Tetrahedral Ti^{4+} in the Solid Solution Ba$_2$Ti$_{1+x}$Si$_{2-x}$O$_8$ (0 ≤ x ≤ 0.14)

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A previously unreported solid solution based on fresnoite, Ba$_2$TiSi$_2$O$_8$, has been found in the BaO : TiO$_2$: SiO$_2$ system. It forms by partial replacement of Si by Ti and has the formula Ba$_2$Ti$_{1+x}$Si$_{2-x}$O$_8$ (0 ≤ x ≤ 0.14). Infrared spectra confirm that the excess Ti is tetrahedrally coordinated. © 1996 Academic Press, Inc.

INTRODUCTION

The preferred coordination of Ti^{4+} in oxides is octahedral. Although some instances of fivefold coordination have been reported (1–5), examples of tetrahedral coordination are uncommon and appear to be limited to Ba$_2$TiO$_4$ (6), Li$_4$TiO$_4$ (7), and Ti-substituted garnets (8). During the examination by electron probe microanalysis (EPMA) of BaTiO$_3$ ceramic, an unexpected impurity phase was found to have a composition similar to that of the mineral fresnoite (3), Ba$_2$Ti$_1$Si$_2$O$_8$, but with a Ti : Si ratio approximately 1.2 : 1.8. The fresnoite structure, as determined by Moore and Louisnathan (3, 4) and Masse *et al.* (5), is rather unusual. It consists of sheets of Ti–O tetragonal pyramids and Si–O tetrahedra held together by Ba–O bonds. If a solid solution forms by the replacement mechanism Si ⇌ Ti, then one may expect excess Ti to occupy Si sites in a tetrahedral coordination. From the work of Tarte (6) and Dubey and West (7), it is clear that tetrahedrally coordinated Ti^{4+} has been detected by characteristic vibrations in the infrared spectrum. The existence of this previously unreported fresnoite solid solution involving the substitution Ti^{4+} ⇌ Si^{4+} is investigated here, and a new example of Ti^{4+} in tetrahedral coordination is shown to exist.

EXPERIMENTAL

Samples were prepared from the reagents BaCO$_3$, TiO$_2$ (Aldrich, 99+%), and SiO$_2$ (Thermal Syndicate Ltd., 99.9%), all of which were dried prior to use. Appropriate stoichiometric quantities were weighed, ground together in an ethanol slurry, dried, and fired at 1000–1200°C for a minimum of 18 h in a Pt crucible in an electric muffle furnace. The samples were then pelleted and fired at temperatures of 1200–1350°C with periodic regrinding. Sam-

ples were characterized by X-ray powder diffraction, XRD (Philips PW1710), and the observed peaks were compared with JCPDS card 22-513. Data for Rietveld refinement were collected on a Stoe Stadi/P automated diffractometer in transmission mode using CuKα_1 radiation (Ge monochromator) and a small, linear position sensitive detector. Compositional analyses were made by EPMA (Cameca SX51). Each sample for EPMA was embedded in epoxy resin, polished to <1 μm surface roughness, and coated with carbon. Analyses were made at 20 keV accelerating voltage and a beam current of 20–50 nA using BaTiSi$_3$O$_9$ (Microanalysis Consultants) as a standard for the Ba$L\alpha$, Ti$K\alpha$, and Si$K\alpha$ lines. Oxygen was determined by stoichiometric calculations. The infrared spectra (ATI Mattson Genesis Series) were measured over the range 4000–400 cm^{-1} at a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Four compositions with the general formula Ba$_2$Ti$_{1+x}$Si$_{2-x}$O$_8$ (x = −0.2, 0, 0.2, 0.4) were prepared using the method described above. The XRD patterns for the fresnoite composition (x = 0) and the small Ti excess (x = 0.2) were found to be essentially identical and free from impurity lines. However, XRD patterns for the Ti deficient (x = −0.2) and the larger Ti excess (x = 0.4) compositions contained additional lines. For x = −0.2, the lines could be assigned to any of three barium silicates, while for x = 0.4, the additional lines were assigned to BaTiO$_3$. Compositional analysis by EPMA showed the presence of more phases than were visible by XRD; no sample was completely phase pure. Table 1 gives the weight percent of each element in the main phase (fresnoite) as measured by EPMA. These values are an average from 7–12 data points. Table 2 compares the EPMA-determined composition of the main phase with the nominal composition of each sample. Figure 1 shows the compositions studied and the phases observed.

