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The magnetoelectric perovskite Sr₃Fe₂TeO₉: An insight from magnetic measurements and neutron powder diffraction

S.A. Ivanov^{a,1}, P. Nordblad^b, S.-G. Eriksson^c, R. Tellgren^{d,*}, H. Rundlöf^d

^a Department of Inorganic Materials, Karpov' Institute of Physical Chemistry, Ul. Vorontsovo Pole, 10 105064 Moscow K-64, Russia ^b Department of Engineering Sciences, University of Uppsala, Uppsala, Sweden ^c Department of Inorganic Chemistry, University of Gothenburg, Sweden ^d Department of Materials Chemistry, The Ångstrom Laboratory, Uppsala University, Uppsala, Sweden

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Abstract

A study of the crystallographic and magnetic structures of the double perovskite $Sr_3Fe_2TeO_9$ has been carried out on a polycrystalline sample using neutron powder diffraction (NPD) data between 10 and 650 K. An analysis of the NPD patterns at room temperature has shown that this compound crystallises in the tetragonal space group *I4/m* with a = 5.5614(7) Å and c = 7.867(1) Å and has a partially ordered arrangement of Fe and Te at the B-sites. The compound undergoes an *I4/m* \rightarrow *Fm-3m* improper ferroelectric phase transition near 460 K. A low-temperature ferrimagnetic ordering (below $T_N = 260$ K) has been followed from the magnetisation measurements and sequential NPD data analysis. In good agreement with magnetic measurements the ferrimagnetic structure with very weak magnetisation is defined by the propagation vector k = (0, 0, 0). In addition to the obtained experimental results on magnetic and electric properties some aspects of magnetoelectricity in this perovskite are also discussed and compared with those of another quaternary oxide $Sr_3Fe_2B^{6+}O_9$.

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1. Introduction

Magnetoelectric compounds (ME), which simultaneously manifest ferroelectric and ferromagnetic properties, have gained renewed and ever increasing research interest during the past years [1,2]. Search and preparation of ME materials would be a milestone for modern electronics and functionalised materials taking an advantage of two coupled degrees of freedom based on local off-centered polar distortion and electron spin [3,4]. Many efforts have been devoted to prepare new ME materials and to find ME properties in known compounds. It is very important to understand under which thermodynamic conditions and chemical environment the coexistence of magnetic and

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^{*} Corresponding author. Tel.: +46 184713776; fax: +46 18513548.

E-mail addresses: ivan@cc.nifhi.ac.ru, Sergey.Ivanov@mkem.uu.se (S.A. Ivanov), per.nordblad@angstrom.uu.se (P. Nordblad),

stene@inoc.chalmers.se (S.G. Eriksson), rte@mkem.uu.se (R. Tellgren).

¹ Fax: +7 95 975 24 50.

ferroelectric orderings can take place. One direction in searching for new ME compositions is to combine ferroelectrics with magnetic materials creating some solid solutions. Another direction is to combine Pb²⁺ and Bi³⁺ cations with lone electron pairs and magnetic cations with d-electrons in the same phase.

However, it is clear now [4] that ferroelectric ferromagnets are rare and mostly exhibit rather weak ferromagnetism. Why and under what circumstances a magnetoelectric coupling will appear is a major open question. This problem has proved difficult to tackle owing to the absence of magnetoelectrics that show such coupling. Much experimental work still needs to be done in order to reach a clear understanding of this coexistence, and eventually to search and design ME compositions. The fundamental physics mechanism behind ME compositions is rich and fascinating to be explored. Although investigation on ME compounds can be traced back to 1950s [5,6], the renaissance of this class of materials was just heralded by the discovery of so-called colossal magnetic resistance (CMR) effect in Sr_2FeMoO_6 [7], signalling a robust interplay between the magnetic and dielectric properties.

Preliminary studies of double perovskites seem to indicate that the occurrence of magnetoelectric properties is a common feature in some of them [8]. Recently, $BiMnO_3$ and Bi_2NiMnO_6 were unravelled to be a supplement to the scarce ME perovskite family [9,10]. In the past few years, there has been renewed interest in studying the iron-based ME perovskites which have higher Curie temperatures and relatively large ME effect [11]. However, very often ME coupling is usually enhanced around magnetic or ferroelectric phase transition temperatures and one strategy for obtaining an attractive ME material is to bring these transitions to around room temperature. Despite the recent progress in understanding the physics of the double perovskites the origin of magnetism and ferroic polar distortion is still controversial. But it is clear now that these physical properties are very sensitive to even small structural changes.

