

EFFECT OF TEMPERATURE ON LINEAGE STRUCTURE IN SOME SYNTHETIC CRYSTALS

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ABSTRACT

Experiments on the growth from solution of large synthetic crystals of lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) demonstrate that lineage structure and attendant cracking in the crystal are eliminated if the crystals are grown at about 94°C . Crystals grown at lower temperatures have considerable lineage structure and are profusely cracked. Earlier theories as to the cause of lineage structure are reviewed and a new theory is presented. It is concluded that increased thermal agitation of the units being added to the growing crystal permit a more ordered arrangement of the atoms that make up the crystal structure.

INTRODUCTION

Geologists and mineralogists are familiar with the fact that characteristics of minerals of the same species differ widely according to the geologic environment in which they are formed. In many cases such differences have been correlated qualitatively with differences in the composition, temperature, pressure, and pH of the depositing solutions. Few workers, however, have marshalled much quantitative or direct experimental evidence in support of their conclusions. The authors contend that many of the features of natural crystals can be duplicated in the laboratory, and knowledge of the factors that control habit, physical properties, electrical properties, and structure of synthetic crystals will undoubtedly lead to a more thorough understanding of the conditions of formation of natural crystals. A relation between the amount of defects and the temperature of formation of pyrite crystals has been postulated by Smith.¹ Pyrite from low temperature deposits commonly shows an extreme development of lineage structure whereas a pyrite crystal from a higher temperature deposit will have less imperfections and lineage structure may not even be recognizable. A similar relationship has been found in synthetic crystals grown recently at the Naval Research Laboratory.

The faces of many crystals are made up of many small units with slightly different orientations. Buerger² recognized that these small sub-units are not separate unrelated units, but that they can be traced back to the original nucleus or seed; consequently he proposed the term lineages for these structures, “. . . whose orientation descend continuously

¹ Smith, F. G., Lineage structure and conditions of deposition of pyrite: *Econ. Geol.*, **37**, 519-523 (1942).

² Buerger, M. J., The significance of “block structure” in crystals: *Am. Mineral.*, **17**, 177-191 (1932).

from the same parent nucleus but whose orientations may differ." The surface between two such structures is, then, a lineage boundary, which may be an actual break or crack in the crystal.

While making a detailed study of some electrical properties of pyrite Smith³ found that the degree of development of lineage structure greatly affected the electrical properties and that the temperature of formation of pyrite apparently could be correlated with the degree of development of the lineage. Laboratory synthesis of crystals under controlled conditions affords proof that crystal imperfections such as a lineage and lineage cracks are related to temperature as Smith postulated.

EFFECT OF TEMPERATURE

Large crystals of lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) have been grown from solution at temperatures ranging from 24°C. to 94°C. The crystals were grown at a precisely controlled temperature from a saturated water solution of lithium sulfate. "Seeds" were attached to a rotating rod in the solution and were freely exposed to the solution at all times during growth. The solutions from which the crystals were grown, were, in all cases, essentially identical except for a difference in temperature and consequently a difference in the concentration of the saturated solution. The concentration of a saturated solution of lithium sulfate decreases but slightly with an increase in temperature. Scores of crystals were grown at 24°C., 43°C., and 94°C. Various types of seed crystals were used; some were tiny perfect crystals, others were cut crystal plates without flaws, and still others were badly flawed and cracked crystal plates. The rate of crystal growth was essentially the same at all temperatures.

The phrase, "lineage cracks" is proposed for those cracks obviously related to structural defects. All lineage units are not bounded by cracks, but it is believed that all are potential cracks. A seed with no cracks can be easily grown (at low temperature) up to a crystal 2 or more centimeters on a side without cracking. However, on further growth cracking may begin in the center of the crystal and gradually progress outward. The final crystal may have numerous cracks starting at or near the seed and extending outward toward the surface. They may or may not extend to the surface of the crystal. In other cases cracking may start at the surface and extend inward toward the original seed, in which case the crack will be propagated outward at the surface as the crystal continues to grow. It must be emphasized that cracking of this type is not restricted to lineage boundaries although the strain developed at lineage boundaries initiates cracking which may then cut through the lineage units themselves.

³ Smith, F. G., *op. cit.*

Those crystals grown at 24°C. are traversed by a multitude of small cracks that formed as the crystal grew. Those grown from perfect seeds are only slightly less cracked than those grown from cracked seeds. Lineage structure is also revealed by a slightly different orientation of reflection from crystal faces (see Fig. 1). In some crystals the cracks are confined to the parts of the crystals that show lineage structure. Apparently these cracks are a manifestation of the lineage structure.

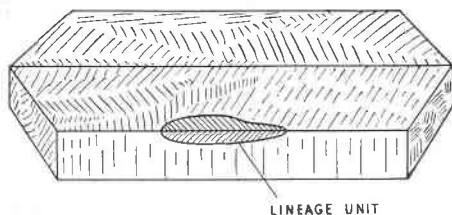


FIG. 1. Sketch of a $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal showing the effect of lineage structure on the orientation of parts of the crystal faces. The lineage unit can be traced back to the seed crystal. The boundary of a lineage unit with neighboring units may be a break or crack in the crystal. The hachure lines in the sketch are not striations, but are merely a way of diagrammatically showing that the lineage units are of slightly different orientation.

Crystals of lithium sulfate monohydrate grown at 43°C. also are traversed by many cracks and possess lineage structure. The quality of the crystals, however, is somewhat better than those grown at lower temperatures.

Crystals grown at 94°C., irrespective of whether they started from perfect or imperfect seeds, are entirely free of cracks and essentially no lineage structure is discernible.

