# THE CONTROL OF CRYSTALLINE GLAZES*

By F. H. Norton

ABSTRACT

In this investigation there is carried out the carefully controlled heat treatment of a single crystalline glaze in which both the crystallizing and growth velocity were determined for the four types of crystal produced. It was found possible to produce crystals at any desired location by seeding; their size could be controlled by the growing time and their shape by the growing temperature. Commercial production of crystalline glazes is possible if close temperature control is maintained.

## I. Crystalline Glazes

This type of glaze is one which upon cooling readily forms comparatively large crystals. The base is a silicate glass, and oxides, such as ZnO or TiO$_2$, are added as crystallizers. Many other oxides, however, will serve, as an examination of the literature will show. Often a coloring oxide is added in small amounts to be differentially absorbed by the crystal and base glass, thus building up color contrasts.

It should be noted that the only crystals large enough to be of direct value in a glaze of this kind are those which can grow mainly in one plane, for the thickness of the glaze layer limits the size of an isometric crystal to a maximum diameter of about 0.5 millimeter. An examination of the crystal systems will show that cubic crystals, for example, can not form in large sizes under these conditions. The hexagonal system seems to be best suited to produce crystals in a plane as, for example, frost on a window.

There is a considerable amount of literature pertaining to crystalline glazes, but it will be found to deal almost entirely with the composition of the glaze. In fact, scarcely a case came to light where the temperature schedule was given throughout the firing with the needed precision. Inasmuch as this paper deals mainly with the heat treatment of the glaze, this literature will not be reviewed.

## II. Theory of Crystal Development from Glasses

It will perhaps be well first to review the present understanding of the glassy state. One of the simplest glasses, vitreous silica, was studied by Warren,[1] who came to the conclusion that the X-ray diagram produced need not be explained by the presence of crystallites, as was previously believed, but could be satisfied by a random network of silicon-oxygen tetrahedrons with a fairly uniform spacing. The binary glasses are more complicated; the soda-silica series, however, has been worked out by Warren and Loring[2] and the lead-silica series by Bair.[3] In both cases, the structure seems to be formed of the same random network of silicon-oxygen tetrahedrons with the cations held in the meshes. This random arrangement is the reason why a continuous series of glasses can be formed with no detectable discontinuities in the properties.

Before this clear picture of the glass structure was presented, Zachariasen[4] advanced the interesting theory that the only glass-forming substances are those in which a small energy difference exists between the fused and crystal state. On this basis he listed the crystal structures that should form glasses, and in practically every case glasses have been made from them. The most important, of course, is silica which is the only one of direct interest here.

Coming next to the formation of crystals from a glass, it is necessary to consider the difference between this action and the formation of crystals from a melt at the liquidus temperature. In the latter case, the process takes place at a constant temperature, and the relatively free and mobile atoms or atomic groups can easily attach themselves onto the growing crystal lattice in a regular manner. In the former case, the process is not as simple because there is a considerable temperature range in which the crystals form, and as the glass is comparatively viscous the atomic groups

[1] B. E. Warren, "X-ray Diffraction of Vitreous Silica," Z. Krist., **86** [5–6] 349–58 (1933); Ceram. Abs., **14** [4] 91 (1935).

[2] B. E. Warren and A. D. Loring, "X-ray Diffraction Study of the Structure of Soda-Silica Glass," Jour. Amer. Ceram. Soc., **18** [9] 269–76 (1935).

[3] G. J. Bair, "Constitution of Lead-Oxide Silica Glasses: I–II," ibid., **19** [12] 339–58 (1936).

[4] W. H. Zachariasen, "Atomic Arrangement in Glass," Jour. Amer. Chem. Soc., **54** [10] 3841–51 (1932); Ceram. Abs., **12** [4] 145 (1933).

can not orient themselves so easily. The extensive work of Tammann[5] has shed a great deal of light on this process, and even though much of his research deals with organic glasses, the principles apply equally to silicates. He shows that crystallization occurs in two steps: the first is the formation of nuclei, that is, properly arranged atoms to form at least one unit cell, and second, the growth of these nuclei by the addition of added atomic groups. He defines two cases: one in which the nuclei form and grow in the same temperature range, and the other, in which the nuclei form at one temperature, but grow at a higher one. Blau[6] has shown how these principles can be applied to controlled production of crystals in opal glass.

