A Fresnoite-structure-related Mixed Valent Titanium(III/IV) Chlorosilicate, $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}$: A Flux Crystal Growth Route to Ti(III) Containing Oxides

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Abstract.

Single crystals of mixed valent barium titanium(III/IV) chlorosilicate, $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$, were grown in a high temperature molten chloride flux involving an *in situ* reduction step. The fresnoite structure related $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ crystalizes in the tetragonal space group $P4/mbm$ with lattice parameters of $a = 8.6717(2) \text{ \AA}$, $c = 18.6492(5) \text{ \AA}$. The title compound exhibits a 3D structure consisting of 2D layers of fused Ti_2O_9 and Si_4O_{12} groups and 2D layers of fused $\text{Ti}_2\text{O}_9\text{Cl}_2$ and Si_2O_7 groups that are linked via barium atoms. The *in situ* reduction of Ti(IV) to Ti(III) is achieved via the addition of metallic Mg to the flux to function as the reducing agent. The temperature dependence of the magnetic susceptibility shows simple paramagnetism above 100 K. There is a discontinuity in the susceptibility data below 100 K, which might be due to a structural change that takes place resulting in charge ordering.

Keywords: Mixed valent titanium silicate, flux crystal growth, Mg reducing agent, magnetic susceptibility

1.Introduction

The majority of known titanium containing oxides contain titanium in its highest oxidation state, Ti(IV), while only a relatively small number of examples of oxides containing Ti(III) or mixed valent Ti(III/IV) are known. The fact that the electronic and magnetic properties of transition metal oxides are determined by their d-electrons makes Ti(III) d^1 rather than Ti(IV) d^0 of particular interest [1–4]. In fact, there are a number of Ti(III) containing oxides that exhibit highly desirable properties, such as superconductivity. Most notable in this regard are the mixed-valence spinel, $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ and the perovskite, SrTiO_{3-x} , both of which exhibit superconductivity at T_c of ~ 13 K and ~ 0.5 K, respectively [5–9]. The T_c of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ is, in fact, quite high for an early transition metal oxide. The stability of the Ti(IV) and Ti(III) oxidation states in oxides and oxo-salts creates opportunities for titanium to adopt a number of structures that require mixed valent cation, such as the NASICON structure, where the titanium containing phase $\text{Na}_x\text{Ti}_2\text{P}_3\text{O}_{12}$ is well known for its ion exchange and ionic conductivity properties [10–13].

The reported Ti(III) oxo compounds include oxides, phosphates, silicophosphates, oxidephosphates, borates, and silicates with different framework structures containing isolated [4,12–17] and corner-shared TiO_6 octahedra [18,19], as well as face-shared Ti_2O_9 double-octahedra [20], and edge-shared TiO_6 octahedral chains [21–26]. Surprisingly, Ti(III) containing silicates, such as the title compound, are quite rare in the literature. Wang et al. reported the first two mixed valent titanium silicates, $\text{La}_4\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{TiO}_2)_{4m}$ ($m = 1, 2$), which contain quasi-two dimensional frameworks [27,28]. To best of our knowledge, $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ is only the third mixed valent titanium silicate reported to date.

Several synthetic routes for the growth of reduced titanates have been reported over the years, including conventional solid-state methods to prepare polycrystalline powders and molten flux approaches used to grow single crystals [9,13,15,19,27,29]. Historically, fluxes such as CaCl_2 , BaCl_2 , and borates were used in conjunction with Ti(III) containing starting materials. Over the last couple of years our group has successfully synthesized reduced early transition metal containing oxides using both low temperature mild hydrothermal and high temperature molten chloride flux methods [30–34]. We are particularly interested in creating reaction conditions that lead to *in situ* reduction involving either organic or inorganic reducing agents. The latter approach was used to obtain single crystals of the title compound and utilize a NaCl/BaCl_2 flux and Mg metal as the reducing agent. Herein, we report on the synthesis,

structural characterization, and magnetic properties of the fresnoite structure related novel compound, $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$.

