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Phase Transitions of the Magnetoelectric A_2NiMoO_6 (A = Ba, Sr) and Ca₂NiWO₆ by Neutron Diffraction

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The magnetic ferroelectric double perovskites A_2NiMoO_6 (A = Ba, Sr), and Ca_2NiWO_6 have been characterised using neutron powder diffraction (NPD) data. The Ba_2NiMoO_6 compound has previously been reported in cubic or hexagonal symmetry which led to investigation of polymorphism. High temperature NPD data of the Sr_2NiMoO_6 compound indicates a continuous structural phase transition from tetragonal to cubic symmetry at approximately 550 K. The reduction in symmetry is linked to spontaneous polarization allowing the structural perturbation to be described as an improper ferroelectric phase transition. The Ca_2NiWO_6 compound shows similar behaviour as Sr_2NiMoO_6 above 700 K, possibly $P2_1/n \rightarrow (I2/m) \rightarrow 14/m \rightarrow Fm-3m$.

Keywords Double perovskite; magnetoelectric; neutron diffraction; phase transition

Introduction

Materials exhibiting both dielectric-dipole and magnetic ordering within a definite temperature range, denoted ferroelectric magnets, have recently gained interest in the scientific community. This combination of properties is very attractive for many technological applications, for example in the design of data storage devices. However, at present there are only a few known candidates and the onset of magnetic order generally occurs well below room temperature for systems such as TbMnO₃ $T_N = 41$ K [1] and RMn_2O_5 , (R = Tb, Ho and Dy) $T_{N,Tb} = 44$ K [2]. In order to induce polarisation a large magnetic field is required and the obtained electrical polarisation is often relatively small. Research aiming to combine polarized and magnetic properties into one material has been widely discussed [3, 4] and the problems associated with achieving this goal in simple perovskite based systems

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are relatively well understood. Essentially, the dipole-electric moment is usually linked to the polarization of a small transition metal ion with an empty *d*-shell configuration. Some displacement of the d^0 ion from the centre of the O₆ octahedra is necessary to break the inversion symmetry and produce a ferroelectric signal as exemplified by the well-known ferroelectric perovskite BaTiO₃ [5]. In contrast, magnetism requires the presence of unpaired electrons in the valence shell, spins, which can then couple to each other ferro-, ferrior antiferromagnetically in the lattice.

Double perovskites described by the general formula A₂BB'O₆, that by definition contain rock salt ordered arrays of distinct B-site species are promising candidates for magnetoelectric materials. The A-site cations determine whether the lattice is cubic or distorted to lower symmetry and cations with different physical properties are found on the B-site. An example is the new magnetoelectric phase Bi₂NiMnO₆ [6] where the Bi³⁺-ions have lone electron pairs which contribute to distortion of the lattice. Double perovskites are known to be extremely thermodynamically stable, however the crystal structure, as a result of the competing bonding preferences of the A, B and B' species, is often unstable [7], in the sense that transitions between forms energetically close to each other can occur. Crystallographic phase transitions as a function of temperature are common, for example Sr₂MnTeO₆ [8], which exhibits several structural phase transitions, $P2_1/n \rightarrow I2/m \rightarrow$ $I4/m \rightarrow Fm\bar{3}m$, and the Sr₂MW⁶⁺O₆ (M = Ni²⁺, Zn²⁺ and Co²⁺) systems which undergo $I4/m \rightarrow Fm\bar{3}m$ transitions have been reported [9]. These structural changes are often intimately linked to the physical properties of the materials.