How does this picture of crystallization harmonize with that of the random network structure? On slowly cooling a glass, the thermal agitation decreases and the bonds become stronger. It may be supposed that when some temperature is reached the bonds representing the crystal structure in certain localized areas form at least one unit cell. At some lower temperature, the random structure becomes so rigid that this shift can not take place. Possibly this temperature is the same as that of the transformation point of the glass. According to Bair, the network is dynamic rather than static, that is, the bonds are continually being broken by thermal agitation of the electrons and continuously re-formed by the attractive forces, or at any one temperature the number of bonds broken per second is equal to those formed per second. As the temperature decreases, the rate decreases until it reaches zero at some temperature. This temperature in an unstressed structure is believed to be the transformation point.

The formation of nuclei would be expected to follow the laws of chance in that occasionally the re-forming bonds will produce a perfect unit cell. The rate at which these happenings occur will depend on the temperature. If it is too high, thermal agitation breaks down the unit cell if it is formed, and if too low, the bonds are too rigid to permit rearrangement. In between, there is a temperature causing a maximum rate of nuclei formation. The number formed would be pro-
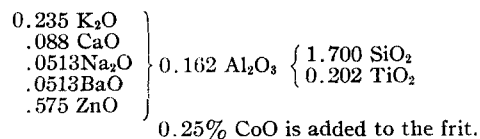
portional to the time as determined experimentally by Tammann.

The growth of the nuclei will depend on two factors: first, a breaking of the bonds to allow attachment of the proper atoms, and second, a transfer of unwanted atoms away from the crystal face. If the composition of the glass is the same as the crystal, the second effect would not take place, and we would expect growth to take place at the nuclei formation temperature. On the other hand, if the crystal is quite different from the glass, then we would expect a high temperature to be needed to give sufficient mobility to the atoms, and the growth temperature would be higher than the nuclei formation temperature. This, however, does not quite fit in with the facts, as some of the pure organic glasses of Tammann showed separate crystallization and growing ranges.

## III. The Glaze Used in This Investigation

The single glaze used was one recently developed by R. O. Lane in this laboratory for use on porcelain. While others, equally good, might have been selected, this one produced such excellent results that it was thought to be quite suitable. The complete glaze is as follows:

$$\left.\begin{array}{l} 0.235 \ K_2O \\ .088 \ CaO \\ .0513 Na_2O \\ .0513 BaO \\ .575 \ ZnO \end{array}\right\} 0.162 \ Al_2O_3 \left\{\begin{array}{l} 1.700 \ SiO_2 \\ 0.202 \ TiO_2 \end{array}\right.$$

0.25% CoO is added to the frit.

All of the composition is fritted except 0.162 $Al_2O_3$ (as kaolin); 0.088 CaO (as $CaCO_3$); and 0.170 $SiO_2$.

It should be kept in mind that the finished glaze may depart widely from this composition, owing to the solution of silica from the tile and to volatilization. The composition also varies with fritting conditions.

The base tile were made from an electrical porcelain body by the usual dust-press method. They were biscuited at 1100°C, which left them quite porous for the application of the glaze by dipping.

## IV. The Kiln and Pyrometer

The tile were fired in a vertical position in a small electric Globar kiln controlled by an induction regulator.

So many inquiries have been received in the

[5] G. Tammann, The Glassy State (Der Glaszustand). Leopold Voss, publisher, Leipzig (1933), 123 pp.; *Ceram. Abs.*, **12** [12] 418–19 (1933).

[6] H. H. Blau, "Crystallization in Glass," *Glass Ind.*, **12** [5] 110–11 (1931); *Ceram. Abs.*, **10** [7] 485 (1931).
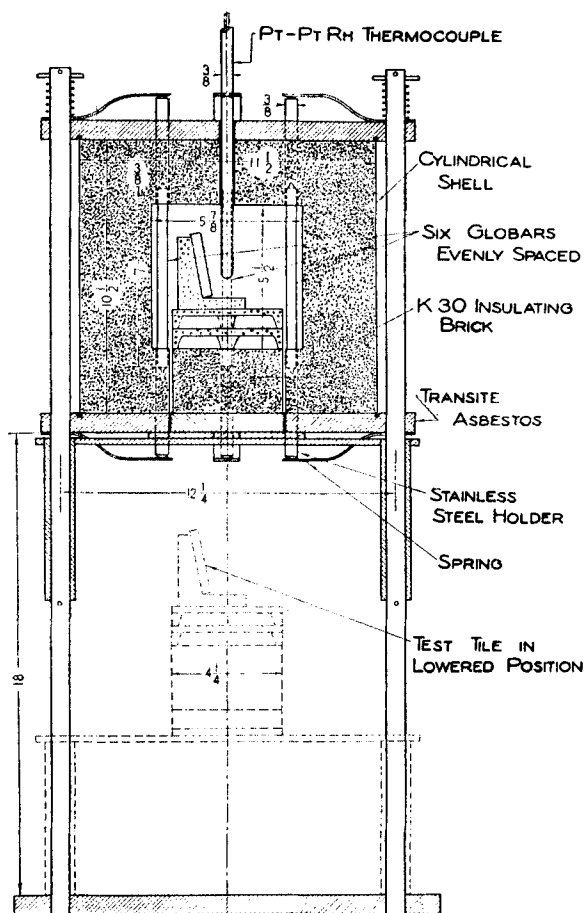
FIG. 1.—Electric kiln.

