

Synthesis and Growth of Fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) from a TiO_2 Flux and Its Relation to the System BaTiO_3 - SiO_2

C. R. Robbins

Institute for Materials Research, National Bureau of Standards,
Washington, D.C. 20234

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Crystals of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (synthetic fresnoite) up to 5 mm in longest dimension have been grown by slow cooling of a TiO_2 -rich liquid of initial composition $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$. The synthetic crystals are essentially identical to their mineral equivalent in morphology, cleavage, optical properties and unit cell dimensions. X-ray powder diffraction data previously reported for the compound BaTiSiO_5 ("barium sphene") is that of $\text{Ba}_2\text{TiSi}_2\text{O}_8$. Apparently the compound BaTiSiO_5 has never been synthesized and the system BaTiO_3 - SiO_2 is not binary.

Key words: $\text{Ba}_2\text{TiSi}_2\text{O}_8$; BaTiSiO_5 ; crystal growth; fresnoite; phosphor; piezoelectric; system BaTiO_3 - SiO_2 ; TiO_2 solvent.

1. Introduction

Crystals of Fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) were found by Alfors, Stinson, Matthews, and Pabst [1]¹ in a study of the minerals of eastern Fresno County, California. The mineral occurs as subhedral to euhedral tetragonal crystals, elongated slightly in the [001] direction, with forms {001}, {110} and one distinct cleavage, (001). Composition was established [1] to be $\text{Ba}_2\text{TiSi}_2\text{O}_8$ with traces of impurities by arc emission spectrographic analyses. The crystals ranged in size from 0.1 to 3 mm with an average longest dimension of 0.3 mm, and exhibited pleochroism in transmitted polarized light (from light yellow to colorless), anomalous blue interference colors and pale yellow fluorescence under ultraviolet light (2652 Å). The optical and x-ray data [1] are summarized in table 1. Alfors et al., also prepared synthetic $\text{Ba}_2\text{TiSi}_2\text{O}_8$ in formula proportions ($5\frac{1}{2}$ hr at 1350 °C) and obtained a sintered compact whose x-ray diffraction pattern was identical with that of the mineral.

The crystal structure of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ was determined by Masse, Grenier, and Durif [2], using synthetic crystals, and independently by Moore [3], using a natural crystal from the type locality. Masse et al. reported growth of crystals from a stoichiometric oxide mixture melted at about 1350 °C and cooled at 40 °C per hour. They obtained a cell of $a=8.52$, $c=5.21$ Å for their synthetic crystals and Moore reported $a=8.52 \pm 0.01$, $c=5.210 \pm 0.005$ Å for the mineral crystal. Both structures were assigned to space group $P4bm$; R values of

Table 1. X-ray and optical crystallographic data for fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$)^a

| X-RAY DATA | |
|---------------------|--|
| System: | Tetragonal |
| Space Group: | $P4/m\bar{b}n$, $P4bm$ or $P\bar{4}b2$ |
| Unit Cell: | $a=8.52 \pm 0.01$ Å, $c=5.210 \pm 0.005$ Å $c/a=0.6115$ |
| Density: | 4.43 ± 0.02 (measured) 4.45 (calculated) |
| Cell content: | $Z=2$ |
| OPTICAL DATA | |
| Optic sign: | Uniaxial (–) |
| Refractive indices: | $w=1.775 \pm 0.003$ $\epsilon=1.765 \pm 0.003$ |
| Pleochroism: | O = colorless E = yellow |

^a Data of [1] for mineral type specimen from eastern Fresno County, California.

11 percent for (hko), 13 percent for (okl) were obtained in reference [2], while an overall R value of 11.1 percent (all reflections) was obtained in reference [3]. Similarities of the structure of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ to that of hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) [2] and that of melilite ($\text{Ca, Na}_2(\text{Mg, Al})\text{Si}_2\text{O}_7$) [3] were noted. In the structure of $\text{Ba}_2\text{TiSi}_2\text{O}_8$, Si_2O_7 groups are linked to square pyramidal TiO_5 groups to form sheets that are

¹ Italicized figures in brackets indicate the literature references at the end of this paper.

parallel to (001) and are held together by Ba ions. An interesting feature of the structure is the presence of Ti in five-fold coordination in the square pyramid, with four Ti-O distances of $2.00 \pm 0.04 \text{ \AA}$ and a fifth Ti-O distance of $1.66 \pm 0.08 \text{ \AA}$ for the pyramidal oxygen atom [3].

