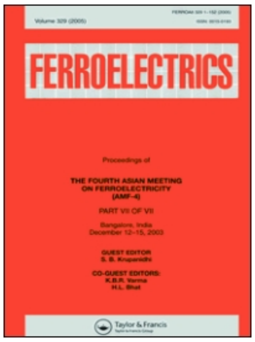

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STRUCTURAL AND MAGNETIC CHARACTERISATION OF THE DOUBLE PEROVSKITES $AA'MnWO_6$ (AA' = Ba_2, SrBa, Sr_2, SrCa and Ca_2)

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The double perovskites $AA'MnWO_6$ (AA'= Ba_2, SrBa, Sr_2, SrCa and Ca_2) have been prepared as pure powders by a conventional solid-state reaction process. Stoichiometric amounts of $BaCO_3$, $SrCO_3$, $CaCO_3$, MnO and WO_3 were mixed, ground and calcined in a nitrogen atmosphere. The materials have been studied by X-ray and neutron powder diffraction (NPD), and magnetization measurements. NPD and magnetization measurements have been carried out at different temperatures in order to correlate their structural and magnetic properties. Susceptibility- Temperature (χ-T) curves were measured between 2K and 200K in field cooled (FC) and zero-field-cooled (ZFC) modes with an applied field (H) up to 3T. Rietveld analysis of NPD data shows that the samples were B-site ordered perovskites with different types of lattice distortions. Magnetisation measurements at low temperatures indicate the antiferromagnetic ordering of magnetic moments.

<u>Keywords</u>: Neutron diffraction; Crystal structure; Double perovskite; Oxides; Magnetic materials.

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INTRODUCTION

Complex metal oxides with the general formula $A_2B'B''O_6$, where B′ and B′′ sites are occupied alternately by different cations, depending on their valences and relative ionic radii, are known as double perovskites or elpasolites[1]. These oxides can be classified into two main types, namely B-site ordered and B- site disordered perovskites. B-site ordered compositions, where B′ is magnetic while B′′ is nonmagnetic, was initially studied by Blasse[2]. It was found that some compounds of this type with an ordered perovskite structure show a considerable tetragonal distortion with $c/a>1$. Some compounds show antiferromagnetic behaviour, because of the superexchange interaction between the magnetic ions via an array of non-magnetic ions.

The structure and physical properties of this type of double perovskites depend considerably on the valence of the B′ and B′′ cations. The modification of structural and magnetic properties by changing the A, B′ and/or B′′ site cations has gained interest in recent years in order to better understand the mechanism of colossal magnetoresistance (CMR)[3,4]. Depending on the ionic radius of the A-site cations, the crystallographic structure can adopt different symmetry[5].

Ba_2MnWO_6 is a face centered cubic with the unit cell parameter a = 8.1985(3)Å (space group Fm-3m)[6]. When the Ba cation is replaced by Sr, the structure adopts the tetragonal symmetry with a = 8.0119 (4)Å, c = 8.0141(8)Å (space group $P4_2/n$)[7]. Furthermore, when Ca cations occupy the positions, the symmetry goes to monoclinic with a = 5.4618(2)Å, b = 5.6545(2)Å, c = 7.8022(4)Å and $\beta = 90.192(3)^0$ (space group $P2_1/n$)[8]. It is also interesting to observe that the antiferromagnetic transition temperature increase with the decreasing radii of A-site cations.

In the continuation of our research on double perovskites with unusual dielectric and magnetic properties, it is interesting to see the behaviour of A-site mixed compounds. We have made $BaSrMnWO_6$ and $SrCaMnWO_6$ double perovskites in single-phase form and characterized the materials by X-ray, neutron diffraction and magnetization measurements, and compared with our previously reported results.

EXPERIMENTAL

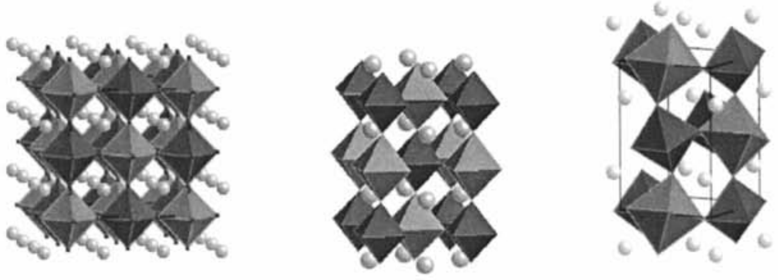
Single-phase powders were prepared by a standard solid state reaction method described elsewhere[8]. X-ray diffraction patterns were obtained from Guinier film data ($CuK_{\alpha 1}$=1.540598 Å). NPD data were collected at the 50 MW R2 research reactor at Studsvik, Sweden. The neutron wavelength was 1.470(1)Å and flux at the sample position was approximately 10^6 neutrons $cm^{-2}s^{-1}$. The step scan covered a 2θ range 4°-139.92° with a step-size of 0.08°. NPD data sets were refined by the Rietveld method using the FullProf software[9].

Magnetization measurements were carried out using a QuantumDesign Superconducting QUantum Interference Device (SQUID) magnetometer. Magnetization versus temperature curves were measured between 5 to 200 K in field-cooled (FC) and zero-field-cooled (ZFC) modes with applied fields ($\mu_0 H$) up to 3T.