PT-PT RH THERMOCOUPLE

CYLINDRICAL SHELL

SIX GLOBARS EVENLY SPACED

K 30 INSULATING BRICK

TRANSITE ASBESTOS

STAINLESS STEEL HOLDER

SPRING

TEST TILE IN LOWERED POSITION

last few years about this kiln that a scale drawing is shown in Fig. 1. The exact control of temperatures and the ability to drop the specimens for examination during the firing makes this kiln ideal for glaze studies.

The temperature was measured by a platinum thermocouple with the junction about 1 centimeter from the center of the tile face. This couple was calibrated several times during these tests by comparing with a standard couple, which in turn was checked at the freezing point of zinc, aluminum, and copper.* The readings can be depended on to ±2°C. Such precision might seem unnecessary from the point of view of the potter but, as will be shown, 5°C makes a real change in the appearance of the glaze.

## V. Experimental Procedure

The sample tile was placed in the furnace in a

* All pure metals were obtained from the National Bureau of Standards.

vertical position and then carried through the desired schedule. While there were some deviations from the desired values in heating and cooling rates, the constant temperatures were held to an average of ±2°F.

The number of crystals on a tile were measured under the microscope using the appropriate objective. Usually ten regularly spaced stations were measured and an average taken, which was then reduced to the number of crystals per square centimeter.

The size of the crystals was measured in the same way, using a graduated ocular. In the case of the large crystals, the measurements of diameter were made with a milliammeter scale.

## VI. Results of Crystal Development

There were four distinct types of crystal produced in this glaze which may be described as follows:

### (1) Crystal (a)

This is the most prominent crystal in glazes of this type because of its rapid growth, brilliant color, and variety of forms. Some writers have referred to it as willemite ($2ZnO \cdot SiO_2$), but this identification is by no means certain. This crystal sometimes starts as a dark blue, hexagonal branching type, but soon grows as the radial light blue type (Fig. 2). The radial type consists of fine rods embedded in glass extending in all directions from the center to form, if unimpeded, a sphere. In the glaze layer, the growth in one direction is restricted to the thickness of
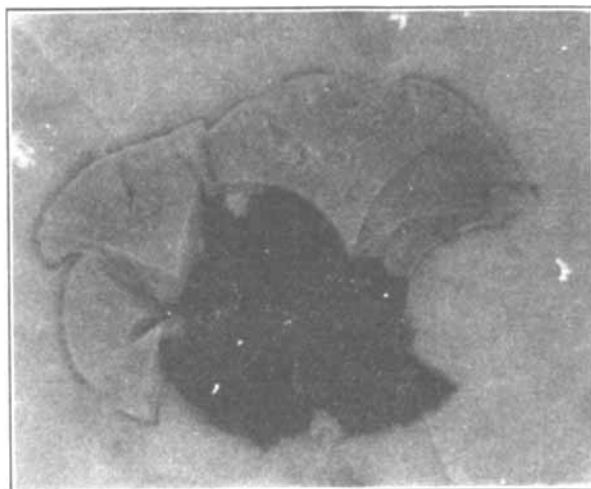


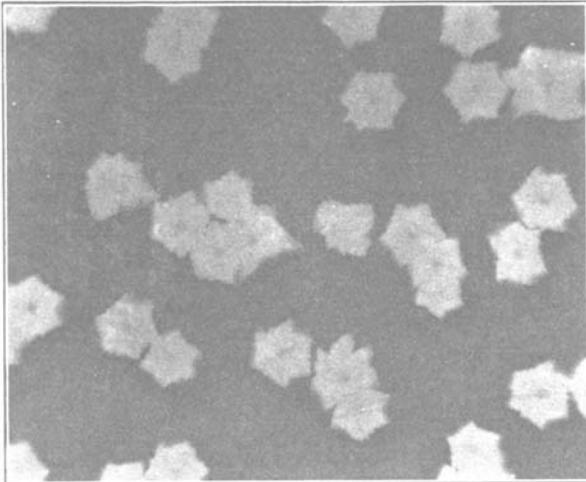FIG. 2.—Crystal (a) showing a dark blue hexagonal center with the light blue form growing out of it; 17×.

