

Evidence for partial cationic disorder in the $\text{BaSrFe}_4\text{O}_8$ type structure: the oxides $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$

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Received 13th November 2001, Accepted 10th January 2002

First published as an Advance Article on the web 18th February 2002

The new oxides $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ have been prepared at 1100 °C in air. XRD characterization gives evidence for a rather wide homogeneity range ($0.8 \leq x \leq 1.3$) of hexagonal phases isotypical with the tetrahedral ferrite $\text{BaSrFe}_4\text{O}_8$. The stuffed tridymite-like structure of these oxides consists of large tetrahedral double layers connected by octahedra. The formation of the solid solution is based on the existence of a partial disorder (18%) of the distribution of the Ba^{2+} and Sr^{2+} cations between the centers of the crowns—twelvefold coordination—and the octahedra. Surprisingly, the Ba^{2+} cations partly occupy the octahedra whatever the composition x , up to a value close to 34% for the Ba-rich limit. The occurrence of such a partial disorder, which also exists in the solid solution $\text{BaSr}_{1-x}\text{Ca}_x\text{Fe}_4\text{O}_8$, seems to be connected to a cooperative rotation of the (FeO_4) tetrahedra resulting in a lengthening of the metal–oxygen distances in the octahedra.

Introduction

The so-called stuffed type $\text{A}_x\text{B}_2\text{O}_4$ oxides constitute an example of the insertion of big A cations ($\text{A} = \text{Ba}, \text{Sr}, \text{K}$) in the voids of vertex-sharing BO_4 ($\text{B} = \text{Al}, \text{Fe}, \text{Ge}, \text{Zn}$) tetrahedra silica-like frameworks.¹ Within this group, the ferrite $\text{BaSrFe}_4\text{O}_8$ ^{2,3} is a rather original case: the six-membered rings of the FeO_4 tetrahedra show a regular $UUUUUU \equiv U_6 (D_6)$ directional sequence along the c axis, resulting in a 2D type structure. More precisely, it consists of large double layers where the larger barium cations occupy the centers of the crowns, these double layers being further connected by strontium cations in octahedral coordination (Fig. 1). The isomorphous calcium compounds $\text{BaCaFe}_4\text{O}_8$,⁴ $\text{BaCaAlFe}_3\text{O}_8$ and $\text{BaCaGa}_2\text{Fe}_2\text{O}_8$ ² were also reported.

The potential interest of $\text{BaSrFe}_4\text{O}_8$ -type oxides stems from the host–lattice properties (cationic mobility) which are expected for the stuffed tridymite-like $\text{A}_x\text{B}_2\text{O}_4$ minerals and synthetic oxides.⁵ Furthermore, in the case of ferrites, investigation of the magnetic properties has to be considered. In this respect, $\text{BaSr}(\text{Ca})\text{Fe}_4\text{O}_8$ are antiferromagnetic and exhibit a rare example of high Néel temperature, close to 800 K.² Under these conditions and in the frame of a systematic work on tetrahedral ferrites, we revisited the crystal chemistry of $\text{BaSrFe}_4\text{O}_8$, trying to understand whether the complete

ordering of Ba^{2+} and Sr^{2+} cations is necessary to ensure the formation of this tetrahedral double layer structure.

We report herein the synthesis and structural characterization of the partly disordered solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ ($0.8 \leq x \leq 1.3$), showing that barium partly occupies the octahedral sites, whatever the value of x , in spite of its larger size.

Experimental

Solid state reactions of appropriate mixtures of barium and strontium carbonates, thoroughly mixed with iron(III) oxide, were carried out in alumina crucibles, in air. After first heating at 600 °C for 6 hours, followed by regrinding, two successive annealings at 950 and 1100 °C for 6 hours, ensured the formation of compositions $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$. The samples were systematically air-quenched.

The cationic composition of different samples was determined by energy dispersive spectroscopy (EDS) using an analyser mounted on a JEOL 200CX electron microscope. The as-prepared compositions were characterized by powder X-ray diffraction (Philips vertical goniometer equipped with a secondary graphite monochromator, $\text{Cu-K}\alpha$ radiation). Rietveld profile calculations (Fullprof program⁶) from diffractograms recorded in the angular range 6–120° 2θ (step 0.025°, counting time 10 s) allowed determination of the values of the parameters of the hexagonal cell and of the distribution of barium and strontium cations between the two possible sites, namely the insertion site and the octahedral one (Fig. 1). Details of the calculation procedure are reported further in the text.

