T10 - Magnetic and Ferroelectric Materials

T10 - P181

EFFECTS OF MAGNESIUM SUBSTITUTION ON THE NUCLEAR AND MAGNETIC STRUCTURES OF Nd$_{0.7}$Sr$_{0.3}$MnO$_3$

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Polycrystalline samples of nominal compositions Nd$_{0.7}$Sr$_{0.3}$Mn$_{1-y}$Mg$_y$O$_3$ (Mg = 0.0, 0.1, 0.2 and 0.3) were synthesized by the standard solid-state reaction method. Rietveld refinement of the neutron powder diffraction data shows that all samples are single phased with perovskite structure of orthorhombic symmetry. The nuclear and magnetic structures of Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ and the Mg substituted samples were studied by neutron powder diffraction and magnetic measurements. It was found that Mg initially preferred to substitute for Nd and only at Mg content greater than 0.1, a measurable and increasing substitution for Mn occurred. The substitution alters the lattice parameters and O-Mn-O bond angles significantly, but the nuclear structure of the compound remains unchanged [1]. The parent compound Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ is a ferromagnetic with a Curie temperature of 210 K and a magnetic moment of Mn = 3.40(4) $_B$ at 10 K, for the substitution up to Mg = 0.1, the

system remains ferromagnetic but the Curie temperature has lowered to T$_C$ = 180 K and the magnetic moment of Mn = 3.09(4) $_B$ at 10 K. The samples with Mg substitution Mg = 0.2 and 0.3 are not ferromagnetic of long range order, but are ferromagnetic of short range order at temperatures below 250 K, and an indication of spin glass-like order is observed at low temperatures in both samples [2].

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T10 - P182

THE EFFECT OF OXYGEN DEFICIENCY ON THE ATOMIC AND MAGNETIC STRUCTURE OF MIXED-VALENCE MANGANATE La$_{1-X}$Sr$_X$MnO$_3$ (X = 0.0, 0.1, 0.2)

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The effect of oxygen deficiency, obtained by high temperature annealing under N$_2$, followed by rapid cooling, on the atomic and magnetic structure of mixed-valence manganate La$_{1-x}$Sr$_x$MnO$_{3-}$ (x = 0.0, 0.1, 0.2) was studied by Rietveld analysis of neutron powder diffraction data. For LaMnO$_3$, the loss of oxygen was accompanied by a change from one orthorhombic structure ('Orto-II') to another ('Orto-I'), both in space group *Pnma*. Also, a transformation from ferromagnetic to antiferromagnetic ordering at low temperature took place. All other samples were either paramagnetic or ferromagnetic. La$_{0.9}$Sr$_{0.1}$MnO$_3$, initially a mixture of orthorhombic and rhombohedral phases at room temperature, became single phased orthorhombic after the

oxygen depletion but also at low temperature. La$_{0.8}$Sr$_{0.2}$MnO$_3$ remained in rhombohedral symmetry. The best-fit magnetic models for the as-prepared and quenched samples were not the same. Consequently, we propose models of the magnetic structure for the oxygen deficient mixed-valence manganates La$_{1-x}$Sr$_x$MnO$_3-$ (x = 0.1, 0.2). In addition, alternating (222) ferromagnetic planes of the two magnetic sublattices in the oxygen deficient La$_{0.8}$Sr$_{0.2}$MnO$_3$ may indicate an ordered state of Mn-ions with different oxidation states.

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CHEMICAL TUNING OF THE INTERLAYER MAGNETIC COUPLING IN TlCo$_2$Se$_{2-x}$S$_X$

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The tetragonal system TlCo$_2$X$_2$ (X = S/Se) belongs to the ThCr$_2$Si$_2$ type family. It contains perfect atomic square-planer layers of cobalt. The layers are separated by the large non-magnetic atoms thallium and selenium/sulphur. The structure can be seen as a layered magnetic structure with two interesting magnetic interactions distances, determining intralayer and interlayer magnetic couplings. In both TlCo$_2$Se$_2$ and TlCo$_2$S$_2$, the magnetic moments are ferromagnetically arranged in the cobalt layers (moments in the ab-plane). The interesting difference between the magnetic structures is the interlayer magnetic coupling. The distance between the cobalt layers is 6.4 Å in TlCo$_2$S$_2$ and the interlayer magnetic coupling is ferromagnetic (T$_C$ = 146 K) [1]. In TlCo$_2$Se$_2$ the distance has increased to 6.8 Å and the compound is instead antiferromagnetic (T$_N$=95 K). It is an incommensurate helical structure running along the c-axis. The turn of the magnetic moments between the cobalt layers is 121 .