FIG. 3.—Crystal (*b*) grown at 973°C; 17×.

the glaze, so that a disk-shaped crystal results. Often the crystal starts out radially without the fern-like center and may present various forms in addition to the disk, as will be discussed later.

## (2) Crystal (b)

This is a fern-like crystal of hexagonal habit, and golden-yellow color. The size seldom exceeds 0.4 millimeter in diameter in a one-hour growing period. A number of these crystals which have been grown at 973°C are shown in Fig. 3. This crystal also shows a considerable variation in form.

## (3) Crystal (c)

This is a disk-like, dark green crystal of fairly rapid growth, occurring only at low temperatures.
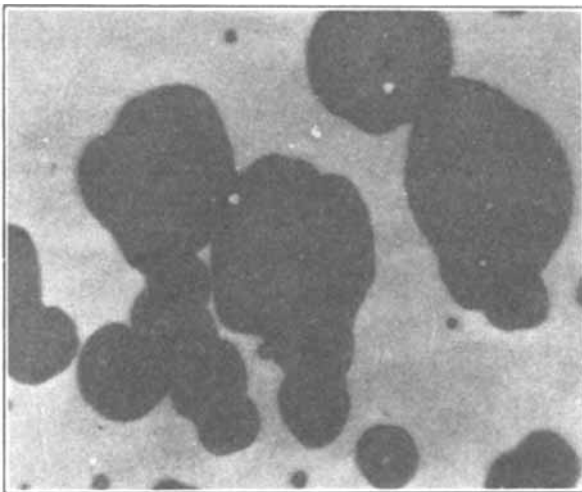


FIG. 4.—Crystal (*c*) grown at 861°C; 17×.

A few of them are shown in Fig. 4. They are evidently made up of radial fibers.

## (4) Crystal (d)

This is a small disk-like crystal, dark blue in color, that occurs in a very narrow temperature range. Some of these, grown at 1100°C, are shown in Fig. 5.

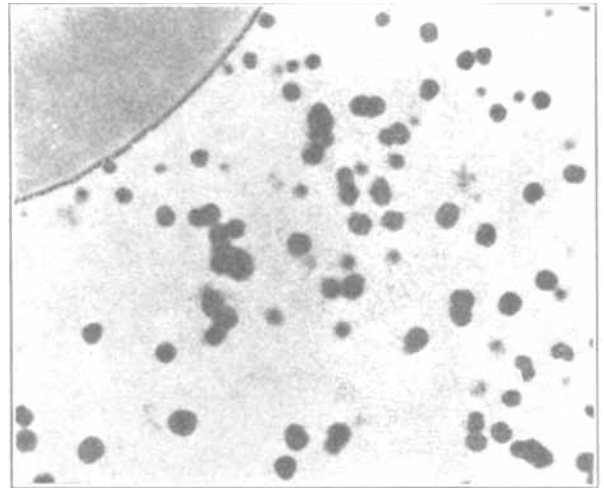A number of tile were glazed and fired at a maturing temperature of 1273°C for one-half



FIG. 5.—Crystals (*d*) grown at 1100°C; 17×.

hour. They were then cooled suddenly to various growing temperatures and held for one hour as shown in *A* of Fig. 6 for a typical case. For each growing temperature, the number and maximum size of each type of crystal was measured, giving the curves shown in Fig. 7. In the case of crystals (*b*), (*c*), and (*d*), the temperature of nuclei formation and growth overlap so that the crystals should vary in size from the smallest to a maximum, as nuclei are forming continuously during the growth period. Crystal (*b*), however, seems to show a predominance of the maximum-sized crystals, which may indicate restriction of growth due to glaze thickness in some cases.

On the other hand, crystal (*a*) has separate growth and nuclei formation ranges so that the crystals can be controlled. The nuclei form so rapidly, however, that it is impossible to complete the lower end of the curve without quenching of greater severity than the tile can withstand. It is also impossible to heat the tile rapidly enough through this range to prevent the formation of many nuclei which give, on growth, a mat glaze.