Results and discussion

Homogeneity range of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$

Pure compositions have been isolated for a wide range of compositions: $0.8 \leq x \leq 1.3$. The EDS analysis, which was carried out on three compositions: 0.8, 1 and 1.3, confirmed the nominal cationic composition without ambiguity. Rich Sr-compositions ($x > 1.3$) and rich Ba-compositions ($x < 0.8$) were never prepared successfully, due to the formation of the more stable ferrites, SrFe_2O_4 and BaFe_2O_4 respectively. The

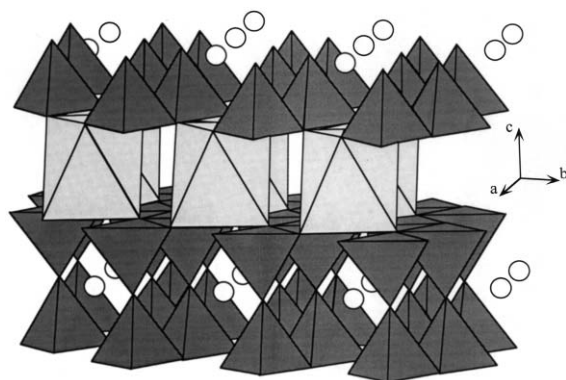


Fig. 1 Perspective view of the structure of $\text{BaSrFe}_4\text{O}_8$ showing the (Fe_4O_8) double tetrahedral layers connected by strontium octahedra. Barium atoms occupy the centers of the crowns.

Table 1 Parameters and volume of the hexagonal unit cell of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$

x	0.8	0.9	1.0	1.1	1.2	1.3
$a/\text{\AA}$	5.4475(2)	5.4456(2)	5.4431(2)	5.4414(2)	5.4388(2)	5.4372(2)
$c/\text{\AA}$	8.1147(4)	8.0990(3)	8.0767(3)	8.0704(3)	8.0591(3)	8.0549(3)
$V/\text{\AA}^3$	208.544(1)	207.995(1)	207.232(1)	206.931(1)	206.454(1)	206.225(1)

diffractograms of six compositions were indexed in an hexagonal cell. The values of a_h , c_h and V_h , the unit cell volume, as-obtained from Rietveld calculations (Table 1) vary continuously (Fig. 2), depending on x , the Sr-composition. The decrease of the unit cell constants *versus* x is rather anisotropic: it concerns mainly the c_h parameter $\Delta c_h = 0.06 \text{ \AA}$, as the extent of variation of a_h is much smaller $\Delta a_h = 0.01 \text{ \AA}$. This is not so surprising if one considers the part that the Ba^{2+} and Sr^{2+} cations play in the structure (Fig. 1): the thickness of the double tetrahedral layers and the interlayer space will be rather sensitive to the size of these cations, whereas the a_h parameter, which defines the periodicity of the hexagonal layers, will be fixed by the Fe^{3+} cations. In any case, the variation of the cell constants gives evidence of the homogeneity of the solid solution. Consequently, the mixed oxide $\text{BaSrFe}_4\text{O}_8$, previously described as a unique compound, has to be understood in terms of the $x = 1$ composition of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ ($0.8 \leq x \leq 1.3$).

Structure calculations: partial disorder of the $\text{Ba}^{2+}/\text{Sr}^{2+}$ distribution

Bearing in mind the previous results concerning the structure of $\text{BaSrFe}_4\text{O}_8$ ^{2,3} which state that the distribution of Ba^{2+} and Sr^{2+} cations is fully ordered, in the twelfold and octahedral sites respectively, we have to understand the distribution of these two species in the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ for $x \neq 1$.