2. Experimental Section

2.1 Reagents

TiO_2 (99.9%, metal basis, Alfa Aesar), BaCO_3 (99.95%, metal basis, Alfa Aesar), Mg powder (99.8%, -325 mesh, Alfa Aesar) were used as received. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (99+%, Alfa Aesar) and NaCl (Certified A.C.S., Fisher) were dried and stored in an oven at 260 °C. A precursor, Ba_2TiO_4 , was synthesized using the conventional solid-state method. Stoichiometric mixture of BaCO_3 and TiO_2 were ground using an agate mortar and pestle, pressed into a pellet, and sintered at 1100 °C in air for 24 h.

2.2 Synthesis

Single crystals of $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ were grown out of BaCl_2 and NaCl eutectic mixture contained in a vacuum-sealed fused silica tube. A mixture of 1 mmol of Ba_2TiO_4 , 1 mmol of Mg powder, and 2 g of a eutectic mixture of BaCl_2 and NaCl (molar ratio 2:3) were placed into a fused silica tube, which acts as the SiO_2 source. Attempts to form the desired product using a direct inclusion of SiO_2 worsened the yield and the crystal quality. The tube was evacuated to a pressure of $\sim 10^{-4}$ Torr and sealed using an oxygen/methane torch. The tube was placed inside a programmable furnace and heated to 1050°C at a rate of 10°C/min, held for 48 hours, cooled to 550°C at a rate of 6 °C/h, and then cooled to room temperature by turning off the furnace. Single crystals were isolated from the flux matrix by dissolving the halide salts in water, assisted by sonication. The reaction yielded a single-phase product consisting of transparent brown square plate crystals in $\sim 65\%$ yield based on Ba_2TiO_4 .

2.3 Single-Crystal X-ray Diffraction

X-ray intensity data from a transparent brown square plate were collected at 300(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å)[35]. The data collection covered 99.8% of reciprocal space to $2\theta_{\text{max}} = 72.9^\circ$, with an average reflection redundancy of 39.5 (Laue class 4/*mmm*) and $R_{\text{int}} = 0.032$ after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs[35]. Final unit cell parameters were determined by least-squares refinement of 9959 reflections taken from the data set. An initial structural model was obtained with SHELXS using

direct methods[36]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014 [36] using the ShelXle interface [37].

The compound crystallizes in the tetragonal system. Systematic absences were consistent with space groups $P4/mbm$, $P-4b2$ and $P4bm$. The centrosymmetric group $P4/mbm$ (No. 127) was confirmed by structure solution. The asymmetric unit consists of two barium atoms, two titanium atoms, two silicon atoms, one chlorine atom and eight oxygen atoms. Barium Ba1, silicon atoms Si1 and Si2, and oxygen atom O3 are located on mirror planes (site $8k$, site symmetry $..m$). Ba2 is located on site $4g$ with $m.2m$ symmetry. Titanium atoms Ti1 and Ti2A/B and the chlorine atom (Cl1/O1B, see below) are located on a fourfold axis (site $4e$, symmetry $4..$). Oxygen atoms O1 and O2 are located on general positions (site $16l$), O4 is located on site $4h$ ($m.2m$ site symmetry), O5 and O6 are located on site $4f$ ($2.mm$ symmetry) and, finally, O7 and O8 are located on sites $2b$ and $2a$, respectively, both with $4/m..$ site symmetry. All atoms were refined with anisotropic displacement parameters. After initial location and normal refinement of all atoms, an electron density peak of $4.1 \text{ e}^-/\text{\AA}^3$ was observed located $0.6 \text{ \AA}$ from the Ti2 site. This was accompanied by a hole of $-2.74 \text{ e}^-/\text{\AA}^3$ centered on the Ti2 site. Taken together these observations suggest a split Ti2 position. Including the smaller peak as a titanium atom and refining the site occupation factors (*sof*) of the Ti2 split position (Ti2A/Ti2B) gave a reasonable model with freely refined Ti2A/Ti2B occupancies summing to one, acceptable displacement parameters for both components and a flattened difference map. The split Ti2 position is coupled with O/Cl disorder of the nearby chlorine site (Cl1). The chlorine *sof* reflects either a Cl vacancy or, more likely, admixture of a lighter atom. With 100% Cl occupancy, the deepest residual electron density hole is $-1.17 \text{ e}^-/\text{\AA}^3$, located on the Cl1 site. The Cl1 *sof* refined to 0.94(1), accompanied by a flattening of the difference map (deepest hole = $-1.03 \text{ e}^-/\text{\AA}^3$ located $0.6 \text{ \AA}$ from Ti1) and a decrease in R -values from $R1/wR2 = 0.0164/0.0373$ to $0.0156/0.0344$. A chlorine vacancy is not likely, as it would leave an open apical coordination site around Ti2. Therefore, a disordered chlorine/oxygen site was assumed. Atomic coordinates and anisotropic displacement parameters for the minor component oxygen atom (O1B) were held equal to those of Cl1. Occupancies of the Ti2A/Ti2B and Cl1/O1B sites were linked such that $\text{sof}(\text{Ti2A}) = \text{sof}(\text{Cl1})$ and $\text{sof}(\text{Ti2B}) = \text{sof}(\text{O1B})$, with each total site occupancy constrained to sum to unity. The final refined occupancies are $\text{Ti2A/Cl1} = 0.911(4)$ and $\text{Ti2B/O1B} = 0.089(4)$. The split Ti2 position and linked Cl/O site disorder was also observed in a second crystal. The largest residual electron