$\text{Ba}_2\text{TiSi}_2\text{O}_8$ was prepared as a crystalline powder by Blasse [4] by heating mixtures of BaCO_3 , TiO_2 and SiO_2 in oxygen at 1000 to 1100 °C. He obtained a unit cell of $a=8.52$, $c=5.21 \text{ \AA}$ (in agreement with [1, 2, 3]) and reported a blue-green fluorescence under excitation with 254 mm radiation and with cathode rays. The spectral energy distribution of emission, the diffuse reflection spectra, the excitation spectra, the decay time of fluorescence ($3 \cdot 10^{-3} \text{ s}$) and the temperature dependence of the phosphor were studied. The exceptionally efficient fluorescent properties of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ at room temperature were attributed to the presence in the structure of the pyramidal TiO_5 group.

The initial objectives of the present study were: (1) to grow small single crystals of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ for other physical property measurements, and (2) to prepare crystals of the compound BaTiSiO_5 (reported by Rase and Roy [5] in their study of the system $\text{BaTiO}_3\text{-SiO}_2$) for x-ray analysis and comparison with crystals of synthetic sphene (CaTiSiO_5) previously described by Robbins [6], and Brower and Robbins [7].

2. Phase Relations

The phase diagram for the ternary system $\text{BaO-TiO}_2\text{-SiO}_2$ in the region of the composition $\text{Ba}_2\text{TiSi}_2\text{O}_8$ has not been reported. The work of Masse et al. [2] indicated congruent melting for $\text{Ba}_2\text{TiSi}_2\text{O}_8$ near 1350 °C.

In the course of the work on their phase diagram for the binary system $\text{BaTiO}_3\text{-SiO}_2$ (fig. 1) Rase and Roy [5] obtained tabular, biaxially positive crystals showing bluish interference colors and having an average

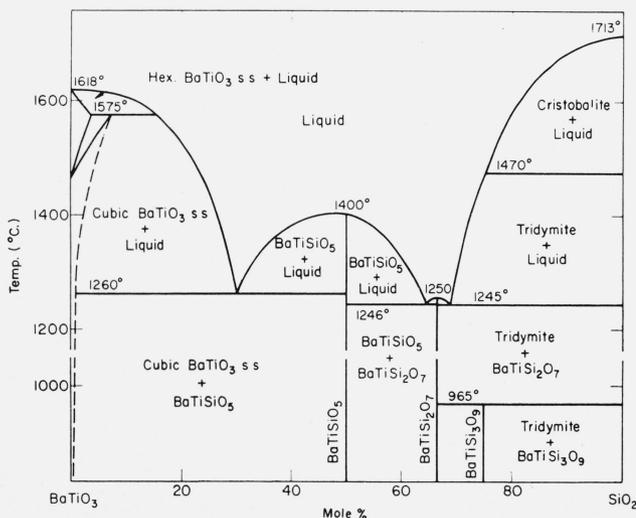


FIGURE 1. Phase equilibrium diagram for the system $\text{BaTiO}_3\text{-SiO}_2$, Rase and Roy [5].

index of refraction of 1.775. They assigned to them the formula BaTiSiO_5 and the congruent melting point 1400 °C. They noted [5] that the refractive index of the glass of mole ratio $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$ was greater than that of the average index of the crystals (1.86 as compared with 1.77). This suggested a negative coefficient of thermal expansion for the crystals but the coefficient was found to be of the order of 50×10^{-7} per °C. Polymorphism was not observed. Rase and Roy [5] reported unindexed x-ray powder data for BaTiSiO_5 and suggested a structural similarity to sphene (CaTiSiO_5). Their x-ray data were subsequently indexed by ASTM personnel (BaTiSiO_5 , card 11-150) on the basis of a tetragonal cell ($a=8.525$, $c=5.22 \text{ \AA}$), the cell later obtained by [1, 2, 3] for fresnoite, $\text{Ba}_2\text{TiSi}_2\text{O}_8$.

The x-ray powder diffraction data for BaTiSiO_5 ([5], ASTM indexing) and for $\text{Ba}_2\text{TiSi}_2\text{O}_8$ [1] are listed in table 2 and shown schematically in figure 2. It may be concluded from comparison of the two patterns that the data are essentially identical, and the two independent studies were of the same compound. The composition $\text{Ba}_2\text{TiSi}_2\text{O}_8$ has been established by chemical analyses [1] and by single crystal x-ray structure determination [2, 3], and is therefore the composition of the phase obtained by Rase and Roy [5] in their study of the system $\text{BaTiO}_3\text{-SiO}_2$ and described by them as BaTiSiO_5 , the barium analog of sphene. Apparently BaTiSiO_5 has not yet been synthesized and the system $\text{BaTiO}_3\text{-SiO}_2$ is not binary. The liquidus surface of the phase diagram for the system (fig. 1, [5]) must be that of a cut in the ternary system $\text{BaO-TiO}_2\text{-SiO}_2$. The congruent melting point of 1400 °C given for BaTiSiO_5 then represents a point on this liquidus surface at which the compound $\text{Ba}_2\text{TiSi}_2\text{O}_8$ would start to crystallize from a TiO_2 -rich liquid of mole ratio $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$. The large observed difference between index of refraction of glass and average index of crystals (1.86 versus 1.77) [5] apparently resulted from comparison of a glass of composition $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$ with crystals of composition $2\text{BaO} \cdot 1\text{TiO}_2 \cdot 2\text{SiO}_2$.