At first, it must be emphasized that the Ba/Sr order precludes the occurrence of a homogeneous substitutional mechanism in

the full range of existence of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$, as it is deduced from the variation of the cell constants. Under these conditions, it seemed to be necessary to revisit the structure of $\text{BaSrFe}_4\text{O}_8$, to check more precisely the hypothesis of the possible existence of some cationic disorder at the Ba and Sr sites. The two sets of data published for the structure of $\text{Ba}_2\text{SrFe}_4\text{O}_8$ both point to unusual values of the isotropic thermal factors at these sites: $-B(\text{Ba}) = 1.03 \text{ \AA}^2$ and $B(\text{Sr}) = 0.14 \text{ \AA}^2$, from X-ray powder diffraction (integrated intensities) at RT;² $-B(\text{Ba}) = 2.1 \text{ \AA}^2$ and $B(\text{Sr}) = 0.6 \text{ \AA}^2$, from neutron powder diffraction (integrated intensities) at $497 \text{ }^\circ\text{C}$.³

Our own X-ray Rietveld calculations, carried out at RT for $\text{BaSrFe}_4\text{O}_8$ in the space group $P\bar{3}1m$ confirm the above reported tendency towards a large difference between the thermal factors of the Ba^{2+} and Sr^{2+} cations: $1.42(5) \text{ \AA}^2$ for Ba and $0.25(7) \text{ \AA}^2$ for Sr. A partial disorder in the Ba/Sr distribution may be the origin of this difference. It was calculated in terms of a refinement of the (Ba, Sr) occupancy of the two sites, by applying the constraint of an overall equal amount of the two metals. After convergence of the calculation procedure, one observes that a mixed occupancy corresponding to the balance $0.82(1)/0.18(1)$ occurs at each site. Simultaneously, there is a significant improvement of the thermal factors: $0.90(7)$ and $0.98(8)$ at the Ba and Sr site respectively, without any significant variation of the R_B factor.

The most important consequence of this result is found in the opportunity to deal in a satisfactory way with the problem of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$. The mixed occupancy of the Ba and Sr sites allows understanding of the existence of this new solid solution and further, the modelling of the variation of the partly disordered distribution of Ba and Sr.

Table 2 lists for six compositions of the solid solution, including $x = 1$, the values of the full sets of variable parameters, namely: the three positional parameters z_{Fe} , x_{O_2} , z_{O_2} , the Ba/Sr balance at the Ba(Sr) sites and the thermal factors of the five independent atoms. The very smooth variation of the positional parameters means that the basic geometrical properties of the tetrahedral ferrite are retained within the homogeneity range of the solid solution. The values of the isotropic thermal factors of the Ba(Sr) sites are always close to 1 \AA^2 or even smaller for the rich Sr-compositions ($x > 1$). As expected, the Ba/Sr balance shows a systematic variation *versus* x : a strontium (barium) enrichment of both the Sr and the Ba sites occurs when the value of x increases (decreases). This is clearly demonstrated in Fig. 3, which gives a graphic representation of the as-calculated Sr(Ba) content of each site *versus* x in comparison with the hypothetical one which is deduced from a fully ordered Ba/Sr distribution of $\text{BaSrFe}_4\text{O}_8$. From this evolution, the following features can be emphasized:

(i) The deviation of the Sr(Ba) content of the Sr(Ba) sites with respect to the theoretical one remains approximately constant within the homogeneity range, *i.e.* a partial disorder of the Ba/Sr distribution close to 18% is found for any composition of the solid solution.

(ii) The limits of the homogeneity range are fixed by the maximum amount of the minor cation in each site, namely: 41% of Sr in the Ba site, for the largest Sr-composition ($x = 1.3$) and 34% of Ba in the Sr site, for the largest Ba-composition ($x = 0.8$). Interestingly, the parts that Ba and Sr play in the existence of the limits of the solid solution are not identical. The ability to get richer Sr-compositions than the Ba one reveals a stabilizing effect of Sr which is larger than that of Ba. At this

