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THE HYDROTHERMAL GROWTH AND THERMAL DECOMPOSITION OF BOEHMITE SINGLE CRYSTALS

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ABSTRACT

Boehmite single crystals measuring up to 2 mm in size were grown hydrothermally with the nutrient temperature at 365°C and a 15°C gradient to the growth zone using 0.5N K_2CO_3 solution as solvent. On heating the crystals on a hot stage microscope, the birefringence decreased reversibly and without hysteresis up to 560°C. Above this temperature, turbid bands of γ-Al_2O_3 nucleate and grow inside the crystals in preferred crystallographic orientation, eventually filling the whole crystal.

Boehmite is a frequent constituent of many bauxite deposits, but the crystals are usually of submicroscopic size. Unusually well-crystallized specimens occur in nepheline pegmatite at the Vishnevye Mountains, Central Urals (Bonshtedt-Kupletskaya, 1947). The mineral is of interest because, although it is readily synthesized, the work of Kennedy (1959) suggested that under the conditions of growth it is always metastable with respect to diaspore, and its supposed phase boundaries with gibbsite, diaspore and corundum (Laubengayer and Weisz, 1943; Ervin and Osborn, 1951; Yanagida and Yamaguchi, 1966) reflect slow reaction rates. Boehmite single crystals are of further interest because the space group may not be *Amam* as had been assumed for X-ray crystal structure analysis (Ewing, 1935; Reichert and Yost, 1946; Milligan and McAtee, 1956). In fact, the O-H . . . O-H . . . O-H . . . chains of hydrogen-bonded oxygen atoms may have oriented polarity throughout the structure making it noncentrosymmetric. Single crystals are therefore required for the measurement of bulk properties, such as ferroelectric properties, which are needed to confirm the crystal structure.

Ervin and Osborn (1951) obtained microscopic size boehmite crystals in a few hydrothermal runs. Milligan and McAtee (1956) obtained slightly larger single crystals by precipitation in 0.1 N $AlCl_3$ and $Al_2(SO_4)^3$ solutions through the addition of a slight excess of NH_4OH, and reacting the precipitate for several days in an autoclave at 350°C–400°C and 3 to 4 kilobars.

The autoclaves used for most of the presently described work were 0.5 inch internal diameter cold seal "test tube" vessels. The nutrient and solution were sealed inside 10 mm diameter gold tubes. Some crystal growth runs were also made in Tem-Pres LRA-150 vessels fitted with a silver liner (Hill and Harker, 1968). For this vessel, a baffle with 3%

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opening was used to separate the growth zone from the nutrient zone. Fine-grained boehmite pressed into pellets was found to be most suitable nutrient. Pressed pellets of gibbsite gave almost equally satisfactory results, and the addition of crushed α-Al_2O_3 crystals to boehmite in the nutrient was also satisfactory. Reagent grade K_2CO_3 was used to make the hydrothermal solution. Solubility and transport of boehmite readily occurred across the thermal gradient. This necessitated the use of dilute K_2CO_3 solution, low thermal gradient, and small baffle opening.

The various crystalline phases were identified using the polarizing microscope and X-ray powder diffraction methods. The thermal decomposition of boehmite single crystals was observed with a polarizing microscope fitted with a high temperature heating stage.

Single crystals of boehmite formed readily at temperatures between 330 and 400°C and at pressures between 1 and 2 kbar in solutions of 0.5 to 2 N K_2CO_3. The optimum conditions for growing boehmite crystals were with the nutrient temperature at 365°C with a 15°C gradient to the growth zone using 0.5 M K_2CO_3 as the solvent. The crystals nucleated on the walls of the upper part of the vessels or sealed tubes. They were usually clear and up to 2 mm in size. Larger crystals were obtained by overgrowing on these as seeds, but these were of poorer quality. The crystals were usually tabular and of hexagonal outline.