In the course of our recent search for new iron-based perovskite magnetoelectrics $A_3Fe_2BO_9$ [12–15], the complex metal oxide $Sr_3Fe_2TeO_9$ (SFTO) has been studied. The importance of this class of perovskites in many applications has encouraged us to throw light on the role of different non-magnetic B'-type cations. In the current case we have studied the crystal structure, magnetic and dielectric properties of $Sr_3Fe_2BO_9$ with B = Te⁶⁺ cation with 4d¹⁰5s⁰5p⁰ electron configuration in an attempt to establish possible correlations between structural features and ME behaviour. Some reported characteristic features of SFTO are quite author-dependent [16-21]. This complex metal oxide was synthesised for the first time almost 30 years ago by Harari et al. [16] and then forgotten for many years. It belongs to the class of perovskite compounds, which simultaneously can exhibit the desired long-range ordering of electrical and magnetic dipoles [18–20]. Later it was reported to be ferrimagnetic with $T_{\rm N} = 240$ K [17] and an improper ferroelectric with $T_{\rm C}$ = 480 K [20]. The crystal structure at room temperature has been reported several times [16–21] but there are some differences in the structural details reported by different authors and still many points remain unclear. In the first reports on the preparations of SFTO [16,17] the crystal structure of this perovskite was studied by X-ray diffraction. The results of the XRD measurements presented in [16-20] led to the conclusion that the symmetry of the SFTO structure is compatible with s.g. Pm-3m. However, some authors [21] did not agree with this conclusion, and affirmed that their XRD data show undoubtedly, at least for the sample they studied, that SFTO compound has a partial ordered perovskite structure with the tetragonal s.g. 14/m. Such confusion is considered to arise from the small deviation from cubic symmetry, possible different composition and temperature treatment. The ME properties of SFTO, which not yet are well understood, need an accurate structural studies. The purpose of the present work is to report new diffraction data (both XRPD and NPD) that confirm some partial ordered arrangement of the Fe and Te cations over the B-sites of the double perovskite structure. The nuclear and magnetic structures were analysed at different temperatures to find out if the compound undergoes any phase transition at high temperatures, like many other perovskites with symmetry I4/m (see, for example [22]). The evolution of both the nuclear and the magnetic structure is analysed from NPD data, complemented by magnetic measurements. It is well known, that NPD is the most useful in the case of structural analysis of ME perovskite oxides because of the high scattering power of the oxygen atoms and the possibility to study the magnetic moments.

2. Experimental

According to the procedure described in [20] a high quality polycrystalline sample of SFTO was prepared by the conventional solid-state reaction from oxides SrO, Fe_2O_3 and TeO_2 (the SrO powder was obtained from a thermal decomposition of $SrCO_3$ at 1500 °C under vacuum). They were first weighed in an appropriate metal ratio, mixed together and ground to a uniform slurry under acetone in an agate mortar protected in a glove-box. The sample was pressed into pellets at 100 MPa and then synthesised at 930–950 °C for two days in air with several intermediate

grindings and pelletings. The maximum heating temperature was set to 950 °C because TeO₂ volatilise at higher temperatures. The samples were heated and cooled at the rate of 5 °C/min. After being allowed to cool to room temperature, the black powder product was removed from the crucible and characterised by X-ray powder diffraction (XRPD) using a Bruker D8/Advance instrument with Cu K α radiation. A step scan mode was employed with a step width of $2\theta = 0.02^{\circ}$ and a sampling time of 5 s per step. The XRPD pattern showed that the prepared sample was a single phase without any detectable impurity including SrTeO₄.

The lattice parameters were calculated using a silicon powder as an internal standard. The cation composition of the SFTO sample was determined by X-ray energy-dispersion spectrometry (EDS) using well-characterised standards. Electron probe microanalyses were performed on 20 different crystallites. The result did not differ significantly; the metal composition of the studied SFTO sample was close to the expected cation ratio, which was estimated to $Sr_{3.03(3)}Fe_{1.98(2)}Te_{0.99(2)}O_9$ if the sum of the elements is assumed to be 6. The size of the crystallites in the obtained powder does not exceed 15 µm.

Medium-resolution NPD data were collected at the Swedish Research reactor R2 in Studsvik with a Huber twocircle diffractometer equipped with an array of 35 ³He detectors. The intensity from each detector was statistically analysed and summed. A monochromator system with two copper crystals (2 2 0) in a parallel arrangement was used. The wavelength was 1.470(1) Å and the neutron flux at the sample position was approximately 10⁶ neutrons cm⁻² s⁻¹. Diffractograms were registered at different temperatures between 10 and 650 K. The powder sample of SFTO (approximately 3 g) was loaded into a thin-walled vanadium container and held in a cryostat. Absorption effects were later corrected for in the Rietveld refinements using experimentally determined value $\mu R = 0.0703$. The step-scan covered a 2θ -range 4–139.92° with a step-length 0.08°, each experiment taking approximately 15 h. The diffraction data were refined by the Rietveld method using the FULLPROF 2000 software [23]. Scattering lengths and form factors for Sr, Fe, Te and O were taken from the library of the program.