Solid solution makes it possible to gradually tune the distance between the magnetic layers and thereby also the interlayer magnetic coupling. The chemistry in the structure is not changed much, due to selenium and sulphur are isovalent. Magnetic SQUID measurements showed a stable antiferromagnetic compound for TlCo$_2$Se$_{2-x}$S$_x$ (x   1.0). For higher sulphur concentration, the absolute values of the susceptibility are increased. The compounds show a weak net moment and are no longer antiferromagnetic. This net moment increases until it is fully aligned for ferromagnetic TlCo$_2$Se$_{0.25}$S$_{1.75}$ [3].

Neutron powder diffraction of TlCo$_2$Se$_{2-x}$S$_x$ samples showed that the helical structure prevails for 0   x   1.5 with a gradual decrease of the coupling angle from 12 to 39 . For x   1.75 the ferromagnetic magnetic structure is stable. The magnetic peaks are shown in Figure 1, the satellites to the (001) reflection for the helix and the (002) peak for the ferromagnetic compounds. The relationship between the coupling angle and the interlayer distance of Co-Co shows an almost linear behaviour.
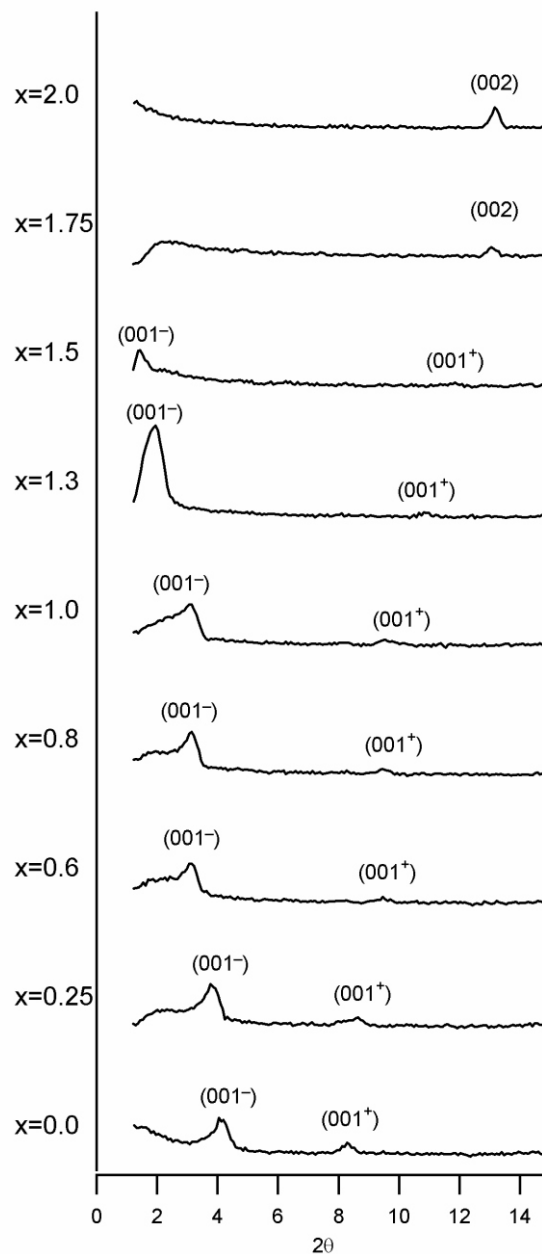
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Figure 1: The measured neutron diffractograms at 10 K for TlCo$_2$Se$_{2-x}$S$_x$