When x = 0, the sample is virtually phase pure, apart from a very small amount of Ba$_2$Si$_3$O$_8$; the Ba : Ti : Si ratio is very close to 2 : 1 : 2 (Table 2), as expected. Increasing the Ti : Si ratio to x = 0.2 gives a product which appears

TABLE 1
EPMA Data

	EPMA weight (%)			
x	Ba	Ti	Si	O
−0.2	53.42(32)	9.55(8)	10.85(9)	24.97(12)
0	53.56(16)	9.69(12)	11.02(10)	25.27(7)
0.2	53.17(19)	10.60(11)	10.31(6)	25.01(4)
0.4	52.97(25)	10.58(9)	10.36(6)	25.04(9)

to be phase pure by XRD, although EPMA shows it to contain a small amount of $BaTiO_3$; see Fig. 1. The main phase of this composition has a higher Ti:Si ratio, 1.14:1.88, than that observed in $x = 0$, suggesting the formation of a solid solution involving the partial replacement of Si by Ti; no noticeable difference in d-spacings of the two compositions was seen, however. To establish the limits of this solid solution, two additional compositions were prepared: Ti deficient ($x = -0.2$) and a larger Ti excess ($x = 0.4$). The products from these two compositions were found to be inhomogeneous by both XRD and EPMA. Table 2 shows the main phase from the Ti-deficient sample ($x = -0.2$) to have a composition very close to that in $x = 0$ which corresponds, therefore, to the lower limit of the solid solution. Furthermore, the main phase composition of the larger Ti excess ($x = 0.4$) was identical, within errors, to that found in $x = 0.2$. This evidence shows that both the $x = -0.2$ and $x = 0.4$ compositions lie outwith the solid solution range and that the limiting values of x are $x = 0.00$ and $x = 0.14(1)$.

From Table 2, the combined (Si + Ti) content is 3, to within one esd, in all samples. There does appear, however, to be a small barium deficiency in all samples, in some cases amounting to several esds; see Table 2. We do not know whether this is a real effect with the implication of a small concentration of Ba vacancies and, to preserve electroneutrality, O vacancies also or whether there is a small systematic error in the Ba analysis.

The stoichiometry of the fresnoite phase, $0 \leq x \leq 0.14$,

TABLE 2
Main Phase Composition

	Nominal composition	EPMA atomic ratios			
x		Ba	Ti	Si	O
−0.2	$Ba_2Ti_{0.8}Si_{2.2}O_8$	1.994(5)	1.023(10)	1.981(10)	8
0	$Ba_2Ti_{1.0}Si_{2.0}O_8$	1.977(5)	1.021(9)	1.990(12)	8
0.2	$Ba_2Ti_{1.2}Si_{1.8}O_8$	1.982(4)	1.135(5)	1.875(5)	8
0.4	$Ba_2Ti_{1.4}Si_{1.6}O_8$	1.971(4)	1.128(9)	1.885(8)	8

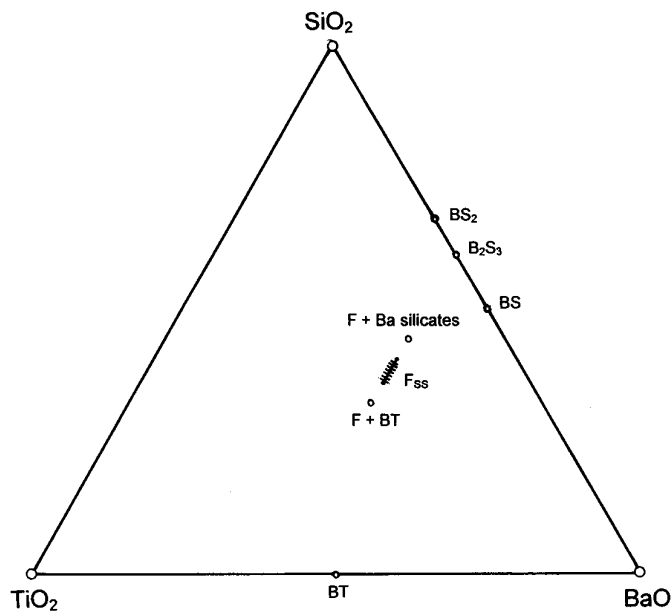**FIG. 1.** Location of the fresnoite solid solutions in the system BaO–TiO₂–SiO₂, showing compositions studied. BT, $BaTiO_3$; BS, $BaSiO_3$; B_2S_3, $Ba_2Si_3O_8$; BS₂, $BaSi_2O_5$; F, fresnoite.

