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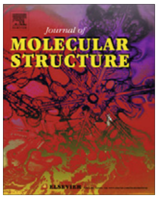

X-ray diffraction and Raman spectroscopy studies of $BaSrMWO_6$ (M=Ni, Co, Mg) double perovskite oxides

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ABSTRACT

In this work we report on the crystal structure and Raman spectroscopy of $BaSrMWO_6$ (M=Ni, Co, Mg) double perovskite oxides. The results showed that the Ni, Co and Mg containing compounds crystallize in a cubic system with the space group Fm-3 m. The double perovskite structure can be represented as a three-dimensional network of alternating MO_6 and WO_6 octahedra, with Ba- and Sr-atoms occupying the interstitial spaces. The Raman spectra of this crystalline perovskite oxides are interpreted by means of factor group analysis in terms of space group Fm-3 m. Assignments of the W—O vibrational stretching and bending modes have been made. High temperature Raman spectroscopy of $BaSrNiWO_6$ showed that all lattice modes illustrate a linear decrease in wavenumbers while temperature is increased. No discontinuities, in the temperature changes, in wavenumber observed for all modes recorded: indicating that the structure remains cubic and stable up the highest temperature studied here.

1. Introduction

Double perovskite oxides of the type $A_2MM'O_6$ (where A is an alkaline earth cation, and M and M′ are two heterovalent transition-metal elements) show a large variety of physical and chemical properties, such as superconductivity, ferroelectricity, antiferroelectricity, piezoelectricity, various optical and magnetic properties or a combination of magnetic and electric interactions. The discovery of low-field colossal magneto-resistance (CMR) in Sr_2FeMoO_6 perovskite up to room temperature [1] caused a renaissance in both fundamental and applied research on various transition-metal double perovskites, as CMR materials are of great significance for applications in magnetic–electric (spintronic) devices. Magnetoelectric (ME) compounds, which simultaneously manifest ferroelectric and ferromagnetic properties, have gained renewed and ever increasing research interest during the past years [2,3]. Search and preparation of ME materials would be a milestone for modern electronics and functionalized materials taking an advantage of two coupled degrees of freedom based on local off-centered polar distortion and electron spin [4,5]. Many efforts have been devoted to prepare new ME materials and to find ME properties in known compounds. It is very important to understand under which thermodynamic conditions and chemical environment the coexistence of magnetic and ferroelectric orderings can take place.

These types of materials are promising candidates for future spin based electronics. Depending on their valences and relative radii, transition metals often occupy the M-site, which can accommodate two different metal ions. When, in a material, one spin channel is metallic and another spin channel is insulating, the material is termed half-metallic (HM). Due to the high order of spin polarization, some of the double perovskites show very good HM characteristics. Ferromagnetism and half-metallicity, with a high spin polarization at the Fermi level, make them promising for spin devices.

In this work we report on the crystal structure study of $BaSrMWO_6$ (M=Ni, Co, Mg) double perovskite oxide which was obtained by using conventional X-ray diffraction and Raman spectroscopy measurements of powder samples.

2. Experimental

2.1. Sample preparation and X-ray diffraction measurements

Well-crystallized powder samples of $BaSrMWO_6$ (M=Ni, Co, Mg) were synthesized by mixing $BaCO_3$, $SrCO_3$, NiO, CoO, $Mg(OH)_2$

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and WO_3 in an agate mortar. The solid state reaction takes place in the following steps: heating of the samples at 400–600 °C, in order to improve the homogeneity of the mixture and to allow the decomposition of carbonates, pellets and grindings were performed after each treatment beyond 800 °C. After being ground, the samples were finally annealed at 1100 °C for 24 h.

The final products of $BaSrMWO_6$ (M=Ni, Co, Mg) have been controlled by X-ray powder diffraction analysis using Cu Kα radiation. The analysis of powders by X-ray diffraction showed some impurities such as $Ba/SrWO_4$ or $(Ba/Sr)_2WO_5$. The structural refinements were undertaken from the powder data. Diffraction data were collected at room temperature on a Phillips D 5000 (θ–θ) diffractometer: Bragg–Brentano geometry; diffracted-beam graphite monochromator; Cu Kα radiation (40 kV, 40 mA); Soller slits of 0.02 rad on incident and diffracted beams; divergence slit of 0.5°; antiscatter slit of 1°; receiving slit of 0.1 mm; with sample spinner. The patterns were scanned through steps of 0.02 (2θ), between 10 and 100 (2θ) for Co and Mg compounds and between 10 and 120 (2θ) for Ni compound with a fixed-time counting. The full pattern refinements were carried out by means of the Rietveld method using the FULLPROF program [6] integrated in WINPLOTR software [7]. The Rietveld refinement of the observed powder XRD data is initiated with zero shift and background parameters and successively other profile parameters and unit cell parameters are included. The background is fitted with a fifth order polynomial. The peak shape is fitted with a Pseudo-Voigt profile function. After an appreciable profile matching the scale, position parameters and isotropic atomic displacement parameters of individual atoms were also refined.

