



Synthesis and crystal chemical evolution of fresnoite powders

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ABSTRACT

(Ba,Sr)₂TiSi₂O₈ fresnoite powders were prepared via a Pechini process in which citric acid and ethylene glycol were used as complexing agents. The resulting gel contained a homogeneous distribution of the metal ions that suppressed the formation of (Ba,Sr)TiO₃ perovskite as a secondary phase during calcination. Phase development was examined as by isochronal and isothermal reaction analysis. A combination of thermo- and differential gravimetric analysis (TGA–DGA), quantitative X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) confirmed that calcination at 900 °C/12 h yielded finely crystalline (~70 nm) Ba₂TiSi₂O₈ (BTS) and Sr₂TiSi₂O₈ (STS). The endmembers and compositional intermediates crystallized directly from the Pechini resin and indirectly through reaction of (Ba,Sr)CO₃, (Ba,Sr)TiO₃ and a silica-rich glass intermediates. This new method for preparing fresnoite yields materials suitable for consolidation as dense monolithic dielectrics or for use as high surface area catalytic powders.

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1. Introduction

Fresnoite, a titanosilicate of ideal composition Ba₂TiSi₂O₈ (BTS), exhibits piezoelectric, ferroelectric, pyroelectric and ion conductivity properties that may prove useful in ultrasonic transduction, memory devices, electro-optical modulation and solid electrolytes [1–4]. These varied applications require the fabrication of BTS powders of defined size and shape, either as functional materials in their own right, or as readily consolidated precursors. Although large single crystals have been melt grown [1,3,5] and BTS glass ceramics synthesized by quenching and annealing powders [6–12], the preparation of phase-pure polycrystalline ceramics has proven difficult. Conventional solid-state syntheses from oxides require high temperatures (> 1200 °C), prolonged sintering (2–3 day) and intermittent grinding, but these products often contain significant quantities of BaTiO₃ and glassy silica [13–15]. Soft chemistry provides alternative routes to obtain homogeneous powders. For example, refluxing barium acetate, tetraethyl silicate and titanium isopropoxide for several hours, followed by slow hydrolysis and calcination (750 °C) permitted tuning of BTS morphology [16,17]. Elsewhere, tetramethyl orthosilicate, titanium isopropoxide and barium metal in

isopropanol were refluxed under nitrogen, with the hydrolysis rate regulated by varying the water:alcohol ratio and the rate of addition to the alkoxides [18]. However, none of these syntheses lead to fine-grained and single-phase BTS that is technologically practical in the broadest sense.

A further consideration is that fresnoite is modulated and of fundamental crystallographic interest. The tetragonal substructure (*P4bm*) with $a=8.550(2)$ Å and $c=5.235(2)$ Å consists of planes of corner-connected TiO₅ pyramids and SiO₄ tetrahedra separated by BaO₁₀ polyhedra (Fig. 1) [3]. The small cation polyhedra may be treated as rigid bodies that oscillate in (0 0 1) leading to the modulation vectors $q_1=0.302 (a^*+b^*)$ and $q_2=0.302 (-a^*+b^*)$ [19]. While several X-ray and electron diffraction studies have confirmed this aperiodic order, the crystals used for these investigations were melt grown, and at micron scales, frequently differentiated into compositionally distinct domains [20]. Therefore, it is intrinsically challenging to obtain equilibrated and non-differentiated fresnoite, although this may be a pre-requisite to control functionality.

This paper describes a simple route of synthesizing fine-grained homogeneous (Ba_{1-x}Sr_x)₂TiSi₂O₈ (0 ≤ x ≤ 1.0) fresnoite (BTS–STS) solid solution series via in situ polymerization, where an esterification reaction between citric acid and ethylene glycol homogeneously immobilizes the cations in a resin that decomposes to the ternary oxide. Also known as the Pechini process [21], metal chelation is a robust means of circumventing differential hydrolysis rates and the selective precipitation of metal ions that promote secondary phase formation [22,23]. Here, direct

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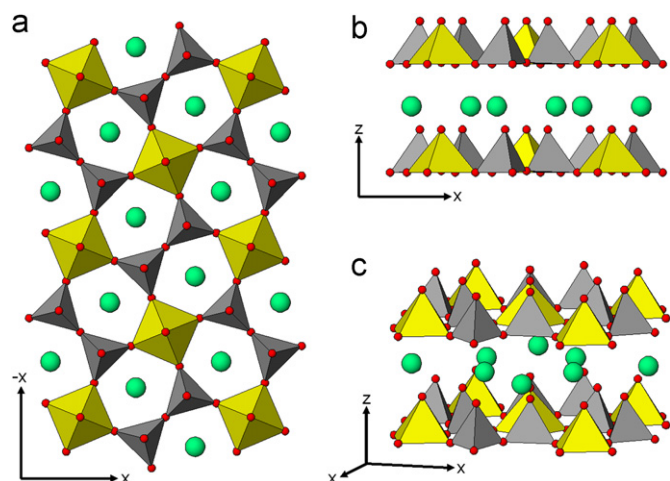