The solution, transport and growth of boehmite occurred at temperatures and pressures at which it is reported to be metastable with respect to diaspore (Kennedy, 1959). A number of runs were therefore made to determine if diaspore would nucleate and grow in the absence of seeds, and also if diaspore would transform to boehmite in the absence of seeds. Diaspore was repeatedly synthesized from both corundum and boehmite at pressures above 2 kbar, and temperatures between 300 and 400°C in runs of three-months duration using 0.5 to 1 N K_2CO_3 solution as mineralizer. The diaspore grown above 350°C particularly at 4 kbar, always consisted of fibrous crystals while those grown nearer 300°C and 2 kbar were equant. The reaction rate below 300°C was extremely slow. In no case could diaspore be transformed into boehmite.

On heating boehmite crystals on a hot-stage microscope, the birefringence decreased reversibly and without hysteresis up to 540°C. Above this temperature, turbid zones nucleate and grow inside the crystals in preferred crystallographic orientation. These bands, presumably of γ-Al_2O_3 eventually grow out, completely filling the whole crystal. If the crystal is cooled after the development of the turbid zones, the birefringence of the remaining clear zones decreases reversibly. The nucleation of the turbid zones occurs mainly inside the crystals, rarely at the surface.

The hydrothermal growth of boehmite crystals rather than diaspore under the conditions described above is dependent on their relative ease of nucleation. The use of polycrystalline boehmite as nutrient definitely minimizes the probability of diaspore nucleating and so facilitates the growth of boehmite. On the other hand, if corundum, which is structurally related to diaspore, is used as nutrient, then the probability of diaspore nucleating is greatly enhanced. Higher pressures and longer reaction times favor the nucleation of diaspore. Of course, if diaspore seeds are present, then overgrowth readily occurs on these seeds. The use of more alkaline solutions to dissolve the Al_2O_3 also favors the nucleation and growth of diaspore. However, new unidentified phases are present when the concentration of the solution is greater than 2 N. Boehmite will also nucleate under all these conditions, but its growth rate decreases with temperature, increased pressure, alkalinity of the solution, and time. It was necessary in these experiments, therefore, to avoid a mechanism which would favor transformation to diaspore.

The decomposition of boehmite to give γ-Al_2O_3 is dependent on the structural control exercised by the Al-O octahedra in the boehmite cell. The octahedra are linked by hydrogen bonds which are broken at higher temperatures and the b-axis shortens to [11.0] of γ-Al_2O_3 due to formation of a vacant octahedral hole.

The decomposition temperature of $540 \pm 10°C$ found here is higher than the 450°C previously reported by Saalfeld (1958), who used polycrystalline boehmite obtained from gibbsite single crystals. The difference is undoubtedly due to the restraining effect exercised by the larger size crystals.

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ANNEALING CHARACTERISTICS OF METAMICT GADOLINITE FROM RODE RANCH TEXAS

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ABSTRACT

Chemically analyzed metamict gadolinite was heated in air at varied temperatures and time intervals. At 1080°C gadolinite was well crystallized by 1 hour. At 880°C samples showed a lesser but constant level of crystallinity. At 780°C and 730° the gamma phase reported at 1300° by Lima-de-Faria (1964) was predominant, but it remained poorly developed after heating for several days. At 680° no recrystallization was detected after one week heating. DTA showed a large exotherm at 810° and smaller exotherms at 850° and 900°. The degree of recrystallization, determined by three X-ray diffractogram peak areas, was influenced more by temperature than by heating time.

INTRODUCTION

Completely metamict gadolinite (having no X-ray diffraction pattern) will recrystallize, giving the X-ray diffractogram of crystalline gadolinite. Problems arise, however, in obtaining consistent results after annealing metamict minerals prior to X-ray analysis if (1) other metamict impurities are present, (2) polymorphs occur, or (3) insufficient or excess temperature is applied during the annealing treatment. The present study describes in detail the annealing character of a chemically analyzed gadolinite; hopefully the data can be used for optimum recrystallization of metamict gadolinite specimens.

Standardized X-ray identification of a number of metamict minerals is considered by Lima-de-Faria (1964), who heated gadolinite in air and nitrogen at fixed conditions of 700°C for 3 hours, 1000° for 1 hour, and