The only way to produce a limited number of (a) nuclei, therefore, is to heat the glaze above the growing range until all but a few are dispersed by thermal agitation, and then, by dropping to the growing range, large crystals will be produced.
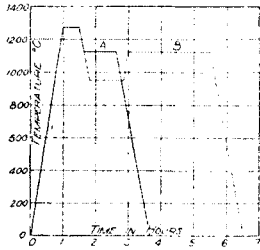


FIG. 6.—Temperature schedules.

By heating a series of tile to different maximum temperatures and then dropping them to the g r o w i n g   r a n g e (1140°C), the number of nuclei can be measured. The relation is shown in Fig. 8, where the logarithm of the number of crystals plotted against the reciprocal of the absolute temperature produces a straight line or,

$$\text{Log } \frac{n_2}{n_1} = A \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Where $n_1$ and $n_2$ = number of nuclei remaining at absolute temperatures, $T_1$ and $T_2$.
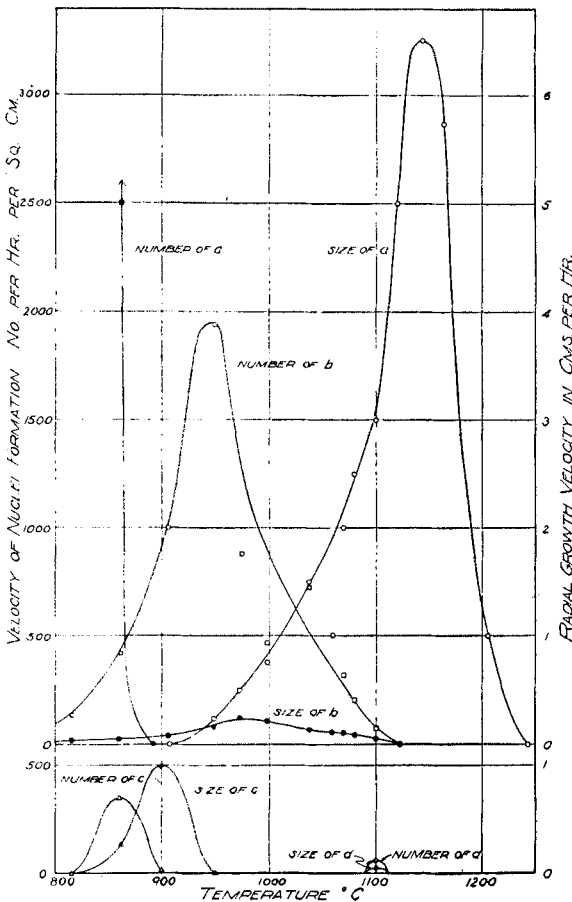
This is the familiar Arrhenius equation for the change-of-reaction rate with temperature.

It was thought at first that the nuclei might be due to undissolved mill addition, but a glaze with 100% frit showed the same effect at a slightly lower temperature. The reason why crystalline glazes must be fluid is now clear for a large part of the nuclei must be dissolved at the maturing temperature and this requires fluidity. Most writers on crystalline glazes have commented on the fact that the glaze runs on vertical surfaces, but no satisfactory explanation has been given for it.
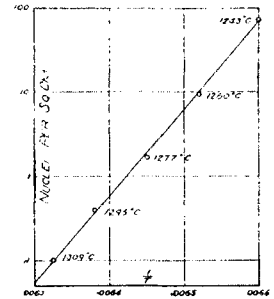
It was noted that all of the (a) crystals were not of the same size, contrary to what would be expected from the nuclei-formation curve.



FIG. 8.—Nuclei solution, crystal (a).

This can be explained either by the fact that the rate of growth is not constant or that a very few nuclei are formed at the higher temperature. It is planned to investigate this matter further, but there is fairly good evidence that the rate of growth is less in the thinner portions of the glaze.

It is of interest to speculate on the reason for several types of crystals separating out of one glass at different temperature levels. The most reasonable explanation would seem to be that, on cooling, the crystal first coming out has an energy level considerably lower than that of the glassy phase and that as the crystals form at lower and lower temperatures their energy level must approach that of the glass. If the identity of these four crystals were known, this hypothesis could be verified.

## VII. Irreversibility of Growth

After a crystal of type (a) is grown to a certain size and then cooled to room temperature, upon reheating it has been found impossible under any condition to continue the growth of the crystal. When about 1185°C is reached, the crystal gradually dissolves, leaving a faint pseudomorph of the original, and myriads of new fine crystals fill the glaze from the nuclei formed on cooling and heating. On the other hand, crystals cooled down to 950°C can be grown again at higher temperatures.