Fig. 1. Polyhedral representation of the $P4bm$ BTS fresnoite subcell. (a) $[0\ 0\ 1]$ projection emphasizing the pentagonal rings created by corner-connection of three SiO_4 tetrahedra and two TiO_5 square pyramids. (b) $[0\ 1\ 0]$ projection showing the interlayer barium atoms. (c) Clinographic projection.

mixing of the ingredients avoids refluxing in an inert (N_2) atmosphere, while crystal growth and phase development evolves via the elimination of organics and reaction with an amorphous silica-rich intermediate.

2. Experimental methods

2.1. Synthesis

BTS powders were synthesized using tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) (Aldrich, 98%), titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (TIP) (Aldrich, 97%), barium acetate $\text{Ba}(\text{CH}_3\text{COO})_2$ (BA) (Aesar, 99%), anhydrous ethylene glycol $\text{OHCH}_2\text{CH}_2\text{OH}$ (EG) (Merck, 99.5%) and citric acid monohydrate $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (CA) (Aldrich, 98%). Citric acid (mole ratio of CA:BTS product=20:1) was dissolved in EG (1:100 parts by volume) and heated to $70\text{ }^\circ\text{C}$ with vigorous stirring to obtain a clear solution. Titanium isopropoxide (1:70 parts by volume of TIP in ethylene glycol) was transferred to the citric acid solution and stirred for 3 h, followed by injection of tetraethyl orthosilicate in Ti:Si=1:2 metal proportions. After aging for 1 h, barium acetate in ethylene glycol (mole ratio 1:150) was added stoichiometrically and stirred vigorously for 2 h to obtain the transparent sol. A brown resin containing the immobilized metals was prepared by drying the sol ($150\text{ }^\circ\text{C}/2\text{ d}$).

Similarly, STS powders were made from the same ingredients as BTS, but with the substitution of strontium acetate $\text{Sr}(\text{CH}_3\text{COO})_2$ (SR) (Aldrich, 99%). The solid solutions of $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ (BSTS) were prepared by introducing strontium and barium acetates separately in the desired alkali earth mole ratios. To study phase development and the kinetics of crystallization the resin precursors were calcined in air as a function of temperature ($650\text{--}900\text{ }^\circ\text{C}/12\text{ h}$) and time (1–48 h/ $900\text{ }^\circ\text{C}$).

The formation of BTS–STS is sensitive to the gelation temperature, rate of TIP addition and drying, and these parameters required optimization to prevent the formation of $(\text{Ba,Sr})\text{TiO}_3$ perovskite and residual amorphous silica. The most favorable temperature for reaction ($70\text{ }^\circ\text{C}$) should be constant, to avoid double citrates $\text{MTi}(\text{CA})_3$ ($\text{M}=\text{Sr}, \text{Ba}$) that are highly stable and once formed will transform to perovskite during calcination. In addition, direct injection of concentrated TIP leads to incomplete dissolution of the alkoxide in CA that is recognizable as white turbidity. To obtain a homogeneous solution, it is essential to dissolve TIP in ethylene glycol before transfer to the CA solution.

Finally, the transparent sol is oven dried until a gummy brown resin forms to ensure the preservation of molecular-scale homogeneity during calcination.

2.2. Characterization

Quantitative phase analysis: Powder X-ray diffraction (XRD) patterns were collected using CuK_α radiation over the 2θ range $10\text{--}140^\circ$ step-scanned at intervals of 0.02° . Phase abundance, unit cell parameters and amorphous content were extracted by the Rietveld method using the fundamental parameters approach implemented in TOPAS 3.0 with reference to an internal CaF_2 standard spiked to 20 wt% (Fig. 3) [24–27]. It is noted that the amorphous content will be systematically slightly overestimated, as CaF_2 is underestimated, due the effects of X-ray microabsorption [21]. Although BTS/STS will be modulated [19], the tetragonal ($P4bm$) sub-structure with $a=8.550(2)\text{ \AA}$ and $c=5.235(2)\text{ \AA}$ was used as for initiating the refinement of accurate lattice parameters, since the weak incommensurate reflections are not observed by laboratory XRD [3]. Quantitative phase analysis was performed by introducing $(\text{Ba,Sr})\text{CO}_3$ witherite-type [22] and $(\text{Ba,Sr})\text{TiO}_3$ perovskite [23] as secondary phases. The absolute CaF_2 content (20 wt%) was only approached after long calcination at higher temperatures when the non-diffracting components were near completely converted to fresnoite.

Thermal analysis: Decomposition and crystallization of the resin was investigated by thermogravimetric analysis (TGA) and differential gravimetric analysis (DGA) (TA Instruments, TGA 2950) in flowing air at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from room temperature to $900\text{ }^\circ\text{C}$.

