The structure of margarosanite is probably very similar to that of synthetic Ca$_2$BaSi$_3$O$_9$. This in turn is closely related to other substances containing X$_3$O$_e$ rings: compare the cell dimensions given.

These data show the existence of a series of metasilicates of large divalent cations containing X$_3$O$_e$ rings. These structures can also exhibit cation ordering; thus the Ca/Ba ratio is known to be fixed in Ca$_2$BaSi$_3$O$_9$, and it does not form solid solutions with either α-CaSiO$_3$ or BaSiO$_3$. Water is not an essential constituent of Ca$_2$BaSi$_3$O$_9$ as crystals are readily grown from melts at ~1320° C.

The authors hope that other less well characterized metasilicates of large cations will be studied to enable an extension of this classification.

REFERENCES


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THE THORITE→HUTTONITE PHASE TRANSFORMATION AS DETERMINED BY GROWTH OF SYNTHETIC THORITE AND HUTTONITE SINGLE CRYSTALS


The phase transformation, tetragonal ThSiO$_4$ (thorite)→monoclinic ThSiO$_4$ (huttonite) is contrary to expectation, in that it involves formation of the denser modification at a higher temperature. The transformation and/or synthesis of either phase have been investigated by Pabst (1951, 1952), Frondel and Collette (1957), Fuchs (1958), Harris (1959) and Mumpton and Roy (1961), none of whom restricted the equilibrium transformation to a narrow temperature interval. Pabst, studying impure natural thorite, suggested that the transformation occurred over the temperature range 700–1200° C. Harris, using solid state methods, was able to synthesize only huttonite at temperatures ≥ 1250° C. Mumpton and Roy indicated the possibility that huttonite is stable at all temperatures, with thorite a metastable phase.

The present authors investigated the transformation using solution growth of the preferred modification of ThSiO$_4$ single crystals as a criterion for phase stability at a given temperature. Experiments designed
to grow ThSiO₄ from alkali ditungstate or dimolybdate solutions revealed that only thorite could be grown below 1225 ± 10° C., whereas above this temperature only huttonite could be grown. These data suggest that the equilibrium transformation temperature (1 atm) is 1225° ± 10° C.

The growth experiments were performed in air atmosphere in covered platinum containers, as described in Fig. 1. Absolute temperatures as well as thermal gradients were determined by use of the Pt-Pt₉₀Rh₁₀ thermocouples shown in Fig. 1. For a given temperature use of Li₂O ·2WO₃, Li₂O ·2MoO₃, or Na₂O ·2WO₃ as solvents for ThSiO₄ (solubility of ThSiO₄ in each of these solvents increases with temperature) resulted in formation of crystals of identical crystallographic modification and crystal habit. Nutrient material, in the hottest region of the container (bottom), was in the form of 1:1 mole ThO₂·SiO₂ pellets, pressed from 99.9% SiO₂ and 99.9% ThO₂ < 200 mesh powders. Supersaturation required to induce nucleation and growth of either modification was obtained using thermal gradients 10–20°/cm. Under these conditions nucleation occurred within 24 hrs at 1200 ± 100° C. in the coolest regions

Fig. 1. Method for growth of thorite and huttonite crystals.
of the solution, usually at solution-platinum interfaces. After runs of three days to one week in duration, the solution was decanted off the crystals at as near as possible their formation temperature. The crystals, adhering to the upper container wall, were readily removed at room temperature.

The synthetic thorite crystals (Fig. 2a), identified by x-ray methods, have a growth habit typical of zircon with well-developed prism \(\{110\}\) and dipyramid \(\{111\}\) forms. The largest crystals attained dimensions 5 mm (parallel to \(\langle c\rangle\)) \(\times\) 2 \(\times\) 2 mm. Good quality crystals are transparent and colorless with indices of refraction, \(\omega = 1.827 \pm 0.003, \epsilon = 1.885 \pm 0.003\). A spectrographic analysis of optically clear crystals revealed

\(<0.1\text{ wt }\%\text{ W as the only detectable impurity. Their density determined by pycnometer is } 6.63 \pm 0.10 \text{ g/cm}^3\text{, comparing to a density of } 6.67 \text{ g/cm}^3\text{, computed from x-ray data.}\)

The growth habit of synthetic huttonite (Fig. 2b) resembles monazite with \(\{100\}\) faces well developed. The largest crystals were 2 \(\times\) 2 \(\times\) 2 mm. Spectrographic analysis of the best crystals revealed approximately 0.1 wt % W (or Mo) as the only detectable impurity. Their pycnometer density is 7.20 \(\pm\) 0.10 g/cm\(^3\), comparing with an x-ray density of 7.18 g/cm\(^3\). The crystals are colorless and transparent with indices of refraction \(\alpha = 1.900 \pm 0.003, \gamma = 1.930 \pm 0.005\). They displayed no sign of inverting to thorite when air-quenched from 1225 to 25\(^\circ\) C.

The general approach of growing single crystals from various solvents at different temperatures as criterion for phase stability may be applica-
ble to the study of other sluggish phase transformations when it is im-
portant to know the true equilibrium crystal structure for a given tem-
perature. The principal limitation is availability of solvents which do not
contaminate the crystallizing phase under study.

References


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A DISTINCTION BETWEEN NATURAL AND SYNTHETIC EMERALDS

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INTRODUCTION

When crystals are grown under different physico-chemical conditions,
their crystal faces exhibit different growth patterns. Growth patterns on
crystal faces vary so sensitively according to the differences in growth
conditions that one can easily notice the difference in localities if he ob-
serves surface structures of crystal faces under a reflection microscope.
The writer previously reported in this journal that hematite crystals
from different localities exhibit different characteristics of surface struc-
tures, from which he deduced the differences in supersaturation condi-
tions of hematite formation between each locality (Sunagawa, 1962).
Tolansky and Sunagawa (1959, p. 60) also observed distinct differences
of surface structures of crystal faces between natural and synthetic
diamonds and discussed the differences of mechanism and conditions of
crystal growth between the two diamonds.

A result of comparative studies on the surface structures of crystal
faces of natural and synthetic emeralds will be reported in this paper.
The present observations using a reflection and phase contrast microscope
have shown that a clear distinction can be made between natural and
synthetic emeralds. These observations have also given information
concerning the differences in conditions of crystal growth between the
two emeralds, which will also be discussed in this paper.

A hexagonal prismatic crystal of Chatham’s synthetic emerald was