The neutron scattering lengths of Fe and Te are different ($b_{\text{Fe}} = 9.94 \text{ fm}$, $b_{\text{Te}} = 5.80 \text{ fm}$), thus the chemical composition of the B-site cations can be observed by NPD with high accuracy. The neutron scattering length of oxygen is comparable to those of the heavy atoms and NPD provide accurate information concerning its position and stoichiometry.

The diffraction peaks were described by a pseudo-Voigt function and a Lorentzian contribution to the Gaussian peak shape was refined. Peak asymmetry correction was made for angles below 35° in 2θ . The background was described by a six parameter polynomial. During the refinements, the two octahedrally coordinated metal cations (Fe and Te) were allowed to vary their proportions on the two possible metal sites. Each structural model was refined to convergence and the best result was chosen on the basis of agreement factors and stability of the refinement.

Magnetisation was measured with a Quantum Design SQUID magnetometer at the different applied fields in the temperature range 5–400 K. Zero field cooled measurements (ZFC) were performed by cooling the samples to 10 K, applying the field, and measuring the magnetisation as the samples were warmed. Magnetisation versus field curves was measured at some temperatures between 10 and 300 K.

An E8-2 bridge was used for the measurement of the dielectric properties (the frequency was 1 kHz and 1 MHz). The transmission ⁵⁷Fe Mössbauer spectra of CFWO were obtained by means of a standard constant acceleration spectrometer using a ⁵⁷Co/Pd source.

3. Results

The dielectric measurements were carried out in the 90–600 K range. The maximum in the dielectric permittivity was found near 460 K, which is in a good agreement with earlier result [20]. A Fe^{3+} charge state for the iron coordinated octahedrally has been clearly confirmed by the isomer shift and hyperfine field determined by Fe^{57} Mössbauer spectroscopy at room temperature.

Figs. 1 and 2 show results from the magnetisation measurements; in Fig. 1 the thermal evolution of the ZFC and FC susceptibility (*M/H*) is plotted under applied fields of 100 Oe and 30 kOe and in Fig. 2 the magnetisation versus field is shown at some different temperatures between 10 and 300 K. The high temperature (300 K) *M* versus *H* curve shows a linear response indicating a paramagnetic character of the sample. At lower temperatures a faster increase occurs at lower fields followed by a quasi-linear regime at higher fields. This behaviour indicates that the sample has attained a weak ferromagnetic moment. From a linear extrapolation to zero field of the curve at 50 K the value amounts to about 0.03 μ_B per iron atom. It is however not possible to distinguish an anomaly that clearly indicates that and where a



Fig. 1. Temperature dependence of the magnetisation of $Sr_3Fe_2TeO_9$ (H = 10 Oe and 30 kOe).

magnetic transition from paramagnetic to a magnetically ordered state occurs from the M/H versus T curves of Fig. 1. A hint that ordering occurs is given by an enhanced irreversibility between the ZFC and FC susceptibility below about 260 K in the 100 Oe measurements. Combining this anomaly with the results from the NPD measurements discussed below, one concludes that ferrimagnetic order, at least on short length scales, occurs below a transition temperature T_N of about 260 K. This ferrimagnetic order is from the NPD data found to sustain to the lowest temperatures of our experiments. In addition, the low temperature behaviour of the ZFC and FC magnetisation indicates that a re-entrant spin glass (SG) like transition occurs at about 60 K, this is suggested by the maximum in the low field ZFC magnetisation and the flattening off of the FC magnetisation at temperatures below 60 K. Also the suppression of the magnitude of M/H and suppression to lower temperature of the maximum in the ZFC susceptibility and the onset of



Fig. 2. M vs. H measurements at different temperatures for Sr₃Fe₂TeO₉.

irreversibility between ZFC and FC curves support this suggestion. This re-entrant spin glass behaviour should be a consequence of the existence of both ferro- and anti-ferromagnetic interactions [24] and disorder amongst these that give rise to the frustration necessary to create as spin glass like state [25]. It should also be pointed out that one of the important characteristics and problem with the re-entrant spin glass state is the apparent coexistence of remaining magnetic order observed by, e.g. neutron diffraction and the simultaneous occurrence of spin glass characteristic macroscopic response in magnetisation and susceptibility measurements. It should also be noted that the *M* versus *H* curves in Fig. 2 have been measured after cooling the sample in zero field, applying 50 kOe and measuring the magnetisation on decreasing the field to zero. This explains why the 10 K curve lies well below the 25 and 50 K curves and also indicates that a comparably large remanent magnetic moment (of order 0.5 emu/g or 0.03 $\mu_{\rm B}$ per iron atom) is achieved after removing a large field after field cooling the sample to 10 K.