2.2. Raman spectroscopy

Experiments have been carried out using a Raman spectroscopic system designed and built at the Department of Earth Sciences, Uppsala University [8,9]. The key system components include a high-throughput, single stage imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems, Inc.) equipped with a holographic transmission grating and thermoelectrically cooled two-dimensional multichannel CCD detector (Newton, Andor Technology, 1600 × 400 pixels, thermoelectrically cooled down to −60 °C), an argon-ion laser (Spectra-Physics, 514.5 nm, 20 mW), and an optical imaging system (magnification 20×, spatial resolution ~1 μm). Two holographic notch filters (Kaiser Optical Systems, Inc.) blocked the Rayleigh line. The spectrometer was calibrated by fluorescence lines of the neon lamp. Non-polarized Raman spectra were collected in the back-scattering geometry, in the range 180–2280 cm^{-1}, at a resolution of about 3 cm^{-1}. Accuracy and precision of spectral measurements, as estimated from the wavelength calibration procedure and peak fitting results, were 1.5 cm^{-1} and 0.1–0.4 cm^{-1}, respectively. The acquisition time varied from 30 to 60 s.

For $BaSrNiWO_6$, heating was accomplished by using a mica insulated band heater (DuraBand, Tempco Electric heater Corporation) mounted around the sample ceramic holder and connected to a variable transformer. Temperature changes during the heating/cooling cycles were induced and controlled by adjusting the transformer's voltage (0–240 V) and monitored with an accuracy of ±1 °C by the K-type thermocouple adjacent to the sample. During the spectral acquisitions, temperatures were stabilized to within 1 and 3 °C, for the low and high temperature measurements, respectively.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1 shows the X-ray powder diffraction patterns of $BaSrMWO_6$ (M=Ni, Co, Mg). Indexing of X-ray powder diffraction patterns for these compositions was performed by means of the computer program DICVOL [10]. The first 15 peak positions, with a maximal absolute error of 0.03° (2θ), were used as input data. The X-ray diffraction patterns were assigned to a cubic and tetragonal symmetries for Ni, Co and Mg compounds (the patterns are similar). The lattice parameters were refined using the complete powder diffraction data sets and the complete powder diffraction data and intensities are given in Table 1. Note here that we will give only the results in the cubic system (because, in the following paragraph, the Raman studies will show that the tetragonal symmetry is to be discarded).

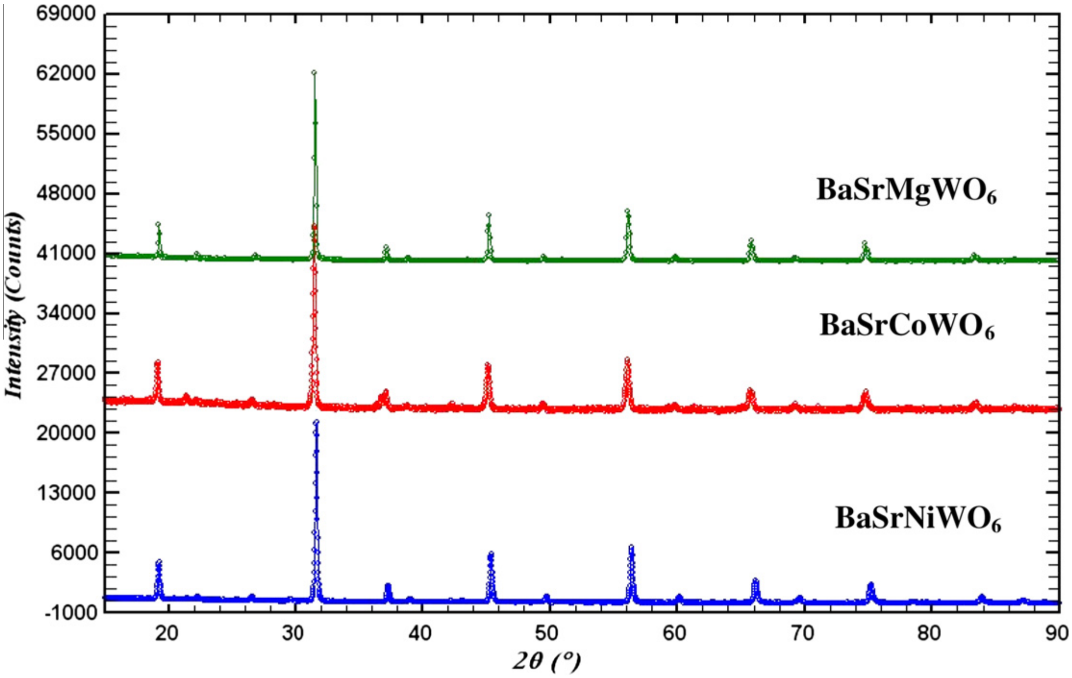

Fig. 1. X-ray powder diffraction patterns of $BaSrMWO_6$ (M=Ni, Co, Mg). The X-ray diffraction patterns were assigned to a cubic symmetry with Fm-3 m as a space group.