Fourier-transform infra-red spectroscopy (FTIR) ($400\text{--}4000\text{ cm}^{-1}$) was performed on KBr pellets (1 part fresnoite: 100 parts KBr by weight or 0.2 g of KBr mixed with 2 mg of sample) with a resolution of 2 cm^{-1} in 30 cycles. The spectra invariably contained broad bands that were analyzed from 450 to 1100 cm^{-1} by deconvolution into 25 Gaussian components before assignment of Ti–O and Si–O stretching and bending modes.

3. Results and discussion

3.1. Reconnaissance studies

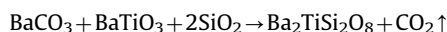
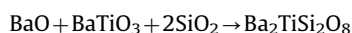
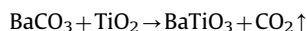
In this study, several different precursors and solvents were trialed. For example, using ethanol as a solvent for the metal alkoxides, and DI water for metal acetates did not lead to fresnoite in high yield, but stabilized intermediates such as BaTiO_3 . Introducing citric acid as a chelating agent enhanced fresnoite formation, but the product remained far from single phase, and refluxing the final mixture did not deliver higher yields. In order to gain better control of moisture uptake, the process was performed under N_2 ; this allowed the reaction to proceed almost to completion but reproducibility was variable. Subsequently, elimination of water from the synthesis by using ethylene glycol as a solvent permitted the sol–gel process to be performed in a fumehood and give single phase fresnoite.

Two unsuccessful synthesis approaches are noted. Sol–gel reaction by direct mixing of TIP, TEOS and BA ethanolic solutions in air yielded, after calcination, BaCO_3 (12.4 wt%), BaTiO_3 (10.6 wt%) and BaTi_4O_9 (24.4 wt%) as intractable secondary phases because TIP hydrolyses more rapidly than TEOS leading to a metal segregated gel. Deploying the same method in a N_2 glove box delayed the hydrolysis of $\text{Ti}(\text{OC}_3\text{H}_7)_4$, but was unable to prevent BaTiO_3 (7.1 wt%) formation.

3.2. Phase evolution

Thermal analysis showed mass loss peaked from 100 to 450 °C during removal of water and organics, with gradual consumption of (Ba/Sr)CO₃ and (Ba/Sr)TiO₃ from 450 to 700 °C (Fig. 2). X-ray diffraction patterns collected from isochronally annealed (12 h) powders are consistent with thermal analysis as fresnoite only forms at 650 °C with intermediates crystallizing at lower temperatures. During isochronal calcination BTS formed to near 100% yield by 700 °C from BaTiO₃, BaCO₃ and a non-diffracting phase presumed to be silica-rich (Fig. 3(a)), while isothermal treatment (900 °C) for 1 h yielded similar results.

However, BTS partially decomposes if held at 900 °C for 12 h, demonstrating that both annealing time and temperature are critical. It is concluded that the optimal synthesis condition for BTS would be 900 °C/12 h, and that the primary oxide reactions are:



For STS and the mixed Ba:Sr=50:50, fresnoite phase development followed similar pathways, but required higher temperatures > 900 °C due to the persistence of perovskite and carbonate phases (Fig. 4(b) and (c)). Isothermal annealing (900 °C) confirmed that STS forms more slowly than BTS (Fig. 4(d)–(f)). A non-diffracting residue (shaded portion of Fig. 4) was retained as a small fraction of all preparations even after extended annealing, and in the strontian materials the high stability of this component may delay fresnoite formation.

3.3. Evaluation of lattice parameter

Although BTS, STS and BSTS (Ba:Sr=50:50) begin to crystallize at lower temperatures (Fig. 5(a)–(c)) lattice parameter dimensions stabilize only after annealing for 12 h at 900 °C (Fig. 5(a)), suggesting that the composition of fresnoite is varying due to

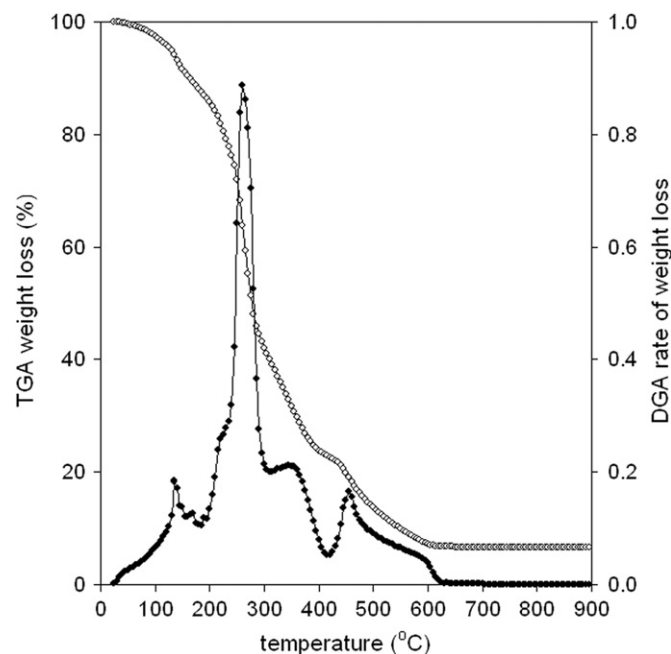


Fig. 2. TGA–DGA of the BTS fresnoite precursor obtained by the Pechini process. Strontian precursors showed similar behavior during heating.