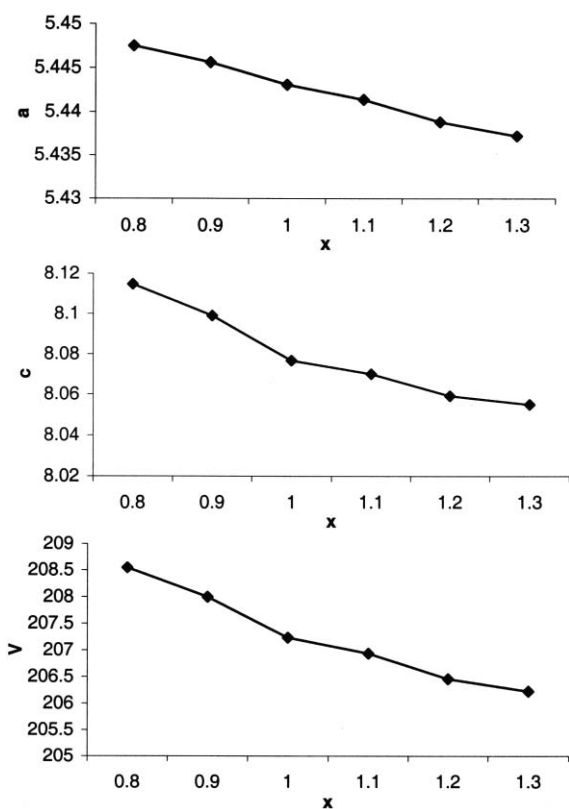


Fig. 2 Unit cell parameters (\AA) and volume (\AA^3) *versus* x in the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$.

Table 2 Atomic parameters of six compositions of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ as obtained from X-ray Rietveld calculations (space group $P\bar{3}1m$)

x	0.8	0.9	1.0	1.1	1.2	1.3
Ba occup.	$\text{Ba}_{0.86}/\text{Sr}_{0.14}$	$\text{Ba}_{0.86}/\text{Sr}_{0.14}$	$\text{Ba}_{0.82}/\text{Sr}_{0.18}$	$\text{Ba}_{0.75}/\text{Sr}_{0.25}$	$\text{Ba}_{0.65}/\text{Sr}_{0.35}$	$\text{Ba}_{0.59}/\text{Sr}_{0.41}$
Ba $B/\text{\AA}^2$	0.99(8)	0.87(7)	0.90(7)	0.86(7)	0.83(6)	0.81(6)
Sr occup.	$\text{Sr}_{0.66}/\text{Ba}_{0.34}$	$\text{Sr}_{0.76}/\text{Ba}_{0.24}$	$\text{Sr}_{0.82}/\text{Ba}_{0.18}$	$\text{Sr}_{0.85}/\text{Ba}_{0.15}$	$\text{Sr}_{0.85}/\text{Ba}_{0.15}$	$\text{Sr}_{0.89}/\text{Ba}_{0.11}$
Sr $B/\text{\AA}^2$	1.1(1)	1.02(7)	0.98(8)	0.75(7)	0.92(6)	0.78(6)
Fe z	0.2249(4)	0.2267(4)	0.2265(3)	0.2259(3)	0.2262(4)	0.2267(4)
Fe $B/\text{\AA}^2$	0.72(7)	0.73(5)	0.61(4)	0.81(5)	0.57(1)	0.53(1)
O_1 $B/\text{\AA}^2$	1.5(4)	2.6(4)	2.1(4)	1.3(3)	2.8(4)	0.2(4)
O_2 x	0.349(2)	0.352(2)	0.348(2)	0.345(2)	0.343(2)	0.338(2)
O_2 z	0.2885(13)	0.2891(12)	0.2923(12)	0.2924(8)	0.2932(9)	0.2907(10)
O_2 $B/\text{\AA}^2$	2.5(3)	2.2(2)	3.2(2)	1.5(2)	1.9(3)	1.6(3)
R_B	0.054	0.051	0.052	0.056	0.051	0.067

stage, it is worthwhile discussing the crystal chemistry of the $\text{BaSrFe}_4\text{O}_8$ -type structure, on the basis of the existence of a partial disorder of the distribution of the two big cations.

New data on the crystal chemistry of the stuffed tetrahedral structure type of $\text{BaSrFe}_4\text{O}_8$

The striking new data regarding the crystal chemistry of the stuffed tetrahedral structure type of $\text{BaSrFe}_4\text{O}_8$ show that a full cationic ordering between the two sites, inside the double layers and in the interlayer space respectively, is not necessary to ensure the formation of the stuffed tetrahedral structure.

The existence of a rather large homogeneity range of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ sets the problem of the lack of miscibility of the 3D structures of BaFe_2O_4 and SrFe_2O_4 . As a matter of fact, and rather surprisingly, the various 3D polymorphous structures of BaFe_2O_4 and SrFe_2O_4 , which bring different examples of (U,D) directional sequences of tridymite-like stuffed tetrahedral structures,⁷⁻¹⁰ never exhibit extended ranges of solid solution. From this, the parts that Ba and Sr play in the existence of these structures seem to be so different, as only a mixed structure which allows a full ordering of Ba and Sr will be able to form. Clearly, this is not true since Ba and Sr can replace each other, to a significant extent, in the twelfold and octahedral sites of the layer structure.