REULTS AND DISCUSSIONS

Structural studies of $BaSrMnWO_6$

The NPD data were collected at 295K and refined using the tetragonal space group I4/m (no. 87). Ba_2MnWO_6 crystallise in the cubic symmetry in the space group Fm-3m. When 50% Sr is introduced in the A-site of the structure, it crystallise in the tetragonal space groups I4/m. The Woodward's notation[10] of the distortion is $a^0a^0c^-$(one tilt system)



Cubic **Tetragonal** **Monoclinic**

FIGURE 1: Schematic representation of the structural phase changes from cubic to tetragonal to monoclinic. Spheres represent the A-site cations. B-site cations are located inside the octahedra.

which can illustrate the combined effect of cation ordering and octahedral tilting (Figure 1).

TABLE 1: Crystallographic parameters, Rietveld reliability factors (at 295K) and Néel temperatures for different compositions.

	Symmetry, Space group	Lattice Parameters (Å)	R-factors (%)	Néel temp
Ba_2MnWO_6 (Ref. 6)	Cubic Fm-3m	a=8.1985(2)	R_p=3.40, R_{wp}=4.53 R_{Bragg}=1.74 χ^2=2.12	9K
$BaSrMnWO_6$	Tetragonal I4/m	a=5.7344(4) c=8.129(1)	R_p=4.50, R_{wp}=5.92 R_{Bragg}=3.79, χ^2=1.43	10K
Sr_2MnWO_6 (Ref. 7)	Tetragonal $P4_2/n$	a=8.0119(4) c=8.0141(8)	R_p=3.89, R_{wp}=5.15 R_{Bragg}=2.97, χ^2=1.81	13K
$SrCaMnWO_6$	Monoclinic $P2_1/n$	a=5.5743(6) b=5.6514(3) c=7.9231(6) β=90.187(7)	R_p=3.30, R_{wp}=4.27 R_{Bragg}=4.14, χ^2=1.47	14K
Ca_2MnWO_6 (Ref. 8)	Monoclinic $P2_1/n$	a=5.4618(2) b=5.6545(2) c=7.8022(3) β=90.192(3)	R_p=3.01, R_{wp}=3.85 R_{Bragg}=1.81, χ^2=2.34	16K

The unit cell parameters are related to that of ideal cubic perovskite as $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$, $a \approx 2a_p$ ($a_p \approx 3.89$ Å). Symmetry, lattice parameters, Rietveld reliability factors and Néel temperature for different compositions are summarised in Table 1. The Wyckoff positions were Mn on 2*b*, W on 2*a*, (Ba,Sr) on 4*d* and O on 4*e* and 8*h*, which gives an ordered perovskite structure of so-called elpasolite type. Mn and W are found to occupy alternate B-sites. The distances between Mn and O in the *ab* plane and parallel to *c*-axis are 2.157(11) and 2.160(4)Å, respectively. The distances between W and O in the *ab* plane and parallel to *c*-axis are about 1.907(1) and 1.906(2)Å, respectively. The MnO_6 and WO_6 octahedra are ordered and alternate along the three directions in the crystal structure in such a way that each MnO_6 octahedra is linked to six WO_6 octahedra and vice-versa (see Figure1).

Bond valence calculation from our observed data shows that the charge distributions of Mn and W cations close to Mn^{2+} and W^{6+}, respectively.

Structural studies of $SrCaMnWO_6$

Rietveld structure refinements of the NPD data confirm the single-phase nature of the sample with cationic and anionic stoichiometry close to the idealised formula of $SrCaMnWO_6$. A-site was equally occupied by Sr and Ca cations within the standard deviations. It is a three tilt system, showing monoclinic distortion with space group $P2_1/n$. Unit cell parameters are related to the ideal cubic perovskite as $a \approx \sqrt{2}a_0$, $b \approx \sqrt{2}a_0$, and $c \approx 2a_0$ ($a_0 \approx 3.8$ Å). The $(a^-b^-b^-)$ tilting (Woodward's notation)[10] of MnO_6 and WO_6 octahedra is readily apparent together with the distribution of Mn and W ions over the B sites in Figure 1. The monoclinic β angle is only slightly different from 90°, ~90.192°, the metric of this structure seems to be strongly pseudo-orthorhombic. The 2*d* and 2*b* sites were fully occupied by Mn and W atoms, respectively. No mixing of sites between Mn and W was found during the Rietveld refinement. The crystal structure is distorted due to the smaller size of A-site cations, which force the $(Mn,W)O_6$ octahedra to tilt in order to optimise the (Ca,Sr)-O bond distances. The MnO_6 and WO_6 octahedra are ordered and alternate along the three directions in the crystal structure (see Fig. 1). The driving force for the B′and B′′ ordering is the size and charge difference between both kinds of cations. Since the six-fold-coordinated ionic radii for Mn^{2+} and W^{6+} ions are 0.97Å and 0.74Å, respectively[11], there will be a tendency for Mn^{2+} ions to occupy larger octahedral sites than W^{6+} ions. The MnO_6 octahedra (volume = 13.4105(2) $Å^3$) is significantly larger than the WO_6 octahedra (volume = 9.4870(9) $Å^3$). Calculation of bond valence sums (BVS), using the Brown's bond valence model[12], from the structural parameters, indicated that Mn and W cations seem to be in their divalent and hexavalent oxidation states, respectively.

Magnetisation measurements:

The temperature dependence of the magnetisation was measured for the samples under both ZFC and FC conditions at different applied fields. Magnetisation measurements in the temperature range 5 to 200K shows that all samples are antiferromagnetic. The antiferromagnetic transition temperature i.e. Néel temperature (T_N) increases with the decreasing size of the A-site cations (see Table 1). Above the transition temperature T_c the sample shows typical Curie-Weiss behaviour.

CONCLUSIONS

Concentration dependence of A-site cations have been investigated in the double perovskite type structures. The increase of the paramagnetic to antiferromagnetic transition temperature with the decreasing A-site cation radius was also seen from the investigation. Magnetic structure studies using low temperature NPD data are in progress.

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