The coexistence of SG and ferrimagnetic order in SFTO may lead to an additional amorphous contribution scattering to the background which was registered in our NPD patterns at low temperatures. As a conclusion, SFTO exhibits a whole range of magnetic states and starting from the paramagnetic range it has a ferrimagnetic character below 260 K, which continues down to some temperature point near 60 K where the "freezing" of the spins starts to grow.

According to the X-ray analysis, the sample was perfectly phase pure (see Fig. 3). The XRD pattern at 295 K shows the splitting of certain peaks, characteristic of a tetragonal distortion of the cubic perovskite structure. XRD pattern could be indexed on the basis of an I-centered tetragonal cell with lattice parameters a = 5.5626(5) Å, c = 7.8634(7) Å. This indexing is only in slight disagreement with the cell parameters reported in [21] but different from the primitive cubic cell parameters found in [16–20]. Such confusion is considered to arise from the small tetragonal distortion of the lattice.

Inspection of the NPD pattern at 650 K provided some evidence for several low intensity superstructure reflections suggesting a doubling of the perovskite unit cell because of the ordering between Fe and Te cations at the B-sites (see Fig. 4). Owing to the existence of these weak peaks in this pattern, possible models based on disordered B-cation distributions were rejected from future consideration for the high temperature phase. The high temperature NPD data collected at 650 K (see Fig. 5a) was refined in space group Fm-3m with a = 7.9128(4) Å (see Table 1). Initially the fractional occupancies of Fe and Te were defined as 67% Fe and 33% Te in accordance with the results of chemical analysis. The Fe/Te arrangement over the two crystallographically distinct B-sites was allowed to vary, with the constraint that the 2:1 composition ratio was maintained. The site occupancy refined by the Rietveld method supports the chosen structural model and indicates some degree of ordering between Fe and Te at the 4a and 4b sites. The contrast in scattering lengths for Fe and Te allows the distribution of these cations over these positions to be determined with a high accuracy. Refinements of the site occupancy factors of the Sr and O atoms did not reveal



Fig. 3. XRD powder pattern for Sr₃Fe₂TeO₉ at room temperature.



Fig. 4. Temperature evolution of NPD patterns for Sr₃Fe₂TeO₉. The superstructure and magnetic peaks are marked.

significant changes from full occupancy (within one standard deviation) and was therefore fixed at unity. The final Fourier difference synthesis calculation using (Fo–Fc) neutron data was without any significant maxima. However, the same structural model could not account for the NPD data starting with 400 K. When the temperature was decreased down to 400 K, some diffraction peaks were split (see Fig. 6). It was found that SFTO adopt a tetragonal distorted perovskite-type structure in the temperature range between 10 and 400 K. It was pointed out in [26] that the most possible space group for this type of double perovskites with tetragonal symmetry is *I*4/*m*. We have tried to fit our data at 400 K using other possible space groups but it was evident that the space group *I*4/*m* provided the best fit to our powder pattern. The *I*4/*mmm* model is less suitable having bad *R*-factors and negative thermal parameter for several cations. The final Fourier difference synthesis calculation showed no significant maxima. Table 1 specifies the refined atomic positions, isotropic displacement parameters, occupancy factors, and agreement factors for SFTO at different temperatures. The quality of the fit is illustrated in Fig. 5. From the Rietveld analysis, Fe and Te were found to occupy the (2a) and (2b) sites with different probability. The Fe₂/Te₂ octahedra are elongated along the *c*-axis. On the other hand, the Fe₁/Te₁ octahedra are compressed along the *c*-axis (see Table 2). Temperature evolution of Fe₁/Te₁ and Fe₂/Te₂ bonds is illustrated in Fig. 7.

The improper ferroelectric phase transition has been observed previously in Sr₃Fe₂TeO₉ near 480 K [20]. There are only three structural degrees of freedom, which may be responsible for this phase transformation: (a) cation shifts, (b) distortions of the oxygen polyhedra coordinating the cations in the A and B-sublattices and (c) tilting of the oxygen octahedra. If one takes the values of the polyhedra distortions into account the ferroic properties of SFTO may be connected with the Sr sublattice. At room temperature it was found that the distortion of the SrO₁₂ polyhedra is significantly larger (19.4 × 10⁻⁴) than for the Fe₁/Te₁ and Fe₂/Te₂ ones (0.17 × 10⁻⁴ and 0.08 × 10⁻⁴, respectively). In the many cases a phase transition with the *Fm*-3*m* \rightarrow *I*4/*m* symmetry change is related to an out-of-phase tilting of the SO₆-octahedra about the *c*-axis (the so-called $a^0 a^0 c^-$ tilt system [26]) owing to some mismatch between the size of the Sr cation and the cubooctahedral interstitial space between these octahedral units.

