

## Phase Transformation and Development of Hourglass Pattern in Synthetic Barium Feldspar

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### Abstract

Hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , nucleated by ZnS impurities, has been grown in glass after heat treatment at  $1000^\circ\text{C}$ . Further annealing at the same temperature causes a polymorphic phase transformation to the monoclinic barium feldspar, celsian. This transformation is accompanied by development of an inclusion hourglass structure within which most of the ZnS impurities are concentrated. The celsian growth rate is about 0.5 mm/hr parallel to the *c*-axis.

### Introduction

#### *Hourglass Structures*

Hourglass structures are divisible into (1) inclusion patterns (Kastner, 1970), and (2) chemical or chemical-optical patterns. In inclusion hourglass patterns the alternate sectors are distinguished by high and low concentrations of primary inclusions (foreign material that existed in the matrix prior to crystallization). In chemical or chemical-optical hourglass patterns the alternate sectors differ in chemical composition because of either solution differences or secondary inclusions derived by post-crystallization unmixing phenomena. Differences in sector coloring may result from differentiation in the distribution of transitional metal ions like  $\text{Ti}^{3+}$  and  $\text{Fe}^{3+}$  between sectors (White and White, 1967; Hollister and Bence, 1967). A chemical hourglass pattern was described in augite by Preston (1966).

Inclusion hourglass patterns (Uhlman, 1963; according to Kastner, 1970) and chemical hourglass patterns are controlled by nucleation and diffusive mechanisms and by the parameters that influence these mechanisms, such as supply of material from the matrix and the viscosity of the matrix. The first group, however, is more dependent on differences of growth rates of various crystal faces. A face with a high rate of growth would incorporate the inclusions, and a face with a lower rate would manage to push away the inclusions. The structures of the second group are governed by the presence of particular ions or ionic groups in the supply material, and by differences in charge balance, atomic geometrical conditions (polyhedral coordination and vacancies),

and rates of growth of the crystal faces (Hollister, 1970).

#### *Synthetic celsian*

The present study is related to an inclusion hourglass structure developed in synthetic celsian (monoclinic barium feldspar) following a polymorphic transformation from hexacelsian (= hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , Yoshiki and Matsumoto, 1951). The hexacelsian is a metastable polymorph below  $1590^\circ\text{C}$  (Lin and Foster, 1968) and is produced by catalyzed crystallization of glass (Bahat, 1969a).

#### *Glass-ceramics*

Catalyzed crystallization of glass (Stookey, 1959) is accomplished by making a molten glass of a desired composition into which a minor catalyst such as ZnS has been added. When the glass is cooled, the catalyst precipitates spontaneously in submicroscopic particles throughout the glass. When the glass is then reheated, the submicroscopic particles promote heterogeneous nucleation and growth of crystals from the glass. The growing crystals are minute (normally 1–10 microns) and are randomly oriented. By this technique metastable rather than stable modifications in the glass are often formed, due mainly to kinetic preferences reflecting high viscosity. Products of catalyzed crystallization of glass are known as glass-ceramics.

### Experimental

A glass of stoichiometric composition  $\text{BaAl}_2\text{Si}_2\text{O}_8$  was prepared from Morgan Sand ( $\text{SiO}_2 = 99.8\%$ ), T-61 aluminum oxide ( $\text{Al}_2\text{O}_3 = 99.7\%$ ), and re-

agent grade barium carbonate, with an excess of 1 percent ZnS as a nucleating agent (Stookey, 1959; Bahat 1969a). The batch materials were weighed to an accuracy of 0.1 g and dry-mixed. A batch mixture of 600 g was melted at 1800°C in a gas-oxygen furnace for 4 hours in 20 percent Rh–80 percent Pt crucibles. A quenched patty was made from the melt by pouring it onto a cold cast-iron plate and annealing at 800°C for 1 hour. Portions of this patty were subjected to various heat treatments, as a result of which controlled nucleation and crystallization of the glass occurred. Glass crystallization was examined by X-ray diffraction.