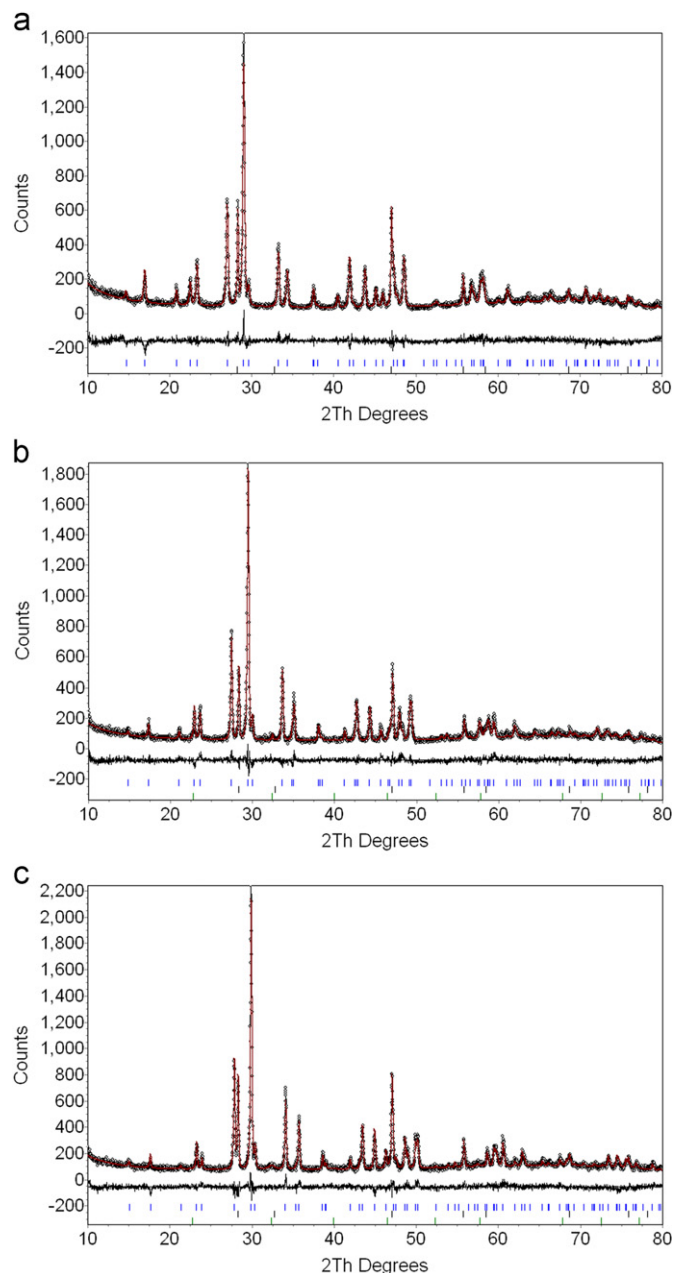


Fig. 3. Rietveld plots for (Ba_{1-x}Sr_x)₂TiSi₂O₈ fresnoites calcined at 900 °C/12 h and spiked with 20 wt% CaF₂ prior to XRD collection. (a) BTS (*x*=0) was single phase within the detection limits of XRD. (b) BSTS (*x*=0.5) contained trace < 1 wt% (Ba,Sr)TiO₃ perovskite. (c) STS (*x*=1) contained < 2 wt% SrTiO₃ of small crystal size (29 nm) suggesting it is finely dispersed. The Bragg markers from top-to-bottom are fresnoite, perovskite and CaF₂.

reaction with the glassy phase. Such equilibrated fresnoites will be optimal for evaluating crystallographic properties. Similarly, higher annealing temperatures lead to a contraction in cell dimensions (Fig. 5(b)). For the equilibrated (Ba_{1-x}Sr_x)₂TiSi₂O₈ (0 ≤ *x* ≤ 1) samples Vegard's Law was obeyed across the entire compositional join (Fig. 5(c)–(e)) indicating complete solid solution and the absence of a miscibility gap. The crystal domain size extracted by analysis of the Bragg peak widths after heat treatment for 12 h/900 °C was ~70 nm.