density peak and hole in the final difference map are +0.75 and -1.03 e⁻/Å³, located 0.75 Å from O1 and 0.58 Å from Ti1, respectively. Crystallographic data, selected interatomic distances, and atomic coordinates for all compounds are listed in Tables 1, 2, and 3, respectively. The Cambridge Crystallographic Data Center (CCDC) number is: 1521414.

2.4 Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction data were collected on a Bruker D2 Phaser powder X-ray diffractometer using Cu K α radiation. The step-scan covered the angular range 5 – 65° 2 θ in steps of 0.02°. Some weak reflections were observed which could not be matched with any known impurity. Magnetic measurement and calculations are consistent with the impurity being non-magnetic. (See supporting information, Figure S1).

2.5 Energy-Dispersive Spectroscopy (EDS)

Elemental analysis was performed on all the reported single crystals using a TESCAN Vega-3 SBU scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 20 s. As a qualitative measure, EDS confirmed the presence of each reported element in the title compounds.

2.6 Magnetic Susceptibility

The magnetic susceptibility of the reported materials was measured using a Quantum Design MPMS SQUID magnetometer. The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2 – 300 K in an applied field of 1000 Oe. The measured magnetic moment was corrected for shape and radial offset effects using the methods reported by Morrison et al. [38], which determines the correction factors by comparing the moments observed from DC and VSM scans at a single temperature, 30 K.

3. Results and Discussion

3.1 Synthesis

Single crystals of Ba₃Ti₂Si₄O₁₄Cl_{0.91}O_{0.09} were synthesized out of a molten chloride flux, which is known to be a redox neutral solvent suitable for the preparation of reduced oxides. The presence of chloride in the product indicates that while redox neutral, the NaCl/BaCl₂ flux is in fact a reactive flux under the reaction conditions used. Limited research available on reduced titanium silicates necessitated finding and optimizing the synthetic conditions to synthesize this new silicate. Initial observations suggested that it was advisable to divide the crystal growth

process into two steps rather than utilizing a single step process starting from either TiO_2 or Ti_2O_3 . Using TiO_2 or Ti_2O_3 as the titanium source resulted in the formation of either oxidized products or known reduced titanium phases. For this reason, the crystal growth process was divided into two steps rather than utilizing a single step process starting from either TiO_2 or Ti_2O_3 . In addition, a titanium precursor, Ba_2TiO_4 , was used to introduce titanium into the melt in one step and, in a second step, mixing the melt with the remainder of the starting materials to grow crystals. A conventional solid-state reaction was used to make the Ba_2TiO_4 precursor by firing stoichiometric amounts of BaCO_3 and TiO_2 at 1000 °C.