The comparison of $\text{BaSrFe}_4\text{O}_8$ and $\text{BaCaFe}_4\text{O}_8$ is worthy of note. CaFe_2O_4 , due to a decrease of the size and the ionic character of Ca^{2+} , cannot exhibit a stuffed tetrahedral structure but rather an octahedral one, built up from corner-sharing double rutile-like chains with Ca^{2+} cations inserted in the tunnels. As a consequence, the formation of a mixed (Ba,

Ca) ferrite is unlikely and the existence of $\text{BaCaFe}_4\text{O}_8$ will strongly depend on the full ordering of Ba and Ca. Revisiting the structure of $\text{BaCaFe}_4\text{O}_8$ shows, as expected, that no disorder of the distribution of Ba and Ca can occur. This is attested by the "good" values of the thermal factors at the Ba and Ca sites, both found to be close to 0.5\AA^2 . In order to learn about the possible simultaneous presence of Ba, Sr and Ca in the $\text{BaSrFe}_4\text{O}_8$ type structure, we have also investigated the Sr \rightarrow Ca replacement. A full homogeneity range of the solid solution $\text{BaSr}_{1-x}\text{Ca}_x\text{Fe}_4\text{O}_8$ ($0 \leq x \leq 1$) is observed. The calculation of the cationic distribution of three selected compositions, $x = 0.2, 0.5, 0.8$ (Table 3), shows the full ordering of Ca which always occupies the interlayer octahedral sites. Moreover, one observes the presence of a small amount of Ba in the octahedral sites, coupled with a corresponding amount of Sr in the twelfold sites of the double layers. Thus, the presence of Ca does not prevent the occurrence of a partial disorder of the pair (Ba, Sr). This tendency remains approximately unchanged with respect to the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$: 16% as an average value in $\text{BaSr}_{1-x}\text{Ca}_x\text{Fe}_4\text{O}_8$ and 18% in $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$. This must be a specific property of the $\text{BaSrFe}_4\text{O}_8$ -type structure.

A detailed understanding of the contribution of each of the components of this partial disorder, *i.e.* the presence of Sr in the twelfold sites and that of Ba in the octahedral sites, can be obtained. As described above, on the basis of the larger tendency of the $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ solid solution toward the Sr-rich compositions, the more favourable effect of Sr has been emphasized. This is not so surprising as the twelfold coordination in the center of the crowns in the double tetrahedral layers shows rather long metal–oxygen distances, in the range 3–3.15 Å. The big cations are not tightly bound to oxygen, and consequently, obtaining mixed occupancy by Ba and Sr cations is very easy. Conversely, the metal–oxygen distances in the octahedral sites of the interlayer space are smaller than the usual distances calculated from the ionic radii: 2.56–2.46 Å, depending on x , the Sr composition, to be compared with 2.75 and 2.58 Å for Ba–O and Sr–O in octahedral coordination, respectively. A tentative explanation of this phenomenon can be found in the existence of cooperative effects of the octahedral coordination with the twelve one, *i.e.* a coupling of the shortening and the lengthening of the metal–oxygen distances, respectively, will allow the existence of the partial disorder of the cationic distribution.

As a logical consequence of this, the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ cannot be thought of as an ideal one. Clearly, a random distribution of Ba(Sr) over the two sites has to be ruled out. In contrast, one can think of local ordering

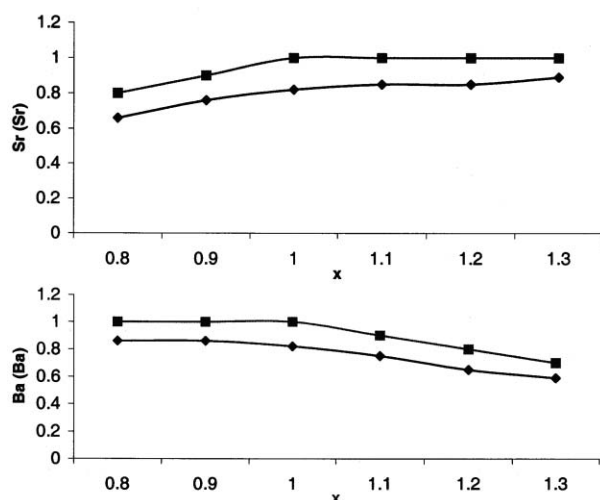


Fig. 3 Graphic representation of Sr(Sr) and Ba(Ba), the Sr and Ba content of the Sr and Ba sites respectively, versus x in the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$. The lower drawing features the as-calculated data and the upper one, the hypothetical data corresponding to a fully ordered Ba/Sr distribution.