T10 - P184

DOPING STUDIES OF $CoSr_2Y_{2-x}Ce_xCu_2O_{9+}$

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Coexistence of weak ferromagnetism and superconductivity have recently been discovered in the 1222 and 1212 ruthenocuprate systems $RuSr_2RECeCu_2O_{10}$ and $RuSr_2RECu_2O_8$[1-3]. The superconductivity originates in the CuO_2 planes below T_c 37 K and the weak ferromagnetism is confined to the ruthenate layers below $T_M = 124 - 215$ K. In order to explore the interplay between ferromagnetism and superconductivity further we have synthesised $CoSr_2Y_{2-x}Ce_xCu_2O_{9+}$ (x = 0.5, 0.6, 0.7, 0.8). The samples are phase pure and excellent Rietveld fits have been obtained for all samples using the *Cmcm* structural model. Weak ferromagnetic order is observed in the CoO_{1+x} plane and T_N increases from 43 K to 70 K as x increases from 0.5 to 0.7 in the $CoSr_2Y_{2-x}Ce_xCu_2O_{9+}$ solid solutions. Low dimensional magnetic order is observed for $CoSr_2Y_{1.2}Ce_{0.8}Cu_2O_{9+}$ with a broad maximum at 130 K. Co is oxidised from Co^{3+} to Co^{4+} with increasing x, in contrast to similar doping studies on $RuSr_2Gd_{2-x}Ce_xCu_2O_{10}$ which showed that Cu is oxidised as x increases [4]. The samples are not superconducting.

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T10 - P185

CRYSTAL STRUCTURE AND MAGNETISM OF $Pr[Fe(CN)_6] \cdot 4D_2O$

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Physical properties of rare-earth ferricyanides $Re[Fe(CN)_6] \cdot nH_2O$, which belong to the group of molecule-based magnets, have been a subject of investigation for a few decades. The crystal structure models for the compounds were worked out on the base of X-ray diffraction techniques [1-4]. However, in the structure description, water molecules location was approximated by position of oxygen atoms. As contribution of the deuterium atoms to the neutron scattering intensity, which is used for magnetic ordering investigation, cannot be neglected, the complete crystal structure including water molecules position must be determined.

We present an analysis of neutron diffraction patterns taken from the powdered $Pr[Fe(CN)_6] \cdot 4D_2O$ at room temperature and in the temperature range from 1.6 to 40 K. Deuterium atoms were localized by direct space method based on a Monte Carlo simulation process, using program FOX [5]. The determined atom positions were refined by Rietveld method [6,7]. Knowledge of the complete crystal structure allows subtracting its contribution to the diffraction pattern so the pure magnetic component can be determined and analyzed.

Although the study of magnetic properties of $Pr[Fe(CN)_6] \cdot 4H_2O$ by NMR spectroscopy, magnetization, DC and AC susceptibility measurements has indicated magnetic correlations in the system (a maximum in AC susceptibility and in zero-field-cooling magnetization curves at about   12 K [8]), no significant difference between low and high temperature pattern has been detected.

Neutron diffraction experiment revealed that the compound does not order magnetically down to 1.6 K, which is consistent with magnetic ordering temperature $T_N < 1$ K suggested in [3]. The phenomenon is probably caused by short range magnetic ordering.

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T10 - P186

PHASE EQUILIBRIA, CRYSTAL AND MAGNETIC STRUCTURE OF SOLID SOLUTIONS $LaFe_{1-x}Co_xO_{3-}$ (0 X 1)