3.4. FTIR analysis

Polymerization of the EG/CA resin yields symmetric and asymmetric carbonyl (COO⁻) vibrations at 1630 cm⁻¹ and

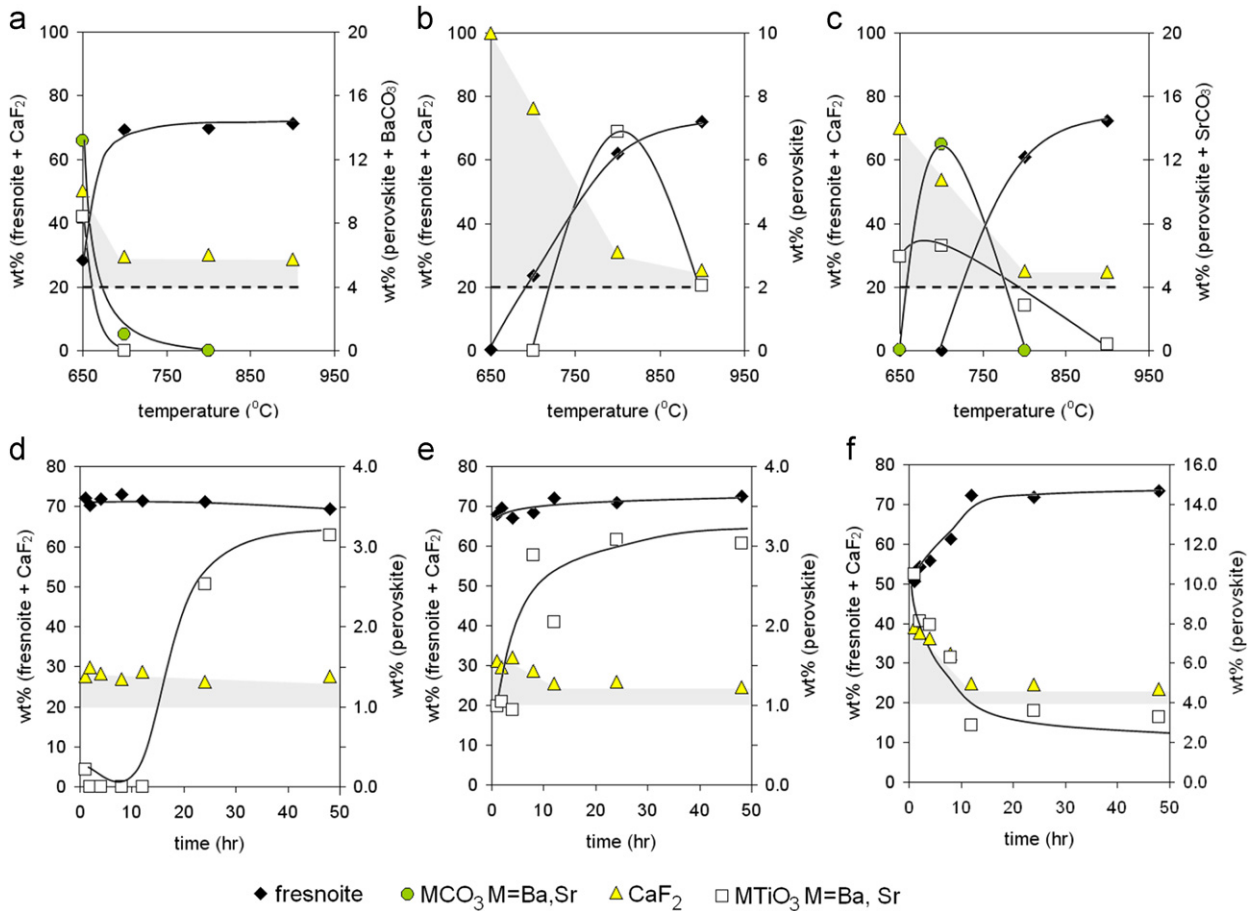


Fig. 4. Phase development during isochronal (12 h) and isothermal (900 °C) synthesis of Ba₂TiSi₂O₈ (BTS), BaSrTiSi₂O₈ (BSTS) and Sr₂TiSi₂O₈ (STS) fresnoites. During isochronal treatment fresnoite crystallizes both directly from the Pechini resin and indirectly from reaction of intermediate carbonate, perovskite and a silica-rich glass (shaded region). For BTS (a and d) crystallization is essentially complete by 700 °C, but for BSTS with $x=0.5$ (b) and (e) and STS (c) and (f) it is delayed until 900 °C. Note all weight percentages sum to 100% inclusive of the CaF₂ spike.