Fig. 8 shows a view of the crystal structure of SFTO. Both Fe and Te cations are located at alternate B-sites as a result of the difference between the sizes and valence charges of these cations. Fig. 9 represents the evolution of the lattice parameters for SFTO. Thermal variations of the unit-cell parameters would be related to the contraction of the lattice due to the magnetic transition at 260 K. The thermal expansion in the paramagnetic phase is significantly larger than in the ferrimagnetic phase. There is also clear evidence of structural phase transition $I4/m \rightarrow Fm-3m$ between 400 and 500 K.

Two major factors will determine the arrangement of different cations at the B-sites in the perovskite structure. The cations can be either ordered or statistically distributed (disordered), and the controlling factors are the difference in ionic charge and in ionic size. The ionic radii of Fe³⁺ and Te⁶⁺ are similar (0.645 and 0.560 Å, respectively) and therefore we



Fig. 5. The observed, calculated and difference plots for the fit to the NPD patterns of $Sr_3Fe_2TeO_9$ after Rietveld refinement of the nuclear and magnetic structure at different temperatures: 650 K (a), 295 K (b) and 10 K (c).

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Table 1 The nuclear and magnetic structure of $Sr_3Fe_2TeO_9$ at different temperatures

Atom	Position	x	у	z	B (Å ²)	n
T = 650 K, s.g.	Fm-3m, a = 7.9128(4)	Å, $R_{\rm p} = 3.48$, $R_{\rm wp} = 4$.63, $R_{\rm B} = 4.25$, $\chi^2 = 1$.	58		
Sr	(8c)	1/4	1/4	1/4	1.25(2)	1.0
Fe ₁ /Te ₁	(4a)	0	0	0	0.47(1)	0.72/0.28(1)
Fe_2/Te_2	(4b)	1/2	1/2	1/2	0.41(1)	0.61/0.39(1)
0	(24e)	0.2551(8)	0	0	1.45(3)	1.0
T = 400 K, s.g.	I4/m, a = 5.5709(8) Å	$c = 7.880(1) \text{ Å}, R_{p} = 3$	$3.93, R_{wp} = 5.06, R_{B} =$	4.56, $\chi^2 = 1.49$		
Sr	(4d)	0	1/2	1/4	1.12(2)	1.0
Fe ₁ /Te ₁	(2a)	0	0	0	0.43(2)	0.72/0.28(1)
Fe_2/Te_2	(2b)	0	0	1/2	0.35(2)	0.61/0.39(1)
O1	(8h)	0.281(1)	0.228(1)	0	1.26(3)	1.0
O2	(4e)	0	0	0.251(1)	1.34(3)	1.0
<i>T</i> = 295 K, s.g.	I4/m, a = 5.5614(7) Å	$c = 7.867(1)$ Å, $R_{\rm p} = 2$	3.51, $R_{\rm wp} = 4.73$, $R_{\rm B} =$	4.09, $\chi^2 = 1.52$		
Sr	(4d)	0	1/2	1/4	0.87(2)	1.0
Fe ₁ /Te ₁	(2a)	0	0	0	0.38(2)	0.72/0.28(1)
Fe ₂ /Te ₂	(2b)	0	0	1/2	0.32(2)	0.61/0.39(1)
O1	(8h)	0.282(1)	0.228(1)	0	1.03(3)	1.0
O2	(4e)	0	0	0.252(1)	1.18(3)	1.0
T = 200 K, s.g.	I4/m, a = 5.5549(8) Å	$c = 7.862(1) \text{ Å}, R_{p} = 2$	3.27, $R_{\rm wp} = 4.53$, $R_{\rm B} =$	4.13, $R_{\rm mag} = 11.2$, χ^2	= 1.52	
Sr	(4d) 0	1/2	1/4	0.66(2)	1.0	
Fe ₁ /Te ₁	(2a)	0	0	0	0.35(2)	0.72/0.28(1)
Fe ₂ /Te ₂	(2b)	0	0	1/2	0.29(2)	0.61/0.39(1)
01	(8h)	0.281(1)	0.228(1)	0	0.86(3)	1.0
O2	(4e)	0	0	0.251(1)	1.04(3)	1.0
T = 100 K, spac	e group $I4/m, a = 5.52$	514(8) Å, $c = 7.857(1)$	Å, $R_{\rm p} = 3.39$, $R_{\rm wp} = 4$.	67, $R_{\rm B} = 3.27$, $R_{\rm mag} =$	10.4, $\chi^2 = 1.55$	
Sr	(4d)	0	1/2	1/4	0.52(2)	1.0
Fe ₁ /Te ₁	(2a)	0	0	0	0.32(2)	0.72/0.28(1)
Fe ₂ /Te ₂	(2b)	0	0	1/2	0.26(2)	0.61/0.39(1)
O1	(8h)	0.280(1)	0.227(1)	0	0.74(3)	1.0
O2	(4e)	0	0	0.251(1)	1.00(3)	1.0
T = 10 K, space	group $I4/m$, $a = 5.55$	08(8) Å, $c = 7.854(1)$ Å	$A, R_{\rm p} = 3.21, R_{\rm wp} = 4.7$	0, $R_{\rm B} = 3.38$, $R_{\rm mag} = 9$	$0.8, \chi^2 = 1.64$	
Sr	(4d)	0	1/2	1/4	0.42(2)	1.0
Fe ₁ /Te ₁	(2a)	0	0	0	0.27(2)	0.72/0.28(1)
Fe ₂ /Te ₂	(2b)	0	0	1/2	0.24(2)	0.61/0.39(1)
O1	(8h)	0.280(1)	0.229(1)	0	0.71(3)	1.0
O2	(4e)	0	0	0.249(1)	0.96(3)	1.0

