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A Neutron Diffraction Study of Magnetically Ordered Ferroelectric Materials

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A number of compounds with perovskite-type structure $A(Fe_{0.67} B_{0.33})O_3$ (A = Ba, Pb, Sr, Ca; B = W, Te) were investigated using X-ray and neutron powder diffraction, dielectric and magnetic measurements and Mössbauer effect. The most striking feature of this type of complex perovskites is the coexistence of magnetic and antiferroelectric types of ordering in a certain temperature range. It was found that ferrimagnetic Ca, Sr and Ba compositions belong to a partially ordered perovskite-related structure, and an antiferromagnetic Pb phase to a disordered one. The possible models for nuclear and magnetic structures were proposed in accordance with the observed dielectric and magnetic properties.

Keywords Complex perovskites; magnetoelectrics; neutron powder diffraction

Introduction

Perovskite oxides of the transition elements have been studied extensively since they present interesting and frequently unexpected electric and magnetic properties [1, 2]. In many such materials the electric and magnetic dipole structures coexist and are coupled in a certain temperature interval [3, 4]. This leads in principle to new potential applications, since it is possible to change magnetic parameters by means of an electric field and vice versa. These properties are strongly influenced by the ordering of B-site cations. Despite the large number of complex perovskites prepared over the years, the problem of cation ordering is only partly understood [5]. One group of compounds which has been investigated is the magnetic perovskite ferrites $A(Fe_{0.67}B_{0.33})O_3$ (A = Ba, Pb, Sr, Ca; B = W, Te). Although

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these phases already have been studied [6–10], the details of the nuclear and magnetic structures as a function of temperature have not yet been described.

Symmetry of different phases is still a matter of discussion and its crystal-chemistry is more complicated than expected earlier. It is very important to indicate also, that these perovskites may be used as model compounds for the study of the relationship between ferroic and magnetic properties. The present paper is a part of our neutron diffraction study of some magnetic ferroelectrics, and describes the results for the indicated ferrites.

Experimental

High quality samples were prepared by a two step calcination method. Electron probe microanalysis shows that the studied samples have close to the expected cation compositions. A Fe³⁺ charge state for iron has been clearly confirmed by Mössbauer spectroscopy. Magnetic measurements were consistent with ferrimagnetic ordering for Ca, Sr and Ba phases and an antiferromagnetic one for the Pb compound. Neutron powder diffraction (NPD) data were collected at the Swedish Research reactor R2 in Studsvik ($\lambda = 1.470$ Å). Diffraction patterns were registered at different temperatures (10–700 K). The step-scan covered a 2- θ range 4.00–139.92° with a step-length 0.08°. The diffraction data were refined by Rietveld method using the FULLPROF software.

Results

The main results from the diffraction, dielectric and magnetic measurements are summarised in Table 1. The type of distorted perovskite structure is a function of A-cation. The structural analysis of $A(Fe_{0.67}B_{0.33})O_3$ (A = Ba, Pb, Sr, Ca; B = W, Te) shows a partial crystallographic order between the Fe³⁺ and W⁶⁺(Te⁶⁺) cations. The distribution of cations in the B sub-lattice was refined and the order parameter was calculated for each phase. Replacement of Ca (or Sr) by Pb leads to the disappearence of this crystallographic order whereas the substitution of Te for W produces an increasing order. The refinement of oxygen occupancy factors did not reveal significant changes from full occupancy. Below T_{CM} the neutron powder diffraction patterns contain a considerable amount of magnetic contributions. To illustrate this Fig. 1 shows the evolution of NPD patterns with temperature from which the nuclear and magnetic structures were refined. The magnetic structure of the title phases consists of two Fe sublattices alternating in all three dimensions. In the case of a ferrimagnetic structural model (for the Ba, Ca and Sr phases), consistent with the results obtained from magnetic measurements, the magnetic moments

A-cation	Pb		Sr		Ca		Ba	
B-cation	W	Te	W	Te	W	Te	W	Te
T _{CE} (K)	178	510	473	430	>600	>600	570	550
T _{NM} (K)	363	380	353	240	323	210	250	220
S.g.	Pm3m	Pm3m	I4/m	I4/m	$P2_1/n$	$P2_1/n$	P6 ₃ /mmc	P6 ₃ /mmc
a(A)	3.980(1)	3.981(1)	5.578(1)	5.561(1)	5.418(1)	5.430(1)	5.743(1)	5.772(1)
b(A)					5.509(1)	5.510(1)		
c(A)			7.864(1)	7.866(1)	7.703(1)	7.712(1)	14.114(2)	14.223(2)
β (deg.)					90.08(2)	90.06(2)		

TABLE 1 Lattice Parameters at 295 K and Transition Temperatures for $A(Fe_{0.67}B_{0.33})O_3$ (A = Ba, Pb, Sr, Ca; B = W, Te)



FIGURE 1 Temperature evolution of NPD patterns of $A(Fe_{0.67}B_{0.33})O_3$ (A = Ca, Pb, Sr; B = W, Te).

of the Fe ions are ordered anti-parallel. The moment of Fe in the B_1 sublattice is substracted from that of the B_2 sub-lattice. The best fit was obtained for a G-type magnetic ordering. For the Pb based compound the interaction between the two magnetic Fe sub-lattices are antiferromagnetic.