In this work we have looked at phase transitions in the double perovskites A₂NiMoO₆ (A = Ba and Sr) and Ca_2NiWO_6 . The Ba_2NiMoO_6 (BNMO) has been described to adopt either cubic [10] or hexagonal [11] symmetry. The cubic compound (sp. $Fm\overline{3}m$) has been described from neutron powder diffraction data (NPD) with lattice parameter a = 8.04862(3)Å and the magnitude of the Ni moment is 2.04(6) $\mu_{\rm B}$ below T_N = 64.3 K. The indexed hexagonal compound from X-ray diffraction data (XRD) has been described as a diffusive ferroelectric material containing micro-domains with lattice parameters of a = 11.35 Å and c = 15.46 Å obtained from a sample annealed at 1473 K. At room temperature (RT) the BNMO has a resistivity of 2.94×10^8 (Ω-cm) and a dielectric constant k = 245 at 400 Hz and 181 at 1 kHz [11]. The compound Sr₂NiMoO₆ (SNMO) has been studied in the early 1960's [12, 13]. The RT crystal structure was initially said to have *I4/mmm* symmetry, with cell parameters a = 3.932 Å, and c = 3.943 Å and the phase was reported to undergo a structural phase transition at 503 K to a cubic structure with cell constant, a = 7.878 Å [13]. Gagulin et al. [14] have recently reported on the dielectric and conductivity properties of the phase, along with the behaviour of the closely related material Sr_2CoMoO_6 . The results of references 12 and 13 were based on XRD data and a more recent structural study of SNMO reported by Martínez-Lope et al. [10], using Neutron Powder Diffraction (NPD) analysis, have shown the RT structure to crystallise with tetragonal, I4/m, symmetry and cell constants, a = 5.54939(5) Å, c = 7.89554(9) Å. Below 80 K new reflections in the neutron diffraction data revealed the establishment of an antiferromagnetically (AFM) ordered Ni²⁺ sublattice, confirming the multiferroic nature of the compound. The more distorted Ca₂NiWO₆ (CMWO) [15] double perovskite due to it's small A-site ion, was from NPD data described as monoclinic (sp. $P2_1/n$) with cell parameters a = 5.4048(1) Å, b = 5.5369(1)Å, c = 7.6889(1) Å and $\beta = 90.246(1)^{\circ}$. Magnetic ordering starts to appear below 56 K in the diffraction pattern.

The main purpose of this work is to characterize in detail the high temperature tetragonal to cubic $(I4/m \rightarrow Fm\bar{3}m)$ phase transition of SNMO using neutron powder diffraction data. We also investigate and characterize the two reported symmetries of BNMO as polymorphism might exist in the material. Finally, we study CNWO for a range of temperatures (10 K–700 K) as a number of phase transitions are expected to exist according to reference 9.

Experimental

The preparation procedure for the compounds was based on the same methods as given in references [10, 14]. A second sample of BNMO was also prepared using the route of reference [11]. The samples were reground at every step, and grinding and pelletising cycles were carried out to ensure the homogeneity of the materials. X-ray powder diffraction patterns were obtained from prepared samples, by a Guinier camera and a Siemens D5000 diffractometer (Cu $K_{\alpha 1} = 1.5406$ Å) to check the purity of the samples. For the Guinier camera, silicon (NBS 640b) was used as an internal standard and a computerised line scanner for evaluation of the films. Neutron powder diffraction (NPD) data was collected on the NPD diffractometer at the Swedish research reactor R2 at Studsvik. The incident wavelength was 1.470 Å and the neutron flux at the sample position was approximately 10^6 neutrons cm⁻² s⁻¹. A typical scan covered the 2θ range 4° -139.92° with a step size of 0.08°. NPD powder patterns were collected in the temperature range 10-700 K. The data sets were analysed by the Rietveld method using the Fullprof (2004) software [16]. Peak shapes were described by a pseudo-Voigt function and background intensities fitted using a Chebyshev polynomial with six coefficients. The value of the absorption correction factor was 0.0915.