3. Experimental Procedure

On the basis of the preceding conclusions two ternary compositions, $2\text{BaO}:1\text{TiO}_2:2\text{SiO}_2$ (fresnoite) and $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$ ("barium sphene"), were prepared in 20 g amounts from high purity BaCO_3 , TiO_2 and SiO_2 , and thoroughly mixed mechanically. The mixtures in 40 ml platinum crucibles were heated in a platinum wound muffle furnace in air to near 1425 °C, held for 1 hr and cooled at 3 deg per hour to 1000 °C and then at 10 °C per hour to room temperature. Products obtained were examined by light microscopy, x-ray powder diffractometry and single crystal x-ray precession methods.

4. Results and Discussion

Crystals of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (fresnoite) up to 5 mm in longest dimension were obtained from the experiment

TABLE 2. X-ray powder diffraction data for BaTiSiO₅ and Ba₂TiSi₂O₈

| BaTiSiO ₅ ^a | | | Ba ₂ TiSi ₂ O ₈ ^b | | |
|-----------------------------------|----------|----------------|---|----------|----------------|
| <i>d</i> (Å) | <i>I</i> | <i>hkl</i> | <i>d</i> (Å) | <i>I</i> | <i>hkl</i> |
| | | | 6.0 | 10 | 110 |
| 5.20 | 15 | 001 | 5.20 | 20 | 001 |
| 4.26 | 10 | 200 | 4.26 | 10 | 200 |
| 3.93 | 15 | 111 | 3.94 | 15 | 111 |
| 3.81 | 25 | 210 | 3.81 + | 20 | 210 |
| 3.29 | 60 | 201 | 3.305 | 50 | 201 |
| | | | 3.01 + | 10 | 220 |
| 2.694 | 30 | 310 | 2.695 | 20 | 310 |
| 2.606 | 45 | 002 } 221 } | 2.610 | 20 | 002 } 221 } |
| 2.394 | 15 | 311 } 112 } | 2.392 | 10 | 311 } 112 } |
| 2.222 | 15 | 202 | 2.222 | 10 | 202 |
| 2.151 | 35 | 212 } 321 } | 2.150 | 30 | 212 } 321 } |
| 2.069 | 25 | 410 | 2.065 | 25 | 410 |
| 2.010 | 10 | 330 | 2.010 | 10 | 330 |
| 1.971 | 15 | 222 | 1.975 | 10 | 401 } 222 } |
| 1.922 | 25 | 302 } 411 } | | | |
| 1.906 | 10 | 420 | | | |
| 1.882 | 30 | 331 } 312 } | 1.870 | 20 | 331 } 312 } |
| 1.621 | 15 | 412 } 431 } | 1.619 | 15 | 412 |
| 1.611 | 10 | 203 | | | |
| 1.593 | 15 | 511 | 1.591 | 15 | 332 |
| 1.582 | 20 | 520 } 213 } | 1.580 | 15 | 520 } 213 } |

^aData of Rase and Roy [5] indexed by ASTM on the basis of a tetragonal cell with $a=8.525$ Å and $c=5.22$ Å. Cu/Ni radiation, $\text{CuK}\alpha=1.5418$ Å.

^bData of Alfors, Stinson, Matthews and Pabst [1]. Their tetragonal unit cell has dimensions: $a=8.52$ Å, $c=5.210$ Å. Intensities were estimated from comparison with a photographic scale. Cu/Ni radiation, $\text{CuK}\alpha=1.5418$ Å.

with the 1BaO:1TiO₂:1SiO₂ (“barium sphene”) mixture described in section 3. The general appearance of the resulting product is shown in figure 3. The crystals are tetragonal first order prisms elongated in the [001] direction with forms {001} and {110}, the morphology previously observed for the mineral [1]. The crystals are transparent, colorless, uniaxial negative and show anomalous blue interference colors in transmitted polarized light. Pleochroism reported for the mineral (O = colorless, E = yellow) [1] was not observed for the synthetic material. Since chemical analyses of the type mineral [1] show a range of Fe content (Fe reported as FeO) of 0.77 to 1.0 weight percent, both the pleochroism and color of the mineral (“lemon or canary yellow” [1]) may result from the

