Selective substitution of vanadium for molybdenum in Sr$_2$(Fe$_{1-x}$V$_x$)MoO$_6$ double perovskites

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Abstract

The crystal and magnetic structures of Sr$_2$(Fe$_{1-x}$V$_x$)MoO$_6$ ($0.03 \leqslant x \leqslant 0.1$) compounds are refined by alternately using X-ray powder diffraction (XRD) and neutron powder diffraction (NPD) data collected at room temperature. The refinement results reveal that the V atoms selectively occupy the Mo sites instead of the Fe sites for $x \leqslant 0.1$. The $3d/4d$ cation ordering decreases with the increase of the V content. Slight distortions in the lattice and metal octahedra are shown at 300 K, and the distortions increase at 4 K. The magnetic structure at 4 K can be modeled equally well with the moments aligning along [001], [110] or [111] directions. The total moments derived from the NPD data for the [110] and [111] direction models agree well with the magnetic measurements, whereas the [001] model leads to a smaller total moment. Bond valence analysis indicates that Sr ions are properly located in the structure and Mo ions are compatible with both the Fe sites and the Mo sites. The electronic effects are suggested to be responsible for the selective occupation of the V on the Mo sites due to the different distortions of the FeO$_6$ and MoO$_6$ octahedra.
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Keywords: Crystal and magnetic structures; Preferential site occupation; Neutron powder diffraction; Double perovskites

1. Introduction

The ordered double perovskite compound Sr$_2$FeMoO$_6$ has received considerable attention in recent years owing to its appreciable room temperature low-field magnetoresistance (LFMR) that offers potential applications in spintronic devices and is of fundamental interest in condensed matter physics. Electronic structure calculations and optical spectroscopy investigations indicate that Sr$_2$FeMoO$_6$ is of half-metallic nature, i.e., the majority spin band is gapped and occupied essentially by the $3d^5$ up-spin electrons of Fe^{3+} ions, while the conduction band is occupied by both the Mo $4d\ t_{2g}$ and the Fe $3d\ t_{2g}$ down-spin electrons, leading to a full polarization of the itinerant carriers [1–3]. Both the ferrimagnetic coupling between the magnetic moments of the Fe and the Mo sublattices and

the metallic conductivity are considered to be induced via itinerant down-spin electrons [2]. The observed LFMR in Sr$_2$FeMoO$_6$ can be attributed to a tunneling of the spin-polarized carriers across grain/domain boundaries [4].

An ideal ordered Sr$_2$FeMoO$_6$ consists of corner-sharing FeO$_6$ and MoO$_6$ octahedra alternately arranged along all three directions with the voids among the octahedra being filled by larger Sr ions. Therefore, Fe and Mo atoms form a rock-salt structure (rock-salt ordering). If one considers a spin-only contribution of 5 Bohr magneton per formula unit (μ_B/f.u.) of the Fe sublattice and 1 μ_B/f.u. of the Mo sublattice, a saturation moment of 4 μ_B/f.u. is anticipated for an ideally ordered Sr$_2$FeMoO$_6$ within the framework of the simplest ferrimagnetic arrangement model (the FIM model), which assumes that the Fe and Mo sublattices couple antiferromagnetically [5]. However, magnetic measurements and crystal structure analysis indicate that Sr$_2$FeMoO$_6$ is not perfectly ordered due to intrinsic antisite defects (AS), i.e., small numbers of Fe and Mo atoms

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exchange sites. This can happen because the valence difference and ionic radius difference between Fe^{3+} and Mo^{5+} fall in the region where ordered and disordered double perovskites can coexist [6]. Both experiments and computer simulation have showed that the LFMR and the saturation moment of Sr_2FeMoO_6 are sensitive to the presence of the AS [5,7,8]. Substitutions of W for Mo [9,10], Cu for Fe [11], and Mn for Fe [12] reduced the AS content. In contrast, substitutions of Cr or V for Fe increased the AS content (i.e. the Mo content on the Fe site) in $Sr_2Fe_{1-x}T_xMoO_6$ (T = Cr, V) [13,14]. For $Sr_2Fe_{1-x}Cr_xMoO_6$ (x = 1/4, 1/2, 3/4 and 1.0), neutron diffraction revealed that Cr preferentially occupied the Mo sites and, interestingly, the population ratio of Cr on the Fe sites to the Cr on the Mo sites was approximately a constant ($\approx$1:2) for $x = 0.25-1.0$ [13]. Oxygen deficiency was detected for the Cr content greater than 0.25. Ritter et al. investigated the structure of a series of 3d-metal doped $Sr_2Fe_{3/4}T_{1/4}MoO_6$ (T = Sc, Ti, V, Cr, Mn, Fe, Co) by X-ray powder diffraction (XRD) and neutron powder diffraction (NPD) [15]. The dopant T distributed unevenly on the Fe and the Mo sites, while a preferential occupation of T on the Fe sites was observed, except for T = Cr. The size and valence state of the dopant are considered to affect the relative distribution of T on the Fe and Mo sites. In comparison to the parent compound Sr_2FeMoO_6 with AS = 0.05, the T-doping increased the Mo content on the Fe sites (AS), i.e. reduced the 3d/4d cation ordering.