Results and Discussion

BNMO

Previous reports concerning the symmetry of BNMO lead us to search for possible polymorphism in the material. The X-ray diffraction pattern of the first sample (Ba1), synthesised according to references 10 and 14, was characteristic of a cubic double perovskite structure, showing superstructure peaks corresponding to Ni/Mo ordering. Rietveld refinement from room temperature NPD data showed a nice fit of the *Fm-3m* space group (no. 225) with cell parameter a = 8.041(2) Å, which is in agreement with reference 10. Structural information for BNMO is found in Tables 1–2. NPD data was collected in the range of 10–700 K to investigate phase transitions. In our 10 K data new magnetic peaks arise at low 2θ angles consistent with the reported antiferromagnetic ordering temperature (T_N) of 64.3 K [10]. A proposed magnetic structure model is shown in Fig. 3a where the propagation vector was indexed to $k = (\frac{1}{2}, \frac{1}{2})$. The orientations of the magnetic moments are not shown as they are difficult to determine.

The high temperature data showed as expected no structural phase transition, as $Fm\bar{3}m$ is of high symmetry. The melting point of BNMO is ~1573 K. The X-ray powder diffraction pattern of the second sample (Ba2) prepared according to [11] was identical to (Ba1). This can be explained that the resolution of the diffraction pattern of [11] was low and therefore an incorrect indexing may have been done.

SNMO

At RT both the X-ray and neutron powder diffraction patterns obtained for the sample could be indexed on the basis of a body centred tetragonal system with cell parameters

| Atom | Х | У | Z | B_{iso} (Å ³) | Occ. |
|-------|-----------|----------------------|-------------------------|-----------------------------|----------|
| | | Ba ₂ N | liMoO ₆ | | |
| Ba | 0.25 | 0.25 | 0.25 | 0.29(8) | 8.09(1) |
| Ni | 0.5 | 0.0 | 0.0 | 0.08(3) | 4.03(1) |
| Мо | 0.0 | 0.0 | 0.0 | 0.67(1) | 4.01(1) |
| 0 | 0.2405(2) | 0.0 | 0.0 | 0.56(2) | 24.01(1) |
| | | Sr ₂ NiM | oO ₆ at RT | | |
| Sr | 0.0 | 0.5 | 0.25 | 0.55(2) | 3.99(1) |
| Ni | 0.0 | 0.0 | 0.5 | 0.31(6) | 1.99(1) |
| Mo | 0.0 | 0.0 | 0.0 | 0.28(1) | 2.01(1) |
| O (1) | 0.2703(5) | 0.2158(4) | 0.0 | 0.80(4) | 8.03(1) |
| O (2) | 0.0 | 0.0 | 0.2417(6) | 0.57(6) | 3.99(1) |
| | | Sr ₂ NiMo | O ₆ at 700 K | | |
| Sr | 0.25 | 0.25 | 0.25 | 1.47(4) | 8.02(3) |
| Ni | 0.0 | 0.0 | 0.5 | 0.34(6) | 4.02(3) |
| Mo | 0.0 | 0.0 | 0.0 | 0.94(1)) | 4.02(3) |
| 0 | 0.2703(5) | 0.2158(4) | 0.0 | 1.80(4) | 24.10(2) |
| | | Ca ₂ N | NiWO ₆ | | |
| Ca | 0.9893(7) | 0.0496(4) | 0.2497(9) | 0.73(6) | 4.01(1) |
| Ni | 0.0 | 0.0 | 0.5 | 0.32(4) | 1.99(1) |
| W | 0.5 | 0.0 | 0.5 | 0.59(8) | 1.99(1) |
| O (1) | 0.0859(5) | 0.4758(4) | 0.2595(5) | 0.71(6) | 4.02(1) |
| O (2) | 0.6913(6) | 0.2844(6) | 0.0449(6) | 0.65(8) | 4.00(1) |
| O (3) | 0.2143(6) | 0.1946(6) | 0.9583(6) | 0.50(8) | 4.01(1) |

 Table 1

 Structural information of BNMO, SNMO and CNWO

a = 5.54726(2) Å and c = 7.89701(3) Å determined from refinement of the neutron data. Splitting of certain reflections, for instance the (004) and (220) peaks, allowed the tetragonal cell to be differentiated from a cubic one. Additional weak intensities at $d \approx 3.20$ Å was identified as the (112) and (013) reflections of the impurity phase SrMoO₄. The phase was fitted with literature data [17] and the amount of impurity phase corresponded to 2.22 weight % of the sample.