Utilization of molten fluxes is a well-known technique for growing crystals, as the use of the flux lowers the reaction temperature and allows the dissolution of a wide range of reactants [39]. To grow crystals containing reduced metal centers it is necessary to use a redox neutral flux, in this case the $\text{BaCl}_2/\text{NaCl}$ eutectic flux. $\text{BaCl}_2/\text{NaCl}$ is stable toward the Mg metal reducing agent, enables the dissolution of the barium titanium precursor along with other starting materials and, finally acts to leach silicon out of the interior walls of the fused silica tube [40]. It was observed that the addition of powdered SiO_2 to the reaction mixture worsened the crystal quality and the yield of the reaction, presumably because the slow dissolution of silicon from the interior wall of the fused silica tube optimized the crystallization of the product.

Mg metal was chosen as the reducing agent for the *in situ* reduction of Ti(IV) to Ti(III). Mg metal with a melting point of 650 °C will be molten at the crystal growth temperature, thereby providing a close contact between the Mg and the Ti cation in the melt. Based on the formation of $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ containing Ti(III), the use of magnesium for the *in situ* reduction is an efficient way of obtaining Ti(III) containing oxides.

3.2 Structure

The compound, $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$, crystallizes in the tetragonal space group $P4/mbm$ and exhibits a three-dimensional structure, shown in Figure 1, consisting of corner shared TiO_5Cl octahedra, TiO_5 square pyramids, and Si_2O_7 and Si_4O_{12} groups connected via Ba cations.

The structure contains two independent Ti coordination environments, TiO_5 square pyramids and TiO_5Cl octahedra. Five coordinated Ti(1) forms TiO_5 square pyramids, with Ti – O distances ranging from 1.8372 to 1.9873 Å. These TiO_5 units dimerize to form Ti_2O_9 apex-shared square pyramids. Ti(2), on the other hand, is six coordinated forming $\text{Ti(2)O}_5\text{Cl}$ octahedra with

Ti – O/Cl distances ranging from 1.8480 to 2.6397 Å. Two of the TiO₅Cl units form vertex shared Ti₂O₉Cl₂ dimers. Additionally, the Ti(2) site in the structure is disordered over two positions, Ti2A and Ti2B. The split Ti2 position is coupled with O/Cl disorder of the nearby Cl site, Cl1. A physically sensible disorder model of the distribution of TiA/B and O/Cl is illustrated in Figure 2.

Silicon, Si(1) and Si(2), in the structure, are each located in a four coordinate tetrahedral coordination environment. Si(1)O₄ corner shares to form Si₄(1)O₁₂ rings that generate [Ti₂Si₄O₁₃] layers by connecting to Ti₂O₉ dimers, Figure 3. Si(2)O₄, on the other hand, corner shares to form bent Si₂(2)O₇ pyrosilicate groups that generate [Ti₂Si₄O₁₅Cl₂] layers by connecting to Ti₂O₉Cl₂ dimers, Figure 4. Si(1) and Si(2) exhibit Si – O distances ranging from 1.5986 to 1.6483 Å, and 1.5868 to 1.6651 Å, respectively.

The structure also contains two crystallographically unique Ba centers, Ba(1) and Ba(2). Ba(1) is located in an irregular eleven-coordinated polyhedron with Ba – O(Cl) distances ranging from 2.7362 to 3.2991 Å, whereas Ba(2) is located in a twelve-fold coordinated polyhedron with Ba – O distances ranging from 2.8112 to 3.1789 Å. Both 2D [Ti₂Si₄O₁₃] layers and [Ti₂Si₄O₁₅Cl₂] layers are linked by interlayer Ba atoms to form the overall 3D structure as shown in Figure 1.

Based on the chemical composition of the reported compound, the average oxidation state of Ti is +3.54, indicating the presence of both Ti(III) and Ti(IV). A bond valence sum (BVS) [41,42] analysis of titanium assuming all titanium is +3 generates valences of 3.23, 3.39, and 3.34 for Ti1, Ti2A, and Ti2B, respectively. Using the identical treatment but assuming all titanium is +4 generates valences of 3.45, 3.83, and 3.55, respectively. These intermediate results between +3 and +4 corroborate the formal oxidation state of +3.54 for titanium. Based on these calculation, it seems that all the titanium sites contain mixed valent Ti(III/IV).