### Results and Discussion

#### *Polymorphic transformation and hourglass development*

After heat treatment at 920°C for an hour, a translucent fine-grained glass-ceramic containing hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$  crystals was obtained which is similar to the glass-ceramics produced by various other nucleating agents (Bahat, 1969b). There was, however, an important difference. Whereas in other

glass-ceramics hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$  was quite persistent at various temperatures within its metastable field and did not transform to the stable modification after prolonged heat treatments, a heat treatment of the glass-ceramic nucleated by ZnS, at 1000°C for 1 hour, was enough for a complete crystallization of the glass to the hexagonal phase and an advanced transformation of the hexagonal phase to the monoclinic phase (celsian). Both processes were accomplished within approximately 30 minutes. After termination of the one-hour heat treatment, the sample was quenched in air to room temperature. The transformation to feldspar was accompanied by a significant crystal growth, from about 1 micron up to about 0.3 mm, with an average crystal growth rate of about 0.5 mm/hr parallel to the *c*-axis of celsian. This transformation was characterized by a concentration of the ZnS nuclei as inclusions on certain faces of the celsian crystals forming an hourglass structure (Fig. 1). The celsian crystals produced are long prisms which resemble certain celsian crystals described by Spencer (1942). In the present celsian, however, Carlsbad twins were not identified. The hourglass structures appear in hyperbolic-like sections on the (110) and (1 $\bar{1}$ 0) planes.

The inclusion hourglass patterns described by previous authors occurred in minerals which had crystallized from liquids. The inclusion hourglass pattern described in the present paper resulted from a solid-state phase transformation that occurred at 1000°C, more than 700°C below the melting point of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Lin and Foster, 1968), namely, under high viscosity conditions. The hourglass pattern was thus developed under apparently conflicting conditions. The abundant availability of supply material for the celsian growth plus the high rate of growth favored hourglass development, but the high viscosity acted as a barrier (apparently ineffective) in rejecting the inclusions. Thus, the impedance imposed on crystal growth due to the presence of inclusions is manifested by an initial rapid growth only in one direction and a relative slow growth in the direction perpendicular to it. The relative rate of growth along the latter direction may or may not increase at a later stage of the hourglass development.

It may be significant that inclusion hourglass patterns described by Buckley (1934) in potassium sulphate, by Kastner and Waldbaum (1968) in authigenic albite, in celsian (this paper), and to some extent in gypsum (Kastner, 1970) have hyperbolic-

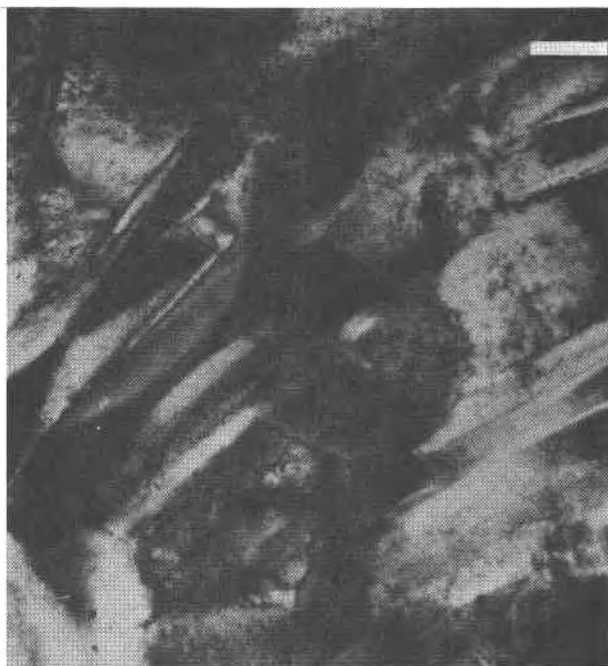


FIG. 1. Photomicrograph of synthetic prisms of celsian after polymorphic transformation from hexacelsian at 1000°C. Hourglass patterns (dark) are visible on various crystals. (Crossed polars). White line in upper right represents 40 microns.

like cross-sections, whereas chemical hourglass patterns described by Preston (1966) and Strong (1969, p. 474), in augite, and sector zoning described in staurolite (Hollister, 1970) and in clinopyroxene (Hollister and Gancarz, 1971) have cross-sections of a triangle or triangles that intersect at their apices. On the basis of kinetics of crystal-growth considerations, Gray (1971) proposed that hyperbolic patterns in authigenic albites (Kastner and Waldbaum, 1968) are expected if the growth of both its (001) and (010) faces is limited by the rate of surface nucleation, whereas triangular patterns with planar sector boundaries could be the result of the growth on each face being limited by the same mechanism—either diffusion, dislocation growth, or a phase boundary reaction.