Initially two different structural models were tested, described using the space groups, I4/m (No. 87) and I4/mmm (No. 139), both of which correspond to the B-site ions being ordered in a rock salt type structure. It quickly became apparent that the greater number of independent oxygen sites available in the I4/m model were necessary to adequately fit the data. A result that confirms the findings of Martínez-Lope et al. [10], and which indicates that at RT the NiO₆ and MoO₆ octahedra are rotated about the *c*-axis, allowing the material to be classified as belonging to the $a^0a^0c^-$ tilt system in the notation proposed by Woodward [18] for 1:1 B-site ordered double perovskites. During the refinement a test was done in order to detect the presence of anti-site disorder between the B-ions (the scattering length factor (b_i) for $b_{Ni^2+} = 10.4$ fm and $b_{Mo^6+} = 6.72$ fm respectively) and no indication of B site mixing was found. Furthermore, it is known that it is possible for MoO₃ to sublime at 923 K. However, during the refinements no indication of molybdenum or oxygen deficiency was detected. The thermal parameters of these atoms were refined to reasonable values

| | | , | | | |
|------------------------------------|----------------------|----------------------------------|----------------------|--|--|
| Bond | 700 K | 295 K | 10/20 K | | |
| | Ba | 2NiMoO ₆ | | | |
| Ва-О | $2.861(2) \times 12$ | $2.844(1) \times 12$ | $2.840(2) \times 12$ | | |
| Ni-O | $2.109(2) \times 6$ | $2.087(1) \times 6$ | $2.089(1) \times 6$ | | |
| Мо-О | $1.936(1) \times 6$ | $1.934(2) \times 6$ | $1.927(1) \times 6$ | | |
| Sr ₂ NiMoO ₆ | | | | | |
| | | $2.942(2) \times 4$ | $2.960(2) \times 4$ | | |
| Sr–O | $2.794(2) \times 12$ | $2.634(2) \times 4$ | $2.611(1) \times 4$ | | |
| | | $2.774(1) \times 4$ | $2.764(1) \times 4$ | | |
| Ni-O | $2.027(1) \times 6$ | $2.047(3) \times 4$ | $2.024(2) \times 4$ | | |
| | | $2.028(6) \times 2$ | $2.026(1) \times 2$ | | |
| Мо-О | $1.925(2) \times 6$ | $1.901(3) \times 4$ | $1.916(2) \times 4$ | | |
| | | $1.923(6) \times 2$ | $1.926(1) \times 2$ | | |
| | C | a ₂ NiWO ₆ | | | |
| Ca–O1 | $2.461(5) \times 1$ | $2.419(3) \times 1$ | $2.402(2) \times 1$ | | |
| Ca–O1 | $2.338(7) \times 1$ | $2.325(5) \times 1$ | $2.315(1) \times 1$ | | |
| Ca–O2 | $2.660(1) \times 1$ | $2.613(6) \times 1$ | $2.586(1) \times 1$ | | |
| Ca–O2 | $2.380(1) \times 1$ | $2.358(6) \times 1$ | $2.361(2) \times 1$ | | |
| Ca–O2 | $2.680(1) \times 1$ | $2.680(7) \times 1$ | $2.697(1) \times 1$ | | |
| Ca–O3 | $2.702(1) \times 1$ | $2.673(7) \times 1$ | $2.653(1) \times 1$ | | |
| Ca–O3 | $2.370(1) \times 1$ | $2.367(6) \times 1$ | $2.360(1) \times 1$ | | |
| Ca–O3 | $2.640(1) \times 1$ | $2.602(6) \times 1$ | $2.598(1) \times 1$ | | |
| Ni-O1 | $2.057(7) \times 2$ | $2.049(4) \times 2$ | $2.049(1) \times 2$ | | |
| Ni-O2 | $2.069(6) \times 2$ | $2.075(3) \times 2$ | $2.076(1) \times 2$ | | |
| Ni-O3 | $2.071(6) \times 2$ | $2.072(4) \times 2$ | $2.066(2) \times 2$ | | |
| W01 | $1.923(7) \times 2$ | $1.918(3) \times 2$ | $1.915(1) \times 2$ | | |
| WO2 | $1.925(6) \times 2$ | $1.921(4) \times 2$ | $1.921(1) \times 2$ | | |
| W03 | $1.928(6) \times 2$ | $1.915(3) \times 2$ | $1.917(1) \times 2$ | | |
| | | | | | |