Several different batches of crystals were grown at the various temperatures and the results were duplicated many times. There can be no doubt that, if factors other than temperature are constant, crystals of lithium sulfate monohydrate grown from solution are more nearly perfect and do not have lineage structure if grown at high temperatures.

DISCUSSION

Buerger⁴ has proposed two causes of lineage structure and the authors propose a third. (1) *Solid solution*: Buerger postulates that foreign atoms in solid solution (a foreign atom proxies for another atom) that are not uniformly arranged within the crystal lattice must cause a structural distortion which may give rise to lineage structure. Buerger⁵ states,

⁴ Buerger, M. J., *op. cit.*

⁵ Buerger, M. J., *op. cit.*, p. 189.

"Unless the crystal is precipitated under equilibrium conditions, its impurity content does not have a chance to acquire a regular distribution."

(2) *Keying of surface cracks*: Buerger⁶ reviews the evidence for the existence and size of submicroscopic cracks that form at the surface of crystals. He states, "The presence of these flaws has been suggested along two main lines of independent evidence; the discrepancies in expected and experimental strengths of solid materials and the calculated surface contraction in ionic crystals."

Convincing evidence for the existence of submicroscopic surface cracks has been presented by Griffith⁷ and Zwicky.⁸ Buerger presents a case for the keying open or plugging of the submicroscopic cracks by the rapid addition of new material either as isolated atoms or as minute crystal blocks. He proposes that rapid growth would cause the atoms or blocks to attach themselves so rapidly that the cracks would be plugged before they were able to close. Submicroscopic surface cracks might also be keyed open by the incorporation of foreign material which would fill or bridge the cracks in the crystal structure. If the foreign atoms were sufficiently large they would keep the crack open and thereby preserve the structural distortion.

(3) *Misoriented minute crystal blocks*: Evidence from a number of different methods of experimentation indicates that crystals grow not by the addition of single atoms (or ions) into the crystal lattice, but rather by the addition of minute crystal blocks or aggregates of atoms that first form in the solution and then are incorporated on the crystal surface.⁹ It is conceivable that not all of the minute crystal blocks would finally come to rest in precisely the correct position for continuation of the ideal crystal structure. Some of the blocks may be too large or the wrong shape to fill a given space between adjacent blocks. Even though the rate of addition of the blocks is very slow it is probable that some of the blocks will not align themselves in their proper place for continuation

⁶ Buerger, M. J., *op. cit.*, p. 182.

⁷ Griffith, A. A., The theory of rupture: *Proc. First Int. Cong. for Applied Mechanics*, Delft, 55-63 (1925).

⁸ Zwicky, F., On the imperfections of crystals: *Proc. Nat. Acad. Sci.*, **15**, 253-259 (1929).

⁹ Volmer, M., Zum Problem des Kristallwachstums: *Zeit. physik. Chem.*, **102**, 267-275 (1922).

Spangenberg, K., Zur Kinetik des Wachstums- und Auflösungs Vorganges von eifachen Ionengittern in wässriger Lösung: *Zeit. Kris.*, **59**, 383-405 (1924).

Volmer, M., and Weber, A., Keimbildung in übersättigten Gebilden: *Zeit. physik. Chem.*, **119**, 277-301 (1926).

Brandes, Herbert, Zur Theorie des Kristallwachstums: *Zeit. physik. Chem.*, **126**, 196-210 (1927).

of the crystal lattice. Brandes¹⁰ proposes a similar mechanism to explain some of the anomalous physical properties of some crystals. Certain anomalous properties are assumed by Smith¹¹ and others, to be a manifestation of the degree of orderliness of the crystal structure.

Buerger ascribes lineage structure to crystallization under non-equilibrium conditions (i.e., from a highly supersaturated solution). If the crystal grows from a highly supersaturated solution it may grow so fast that submicroscopic surface cracks are keyed open and added material will come to rest where it first entered the crystal lattice, and the defect may be sealed over before it can be uniformly distributed and oriented in the crystal lattice. If structural distortion is actually caused by misorientation of minute crystal blocks, then too rapid growth may cause the blocks to be covered over before they are reoriented to fit precisely in the crystal lattice.

The authors suggest that the amount of thermal agitation of the materials being added to the crystal, be they single atoms or groups of atoms, is a dominant factor in the development of lineage structure in crystals. Regardless of whether lineage structure is ascribed to foreign materials in solid solution, to the keying open of submicroscopic surface cracks, or to a misoriented grouping of minute crystal blocks, it seems plausible that the material being added to a growing crystal will be more likely to assume a position in harmony with the ideal crystal structure the greater the agitation and energy of the material. The higher the temperature of growth the greater the agitation of the material being added to the crystal. Therefore, crystals grown at high temperatures will have fewer structural defects (less lineage structure) than those grown at lower temperatures. This conclusion is substantiated by the experiments on the growth of crystals of lithium sulfate monohydrate described elsewhere in this paper.

CONCLUSION

It has been demonstrated that for the crystal $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ lineage structure and attendant cracking are essentially eliminated if the crystal is grown at high temperatures. It is concluded that increased thermal agitation at the higher temperatures permits the units that are being added to the crystal to assume a more orderly position in the lattice, whether the lineage be caused by solid solution impurities, by keying open of submicroscopic surface cracks or by a disordered arrangement of groups of atoms on the growing crystal surface.

¹⁰ Brandes, H., *op. cit.*

¹¹ Smith, F. Gordon, Variation in the electrical conductivity of pyrite: *Univ. Tor. Studies*, Geol. Ser., **44**, 83-93 (1940); and Variation in the properties of pyrite: *Am. Mineral.*, **27**, 1-19 (1942).