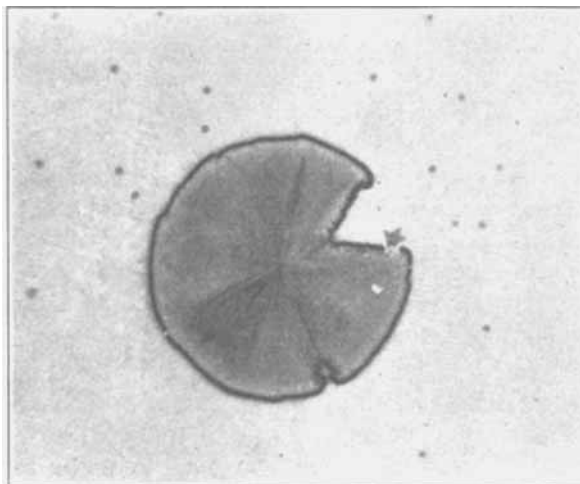FIG. 7.—Number and size of crystals at various growing temperatures.

FIG. 9.—Crystal (*a*) grown at 994°C; 17×.

It would seem plausible from this picture of the glass structure that the transformation temperature is the lower limit for regrowth. If the crystal falls below this temperature, it is surrounded by a rigid network of atoms where no thermal breaking of bonds occur. On raising the temperature, thermal agitation would seem to disrupt the crystal, as well as the glass, owing to the nearly equal energy contents of the two. We do not know how general this irreversibility is, but further research along this line should aid considerably in studies on the constitution of glass.

## VIII. Change in Crystal Form with Growing Temperature

Crystal (*a*) varies in shape and color as the growing temperature is increased. We must deal
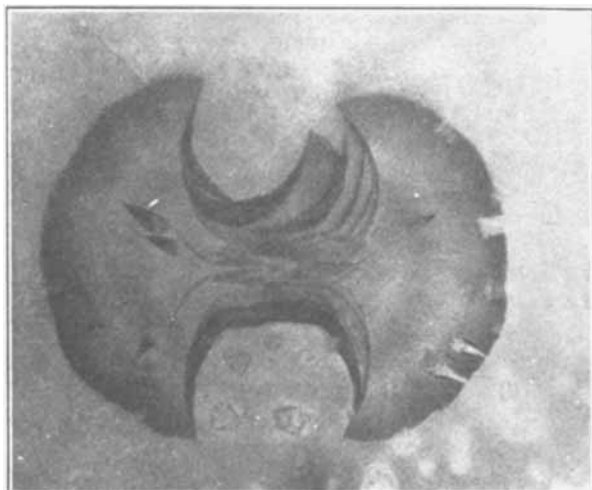


FIG. 10.—Crystal (*a*) grown at 1100°C; 17×.

in averages, of course, because there is some variation in the crystal shapes grown at any one temperature. The series of photomicrographs in Figs. 9 to 12 show this variation in shape as the growing temperature rises from 994° to 1206°C.

The color also varies from a pale green at the lower temperature to a deep blue at the higher. This fact can be utilized to grow, for example,
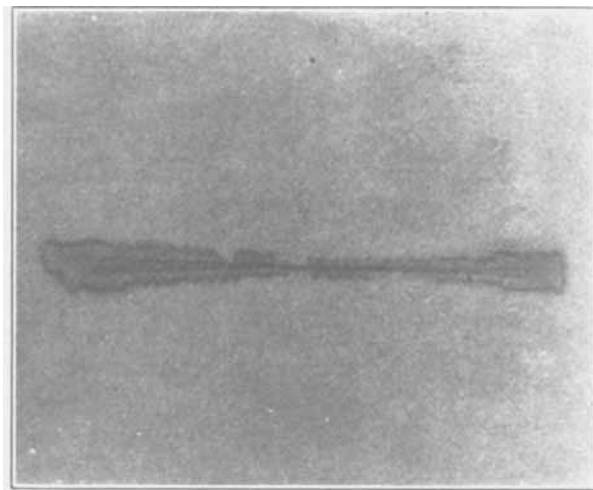


FIG. 11.—Crystal (*a*) grown at 1164°C; 17×.

very interesting flower-like crystals with a green center and blue border by following the schedule in *B* of Fig. 6. Crystals can also be grown with concentric bands by dropping the growing temperature periodically.

Crystals (*b*) show a great variation in shape with a change in growing temperature; but as this alteration is not so clear in photomicrographs as for crystal (*a*), the drawings in Fig. 13 were made to show this change. Several forms may occur at one temperature, and the similarity to snow crystals is rather striking.