appears to be temperature independent. Samples of $x = 0, 0.2$ were heated to 1250, 1270, 1300, and 1350°C followed by quenching to room temperature; they showed no observable fluctuation in composition or variation in solid solution limits by EPMA. Similarly treated samples which were slow cooled to room temperature showed no compositional fluctuations either. These combined results indicate that, at the high temperatures over which the fresnoite
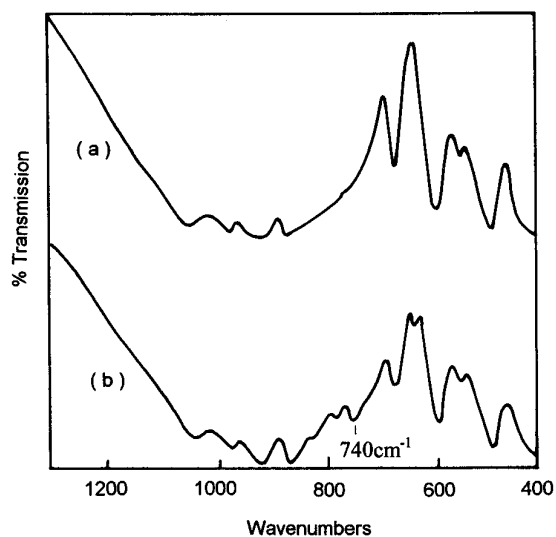

FIG. 2. Infrared spectrum of (a) $x = 0$ and (b) $x = 0.2$.

phase is likely to be formed in ceramics, its stoichiometry range is essentially fixed.

In an attempt to confirm the solid solution mechanism, Rietveld refinements using the Stoe in-house program PFSR (profile-fitting structure refinement) were carried out on XRD data from the Ti excess composition, $x = 0.2$. Two models were compared using starting parameters taken from Moore and Louisnathan (3) (i) $x = 0.2$ with the excess Ti substituted on Si sites and (ii) $x = 0$, i.e., with no excess Ti. For model (i), R_p and R_{wp} were 4.64 and 6.66, respectively, while for model (ii), R_p and R_{wp} were 4.65 and 6.68, respectively. These R values are essentially identical and therefore, it is not possible to confirm the partial substitution of Ti onto Si sites by powder XRD.

Tarte (6) showed that tetrahedrally coordinated Ti, [TiO$_4$], has a characteristic vibration between 720 and 740 cm^{-1}, while [TiO$_6$] octahedra absorb at ~500–600 cm^{-1}. If the excess Ti in fresnoite substitutes directly for Si then it is expected to occupy tetrahedral sites. Comparing the infrared spectra from $x = 0$ and $x = 0.2$, Fig. 2 shows the appearance of a prominent band at 740 cm^{-1} in $x = 0.2$ that is clearly absent from $x = 0$. This strongly suggests the presence of tetrahedrally coordinated Ti^{4+} in $x = 0.2$.

CONCLUSIONS

A solid solution with the general formula Ba$_2$Ti$_{1+x}$Si$_{2-x}$O$_8$ ($0 \leq x \leq 0.14$) has been identified by XRD and EPMA. The direct substitution of Ti for Si in fresnoite is confirmed by IR data which clearly show the presence of tetrahedrally coordinated Ti^{4+}. Rietveld refinements proved to be insufficiently sensitive to detect whether the Si sites contained a small amount of substituted Ti and no lattice parameter shifts were detected.

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