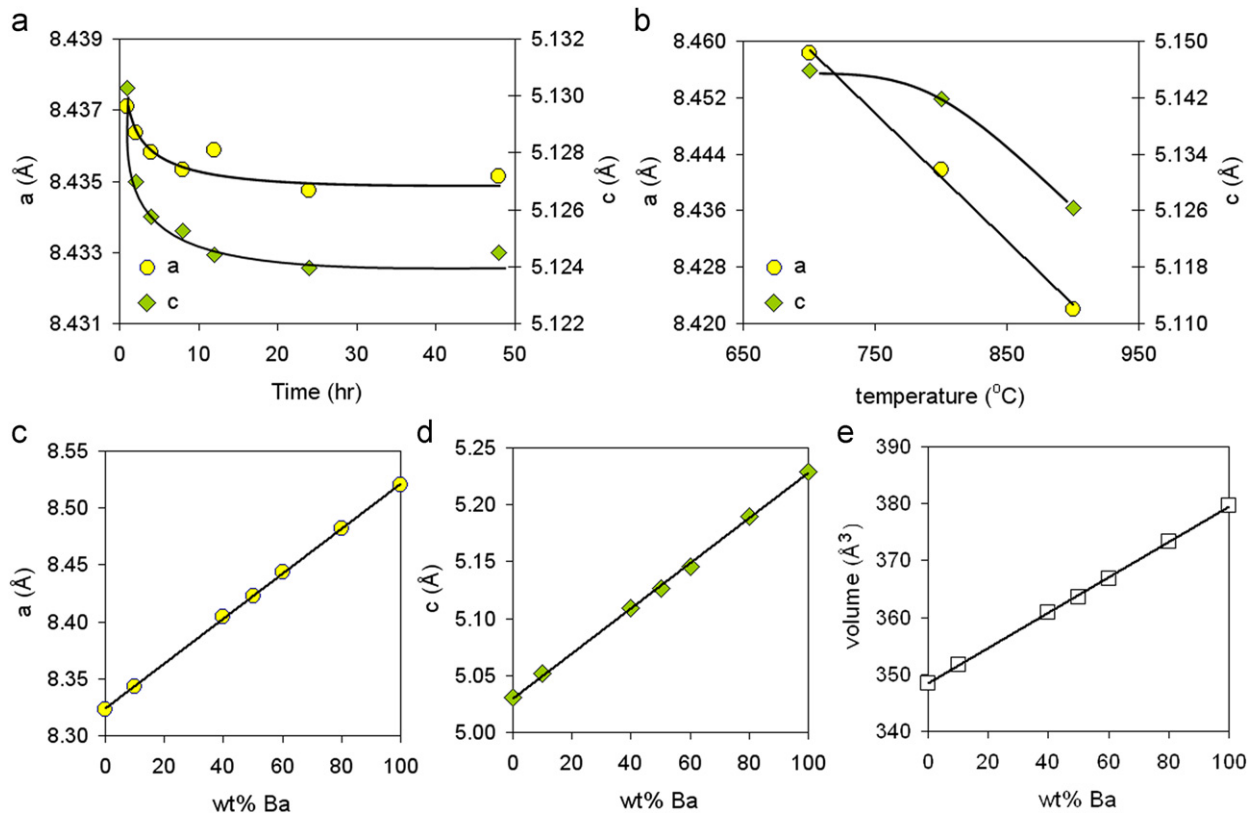


Fig. 5. For BTS both (a) isothermal and (b) isochronal syntheses show that firing for 12 h at 900 °C is required to bring the material to near equilibrium and stabilize the unit cell parameters. For the equilibrated (Ba_{1-x}Sr_x)₂TiSi₂O₈ (c)–(e) the lattice parameters dilate linearly as barium replaces strontium.

1380 cm^{-1} [28], an intense band at 1725 cm^{-1} arising from C–O stretching, C–H stretching at 2950 cm^{-1} and 2880 cm^{-1} [29] and C–C–O stretching at 1186 cm^{-1} with the latter two vibrations arising from ethylene glycol [28]. These vibrations are consistent with chelation between metal ions during polymeric reactions that lower the temperature for fresnoite formation, as compared to conventional solid-state reactions. Subsequently, as the calcination temperature increases, the precursor slowly forms fresnoite by releasing volatile organics with the Ti–O and Si–O stretching and Si–O–Si bending modes at 600 °C, characteristic of BTS, becoming increasingly evident at higher calcination temperatures (Fig. 6) [30].

