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Crystal structures and high-temperature phase-transitions in SrNd*M*RuO$_6$ (M=Zn,Co,Mg,Ni) new double perovskites studied by symmetry-mode analysis

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ABSTRACT

Crystal structures of SrNdZnRuO$_6$, SrNdCoRuO$_6$, SrNdMgRuO$_6$ and SrNdNiRuO$_6$ double perovskites have been studied by X-ray, synchrotron radiation and neutron powder diffraction method, at different temperatures, and using the symmetry-mode analysis. All compounds adopt the monoclinic space group $P2_1/n$ at room-temperature, and contain a completely ordered array of the tilted MO$_6$ and RuO$_6$ octahedra, whereas Sr/Nd cations are completely disordered. The analysis of the structures in terms of symmetry-adapted modes of the *parent* phase allows the identification of the modes responsible for the phase-transition. The high-temperature study (300–1250 K) has shown that the compounds present a temperature induced structural phase-transition: $P2_1/n \rightarrow P4_2/n \rightarrow Fm\bar{3}m$.

1. Introduction

In recent years, double perovskites ruthenates (A_2MRuO$_6$ or $AA'M$RuO$_6$) have gain much interest due to their novel and diverse physical and magnetic phenomenon. The ideal structure of a double perovskite (space group $Fm\bar{3}m$ (ITA no. 225) or $Pm\bar{3}m$ (ITA no. 221)) consists of a regular array of corner-sharing BO$_6$ and B'O$_6$ octahedra connected in three dimensions, with B and B' cations joined by linear bonds and A cations filling the space between the octahedra. However, because of the numerous combinations of cations with different ionic radii, this ideal structure is seldom obtained. Instead structures with reduced symmetry are more common. Depending on the relative size of the B and B' cations with respect to the A cations, the most reported crystal symmetries are cubic ($Fm\bar{3}m$ [1]), and monoclinic ($P2_1/n$ [3,4]). A smaller number of materials have been found to have rhombohedral ($R\bar{3}m$ [5], $R\bar{3}$[1]), tetragonal ($I4/mmm$ [6], $P4/mnc$ [7], $I4/m$ [8], $P4_2/n$ [9,10]), orthorhombic ($Pmm2$ [11]), monoclinic ($I2/m$ [8], $P2_1/m$ [12]) or triclinic symmetries ($P\bar{1}$ [13]). Temperature and pressure variation can induce several phase transitions between the monoclinic ($P2_1/n$) and the cubic ($Fm\bar{3}m$) symmetries: $P2_1/n$–$I2/m$–$I4/m$–$Fm\bar{3}m$ [14], $P2_1/n$–$I2/m$–$R\bar{3}$–$Fm\bar{3}m$ [2], $P2_1/n$–$I4/m$–$Fm\bar{3}m$ [15], or $P2_1/n$–$R\bar{3}$–$Fm\bar{3}m$ [3].

The structural properties of double perovskites materials with general formula SrLaMRuO$_6$ (M transition metal) have been reported in several occasions [3,4,16–18]. All these compounds have shown a disordered distribution of Sr and La atoms over the A-site of the perovskite structure; and either ordered [3,4,16] or disordered [17,18] arrangement of the M and Ru atoms over B-site. The room-temperature space group for SrLaMRuO$_6$ (Ni,Cu,Co) [3,4,16] was reported to be $P2_1/n$ (ITA no. 14, non-standard setting), whereas $Pbnm$ (ITA no. 62, non-standard setting) for SrLaMnRuO$_6$ and SrLaFeRuO$_6$ compounds [17,18]. Crystallographic phase-transitions as a function of temperature are common, for example, SrLaCuRuO$_6$ and SrLaNiRuO$_6$ reported in [3] showed that the compounds present the following temperature induced structural phase-transition: $P2_1/n \rightarrow R\bar{3}$ (ITA no. 148). These structural changes are often intimately linked to the physical properties of the materials.

The aim of the present work is to analyze the room-temperature structures and the possible temperature-induced structural phase-transitions of SrNdMRuO$_6$ (M=Zn,Co,Mg,Ni), as there are no previous studies neither on room-temperature nor on the temperature-dependent structural modifications of this new family of double perovskite materials.

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2. Experimental

2.1. Sample preparation

Polycrystalline samples of the SrNdMRuO$_6$ (M=Zn,Co,Mg,Ni) compounds were prepared by the standard method of the solid-state reaction. Stoichiometric amounts of SrCO$_3$ (99.995%), Nd$_2$O$_3$ (99.99%), RuO$_2$ (99.9%), MgO (99.998%) or CoO (99.99%) or NiO (99.99%) or ZnO (99.999%) were mixed according to the following chemical reaction:

$$2\mathrm{SrCO_3}+\mathrm{Nd_2O_3}+2\mathrm{RuO_2}+2M\mathrm{O} \Rightarrow 2\mathrm{SrNd}M\mathrm{RuO_6}+2\mathrm{CO_2}$$

All reacting compounds were used as received (all from Sigma-Aldrich). The starting materials were mixed and ground in an agate mortar with acetone and subsequently heated in air, in alumina crucibles. The following heat treatment was used: 24 h at different temperatures, from 770 to 1470 K every 100 K and 48 h at 1520 K. After each heating, the samples were cooled down slowly (3 K/min); and reground to improve homogeneity. In order to control the quality of the obtained material, X-ray diffraction measurements were performed after each heating. An amount ($\approx$4.84%) of the impurity NiO was found in the SrNdNiRuO$_6$ final material; this impurity was included as a known additional phase in the Rietveld refinements of the structure of the compound.