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Perovskite-type oxides $La_{1-x}A_xMeO_3$ (A=Ba, Sr, Ca; Me-transition metal) have been extensively studied for over four decades due to their catalytic activities, unique magnetic, electrical and transport properties [1, 2] making these materials promising for different applications. In these compounds the rare earth element plays an important role to stabilize the structure, and the electronic ground state of 3d-transition metal (TM) 'B' is responsible for the magnetic and transport properties. The similarity of the structure to high-T_C superconductors and recent observation of giant magneto-resistance in hole doped $LaMnO_3$ have attracted a great interest in these compounds [3–5]. Therefore, manganites have been intensively investigated in recent years. At the same time Sr-, Ca- and Ba-doped cobaltites and ferrites can be used as gas-dense oxygen permeable ceramic membranes for gas conversation [6-8]. The possibility of creation of such devices is being studied nowadays. A number of scientific papers give much information about the phase equilibria and physical properties of solid solutions $LnFe_{1-x}Co_xO_3$, as a rule, when Ln = $(La_{0.3}Sr_{0.3})$ the structure is stabilized by Sr and therefore this solution exists in a continuous range of concentration [9]. However, no detailed structural $LaFe_{1-x}Co_xO_{3-}$ studies have been carried out.

The samples of the general composition $LaFe_{1-x}Co_xO_{3-}$ (0 x 1) with a step of 0.05 were prepared using different routes. First route was a traditional ceramic technique of three-stage firing in air in the temperature range of 850-1100 C for 100-300 hours with intermediate regrinding in ethanol. Another routes were preparation through amorphous precursors using nitric or citric acid as solvent. The final thermal treatment involved heating in air at 1100 C for about 150 hours. In order to identify phase composition all samples were examined by X-ray diffraction using a DRON-3 diffractometer with Cu-K radiation (10 2 75). It is known that determination of the oxygen location in solid oxides by means of X-ray diffraction analysis lead to relatively large uncertainties. Therefore, neutron diffraction was used additionally for the crystal and magnetic structure determination. The powder neutron diffraction profiles were measured using neutron diffractometer D7a (wavelength of 1.5152 Å) at room temperature at the research reactor IVV-2, located near Yekaterinburg, Russia. For all single phase samples unit cells parameters and magnetic structure were calculated and refined by Rietveld analysis. Structural analysis was carried out by simultaneous refinement of neutron and X-ray powder diffraction data.

According to the X-ray analysis initial $LaCoO_{3-}$ has a cubic perovskite structure with rhombohedral distortions (space group *R-3c*). Rietveld neutron powder diffraction

profile of this sample at room temperature is shown in figure 1. Single phase of the solid solution of following composition $LaFe_{1-x}Co_xO_{3-}$ was obtained in a range of concentrations 0 x 0.25. It is shown that the volume and unite cell parameters are continuously increase as the iron content increases. It caused by the ionic size difference: an ionic radius of Fe^{3+} is larger than ionic radius of Co^{3+}.

Lanthanum ferrite $LaFeO_3$ was described in *Pbnm* space group with orthorhombic distortions [10]. All single phase samples $LaCo_{1-y}Fe_yO_3$ exist within the composition range 0.775 y 1.0. In the samples in intermediate region both orthorhombic and rhombohedral boundary phases were simultaneously identified as $LaCo_{0.75}Fe_{0.25}O_3$ and $LaCo_{0.225}Fe_{0.775}O_3$.

It should be noted that single phase regions of $LaCo_{1-y}Fe_yO_3$ are narrower than the regions of Sr-stabilized solutions $La_{0.7}Sr_{0.3}Co_{1-y}Fe_yO_3$ [9].
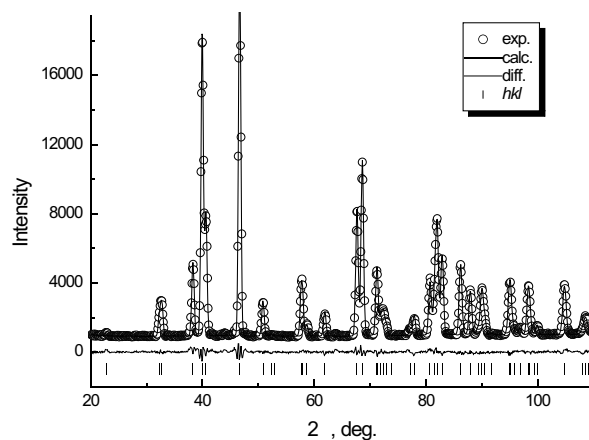