3.3 Relationship to the Fresnoite Structure

In Ba₃Ti₂Si₄O₁₄Cl_{0.91}O_{0.09}, the titanium is present as TiO₅ square pyramids and TiO₅Cl octahedra. These species are arranged into two types of layers, those containing fused Ti₂O₉ and Si₄O₁₂ groups and those containing fused Ti₂O₉Cl₂ and Si₂O₇ groups. These two layer types are connected into a three-dimensional structure by the presence of interlayer barium cations. This arrangement is very reminiscent of fresnoite, a titanium containing silicate mineral, Ba₂(TiO)Si₂O₇, in which titanium takes on the +4 oxidation state [43]. There exists an

extensively studied, large structural family related to fresnoite of general formula $A_2MM'_2O_8$ ($A = Sr^{2+}$ or Ba^{2+} , $M = Ti^{4+}$, and $M' = Si^{4+}$ or Ge^{4+}), which consists of two-dimensional layered crystal structures [44–49]. These layers contain corner sharing MO_5 square pyramids isolated from each other by M'_2O_7 groups. Conceptually, the structure of $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$ can be obtained from the fresnoite, $Ba_2(TiO)Si_2O_7$, in three steps. The first step consists of mirroring one of the Ti/Si layers of fresnoite and the second step consists of adding a sixth oxygen atom to the square pyramids of the other layer to form Ti octahedra and mirroring this new Ti/Si layers. Finally, $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$ can be obtained via a third and final step by substituting the apex oxygen atoms present in the octahedral Ti with Cl atoms. (Figure 5)

3.4 Magnetic Susceptibility

The temperature dependence of the magnetic susceptibility of $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$ was measured in an applied field of 1000 Oe and is shown in Figure 6. In $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$, the Ti_2O_9 and $Ti_2O_9Cl_2$ groups are isolated from one another by intervening Si_2O_7 and Si_4O_{12} groups, respectively, limiting the possibility of long range magnetic order. One might consider the possibility of forming spin dimers, however, the data reveal no deviation from the Curie-Weiss (C-W) at high temperatures. This is not surprising as the titanium dimers are all mixed Ti(III/IV), where statistically only 25% of them would have potential d^1 - d^1 interactions, an effect not expected to become noticeable at high temperatures. There is a discontinuity in the susceptibility data below 100 K, which might be due to a structural change that takes place resulting in charge ordering. Future work will focus on lower temperature structural studies at synchrotron or neutron facilities. The inverse susceptibility is linear at high temperatures (150 K – 300 K) and the effective magnetic moment of $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$ is $1.64 \mu_B$ /formula unit, which is in good agreement with the theoretical value of $1.65 \mu_B$. The associated Weiss constant is -12.8 K suggesting the presence of antiferromagnetic interactions between the Ti(III) species.

4. Conclusion

A new mixed valent Ti(III/IV) containing silicate, $Ba_3Ti_2Si_4O_{14}Cl_{0.91}O_{0.09}$, was obtained in single crystal form via high temperature molten chloride flux growth. Metallic Mg was used to reduce, *in situ*, Ti(IV) to Ti(III). The material consists of 2D layers of fused Ti_2O_9 and Si_4O_{12} groups and 2D layers of fused $Ti_2O_9Cl_2$ and Si_2O_7 groups connecting via Ba cations to create an extended 3D structure. The magnetic susceptibility shows simple paramagnetism at high

temperatures (>100 K). Below 100 K, there might be a structural change taking place, which resulting in charge ordering.

Supporting Information

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD-431935.

Acknowledgement

Financial support for this work was provided by the National Science Foundation through award DMR-1301757 and is gratefully acknowledged.

Table 1. Crystallographic Data for Ba₃Ti₂Si₄O₁₄Cl_{0.91}O_{0.09}.