Table 3 Occupancy of the twelfold and octahedral sites for three compositions of the solid solution $\text{BaSr}_{1-x}\text{Ca}_x\text{Fe}_4\text{O}_8$

x	0.2	0.5	0.8
CN XII	$\text{Ba}_{0.89}/\text{Sr}_{0.11}$	$\text{Ba}_{0.90}/\text{Sr}_{0.10}$	$\text{Ba}_{0.97}/\text{Sr}_{0.03}$
CN VI	$\text{Ca}_{0.20}/\text{Sr}_{0.69}/\text{Ba}_{0.11}$	$\text{Ca}_{0.50}/\text{Sr}_{0.40}/\text{Ba}_{0.10}$	$\text{Ca}_{0.80}/\text{Sr}_{0.17}/\text{Ba}_{0.03}$

phenomena in terms of “aggregation” of the cations in rich Ba(XII)–Sr(VI) and Sr(XII)–Ba(VI) microdomains, respectively. In any case, the increase of the Ba content of the solid solution, which results in a continuous increase of the amount of Ba in octahedral coordination, will destabilize the overall structure rather quickly.

Concluding remarks

The existence of the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$ is based on the ability of Ba and Sr to occupy simultaneously the two different sites of the stuffed tetrahedral structure, namely: the twelvefold one, in the crowns of the double layers, and the octahedral one, in the interlayer space. The extent of disorder of the cationic distribution is limited, due to the constraints resulting from the presence of Sr in the crowns and above all, Ba in the octahedral sites. In this respect, a similarity can be found with the case of the mineral α -celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$.¹¹ This stuffed tetrahedral aluminosilicate exhibits another example of a $U_6(D_6)$ directionality of the $\text{Al}(\text{Si})\text{O}_4$ tetrahedra, resulting in a double layer structure. The topology of the double layer is modified, involving a cooperative rotation of the tetrahedra, which transforms the triangular window into a hexagonal one (Fig. 4). Consequently, the coordination of the cation inserted in the interlayer space moves from an octahedral one to a twelvefold prismatic one. These sites are large enough to receive Ba^{2+} cations, while the centers of the crowns are unoccupied.

From this, one can propose that in the solid solution $\text{Ba}_{2-x}\text{Sr}_x\text{Fe}_4\text{O}_8$, some degree of cooperative rotation of the tetrahedra will allow a lengthening of the metal–oxygen distances in the interlayer site. This will occur specifically when Ba occupies this site. At this stage, no clear experimental evidence for this phenomenon was obtained; nevertheless, the somewhat abnormally large standard deviation on the $\text{O}_{(2)}$ atoms, as previously reported,² may be its signature.

The work in progress takes into account, at first, the potential cationic mobility properties of the $\text{BaSrFe}_4\text{O}_8$ -type

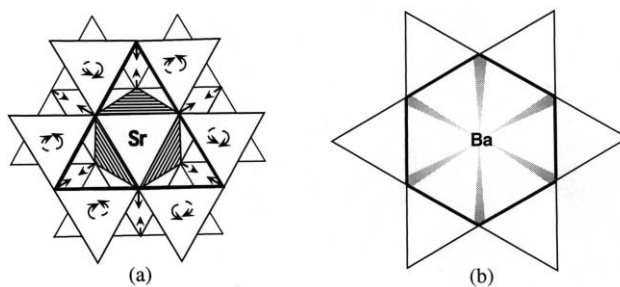


Fig. 4 Cooperative rotation of the tetrahedra in the $\text{BaSrFe}_4\text{O}_8$ type structure (a), transforming the triangular window of the double layer into the hexagonal one of the α -celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$ -type structure (b).

oxides. The rather large space which is offered in the crowns suggests mobility pathways. Application of the usual candidates to these properties, such as alkaline cations, is currently under investigation.

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