Structural refinement of Pb(Fe_{0.67}W_{0.33})O₃ (PFW) provides a strong evidence for the presence of disordered atomic displacements of Pb cations. Such behaviour is typical for cubic perovskites containing a Pb²⁺ cation on the A-site, due to the presence of a stereoactive electron pair. A disordered cubic structure model was proposed in which the Pb cation on the A-site is in reality located in disordered (x, x, x) sites (x = 0.042(4)). A displacement of Pb cations along the $\langle 111 \rangle$ direction increases slightly the angles between the lone pair and all the Pb–O bonds, minimising the repulsion effects. This displacement would lead to a rhombohedral lattice distortion but in the case of our experimental data it is very difficult to conclude about the possible existence of a less symmetric but ordered model.

The evolution of the NPD patterns of PFW in the antiferromagnetic region indicated magnetic peaks that could be indexed on a cubic unit cell doublet in three directions as compared to the chemical one. The best model, giving the lowest R-values, was associated with a G-type antiferromagnetic structure. Each Fe couples to six other Fe with an antiparallel magnetic coupling. The refined value of the magnetic moment for Fe cations at 10 K is $3.65(3)\mu$ B.

The Ca compound crystallizes in the monoclinic symmetry with the partial ordering between Fe and W cations at the B sites. The refinement yielded the order parameter $\lambda = 0.21(3)$.

Below T_{CM} new peaks of magnetic origin appear which can be indexed using a propagation vector k = (1/2, 1/2, 0). The ferrimagnetic structure consists of two Fe³⁺ antiparallel sublattices alternating the in c-direction. The moment of Fe³⁺ in the B₁ sublattice (3.88(6)µB) is subtracted from that of the B₂ sublattice (-3.08(7)µB). It was found that space group I4/m provided the best fit to our powder patterns for the Sr containing compounds. Figure 1 shows the evolution of the NPD patterns with temperature for the compositions x = 0, 0.5 and 1.0. The magnetic structure consists of two Fe³⁺ sublattices alternating in all three directions. The moment of Fe³⁺ in the B₁ sublattice is subtracted from that of the B₂ sublattice. The best fit was obtained for a G-type magnetic ordering. The magnetic interactions originate from long range super exchange interactions via O and W(Te) ions decreasing with concentration of Te. Comparing W and Te containing compounds, the difference in T_N is attributed to the difference in the bond angles of Fe–O–W and Fe–O–Te.

Finally the Ba based compound adopt a hexagonal structure with $W(Fe)_2O_9$ dimers, made from face shared $W(Fe)O_6$ octahedra, interconnected by corner-sharing FeO₆ octahedra. A considerable amount of mixing between Fe and W was found, although Fe prefers an isolated octahedron but not the dimer site. The magnetic cell which is doubled in the c-direction suggests a simple antiparallel coupling of ferromagnetic (001) planes of Fe moments.

Conclusions

A combination of NPD, magnetometry, dielectric and Mössbauer spectroscopy was used for study of ferroelectromagnets with formula $A(Fe_{0.67}B_{0.33})O_3$ (A = Ba, Pb, Sr, Ca; B = W, Te) in which the magnetic and ferroelectric ordering occurs simultaneously. It was shown that they are perovskite-type phases showing different types of lattice distortions and crystallographic order. The deviation from high symmetry is caused by a relatively small ionic displacements from their ideal positions. The main factor influencing the ferroic phase transition temperature is the lattice distortion degree. The symmetry of the nuclear structure increases with ionic radius from monoclinic (Ca) to tetragonal (Sr) and finally cubic (Pb).

The magnetic properties are strongly influenced by the ordering and the nature of the nonmagnetic B-site cations. Ca and Sr compounds are ferrimagnetic, showing oppositely directed Fe^{3+} magnetic moments of different magnitude (related to the two different B sublattices). The magnetic ordering of the Pb phase is antiferromagnetic. All the compounds have the G-type magnetic structure. Reasonable agreement has been found between the total magnetic moments determined from NPD data and magnetisation measurements.

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