Formula weight	877.91
Temperature (K)	300(2)
Crystal system	Tetragonal
Space group	<i>P4/mbm</i>
<i>a</i> (Å)	8.6717(2)
<i>c</i> (Å)	18.6492(5)
Volume (Å ³)	1402.39(7)
<i>Z</i>	4
Density (g/cm ³)	4.158
Abs coeff (mm ⁻¹)	9.979
Cryst size (mm ³)	0.100 X 0.060 X 0.030
θ ° range	2.184– 36.447
Completeness to θ _{max} (%)	99.8
<i>R</i> (int)	0.0324
GOF (<i>F</i> ²)	1.215
<i>R</i> (<i>F</i>) ^{<i>a</i>}	0.0156
<i>R</i> _w (<i>F</i> _o ²) ^{<i>b</i>}	0.0337
^{<i>a</i>} <i>R</i> (<i>F</i>) = Σ <i>F</i> _o – <i>F</i> _c /Σ <i>F</i> _o . ^{<i>b</i>} <i>R</i> _w (<i>F</i> _o ²) = [Σ <i>w</i> (<i>F</i> _o ² – <i>F</i> _c ²) ² /Σ <i>w</i> (<i>F</i> _o ²) ²] ^{1/2} .	

Table 2. Selected Interatomic Distances (Å) for Ba₃Ti₂Si₄O₁₄Cl_{0.91}O_{0.09}.

Ba(1)–O(3)	2.7362(16)	Ba(2)–O(1) X 4	2.8112(13)
Ba(1)–O(3) X 2	2.8365(10)	Ba(2)–O(6) X 2	2.9316(15)
Ba(1)–O(2) X 2	2.8670(11)	Ba(2)–O(1) X 4	3.0289(15)
Ba(1)–O(5)	2.9146(15)	Ba(2)–O(8)	3.1789(1)
Ba(1)–O(2) X 2	2.9898(11)	Ti(1)–O(7)	1.8372(6)
Ba(1)–O(1B)	3.2991(2)	Ti(1)–O(2) X 4	1.9873(11)
Ba(1)–Cl(1) X 2	3.2991(2)	Ti(2B)–O(1) X 4	2.0280(30)
Ti(2A)–O(8)	1.8480(11)	Ti(2B)–Cl(1)	2.1710(11)
Ti(2A)–O(1)X 4	1.9710(12)	Ti(2B)–O(8)	2.3170(11)
Ti(2A)–Cl(1)	2.6397(14)	Si(2)–O(3)	1.5868(16)
Si(1)–O(4)	1.5986(5)	Si(2)–O(1) X 2	1.6148(12)
Si(1)–O(2) X 2	1.6048(11)	Si(2)–O(6)	1.6651(10)
Si(1)–O(5)	1.6483(8)		

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Ba₃Ti₂Si₄O₁₄Cl_{0.91}O_{0.09}. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	Occ.	x	y	z	U(eq)
Ba(1)		1725(1)	3275(1)	2815(1)	10(1)
Ba(2)		6815(1)	1815(1)	0	11(1)
Ti(1)		0	0	4015(1)	12(1)
Ti(2A)	0.911(14)	0	0	991(1)	8(1)
Ti(2B)	0.089(4)	0	0	1242(6)	8(1)
Si(1)		3712(1)	1288(1)	4144(1)	7(1)
Si(2)		3745(1)	1255(1)	1363(1)	8(1)
Cl(1)	0.911(4)	0	0	2406(1)	14(1)
O(1B)	0.089(4)	0	0	2406(1)	14(1)
O(1)		2143(1)	756(2)	987(1)	23(1)
O(2)		2112(1)	750(1)	3792(1)	12(1)
O(3)		3760(1)	1240(1)	2214(1)	12(1)
O(4)		3660(2)	1340(2)	5000	16(1)
O(5)		0	5000	3890	14(1)
O(6)		5000	0	1023	24(1)
O(7)		0	0	5000	13(1)
O(8)		0	0	0	16(1)

Figure 1. Extended structure of $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$, along the A) crystallographic $[101]$ direction and B) c -axis. The purple, gray, blue, cyan, green, and red represent Ba, Si, TiO_5Cl octahedra, TiO_5 square pyramids, Cl, and O, respectively. Ba connectivities are not shown for clarity.