## IX. Seeding Crystals

There has always been a desire on the part of potters to produce crystals at a definite place on the glaze surface. This can be done when the mechanism of crystallization is understood. It is first necessary to have a glaze free from nuclei, and, while it is at the growing temperature, to apply nuclei-forming material at the desired point. This material can consist apparently of any material changing the viscosity of the glaze locally. In this case, crystal (*a*) was produced by $Na_2CO_3$, $CaCO_3$, and ZnO, and crystal (*b*) was
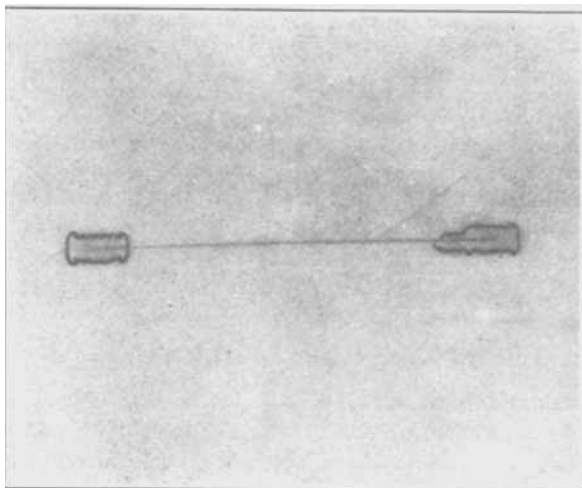
FIG. 12.—Crystal (*a*) grown at 1206°C; 17×.

formed by $SiO_2$. The particles can be applied by blowing a few of them into the hot glaze through a tube or by attaching a particle to a steel point and applying to the glaze. It is possible that particles which do not go into solution in the glaze may form crystallizing centers.

Many crystals were produced by both methods fairly consistently, but it was found difficult with the set-up used to provide a nuclei-free glaze as a base. This may have been due to dust in the kiln or particles freed from the tile base. There seems to be no reason why tile, for example, could not be produced with a three-inch round crystal in the center of each, or vases, with the crystal arranged in a definite pattern. Further investigation of this problem is being carried out at present.

## X. Influence of the Body on the Development

The solution of the base tile in a glaze alters the composition of the original glaze, oftentimes profoundly. Much theorizing has been done on the erroneous assumption that the finished glaze was of the same composition as the unfired batch. Shaw[7] noted that in a lead glaze the silica content increased between 90 and 252% on firing for a comparatively short time at 1000°C.

It is well known that a given glaze will often yield a different result when used on one body or another, which is due to the difference in absorption of the materials of the body into the glaze. In the case of this crystalline glaze, changing from

[7] D. T. H. Shaw, "Color Formation in Plumbic Glazes," Doctor's Thesis, Mass. Inst. of Tech. (1931); a portion of this thesis was published in *Jour. Amer. Ceram. Soc.*, **15** [1] 37–58 (1932).

the regular porcelain body to one containing 98%, silica altered the character of the (*a*) crystals quite materially.

## XI. Conclusions

It is realized that this study is not by any means complete, but it is hoped that the fundamentals are brought out so that further work can be carried out in a logical manner. While it is dangerous to draw very general conclusions from the results on one glaze, the following are offered with this limitation.

(1) The formation of crystals in the glaze proceeds in the same manner as for crystallization from any glass: first, a formation of nuclei and then a crystal growth. There can be either separate or simultaneous temperature intervals for nuclei formation and growth.

(2) Large crystals in a glaze can not belong to the isometric system. The hexagonal system seems to be best adapted to produce large crystals.

(3) The common type (*a*) crystals, which occur in most crystalline glazes, form nuclei so rapidly on heating up that a high maturing temperature with consequent fluidity is needed to dissolve all but a few of them. They can then be permitted to grow at a lower temperature.

(4) By proper temperature control, a single crystalline glaze can produce an almost infinite variety of effects.

(5) The conditions for crystal growth appear to be irreversible; that is, a crystal once cooled below a certain temperature can never be increased in size by raising the temperature.