 Table 2

 Bond distances of BNMO, SNMO and CNWO

and variation of the site occupancy factors also revealed no significant changes from full occupancy, see Table 1. The previous report of a tetragonal to cubic phase transition at 503 K [13], lead us to collect high temperature NPD data in order to characterise the structural change in more detail. We have in a previous work [19] shown that the phase transition is a continuous process, consistent with a second order phase transition. Consequently the symmetry sub-group relationship applies and the transition can be identified as an I4/mto $Fm\bar{3}m$ transformation [9]. The main difference between the low temperature and high temperature structures is the presence of rotations of the MO_6 octahedra in the tetragonal phase. These distortions must occur due to the competing bonding preferences of the Sr and B site ions. At high temperatures both the expanded cell, and the greater thermal motion of the atoms, allows these to be satisfied in a cubic cell, however, on cooling the increased bond strain drives the tetragonal distortion. The order parameter for the structural phase transition is the angle of rotation of the NiO₆ and MoO₆ octahedra which itself is defined by the displacement of the oxygen atoms within the *ab*-plane (Fig. 1). The phase transition exhibited by SNMO is described as an improper ferroelectric phase transition as the polarisation develops after a change between two centro-symmetric, and therefore



Figure 1. The tetragonal to cubic structural phase transition at 550 K is related to the angle of rotation of the NiO₆ and MoO₆ octahedra. (See Color Plate XVI)

non-polar, space groups. Development of a net polarisation within the material is possible due to the gradual growth of domains in which local displacements of the ions produce a dipole. There are two candidates for the origins of the ferroic behaviour, displacements of the Sr^{2+} ions and/or the Mo^{6+} ions. Figure 2 shows a significant deformation of the SrO_{12} cubo-octahedron as a result of the phase transition. In comparison the elongation of the MoO_6 octahedra in the tetragonal structure is relatively small (see Table 2), and we therefore conclude that ferroelectric signal is mainly associated with the Sr sublattice. However, it is possible that small local displacements of the highly charged Mo ions are also present below the phase transition and that these also contribute.

The magnetic structure was introduced as a second phase (space group P1). Only models with a finite moment located on the Ni site were considered as the Mo⁶⁺ ion is in a d^0 electron configuration. The magnetic reflections could be defined by the propagation



Figure 2. The distorted (left) and symmetric (right) SrO₁₂ cubo-octahedron obtained at 295 K and 600 K respectively. (See Color Plate XVII)



Figure 3. Magnetic structure of (from left) a.) BNMO, b.) SNMO and c.) CNWO where ferromagnetic layers are coupling antiferromagnetically. (See Color Plate XVIII)

vector k = (1/2, 0, 1/2) and the best fit to the experimental data was achieved for an antiferromagnetic (AF) model. Figure 3b shows the orientation of the Ni moments in the unit cell. The magnetic structure can be described as alternating sets of (2 0 2) ferromagnetic planes that couple antiferromagnetically to each other. The refined moment of 1.88(8) μ_B at 20 K, is in good agreement with the work of Martínez-Lope et al. [10] where the net magnetic moment was found to be 1.92(6) μ_B at 2 K, and is consistent with the presence of Ni²⁺ (s = 1).