Figure 2. Physically sensible disorder model of the distribution of TiA/B and O/Cl in $\text{Ti}_2\text{O}_9\text{Cl}_2$ octahedral dimers.

Figure 3. $[\text{Ti}_2\text{Si}_4\text{O}_{13}]$ layers composed of Ti_2O_9 apex-shared square pyramids and $\text{Si}_4(1)\text{O}_{12}$ rings.

Figure 4. $[\text{Ti}_2\text{Si}_4\text{O}_{15}\text{Cl}_2]$ layers composed of fused $\text{Ti}_2\text{O}_9\text{Cl}_2$ vertex-shared octahedra and bent $\text{Si}_2(2)\text{O}_7$ pyrosilicate groups.

Figure 5. Conceptual relationship of the $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ to Fresnoite.

Figure 6. Temperature dependence of the molar magnetic susceptibility, χ , and inverse susceptibility, $1/\chi$, of $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}_{0.91}\text{O}_{0.09}$ in an applied field of 1000 Oe.

Reference

- [1] M. Evain, M.H. Whangbo, L. Brohan, R. Marchand, *Inorg. Chem.* 29 (1990) 1413-1416.
- [2] S.J. Clarke, A.J. Fowkes, A. Harrison, R.M. Ibberson, M.J. Rosseinsky, *Chem. Mater.* 10 (1998) 372-384.
- [3] L. Brohan, R. Marchand, M. Tournoux, *J. Solid State Chem.* 72 (1988) 145-153.
- [4] S. Wang, S.-J. Hwu, *J. Solid State Chem.* 90 (1991) 377-381.
- [5] J.F. Schooley, W.R. Hosler, M.L. Cohen, *Phys. Rev. Lett.* 12 (1964) 474-475.
- [6] J.F. Schooley, H.P.R. Frederikse, W.R. Hosler, E.R. Pfeiffer, *Phys. Rev.* 159 (1967) 301.

- [7] D.C. Johnston, H. Prakash, W.H. Zachariasen, R. Viswanathan, Mater. Res. Bull. 8 (1973) 777-784.
- [8] D.C. Johnston, J. Low Temp. Phys. 25 (1976) 145-175.
- [9] M.P. Rogge, J.H. Caldwell, D.R. Ingram, C.E. Green, M.J. Geselbracht, T. Siegrist, J. Solid State Chem. 141 (1998) 338-342.
- [10] H.-P. Hong, Mater. Res. Bull. 11 (1976) 173-182.
- [11] M. Barj, H. Perthuis, P. Colomban, Solid State Ionics 11 (1983) 157-177.
- [12] S. Wang, S.-J. Hwu, J. Solid State Chem. 90 (1991) 31-41.
- [13] A. Leclaire, A. Benmoussa, M.M. Borel, A. Grandin, B. Raveau, J. Solid State Chem. 77 (1988) 299-305.
- [14] S. Wang, S.J. Hwu, Chem. Mater. 4 (1992) 589-595.
- [15] S. Wang, S.-J. Hwu, J. Solid State Chem. 92 (1991) 219-226.
- [16] A. Benmoussa, M.M. Borel, A. Grandin, A. Leclaire, B. Raveau, J. Solid State Chem. 84 (1990) 299-307.
- [17] A. Leclaire, A. Benmoussa, M.M. Borel, A. Grandin, B. Raveau, J. Solid State Chem. 78 (1989) 227-231.
- [18] A. Benmoussa, M.M. Borel, A. Grandin, A. Leclaire, B. Raveau, Acta Crystallogr. C47 (1991) 936-938.
- [19] M. Ohashi, M. Sarubo, S. Yamanaka, M. Hattori, Solid State Ionics 53-56 (1992) 534-538.
- [20] M. Schoneborn, R. Glaum, F. Reinauer, J. Solid State Chem. 181 (2008) 1367-1376.
- [21] A. Haberer, H. Huppertz, J. Solid State Chem. 182 (2009) 484-490.
- [22] M.J. Geselbracht, A.S. Erickson, M.P. Rogge, J.E. Greedan, R.I. Walton, M.W. Stoltzfus, H.W. Eng, P.M. Woodward, J. Solid State Chem. 179 (2006) 3489-3499.

