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Contributions in Synthesis and Characterisation of the Double Perovskites Oxides in $Sr_2Ni_{1-x}Mn_xWO_6$ Series

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Abstract: The double perovskites $Sr_2Ni_{1-x}Mn_xWO_6$ (x = 0; 0.15; 0.20; 0.40; 0.60; 0.80; 1.00) were synthesised by modified ceramic method and characterised by infrared spectra and DRX analysis. The infrared spectra of the powders were collected in order to check the formation of the $Sr_2Ni_{1-x}Mn_xWO_6$ double perovskite.

Keywords: Double perovskites; DRX; IR spectra.

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Introduction

Some of the oxides of the double perovskites family $A_2B'B''O_6$ (A is an alkaline earth; B', B'' are heterovalent transition metals) have recently been described to exhibit half-metallic ferromagnetism with a high spin polarization at the Fermi level, making them promising candidates for future spin electronics.[1-3] The modification of structural and magnetic properties of B-site (B' and B'' on the octahedral places) ordered double perovskite oxides, caused by a change of B-site cations, is of great interest, and of use when trying to understand the mechanism of e.g. colossal magnetoresistance. Some compounds with ordered perovskite structure show a considerable distortion with ratio between cell parameters $\frac{c}{a} > 1$ which depends on the radius of the A-site cations and/or of a Jahn–Teller effect. These structural distortions are of interest not only from a crystallographer's point of view, but also because they can have important effects on the physical properties of perovskite compound, particularly its electric and magnetic properties. Recently, motivated by the theoretical and experimental studies, it was studied the room temperature to low temperature structural and magnetic properties of the series A_2MnWO_6 (A = Ca, Sr, Ba).[4-7]

Nickel containing perovskites have been suggested as possible materials for reduced dielectric constant substrates for high-temperature superconductors and even as possible high-temperature superconductors themselves. The purpose of this study is to survey possible nickel-containing compositions that might be suitable for substrate materials. The basic perovskite composition is ABO_3 where A is a large ion suitable to the 12-coordinated cube-octahedral site and B is a smaller ion suitable to the 6-coordinated octahedral site. Complex perovskites with ordered mixed

species on a site (particularly the B site) may be represented by multiples of this formula unit and larger unit cells. Such a compound could be expressed as $A(B_xB'_{1-x})O_3$ or as a multiple of this unit that would yield all-integer subscripts. Nickel occurs in the 2 + valence state and the Ni^{2+} ionic radius make it a good fit to the octahedral B site. Perovskites form most readily if there is a large difference in ionic radius between the A- and B-site ions. Formation of cubic perovskites that are most desirable as substrates requires an even larger difference in ionic radii. Ni^{2+} is a moderate-to-large size ion for the B site, therefore, only large A-site ions were considered. The simple $A^{4+}Ni^{2+}O_3$ perovskites would maximize the nickel concentration, but unfortunately the A^{4+} ions are mostly impractical (i.e. U^{4+} and Th^{4+}). Only Ce^{4+} was considered. La^{3+}, the largest of the lanthanides, was the only 3 + ion considered. The other lanthanides are chemically similar, but have smaller ionic radii, which are less suitable. The alkaline earths are all good perovskite formers on the A site, but only Sr^{2+} and Ca^{2+} form perovskites with the proper lattice parameter for substrates for high temperature superconductors. At the B'-site ion, the choices were also limited. Mo^{6+} and W^{6+} are the most stable 6 + ions.[8]

Results and discussions

We can write the following formation reaction of compounds of $Sr_2Ni_{1-x}Mn_xWO_6$ series:

$$2SrCO_3 + (1-x)NiO + xMn(CH_3COO)_2.4H_2O + WO_3 + 4xO_2 = Sr_2Ni_{1-x}Mn_xWO_6 + 2(1+2x)CO_2 + 7xH_2O$$

The infrared spectra of the powders were collected in order to check the formation of the $Sr_2Ni_{1-x}Mn_xWO_6$ double perovskite. The vibrational behavior of these materials is expected to be rather complex, taking into

account that the crystal lattice is built up by two different metal oxygen polyhedra and that one of them contains metallic cations of different charge and size. On the other hand, symmetry reduction observed in numerous of the investigated materials allows predicting additional spectral complexities.