may say that this combination of cations in general favours a disordered arrangement. By using a long-range order parameter η , introduced in [27] for characterisation of the degree of order in the arrangement in B-sites of double perovskite lattices, the ionic distribution of Fe³⁺ and Te⁶⁺ cations for SFTO may be represented by the formula:

$$Sr[Fe^{3+}_{(2+\eta)/6}Te^{6+}_{(1-\eta)/6}]_{B1}[Fe^{3+}_{(2-\eta)/6}Te^{6+}_{(1+\eta)/6}]_{B2}O_{3}$$

The Fe³⁺ cations at the B₁ site are surrounded by six B₂ sites, which are occupied on average 61% by Fe³⁺ and 39% by Te⁶⁺ ions on average. A Fe³⁺ cation on a B₂ site is surrounded by six B₁ sites, which are occupied on average 72% by Fe³⁺ ions and 28% by Te⁶⁺. The Fe³⁺ cations provide much greater internal magnetic field to the neighbouring iron sites than Te⁶⁺ ions, and therefore the magnetic moments are expected to differ for Fe³⁺ ions on B₁ and B₂ sites, respectively. From the results obtained from analysis of our NPD data a long-range parameter η was estimated as 0.16 and the atomic arrangement in our SFTO sample can be represented as follows:

$$Sr[Fe_{0.360}^{3+}Te_{0.140}^{6+}]_{B1}[Fe_{0.306}^{3+}Te_{0.194}^{6+}]_{B2}O_3$$

The value of the magnetic transition temperature can be calculated following the hypothesis [27,28], that a magnetic ion which has no magnetic neighbours or only one magnetic neighbour does not take part in magnetic ordering. In our case there are two magnetic sublattices with octahedral sites, and k_1 and k_2 are the fractions of non-magnetic ions in the



Fig. 6. Details of selected portions of the NPD patterns at different temperatures. Splitting of some reflections at 400 K indicates the cubic to tetragonal structure change.

sublattices B_1 and B_2 , respectively. $E(k_1)$ (or $E(k_2)$ are the probabilities that a given ion of the sublattice B_2 (or B_1) has not more than one magnetic neighbour in the sublattice $B_1(B_2)$.

The number of magnetically active ions and the number of effective magnetic interactions per molecular unit are given as:

$$N = 0.5(1 - k_1)[1 - E(k_2)] + 0.5(1 - k_2)[1 - E(k_1)]$$

$$n = 6(1 - k_1)[1 - E(k_2)](1 - k_2)[1 - E(k_1)]$$

where 6 is the coordination number for a cation at the B-site of the perovskite lattice. The magnetic transition temperature of our SFTO composition $T_N(k_1, k_2)$ is related to the standard Neel temperature $T_N(0, 0)$ by

$$T_{\mathrm{N}}(k_1, k_2) = \frac{1}{6} \times \frac{n}{N} \times T_{\mathrm{N}}(0, 0)$$

where we take $T_N(0, 0) = 643$ K is the Neel temperature of perovskite with only Fe³⁺ in the B-site (BiFeO₃) in agreement with [27]. The comparison of the calculated (313(25) K) and observed (260 K) values of T_{CM} computed for our SFTO sample, on the basis of the iron content obtained from our NPD data, shows relatively good agreement.