Fig.1. Neutron-diffraction pattern of $LaCoO_3$
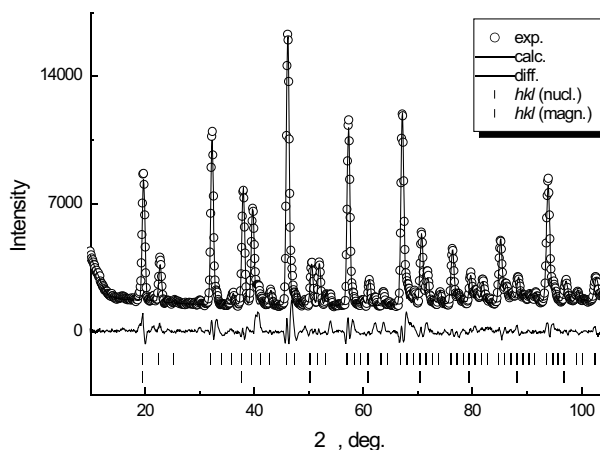

Fig.2. Neutron-diffraction pattern of $LaCo_{0.1}Fe_{0.9}O_3$

In several reflexes some additional intensity of $LaCo_{0.1}Fe_{0.9}O_3$ was determined. It is known that the pure lanthanum ferrite is an antiferromagnetic (G-type) with T_N = 750K [11-12]. Analysis of magnetic reflexes of experimental neutron diffraction profile of composition $LaCo_{1-y}Fe_yO_{3-}$ shows that antiferromagnetic G-type structure realize in this compound at room temperature (Fig.2). The magnitude of magnetic moment is 3.55(5) μ_B on "average" iron atom in a unite cell.

All rhombohedral phases $LaCo_{1-y}Fe_yO_{3-}$ don't have a magnetic moment at room temperature what is in a good agreement with data obtained for the $LaCoO_{3-}$ in [13-14].

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T10 - P187

SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF THE DOUBLE PEROVSKITES OF THE TYPE A_2MnBO_6 AND A_2FeBO_6 (A = Ca, Sr, Ba; B = W, Mo)

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Double perovskite oxides are becoming more and more important in various technological applications. There is a need to improve our detailed understanding of the structural and magnetic properties of such materials and how the atomic structure is related to macroscopic physical properties. Neutron diffraction in combination with Rietveld refinements and magnetization measurements has proved to be a very useful tool in the study of structural and magnetic properties of double perovskites. The structure and physical properties of this type of double perovskites depend considerably on the size, valence and order of the A and B site cations. We have studied the A_2MnBO_6 and A_2FeBO_6 (A = Ca, Sr, Ba; B = W, Mo) [1-6] system to know the structural and magnetic details, and concentration dependence of A-site cations.

Polycrystalline samples were prepared by solid-state sintering of metal oxides and carbonates. The samples were preliminary characterised by X-ray powder diffraction in order to examine the purity of the products solid solubility, and to obtain preliminary information about space group symmetry. Then neutron powder diffraction and magnetization measurements were carried out to study the structural and magnetic properties. Other characterization methods like ED, HRTEM, SEM, EDX were performed according to the necessity.

The room temperature and low temperature structures of these compounds were refined by the Rietveld method to know the structural details and correlation between the compounds. The structure changes from monoclinic through tetragonal to cubic with the change of A-site cation as well as with the change of temperature. A structural and magnetic phase diagram is proposed for A_2MnWO_6 (Ca, Sr, Ba) compounds from the study. All samples were B-site ordered double perovskites. The magnetic transition temperature depends on the B-site bond distances, interaction and ordering. Moreover a decrease of the paramagnetic to antiferromagnetic transition temperature with an increase in the A-site cation radius was also observed in the compo-

sitions A_2MnWO_6 (Ca, Sr, Ba) and A_2FeWO_6 (Sr, Ba). Bond valence sum calculations indicate that the charge distribution between Mn, and W in A_2MnWO_6 (Ca, Sr, Ba) were Mn^{2+} and W^{6+}, and in A_2FeWO_6 (Sr, Ba) and A_2MnMoO_6 (Sr, Ba), there were mixed valence states between Fe^{2+}/Fe^{3+}, W^{6+}/W^{5+} Mn^{2+}/Mn^{3+}, and Mo^{6+}/Mo^{5+}, respectively.