The IR absorption spectra of samples $Sr_2Ni_{1-x}Mn_xWO_6$ annealed at 1563 K are depicted in Figure 1. The spectra of all samples $Sr_2Ni_{1-x}Mn_xWO_6$ are very similar, showing two strong and well-defined absorption bands, typical of perovskite materials.[9-11]

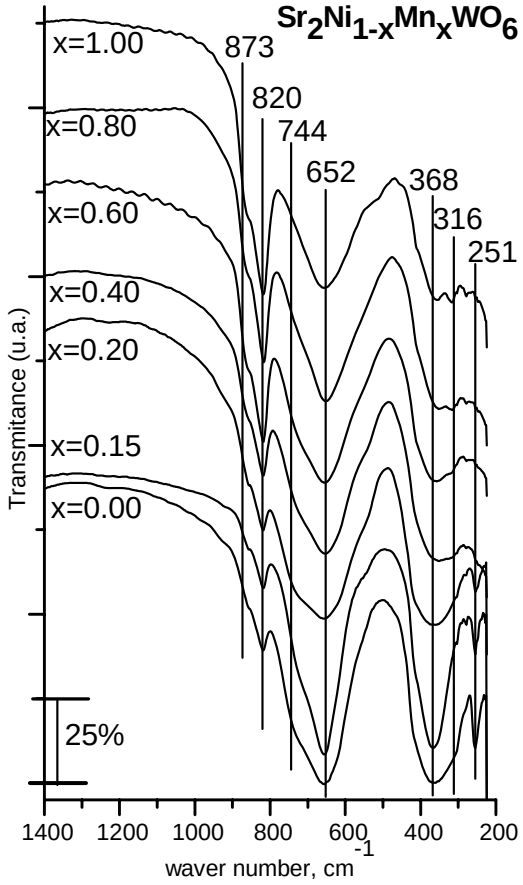

Figure 1. FTIR spectra of $Sr_2Ni_{1-x}Mn_xWO_6$ sintered at 1563 K

The spectra of all samples $Sr_2Ni_{1-x}Mn_xWO_6$ are very similar. The two main absorptions are clearly split, probably as a consequence of the tetragonal distortion of the unit cell. The strong high-energy band centered at about 652 cm^{-1} can surely by assigned to the antisymmetric stretching mode of the WO_6-octahedra, due to the higher charge of this cation. Another interesting point raised by this spectrum is the presence of the medium intensity band at 820 cm^{-1} which can eventually be assigned to the symmetric stretching vibration of these octahedra. The position of these bands suggests relatively long W–O bonds.

X-ray diffraction analysis was performed to determine the phase purity of the compounds of $Sr_2Ni_{1-x}Mn_xWO_6$ series, after sintering at 1563K.

The XRD patterns in Figure 2 show single-phase structure for $Sr_2Ni_{1-x}Mn_xWO_6$ with traces of $SrWO_4$ (PDF 850587) as impurity, which inevitably formed in many solid state reaction routes and even in some chemical wet routes. Superstructure reflections can be clearly seen around 19° and 38°, corresponding to the B sites Ni/W ordering. Structural analysis was performed using FullProf program. The crystal structures belong to the tetragonal *I 4/m* space group. In fact, Philipp et al.[12] have formulated the following empirical rule: for $0.96 \leq t \leq 1.06$ in the majority of cases the double perovskites are cubic/tetragonal. The definition of t is given by :

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Here, $<r_B>$ means the average ionic radius for the ions on the B site. The values of t for our compounds $Sr_2Ni_{1-x}W_xO_6$ are 0.98, suited to this empirical rule. The cell parameters are calculated as follows: a=b=5.561 ± 0.001 Å, 7.911 ± 0.002 Å for Sr_2NiWO_6. Our results are

comparable with the previous reports.[13-16]

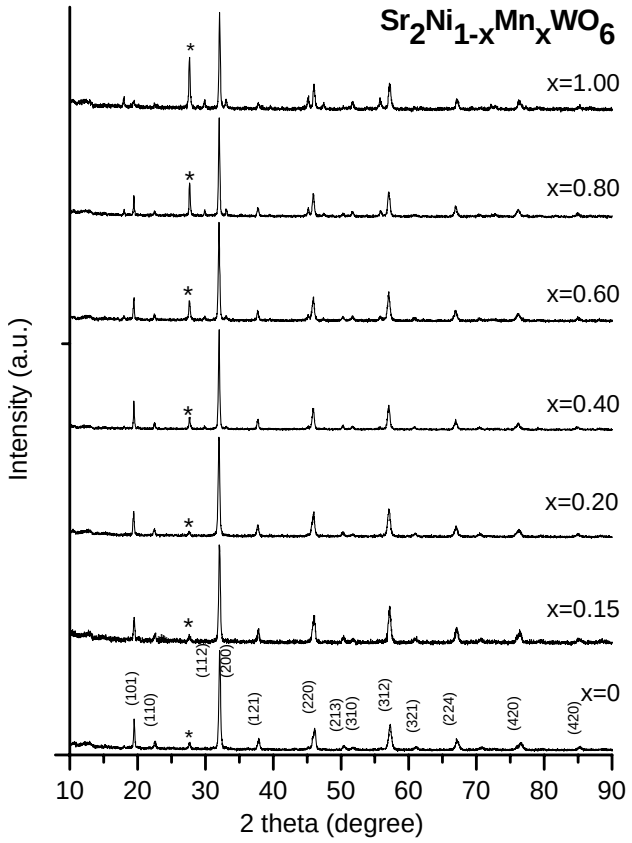

Figure 2. X-ray powder diffraction patterns of $Sr_2Ni_{1-x}Mn_xWO_6$, sintered at 1563 K (PDF file: * $SrWO_4$ 85-0587)

According to the X-ray powder diffraction patterns (PDF file 710754 for Sr_2NiWO_6), the presence of a perovskite superstructure is clearly confirmed, as already found for numerous $A_2BB'O_6$ materials.[17-22] This behavior resulted from the ordering of the B and B' cations on the octahedral sites of the unit cell. The determined structural parameters and cell symmetries are shown in Table 1.