After prolonged calcination (900 °C for 12 h) the FTIR spectra are dominated by Ti–O and Si–O stretching and Si–O–Si bending modes [30,31]. The bands are quite broad, and increasingly so, as strontium replaces barium indicating a greater level of disorder and bond strain related to the inherent structural modulation. Using earlier studies as a guide, these features have been separated into distinct vibrational modes, especially for BTS (Fig. 7). As strontium replaces barium, the bands are displaced towards higher wavenumbers as molecular oscillations increase

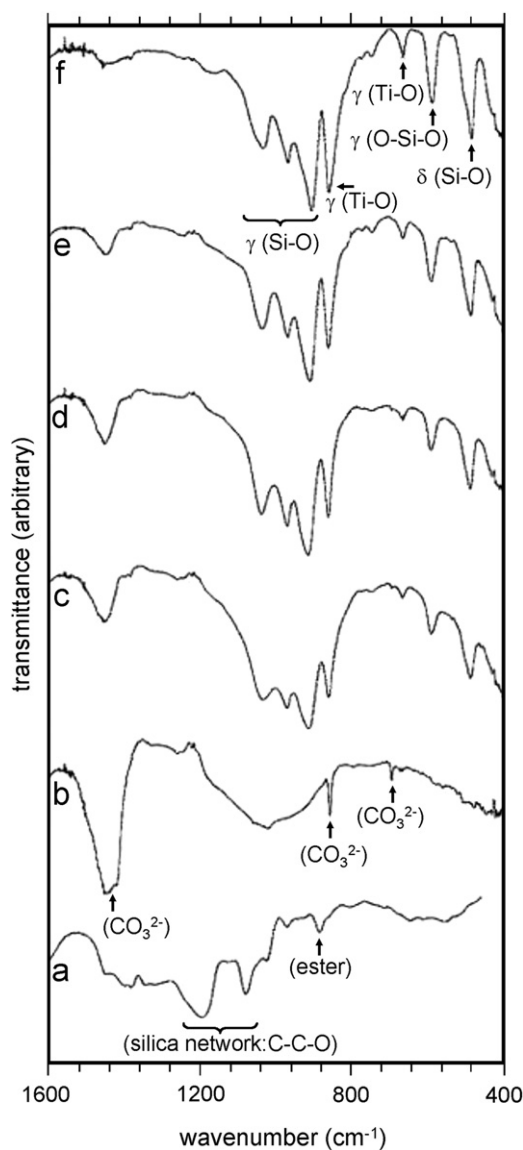


Fig. 6. FTIR spectra showing BTS phase evolution during isochronal (12 h) calcination. (a) precursor, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C.

in frequency leading to stronger mixing of the Si–O and Ti–O vibrations.

3.5. Advantages of Pechini process

Recent studies by Wong et al. [32] and Nagel et al. [33] have shown extreme difficulty in obtaining homogeneous, single crystal of BTS and STS fresnoites, which show a proclivity towards hierarchical structures at nanometric and micrometric scales. Indeed, such structures can be embedded even in appreciable 'single' crystals with well-developed facets, and as pointed out by Wei et al. [34], these features destroy simple correlations between the magnitude of incommensuration (measured through q vectors) and composition, whereas such trends can be established in the related melilites. The Pechini method offers a possible means to avoid or minimize these features and avoid trapping of internal strains when fabricating fully dense BTS by spark plasma sintering [35]. In addition, it has been found in the vanadate fresnoite $\text{Ba}_2\text{VSi}_2\text{O}_8$ that sol–gel methods allow superior control of transition metal oxidation states [36] and this may also be important in titano-silicates. Confirmation of the synthesis of high quality fresnoites should ideally include examination by transmission electron microscopy, either using diffraction or energy loss spectroscopy, but these approaches often lead to rapid amorphization or volatilization. While this limitation might in some cases be minimized by specimen cooling, to slow damage, or warming, to accelerate self-repair, a superior approach may be solid state NMR as already used to examine the atomic scale structure of sol–gel prepared fresnoite [37].

4. Conclusion

In the present study, ethylene glycol is both the solvent and chelating agent, with the former role of particular importance, as water need not be introduced to dissolve barium and strontium acetates. This circumvented controlling the water to solvent ratio to avoid hydrolysis and low yields. Chelation of TIP is essential as previous attempts to synthesize fresnoite without citric acid were unsuccessful. Moreover, the sequence of chelation must be regulated as chelating TEOS with citric acid followed by TIP lead to incomplete fresnoite formation. Slow dissolution of TIP into ethylene glycol with moderate stirring is essential to minimize reaction with air that precipitates TIP and prevents complete chelation of the Ti–CA complex. Too little ethylene glycol solvent hinders TIP and TEOS dissolution resulting in segregation and precipitation of metal ion chelates.

In summary, $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ ($0 \leq x \leq 1$) fresnoites were prepared by calcination (900 °C) of a resin obtained by esterification of $\text{Ba}^{2+}/\text{Sr}^{2+}-\text{Ti}^{4+}$ -citrate and Si^{4+} -citrate complexes that are resistant to accelerated hydrolysis. In this manner, metal alkoxides are immobilized in a rigid polyester framework by ethylene glycol polymerization which eliminates metal segregation during hydrolysis/pyrolysis. This inhibits the formation of perovskite, and other alkali earth titanates, as significant secondary phases. Chelation also circumvents the need for an inert atmosphere (N_2) blanket during hydrolysis.

