compositions—structure-phases—listed in Table 1 are of structural importance in the three-component system $CaO \cdot Na_2O \cdot SiO_2$. The structure-phases are

TABLE 1. RATIONAL COMPOSITIONS OF STRUCTURAL IMPORTANCE

SiO_2	$Na_4Si_7O_{16}$	$Ca_2Si_4O_{10}$	$Ca_3Na_2(Si_4O_{10})_2$
	$Na_4Si_4O_{10}$	$Ca_3Si_4O_{11}$	$CaNa_2Si_4O_{10}$?
	$Na_6Si_4O_{11}$		$Ca_2Na_2Si_4O_{11}$
			$CaNa_4Si_4O_{11}$?

joined by straight lines, which are the boundaries of areas in which the surface of the solid diagram is planar. Those boundaries which follow rational compositions may themselves be looked upon as being structure-phases. In any one field, the density varies as a straight line in any direction, a fact which is of practical as well as theoretical significance.

CONCLUSIONS

As has been emphasized, many of the structure-phases listed in Table 1 must be considered as tentative. While it is true that the data can be represented adequately by such planes as are outlined in the diagrams, Figs. 2 and 3, the exact locations of the boundaries have been guided in part by theoretical considerations. An exception to this is the boundary which represents saturation of the framework. Eight individual sections crossing this line revealed discontinuities in the proper positions. The field delineated this line and, probably, that representing the composition $Ca_xNa_ySi_4O_{10}$ can be considered as being well established. In this field, the framework is essentially cristobalite-like, with sodium and calcium atoms in the interstices. (The validity of including the region of low Ca/O ratio and very low Na/O ratio is open to question. It is in this region that the melt consists of two liquids and homogeneous glasses cannot be made.)

It would be desirable to prepare a series of glasses of specially selected compositions which will cover the structure-phase diagram with a grid of observed values. Data will lie on straight lines, and one should be able to determine the boundaries with accuracy. Until such time, no theoretical interpretation of the diagrams is possible.

Whatever the compositions of the structure-phases may be or their theoretical interpretation, the fact that the data can be well represented

by planes is of practical value in the study of glass systems. The boundaries of the planes are dependent upon the manner of linkage of the silicon-oxygen tetrahedrons. The effects of other modifying metals can be determined with a minimum of experimental effort, since the attitude of a plane can be determined from three points. In addition to specific gravity studies, the investigation of optical properties will be facilitated. The close relation between index of refraction and density suggests, for instance, that the surface representing the refractive indices as functions of Ca/O and Na/O should be made up of planes, intersecting in the same boundaries. This appears to be the case with the data already studied.

REFERENCES

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