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T10 - P188

STRUCTURAL AND MAGNETIC STUDY OF MAGNETOELECTRIC PEROVSKITE Sr_2CoMoO_6

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Some complex metal oxides with perovskite-related structure exhibit both electric-dipole and magnetic ordering within a definite temperature range (so-called ferroelectric magnets).

We describe in the present communication the synthesis, structural characterisation by X-ray (XRD) and neutron (NPD) powder diffraction, thermal analysis, dielectric, conductivity and magnetic measurements of the complex perovskite Sr_2CoMoO_6. The pure ceramic sample of the title compound was prepared by solid state reaction in air. At room temperature, the crystal structure is tetragonal (s.g.I4/m) with a= 5.5616(2) and c= 7.9470(3) Å. The diffraction data obtained confirmed the complete ordering of the B-site cations. The structure contains alternating Co and Mo octahedra, tilted by 7.1° in the (110) plane along the [001] direction. The temperature dependence of permittivity and loss tangent of Sr_2CoMoO_6 show a peak at 563 K which can be attributed to the improper ferroelectric phase transition. XRD and NPD measurements as a function of temperature indicate a structural phase transition from tetragonal (s.g.I4/m) to cubic (s.g.Fm3m) at about 560 K. The order parameter of this transition is related to the angle of rotation of the Co and Mo octahedra. Magnetic measurements indicate an antiferromagnetic ordering below T_N = 36K. The antiferromagnetic ordering has been followed from low temperature NPD patterns which have been collected at the Swedish Research Reactor R2 (Studsvik). It was found that the set of magnetic reflections appear in the NPD patterns of tetragonaly-distorted Sr_2CoMoO_6 below T_N. The obtained diffraction data were analyzed with the FULLPROF software in order to characterize the temperature-induced phase transformation, and to determine the nuclear and magnetic structures. The G-type magnetic structure is defined by the propagation vector **k** =(1/2,0,1/2). The antiferromagnetic structure can be modeled with magnetic moments at the Co positions providing the couplings between each Co magnetic moment and the six nearest neighbors using O-Mo-O paths. It was experimentaly found that the magnetic moments aligned along the [110] directions. There appears to be no magnetic contribution from the Mo sites. Such an observation supports the presence of Co^{+2} -O- Mo^{+6} pairs in Sr_2CoMoO_6 . The refined magnitude of the magnetic moment and bond valence sums also suggest a divalent oxidation state of cobalt. The correlation between ferroic distortions and the magnetic ordering is briefly discussed. Possible influence of doping in the A and B perovskite sublattices on magnetic, dielectric and structural properties is also estimated.

T10 - P189

STRUCTURAL AND MAGNETIC CHARACTERISATION OF THE MAGNETOELECTRIC DOUBLE PEROVSKITE Sr_2NiMoO_6

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Complex metal oxides with the perovskite-related structure can exhibit both electric-dipole and magnetic ordering within a definite temperature range, (so-called ferroelectric magnets) and this combination of properties is very attractive for many technical applications.

In the present work we describe the synthesis, structural characterisation by X-ray (XRD) and neutron powder diffraction (NPD), thermal analysis and magnetic measurements of the compound Sr_2NiMoO_6 adopting a double perovskite-type structure.

The compound was prepared by a standard solid-state reaction method in air. X-ray diffraction patterns were obtained after the 1523 K and 1623 K sintering steps by a Guinier camera (Cu K $= 1.54059$ Å) in order to check the purity of the sample and to index and refine lattice parameters. Indexing of the Bragg reflections for the sample heated at 1623 K, were made with the program TREOR90.

From NPD data, collected at 300 K, at the Swedish Research Reactor R2 (Studsvik), one could find that the compound adopted a tetragonal unit cell. The space group was I4/m, with lattice parameters a = 5.5448(1) Å, and c = 7.8936(3) Å. Rietveld refinement indicated the Ni^{2+} and Mo^{6+} ions to be B-site ordered. The refinement estimated some oxygen deficiency to a total of 5.8 oxygen atoms.