2.2. Diffraction measurements

High-quality room-temperature diffraction data were obtained on a Bruker D8 Advance diffractometer equipped with a primary germanium parafocusing monochromator and Bragg–Brentano geometry, using Cu Kα_1 = 1.5406 Å radiation. A Sol-X energy dispersive detector was used, with a detection window optimized for Cu Kα_1, in order to avoid the fluorescence radiation from the samples. The data were collected between 15° and 110° in 2θ, with steps of 0.01° (2θ) and counting time of 12 s per step.

High-temperature diffraction data were collected on a similar diffractometer (Bruker D8 Advance), but equipped with a Våntec high speed one-dimensional detector (with 3° angular aperture), using Cu Kα radiation. An Anton Paar HTK2000 high-temperature chamber with a direct sample heating (Pt filament) and a temperature stability of 0.5 K was used. The specimens for high-temperature measurements were prepared by mixing the material under study with acetone. Then, the mixture was "laid" over the Pt-strip heater (high-temperature) of the evacuated chamber.

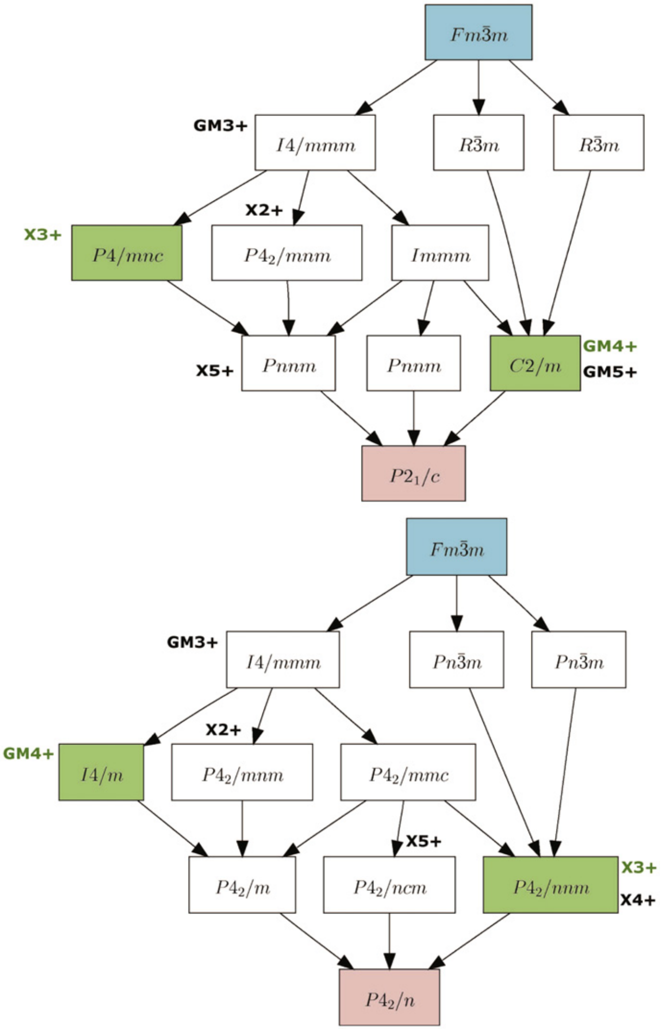

Fig. 1. Graph of maximal subgroups relating the space groups of the parent (highlighted in blue) and distorted $P2_1/n$ and $P4_2/n$ phase (highlighted in red) of SrNdMRuO$_6$ compounds. For each subgroup any irrep yielding this symmetry is indicated and the two primary active irreps evidenced by the Rietveld refinement are highlighted in green. In the scheme we are using the standard settings of the space groups as the BCS does for generating these graphs. $P2_1/c$ is the standard setting of $P2_1/n$. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

Table 1
Input information for AMPLIMODES for FullProf: high-symmetry phase information (virtual prototype structure), low-symmetry structure information (cell-parameters obtained by XRPD data profile matching) and transformation matrix for SrNdCoRuO$_6$. $P2_1/n$ (ITA no. 14, non-standard setting), $P4_2/n$ (ITA no. 86, standard setting) and $Fm\overline{3}m$ (ITA no. 225, standard setting).

High-symmetry structure
225
7.9209 7.9209 7.9209 90.00 90.00 90.00
4

Ru	1	4a	0.00000	0.00000	0.00000
Co	1	4b	0.50000	0.50000	0.50000
Sr	1	8c	0.25000	0.25000	0.25000
O	1	24e	0.24714	0.00000	0.00000

Low-symmetry structure
014
5.5487 5.5587 7.8412 90.00 89.98 90.00

Transformation matrix

$$\left(\begin{array}{ccc|c} 1/2 & 1/2 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array}\right)$$

Low-symmetry structure
086
7.8688 7.8688 7.8728 90.00 90.00 90.00

Transformation matrix

$$\left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array}\right)$$