CNWO

NPD data was obtained in the T range of 10–700 K from a light green homogeneous crystalline powder of CNWO. In Fig. 4 diffraction patterns from 10 K, RT and 700 K are



Figure 4. Neutron diffraction patterns of CNWO as a function of temperature. (See Color Plate XIX)

shown. The arrows at low 2θ -angles indicate peaks originating from magnetic ordering in the low T data. Structural refinement of the RT pattern correspond well to the monoclinic space group $P2_I/n$ (no. 14, unique axis b) with cell parameters, a = 5.403(3) Å, b =5.538(3) Å, c = 7.689(4) Å and $\beta = 89.766(6)^{\circ}$. The Ca atoms were located at the 4*e* positions, Ni at 2*d*, Mo at 2*b* and the O1, O2 and O3 ions were located on 4*e* sites. The good agreement between the observed and the calculated patterns indicated no anti-site disorder between Ni/W, which was confirmed by a variation of less than 1% in a refinement test (the scattering length factor (b_i) for $b_{Ni^2+} = 10.3$ fm and $b_{W^6+} = 4.86$ fm respectively). The final atomic coordinates are found in Table 1, which also show no sign of any oxygen vacancies within the standard deviations.

The distorted structure of CNWO is linked to the small size of the Ca cations, which force the NiO₆ and WO₆ octahedra to tilt in order to optimize the Ca-O bond distances, see Table 2. The structure corresponds to the $a^+ b^- b^-$ Glazer notation as derived by Woodward for 1:1 ordered double perovskites [18].

The Ca compound, similar to the A₂NiMoO₆, A = Ba, and Sr phases, reveals long range magnetic order at 10 K as seen in the NPD data. The magnetic reflections were indexed with the propagation vector k = (1/2, 0, 1/2) and the magnetic moments were determined to 1.94(2) $\mu_{\rm B}$, which is the same value as [15]. The magnetic structure can be described in a similar way as SNMO with ferromagnetic layers coupled antiferromagnetically as shown in Fig. 3c.

As proposed by Gateshki et al. monoclinic CNWO is expected to undergo at least one structural phase transition, $P2_1/n \rightarrow (I2/m) \rightarrow I4/m \rightarrow Fm-3m$ as temperature increases. However the 700 K data set does not differ much from the RT data, which must indicate that the phase transition occurs above 700 K. The bonding energy of Ca-O is higher than for Ba-O and Sr-O, which indicate higher temperatures for a structural transformation.

Conclusions

The magnetic ferroelectric double perovskites A_2NiMoO_6 (A = Ba, Sr) and Ca_2NiWO_6 have been studied by X-ray and neutron powder diffraction. Only one cubic phase ($Fm\overline{3}m$) of BNMO was found in the search of polymorphism in the material. The SNMO undergoes a $Fm\overline{3}m \rightarrow I4/m$ structural phase transition as a result of antiphase octahedral rotations around the *c*-axis at approximately 550 K. The driving force for the phase transition is the bonding demands of the Sr A-sites cation which adopt a distorted SrO_{12} coordination in the low temperature tetragonal structure. The ferroelectric properties that develop below the transition may be linked to displacements of the Sr^{2+} ion within the distorted cubooctahedral cage. The environment of the highly polarisable d⁰ Mo⁶⁺ also becomes more distorted below the transition. The structure of CNWO can be described in the monoclinic (P2₁/n) system at low and room temperature. Structural phase transitions probably occur above 700 K as the Ca–O bonding energy is more stable than Ba–O and Sr–O. All three compounds show antiferromagnetic ordering in our 10 K NPD data sets.

References

- 1. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Magnetic control of ferroelectric polarisation. *Nature* **426**, 55 (2003).
- G. R. Blake, L. C. Chapon, P. G. Radaelli, S. Park, N. Hur, S.-W. Cheong, and J. Rodríguez-Carvajal, Spin structure and magnetic frustration in multiferroic *RMn*₂O₅ *R* = Tb,Ho,Dy. *Phys. Rev. B* **71**, 214402 (2005).