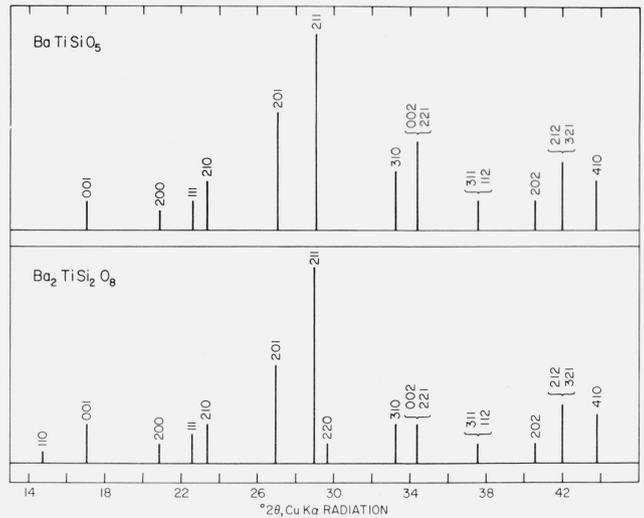


FIGURE 2. Schematic partial x-ray powder diffraction patterns for BaTiSiO₅ and Ba₂TiSi₂O₈.

The data for BaTiSiO₅ is from Rase and Roy [5] (ASTM indexing) and the data for Ba₂TiSi₂O₈ is from Alfors, Stinson, Matthews, and Pabst [1].

presence of Fe ions as a major impurity. The (001) cleavage reported for the mineral [1] was observed for the synthetic crystals. The piezoelectric response reported by [2] for synthetic Ba₂TiSi₂O₈ was also observed in this study. Unit cell dimensions obtained by x-ray powder diffractometry agree within limits of error, with the values $a=8.52$, $c=5.21$ Å reported by

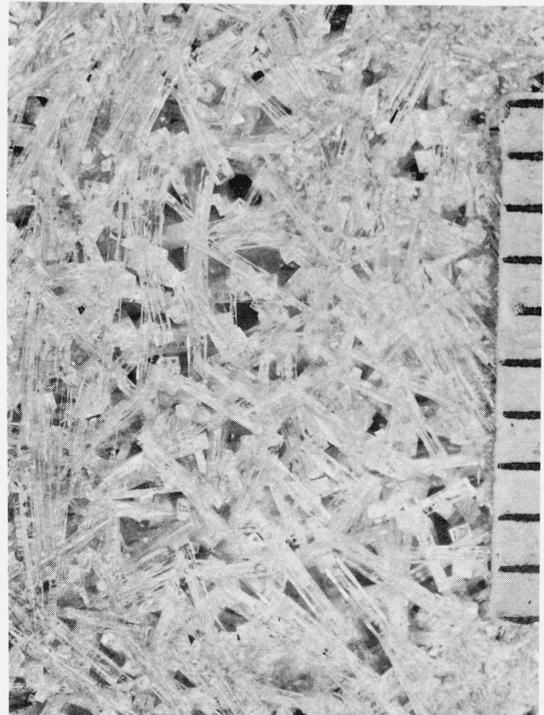


FIGURE 3. Single crystals of Ba₂TiSi₂O₈ grown by slow cooling of a melt of initial mole ratio 1BaO:1TiO₂:1SiO₂.

The smallest division of the scale is 1 mm.

[1, 2, 3]. Optical and x-ray examination of a bulk sample of crystals and matrix from this experiment showed the presence of additional phases. The compound BaTi_4O_9 (Rase and Roy [8]) was identified by x-ray powder diffractometry as the next most abundant phase and was present in appreciable amounts.

The $2\text{BaO}:1\text{TiO}_2:2\text{SiO}_2$ experiment of section 3 gave sintered microcrystalline $\text{Ba}_2\text{TiSi}_2\text{O}_8$. The general appearance of the material suggested incipient melting. Unit cell dimensions agreed with those of crystals obtained by growth from the TiO_2 solvent ($1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$ mixture) indicating only slight solubility of TiO_2 in $\text{Ba}_2\text{TiSi}_2\text{O}_8$. Differential thermal analysis of the material to 1000°C gave no indication of a phase transformation.

5. Summary and Conclusions

Crystals of synthetic fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) up to 5 mm in longest dimension have been grown by slow cooling of a TiO_2 -rich melt of initial composition $1\text{BaO}:1\text{TiO}_2:1\text{SiO}_2$ in a small-scale experiment. The solubility of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ in this liquid at 1400°C is of the order of 86 percent by weight. The synthetic crystals are essentially identical to their mineral equivalent in morphology, cleavage, indices of refraction, anomalous interference colors and unit cell

dimensions. The color and pleochroism of the type mineral may result from the presence of Fe ions as a major impurity. Solubility of TiO_2 in $\text{Ba}_2\text{TiSi}_2\text{O}_8$ is small. The system $\text{BaTiO}_3\text{-SiO}_2$ is not binary and the compound BaTiSiO_5 ("barium sphene") apparently has never been synthesized.

6. References

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