Most publications that describe hourglass patterns are confined to crystals of low symmetries, mainly monoclinic and triclinic (a few examples were mentioned above). This may indicate that low symmetry increases the probability of differentiation of faces in a crystal in terms of structural variabilities (in charge balance and atomic geometrical conditions) which would permit sector zoning and differences in growth rates.

#### *Inclusions of ZnS*

The heat treatment of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  at  $1000^\circ\text{C}$  was initiated on a colorless, fully transparent glass. In this glass ZnS particles were uniformly distributed with grain sizes a few orders of magnitude below 1 micron. At the end of the heat treatment the material obtained became partly opaque and gray white. The change from colorless transparency resulted in part from growth of both hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$  and ZnS crystals. It is likely that during or before the growth of celsian, the growth of ZnS crystals had started. The polymorphic transformation of sphalerite to wurtzite occurs at  $1020^\circ\text{C}$  which is close to the present annealing temperature; it is possible that near this transformation temperature, ZnS ionic disordering was instrumental in ZnS crystal growth. This transformation may have also triggered the polymorphic transformation of  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , (because a relatively rapid transformation of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  occurred only in glass-ceramics which had initially been nucleated by ZnS, whereas in glass-ceramics nucleated by other nucleating agents hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$  was quite persistent within its metastable field).

The darkness of the hourglass patterns is not uni-

form (Fig. 1). The narrow central portion of the patterns is brighter than the wide parts of it. This may be explained by differences in ZnS crystal sizes. At the initial stages of hourglass development, ZnS particles were minute and were rejected by the advancing face. However, rapid ZnS crystal growth that took place at later stages caused a more intensive incorporation of ZnS crystals in the hourglass pattern. This interpretation assumes a relative uniformity in celsian's rate of growth. A constant rate of hourglass growth in authigenic albite was suggested by Kastner and Waldbaum (1968).

If, however, it should be proved that crystal growth of ZnS has not occurred during the hourglass development, then an alternative explanation for the non-uniformity of hourglass darkness would be required, namely, a change in celsian growth rate with slow growth at the beginning and rapid growth at later stages. Nonuniformity in the rate of phase transformation of this polymorphic couple has been observed before (Bahat, 1970), but with an opposite trend; a high rate of growth observed at the start and a lower rate at later stages of transformation. This of course indicates different mechanisms of both nucleation and crystal growth. The latter transformation (Bahat, 1970) was observed on stoichiometric powders without the presence of inclusions such as ZnS.

#### **Summary**

An inclusion hourglass pattern with an hyperbolic-like cross-section was artificially produced in celsian, following a polymorphic transformation from its hexagonal metastable modification ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ). The crystal growth of celsian took place at  $1000^\circ\text{C}$  under high viscosity conditions with an average growth rate of about 0.5 mm/hr. The non-uniformity in darkness of the hourglass pattern, which stems from variations in the concentration of ZnS inclusions at different regions of the pattern, resulted from changes of growth rate of either ZnS or of the celsian crystals at different stages of the  $\text{BaAl}_2\text{Si}_2\text{O}_8$  transformation. The transformation temperature of sphalerite to wurtzite is close to the temperature at which the polymorphic transformation of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  occurred, and it is possible that the former transformation triggered the latter.

#### **Recommendations for Further Research**

The hourglass pattern in the synthetic celsian described above is an example of a reproducible

process with a number of controllable variables. The kinetics of the celsian growth can be quantitatively investigated (Bahat, 1970). If such an investigation were to be accompanied by a hot-stage microscopic examination, additional valuable information on the hourglass pattern development would be gained, possibly even in relation to twinning. A simultaneous electron microscopic study of the growth of ZnS crystals in the process, as well as shape development, would be rewarding. Other methods of following the polymorphic transformation in ZnS, such as X-ray diffraction, should be considered as well. Approximate viscosity data may be obtained by dilatometric techniques, accurate determinations of viscosity can be carried out by the beam-bending method (Hagy, 1963), and some sophisticated crystal growth experimentation under controlled viscosity conditions may be accomplished by the automatic viscosity control method (Hagy, 1964). The interdependent relationship between the transformation of hexagonal  $\text{BaAl}_2\text{Si}_2\text{O}_8$  to celsian and the presence of ZnS might then be more clearly understood.

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