NPD measurements at 700 K indicated a structural phase transition from a tetragonal to a cubic structure. The space group in the cubic phase is F m$\overline{3}$m with a = 7.901(3) Å. The order parameter of this transition (I4/m-Fm$\overline{3}$m) is related to the angle of rotation of the Ni and Mo octahedra and possibly also to some loss of oxygen in the structure.

Extra Bragg peaks due to magnetic scattering appeared at 20 K in the NPD dataset in the 2 range 17° to 32° in the tetragonal system, which indicate antiferromagnetic ordering.

These new peaks arise from the $3d^8$-spins of the Ni^{2+} ion sublattice and are defined by a propagation vector $\mathbf{k} = ''$, 0, ''. The net magnetic moment was for the 20 K data refined to $1.88\mu_B$.

The obtained NPD diffraction data at different temperatures were analysed with the FULLPROF software in order to characterise the temperature induced phase transformation, and to determine the temperature evaluation of nuclear and magnetic structures.

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XRD ANALYSIS OF HIGHLY-ORIENTED $Pb(Mg,Nb)O_3$-$PbTiO_3$ PEROVSKITE LAYERS

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Layers of the perovskite solid solution $[Pb(Mg_{0.33}, Nb_{0.67})O_3]_{1-x}$-$[PbTiO_3]_x$ were deposited on MgO (1 0 0) single crystals. The layers were characterised with several X-ray diffraction techniques. Grazing incidence measurements at different incidence angles showed that the layers consist of {1 0 0} oriented as well as polycrystalline material, with the polycrystalline material being mainly located at the top of the layers. Pole figure measurements revealed that the oriented material does not have the expected {1 0 0} fibre texture, but has grown largely epitaxially on the single crystalline substrates. High resolution reciprocal space maps indicated that the layers are not strained and that the lattice planes exhibit rather large tilt variations, probably due to orientation differences of the individual perovskite grains (mosaic structure). High-resolution transmission electron microscopy confirmed the mosaic structure of the layers. Misorientations of the perovskite grains with respect to the MgO substrate ranging from 0° up to 10° were observed.

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STRUCTURE AND PHASE CONTENT OF PZT NEAR ITS MPB WITH AND WITHOUT THE INFLUENCE OF AN ELECTRIC FIELD

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Ferroelectric lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$ (PZT), ceramics are used in a variety of piezoelectric, pyroelectric and ferroelectric devices. Questions remain concerning the crystal structures of PZT and the compositional range of the morphotropic phase boundary (MPB). By considering the average structure, Noheda et. al. [1] have confirmed the existence of a "bridging" monoclinic *Cm* phase at the MPB in 1999 [2]. However, very little work has been conducted on phase fractions and influences of electric field and real structure effects on crystal structure and diffraction profiles. This kind of information is vital for studying structural changes produced by electrical cycling of the material, in order to gain an insight into the effects of electrical fatigue on the local and average structure [3].

In order to investigate these phenomena, a series of high-resolution and in-situ electric field synchrotron studies in a compositional range of $x = 0.40$, $x = 0.45 – 0.48$ and $x = 0.55$ – being equivalent to PZT of rhombohedral, morphotropic and tetragonal composition, respectively - have been undertaken at the beamline B2, Hasylab, Hamburg, Germany. Following single crystal studies in PZN-x%PT, which show a change in domain structure and phase [4] under electric field, and computational studies on PZT [5], structure and phase content of polycrystalline PZT pellets across the MPB will be discussed. With decreasing Ti content the tetragonality of the tetragonal phase decreases in the same degree as its phase fraction in comparison to the monoclinic phase in the area of the MPB.

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2) $CdHfO_3$ ceramic (perovskite phase) in the interval 20 T 900 ℃;

3) $CdSnO_3$ ceramic (perovskite phase) at room temperature.

With using the computer program PowderCell 2.3 the structures of these compounds were established (table 1).