Table 1. Structural data of the investigated materials

Compounds	Cell symmetry	Determined unit cell parameters (Å)	Tolerance factor, t
Sr_2NiWO_6	Tetragonal	a = 5.561 +/- 0.001 c = 7.911 +/- 0.002	0.98
$Sr_2Ni_{0.85}Mn_{0.15}WO_6$	Tetragonal	a = 5.563 +/- 0.002 c = 7.905 +/- 0.002	0.977
$Sr_2Ni_{0.80}Mn_{0.20}WO_6$	Tetragonal	a = 5.593 +/- 0.009 c = 7.881 +/- 0.003	0.975
$Sr_2Ni_{0.60}Mn_{0.20}WO_6$	Tetragonal	a = 5.581 +/- 0.001 c = 7.912 +/- 0.001	0.968
$Sr_2Ni_{0.40}Mn_{0.60}WO_6$	Tetragonal	a = 5.583 +/- 0.001 c = 8.030 +/- 0.005	0.962
$Sr_2Ni_{0.20}Mn_{0.80}WO_6$	Tetragonal	a = 5.585 +/- 0.001 c = 8.017 +/- 0.006	0.956
Sr_2MnWO_6	Tetragonal	a = 5.574 +/- 0.002 c = 8.028 +/- 0.005	0.949

Based on XRD, were determined the volumes of unit cells of the compounds of the series $Sr2Ni_{1-x}Mn_xWO_6$ (x = 0, 0.15, 0.20, 0.40, 0.60, 0.80, 1). The variation of the volumes of elementary cells in function of x is shown in Figure 3.

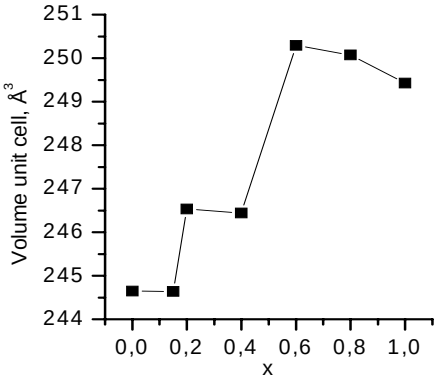

Figure 3. Volume unit cell for $Sr_2Ni_{1-x}Mn_xWO_6$

(x = 0, 0.15, 0.20, 0.40, 0.60, 0.80, 1) series samples

Experimental

The double perovskites oxides in $Sr_2Ni_{1-x}Mn_xWO_6$ (x = 0, 0.15, 0.20, 0.40, 0.60, 0.80, 1) series were obtained by modified ceramic method. Stoichiometric amounts of high purity powder of $SrCO_3$, $Mn(CH_3COO)_2.4H_2O$, NiO and WO_3, were mixed in an agate mortar. The mixed powder was placed in an alumina crucible and calcined at 773K for 24 h. The sample was pressed into a pellet and sintered at 1273K for 20 h and 1563K for 20 h. The sample was reground in each step, and grinding and pelletising cycles were carried out to insure the homogeneity of the sample.

The X-ray data were collected on polycrystalline samples at room temperature using a Seifert (type XRD 3003 PTS) X-ray diffractometer mounted in a Bragg–Brentano configuration with Cu Kα radiation. The scan was collected from 15° to 120° (2 theta) using a 0.02° step-interval with a counting time of 14 s/step. The structural refinement was performed using the FullProf suite. The shape of the peaks was described by a Pseudo-Voigt function and the background was fitted based on linear interpolation between a set of about 50 background points with refinable heights. The scattering factors of all elements were used.

The corresponding IR absorption spectra were recorded on a FT-IR NEXUS NICOLET Spectrometer at room temperature from 250 to 4000 cm^{-1} with 2 cm^{-1} resolution, using the CsI pellet technique.

Conclusions

The synthesis method used led to compounds of the series $Sr_2Ni_{1-x}Mn_xWO_6$ (x = 0, 0.15, 0.20, 0.40, 0.60, 0.80, 1), characterized by a single phase. In all samples there is $SrWO_4$ as impurity, formed in the

synthesis.

The IR absorption spectroscopy has been used as a method to monitor the formation of the perovskite phase. DRX method confirmed the formation of the perovskite phase observed by IR and allowed the structural characterization of samples with different degrees of substitution of Ni with Mn.

Research will continue to find a synthesis method of samples without $SrWO_4$ as impurity, which can change the electrical properties of these compounds.

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