- [23] N. Kinomura, F. Muto, M. Koizumi, J. Solid State Chem. 45 (1982) 252-258.
- [24] J. Akimoto, H. Takei, J. Solid State Chem. 85 (1990) 8-14.
- [25] J. Akimoto, H. Takei, J. Solid State Chem. 90 (1991) 147-154.
- [26] J. Akimoto, H. Takei, J. Solid State Chem. 79 (1989) 212-217.
- [27] S. Wang, S.J. Hwu, J. Am. Chem. Soc. 114 (1992) 6920-6922.
- [28] S. Wang, S.-J. Hwu, Inorg. Chem. 34 (1995) 166-171.
- [29] B. Hessen, S.A. Sunshine, T. Siegrist, J. Solid State Chem. 94 (1991) 306-312.
- [30] D. Abeyasinghe, M.D. Smith, J. Yeon, G. Morrison, H.-C. zur Loye, Cryst. Growth Des. 14 (2014) 4749-4758.
- [31] D. Abeyasinghe, A.J. Cortese, J. Yeon, H.-C. zur Loye, Am. Cryst. Assn. Symp. Trans.45 (2015) 20-30.
- [32] D. Abeyasinghe, B. Gerke, G. Morrison, C.H. Hsieh, M.D. Smith, R. Pöttgen, T.M. Makris, H.-C. zur Loye, J. Solid State Chem. 229 (2015) 173-180.
- [33] D. Abeyasinghe, M.D. Smith, J. Yeon, G. Morrison, H.-C. zur Loye, Inorg. Chem. 55 (2016) 1821-1830.
- [34] A.J. Cortese, D. Abeyasinghe, B. Wilkins, M.D. Smith, G. Morrison, H.-C. zur Loye, Inorg. Chem. 54 (2015) 11875-11882.
- [35] APEX Version 2014.9-0, SAINT+ Version 8.34A and SADABS Version 2014/4. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2014.
- [36] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112-122.
- [37] C.B. Hubschle, G.M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 44 (2011) 1281-1284.
- [38] G. Morrison, H.-C. zur Loye, J. Solid State Chem. 221 (2015) 334-337.
- [39] D.E. Bugaris, H.-C. zur Loye, Angew. Chem. Int. Ed. 51 (2012) 3780-3811.
- [40] A.J. Cortese, B. Wilkins, M.D. Smith, G. Morrison, H.-C. zur Loye, Solid State Sci. 48

(2015) 7-12.

- [41] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244-247.
- [42] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192-197.
- [43] P.B. Moore, S.J. Louisnathan, *Z. Kristallogr.* 130 (1969) 438-448.
- [44] T. Hoche, C. Russel, W. Neumann, *Solid State Commun.* 110 (1999) 651-656.
- [45] E.E. Abbott, M. Mann, J.W. Kolis, *J. Solid State Chem.* 184 (2011) 1257-1262.
- [46] S.A. Markgraf, A. Halliyal, A.S. Bhalla, R.E. Newnham, C.T. Prewitt, *Ferroelectrics* 62 (1985) 17-26.
- [47] M. Kimura, K. Doi, S. Nanamatsu, T. Kawamura, *Appl. Phys. Lett.* 23 (1973) 531-532.
- [48] J. Yeon, A.S. Sefat, T.T. Tran, P.S. Halasyamani, H.-C. zurLoye, *Inorg. Chem.* 52 (2013) 6179-6186.
- [49] G. Morrison, M.D. Smith, T.T. Tran, P.S. Halasyamani, H.-C. zur Loye, *CrystEngComm* 17 (2015) 4218-4224.