Following the results of dielectric and magnetic measurements below 260 K SFTO exists in antiferroelectric and ferrimagnetic states. As the SFTO sample show ferrimagnetic order the nuclear and magnetic periodicity is the same, i.e., the two contributions occur at the same scattering angle. In the simplest case of ferrimagnets there are two sublattice systems. The magnetic moments at each sublattice differ in magnitude, and they are oppositely oriented. In our NPD spectra registered below 260 K the set of magnetic reflections was observed. Because the selected perovskite

Table 2 Selected interatomic distances (Å) for $Sr_3Fe_2TeO_9$ at different temperatures

650 K	295 K	200 K	10 K
	2.635(2) × 4	2.636(2) × 4	$2.637(2) \times 4$
$2.799(2) \times 12$	$2.781(2) \times 4$	$2.778(2) \times 4$	$2.775(2) \times 4$
	$2.935(3) \times 4$	$2.930(3) \times 4$	$2.923(3) \times 4$
$2.018(3) \times 6$	2.017(3) × 4	$2.011(3) \times 4$	$2.005(3) \times 4$
	$1.981(3) \times 2$	$1.975(3) \times 2$	$1.972(3) \times 2$
1.939(3) × 6	1.954(3) × 2	1.959(3) × 2	$1.956(3) \times 2$
	$1.939(3) \times 4$	$1.941(3) \times 4$	1.938(3) × 4
	650 K 2.799(2) × 12 2.018(3) × 6 $1.939(3) \times 6$	650 K295 K $2.799(2) \times 12$ $2.635(2) \times 4$ $2.799(2) \times 12$ $2.781(2) \times 4$ $2.935(3) \times 4$ $2.018(3) \times 6$ $2.017(3) \times 4$ $1.981(3) \times 2$ $1.939(3) \times 6$ $1.954(3) \times 2$ $1.939(3) \times 4$ $1.939(3) \times 4$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



Fig. 7. Temperature behaviour of Fe/Te–O bond lengths for Sr₃Fe₂TeO₉.

unit cell is already doubled by partial ordering of Fe/Te cations, all magnetic reflections are coincident with nuclear reflections. Primarily attempts were made to refine the NPD patterns at these temperatures using a model assumed in accordance with space group *I4/m*. These calculations resulted in non-acceptable high *R*-factors: in particular, big differences were found between observed and calculated intensities in the low angle 2θ region. The agreement between the observed and calculated intensities did not improve due to shifting of atoms from their idealized positions. The higher angle data covering $70^{\circ} < 2\theta < 139.92^{\circ}$ were refined using the initial model in s.g *I4/m* resulting in satisfactory *R*-factors. It also gave quite reasonable structural parameters, including the isotropic displacement parameters. These results indicate that the extra intensities decrease rapidly with increasing 2θ -angle and are most likely due to magnetic ordering of the iron cations. The additional scattering was found to disappear above 260 K. To verify that the observed



Fig. 8. A polyhedral view of the tetragonal crystal structure of Sr₃Fe₂TeO₉ at room temperature.



Fig. 9. The temperature dependence of the lattice parameters for Sr₃Fe₂TeO₉.

extra intensities indeed were magnetic to its origin, X-ray diffraction measurements were carried out at low temperatures.

Worthwhile to notice is that below 260 K there are no further changes in the NPD patterns except a progressive increase in intensity of weak magnetic reflections. This indicates that the magnetic structure remains stable across the temperature range 10–260 K. The NPD patterns of SFTO below 260 K were refined with both a nuclear and magnetic structure simultaneously. The parameters varied in the refinement of the magnetic structure were the magnitudes and the canting angles of the moments.

A ferrimagnetic structure was modeled with magnetic moments at two possible Fe positions. Magnetic moments were refined both along the a- and the c-axis. A significantly better fit to the data was obtained when refined in the c-direction. The ordered moment was constrained to lie along the c-axis, but a small component (in the frame of one standard deviation) along the a- or b-axis is possibly given within the resolution of our data. The best fit was obtained for a G-type magnetic ordering. Within this model a given moment is coupled antiparallel to its six nearest neighbours



Fig. 10. A sketch of the magnetic structure for Sr₃Fe₂TeO₉ at 10K. Diamagnetic ions are omitted.



Fig. 11. The temperature dependence of the magnetic moments of the Fe1 and Fe2 sub-lattices in Sr₃Fe₂TeO₉.

(see Fig. 10). Temperature evolution of the refined magnetic moments of B_1 and B_2 sites are shown in Fig. 11. The observed moments are related to the antisite disorder and could be evaluated for the simplest ferrimagnetic arrangements between Fe₁ and Fe₂ sublattices which produce a net magnetisation $M_s = m_{BFe1} - m_{BFe2}$.