- 3. C. Ederer and N. A. Spaldin, A new route to magnetic ferroelectrics, Nature Mat. 3, 849 (2004).
- 4. D. V. Efremov, J. van den Brink, and D. I. Khomskii, Bond- versus site-centred ordering and possible ferroelectricity in manganites. *Nature Mat.* **3**, 853 (2004).
- 5. B. Matthias and A. von Hippel, Domain Structure and Dielectric Response of Barium Titanate Single Crystals. *Phys. Rev.* **73**, 1378 (1948).
- M. Azuma, K. Takata, T. Saito, S. Ishiwata, Y. Shimakawa, and M. Takano, Designed Ferromagnetic, ferroelectric Bi₂NiMnO₆. J. Am. Chem. Soc. 127(24), 8889 (2005).
- 7. E. Salje, Characteristics of perovskite-related materials. *Phil. Trans. R. Soc. London* A328, 409 (1989).
- L. Ortega-San Martin, J. P. Chapman, E. Hernández-Bocanegra, M. Insausti, M. I. Arriotua, and T. Rojo, Structural phase transitions in the ordered double perovskite Sr₂MnTeO₆. *J. Phys. Condens. Mat.* 16, 3879 (2004).
- M. Gateshki, J. M. Igartua, and E. Hernández-Bocanegra, X-ray powder diffraction results for the phase transitions in Sr₂MWO₆ (M = Ni, Zn, Co, Cu) double perovskite oxides. *J. Phys. Cond. Mat.* 15, 6199 (2003).
- M. J. Martínez-Lope, J. A. Alonso, and M. T. Casais, Synthesis, crystal and magnetic structure of the double perovskites A₂NiMoO₆ (A = Sr, Ba): A neutron diffraction study. *Eur. J. Inorg. Chem.* 15, 2839 (2003).
- N. G. Durge, M. S. Nadkarni, and S. V. Salvi, Characterization of a new relaxor perovskite of Ba(Ni_{1/2}Mo_{1/2})O₃. J. Mat. Sci. 39, 2547 (2004).
- 12. L. Brixner, Preparation and structure determination of some new cubic and tetragonally-distorted perovskites, *J. Phys. Chem.* **64**, 165 (1960).
- M. F. Kupriyanov and E. G. Fesenko, X-ray structural studies of phase transitions in perovskitetype compounds. *Kristallogr* 7, 451 (1962).
- V. V. Gagulin, S. K. Korchagina, V. V. Ivanova, and Yu. A. Shevchuk, Synthesis and Properties of Sr₂CoMoO₆ and Sr₂NiMoO₆, Shevchuk. *Neorg. Mater.* (Russia) **39**, 739 (2003).
- M. J. Martínez-Lope, J. A. Alonso, M. T. Casais, and M. T. Fernández-Díaz, Preparation, crystal and magnetic structure of the double perovskites Ca₂TWO₆ (T = Co, Ni). *Z. Naturforsch* 58b, 127 (2003).
- J. Rodriguez-Carvajal, FULLPROF, A Program for Rietveld Refinement and Pattern Matching Analysis Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France 127 (1990).
- 17. E. Guermen, E. Daniels, and J. S. King, Crystal Structure Refinement of SrMoO₄, SrWO₄, CaMoO₄, and BaWO₄ by neutron diffraction, *J. Chem. Phys.* **55**, 1093 (1971).
- P. M. Woodward, Octahedral tilting in perovskites. I. Geometrical considerations. *Acta Cryst. B* 53, 32 (1997).
- A. K. Eriksson, S.-G. Eriksson, S. A. Ivanov, C. S. Knee, J. Eriksen, H. Rundlöf, and M. Tseggai, High temperature phase transition of the magnetoelectric double perovskite Sr₂NiMoO₆ by neutron diffraction. *Mat. Res. Bull.* (2005) In press.