(6) Crystals can be produced in any desired place by applying seeds to the glaze at the growing temperature. The use of various seeding materials will allow the growth of more than one type of crystal at the same time. The seeds need
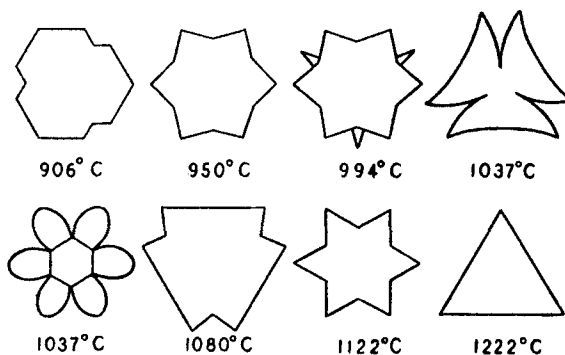


FIG. 13.

not be fragments of the same crystal that it is desired to grow.

(7) The composition of the body has quite a marked influence on the appearance of the crystal glaze due to solution of the body constituents in the fluid glaze.

(8) With a knowledge of the mechanism of crystal formation and growth and an accurate temperature control, there is no reason why com-

mercial production of crystalline glazes can not be carried out.

# THE EFFECT OF ALUMINA ON THE SURFACE TENSION OF MOLTEN GLASS*

BY C. W. PARMELEE AND C. G. HARMAN

ABSTRACT

The maximum bubble-pressure method has been used to determine the surface tensions of molten glasses. The compositions of the glasses were those typical of certain types of commercial products. A brief summary of the theory and application of the method is presented. The surface tensions of the glasses studied were of the order of 300 dynes per centimeter and the temperature coefficients were − 0.017 dyne per centimeter per degree centigrade. It was found that $Al_2O_3$ raised the surface tension of soda-lime-silica glass, the increase being almost linear between 2% $Al_2O_3$ and 8% $Al_2O_3$.

## I. Introduction

### (1) Purpose of the Investigation

The primary purpose of this work was to study the effect of alumina on the surface tension of soda-lime-silica glasses. A second purpose was to make a further study of the technique involved in the measurement of the surface tensions of glasses by the maximum bubble-pressure method.

### (2) The Value of Surface-Tension Data

Surface-tension data may be helpful for studying the liquid state of matter. There is less known concerning liquids and solutions than of the other states of matter. Surface tension is a property of liquids and solutions and should have some connection with their structure or physical make-up. It is responsible for much of the beauty of surfaces. Since it will cause the withdrawal of sharp edges and affects the rate of fining and planing of glass, it is an important factor in commercial operations.

## II. Historical

### (1) Previous Work on the Surface-Tension Determinations of Glasses

Tillotson,[1] by weighing the drops which fell

from a glass rod when heated in a blast-lamp flame, studied the surface tensions of several commercial glasses. Griffith,[2] by the use of the Quincke drop-shape method, measured the surface tensions of glasses at about 1100°C. Measurements were also made between 900 and 730°C by measuring the sag of glass fibers. Washburn and Libman[3] used a dipping cylinder method to determine the surface tensions of several glasses at 1206 and 1454°C. Lecrenier[4] used a modified form of the drop-weight method and measured the surface tensions of several glasses. Pietenpol[5] measured surface tensions of glasses at 550 to 900°C.

[2] A. A. Griffith, "Phenomena of Flow and Rupture in Solids," Phil. Trans. Roy. Soc. [London], 221A, 163 (1920).

[3] (a) E. W. Washburn and G. R. Shelton, "Viscosities and Surface Tensions of Soda-Lime-Silica Glasses at High Temperatures: I, Viscosities of Glasses at High Temperatures," Univ. Ill. Eng. Expt. Station Bull., No. 140, pp. 8–50 (April 14, 1924).

(b) E. W. Washburn and E. E. Libman, "II, Surface Tensions of Glasses at High Temperatures," ibid., pp. 53–71.

EDITOR'S NOTE: A detailed abstract of this reference is published in Ceram. Abs., 3 [12] 336–44 (1924). Tables 10, 15, 17, 23, and 24 are given in full and Figs. 1, 2, 10, 12 to 18, and 22 are reproduced.

[4] (a) A. Lecrenier, "Measurement of the Surface Tension of Glass," Bull. soc. chim. Belg., 33, 119–22 (1924); Ceram. Abs., 3 [9] 275 (1924).

(b) A. Lecrenier and P. Gilard, "Surface Tension of Molten Glass," Bull. soc. chim. Belg., 34, 27–34 (1925); Ceram. Abs., 4 [7] 190 (1925).

[5] W. B. Pietenpol, "Surface Tension of Molten Glass," Physics, 7 [1] 26 (1936); Ceram. Abs., 15 [8] 235 (1936).

[1] E. W. Tillotson, "Surface Tensions of Molten Glasses," Jour. Ind. Eng. Chem., 3, 631 (1911); 4, 651 (1912).