Crystallization of fresnoite occurs, in part, via $(\text{Ba,Sr})\text{CO}_3$ and $(\text{Ba,Sr})\text{TiO}_3$ which are eliminated by reaction with a silica-rich non-diffracting phase, and at higher temperatures (> 800 °C) phase-pure BTS–STS fresnoite was obtained. To date, the development of fresnoite as a functional material has been hampered due to the difficulty of obtaining reactive single phase powders. The new Pechini process described here yields homogeneous fresnoite powders and will simplify deployment as photocatalysts, dielectric materials and ion conductors.

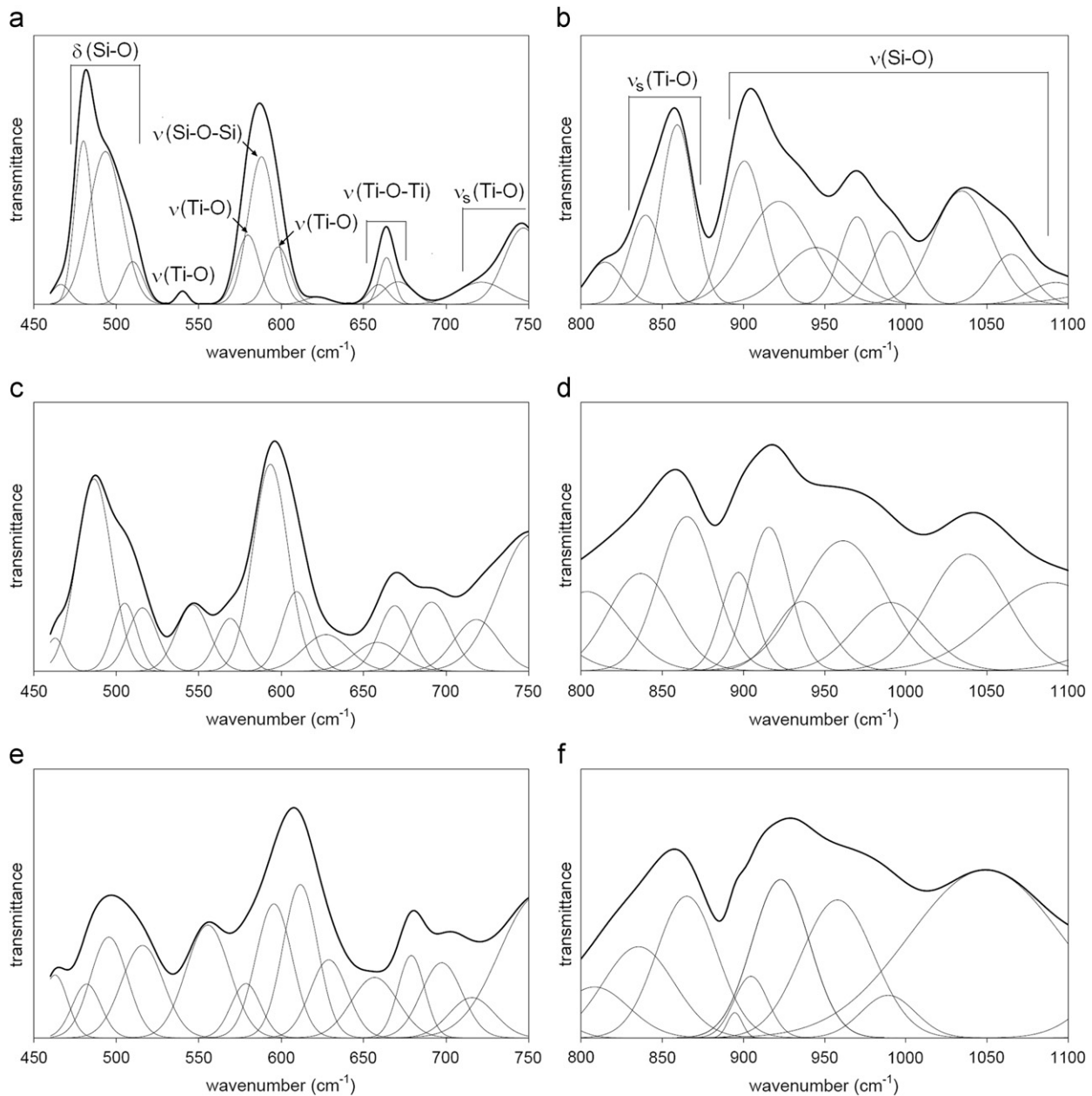


Fig. 7. FTIR spectra of (a,b) $\text{Ba}_2\text{TiSi}_2\text{O}_8$; (c,d) $\text{BaSrTiSi}_2\text{O}_8$; and (e,f) $\text{Sr}_2\text{TiSi}_2\text{O}_8$ show progressive broadening of the vibrational bands and their displacement to larger wavenumbers as Ba is replaced by Sr leading to higher frequency oscillations of the Ti–O and Si–O bonds.

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