4. Discussion

The refined atomic coordinates and bond distances for SFTO (see Tables 1 and 2) confirm the basic structural features of the proposed tetragonal perovskite structure. Fe and Te were found to occupy the (2a) and (2b) sites with different probability. The average Fe₁–O bond length is very similar to that found in other oxides with Fe³⁺ cations [29] and close to Fe³⁺–O length calculated from Shannon's ionic radii [30] for high spin electron configuration in octahedral coordination. The Fe–O–Fe superexchange pathways deviates from linear (Fe–O–Fe angle changes from 168° (10 K) up to 172° (400 K)). The observed magnetic moments of Fe are smaller than what is expected for Fe³⁺ (5.0 μ_B). In order to get some insight into the cation distribution, we carried out a bond-valence calculation by means of the Brown model [31], which gives a relationship between the formal valence of a bond and the corresponding bond



Fig. 12. Details of composition dependence of NPD patterns at 10 K for selected samples in $Sr_3Fe_2W_{1-x}Te_xO_9$ solid solutions. The decrease of integrated intensities for some magnetic reflections with Te doping is shown.



Fig. 13. Dependence of the magnetic phase transition temperature T_N from ionic radii for the series $Sr_3Fe_2B^{6+}O_9$. The uncertainty of T_N was estimated for all published data.

lengths. In non-distorted structures, the bond-valence sum rule states that the valence of the cation (V_i) is equal to the sum of the bond-valences (v_{ij}) around this cation. From individual cation–anion distances at room temperature the bond-valence sums were calculated. Fe₁ and Fe₂ cations exhibit valences 3.13(1) and 3.35(1), slightly different from those expected in this compound, of +3. Following the results of Mössbauer measurements we can conclude that the Fe cations have formally +3 valence in both oxygen environments.

The important question concerns the striking difference of NPD patterns of $Sr_3Fe_2TeO_9$ ($\eta = 0.16$) and $Sr_3Fe_2WO_9$ ($\eta = 0.33$) which was studied earlier [12] (see Fig. 12). Strong decreasing of magnetic scattering could arise from the difference of electronic states in addition to the ionic radius between W^{6+} ($5d^06s^0$) and $Te^{6+}(4d^{10}5s^05p^0)$. The same degradation of magnetic properties of Te compound in comparison with W analogue was previously reported for perovskites Sr_2CuBO_6 [36] and Sr_2NiBO_6 [37] (B = W, Te).

It can be noted that other oxides $Sr_3Fe_2B^{6+}O_9$ ($B^{6+} = Mo$, W, Te, Re, U) with perovskite structure also show the magnetic properties [12,32–35] (see Fig. 13). It is important to understand the possible influence of the B-site cations on T_N remembering that it is strongly related with the value of the $B^{3+}-O-B^{6+}$ angle and with lattice distortions. In order to establish correlation between the structural and magnetic properties the T_N values are shown in Fig. 13 as a function of the ionic radius. It should be emphasised as a tendency that T_N increases with an increasing size of the different B^{6+} cations. At the same time the influence of the degree of crystallographic order/disorder in Fe-sites and/or the oxygen deficiency on T_N still remains to be solved because the available physical and structural data are very restricted. At this stage, one cannot draw definite conclusions about this dependence and additional experimental data should be obtained. It is well known that the magnetisation of double perovskites decreases systematically with the anti-site defect concentration [38]. The actual degree of Fe/Te order depends on synthesis conditions and as a rule an increased order may be obtained by different treatment conditions [38,39]. More investigative work is needed to resolve this issue in the case of $Sr_3Fe_2B^{6+}O_9$ oxides. Studies of heat treatment effects on the structural and magnetic properties of SFTO are in progress and we shall return to this theme in our future publication.

5. Concluding remarks

We have revised some experiments that may provide key ingredients for clear understanding of the magnetoelectric properties of SFTO. The most striking feature of this compound is the coexistence of ferrimagnetic and antiferroelectric types of ordering below $T_N = 260$ K. Our NPD investigation has shown that the previous description of Sr₃Fe₂TeO₉, as being a simple cubic perovskite with s.g. *Pm-3m* at room temperature [16–20], was wrong. The

symmetry was overestimated. The ideal elpasolite-type structure with s.g. Fm-3m was found for SFTO only above $T_{\rm C} = 460$ K. The phase-pure sample of the perovskite ${\rm Sr_3Fe_2TeO_9}$ was synthesised, magnetically and structurally characterised applying the Rietveld analysis of NPD data at different temperatures. This compound shows one structural phase transition $Fm-3m \rightarrow I4/m$, and the tetragonal superstructure arises from the combination of partial cation ordering and small tilting of the oxygen octahedral (about 6°). The Fe and Te cations are partially ordered into B-sites (2a) and (2b). The precise metal–oxygen distances derived from NPD data made it possible to calculate the valences of the cations and the distortion of their polyhedra. These results suggest the electronic configuration to be Fe³⁺–Te⁶⁺. The proposed model for the ferrimagnetic structure (below $T_{\rm N}$) can be modelled with magnetic moments at two Fe positions (2a) and (2b) aligned along the [0 0 1] direction. Structural and magnetic features of magnetoelectric Sr₃Fe₂TeO₉ are considered and compared with those of other quaternary complex perovskite oxides.

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