Since the LFMR and the saturation moment of Sr_2FeMoO_6 are sensitive to the presence of the AS [5,7,8], detailed information on structure stability, atomic occupancies, cation ordering and magnetic structure is indispensable for understanding the physics of the LFMR of the double perovskite compounds. Many neutron diffraction studies have been carried out on parent compound Sr_2FeMoO_6 [15–18] and heavily doped $Sr_2(Fe_{1-x}T_x)MoO_6$ ($x \geqslant 0.25$) [13,15]. However, similar work on lightly doped compounds is less reported in literature. The relatively light doping provides an opportunity to examine the perturbation of the doping to the stability and physical properties of the double perovskite compounds.

The crystal structure, electrical transport and magnetic properties of the lightly V-doped $Sr_2(Fe_{1-x}V_x)MoO_6$ compounds ($0 \leqslant x \leqslant 0.1$) have been reported previously [14]. Based on X-ray diffraction, it was revealed that the 3d/4d cation ordering decreased with the V content. Because of the tiny difference in X-ray atomic scattering factor between Fe and V, the (Fe, V) was treated as a single entity and the occupancy of Mo on the Fe sites (= the occupancy of (Fe, V) on the Mo sites) was refined as the AS. The derived AS was greater than the V content, x, for all the investigated $Sr_2(Fe_{1-x}V_x)MoO_6$ ($0 \leqslant x \leqslant 0.1$). On the assumption that the V occupied exclusively the Mo sites, i.e. $Sr_2(Fe_{1-AS}Mo_{AS})(Mo_{1-AS}Fe_{AS-x}V_x)O_6$, the FIM model reasonably reproduced the experimental magnetic moments as a function of the V content. However, the

assumed distribution of V in the investigated compounds is in contradistinction to the cases of the heavily doped $Sr_2Fe_{3/4}V_{1/4}MoO_6$ [15] and $Sr_2(Fe_{1-x}Cr_x)MoO_6$ ($x \geqslant 0.25$) [13]. In this paper, we combine XRD and NPD techniques to ascertain the distribution of Fe, Mo, and V cations in the lightly V-doped $Sr_2(Fe_{1-x}V_x)MoO_6$ compounds ($0 \leqslant x \leqslant 0.1$). In addition, magnetic structure of $Sr_2Fe_{0.9}V_{0.1}MoO_6$ at 4 K is modeled by considering different alignments of magnetic moments.

2. Experimental

The preparation of polycrystalline $Sr_2(Fe_{1-x}V_x)MoO_6$ ($0 \leqslant x \leqslant 0.1$) was described in detail previously [14]. The samples were synthesized by standard solid-state reactions at 1280 °C under a reduction atmosphere (flowing 5% H_2/Ar gas) with several intermediate grindings. XRD detected no impurity phases in the samples. The XRD was performed on a Rigaku D/max 2500 diffractometer with Cu$K\alpha$ radiation (50 kV × 250 mA) and a graphite monochromator for the diffracted beam in Bragg–Brentano geometry. The patterns were collected between $2\theta = 15°$ and $100°$ in a step of $0.02°$ with a sampling time of 1 s per step. The NPD experiments were performed at NIST Center for Neutron Research (NCNR) on the high-resolution, 32-counter BT-1 diffractometer with a monochromatic neutron beam of wavelength 1.5403(2) Å. Collimators with horizontal divergence of 15, 20, and 7 min of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the 2θ range of 10–160° with a step of 0.05°. The crystal and magnetic structures were refined using the program FULLPROF [19].

3. Results

The crystal structure of the V-doped $Sr_2(Fe_{1-x}V_x)MoO_6$ was refined based on space group $I4/m$ as mostly reported for the parent compound Sr_2FeMoO_6 with the rock-salt ordering [13,16,20]. The space groups $I4/mmm$ [9] and $P4_2/m$ [17] have also been suggested for Sr_2FeMoO_6. These three space groups are in fact only slightly different in describing the symmetry of Sr_2FeMoO_6 and become equivalent, provided that some reasonable constraints on the position parameters of oxygen are applied [13].

It is well known that determination of the distribution of three different kinds of atoms (Fe, V, Mo) on two available crystallographic sites (2a and 2b in $I4/m$) requires, in principle, at least two sets of diffraction data with differing atomic cross sections that can provide two linearly independent structure factors [21] and even then is nontrivial by Rietveld refinement. Since it is difficult in practice to measure absolute intensities with precision, a scale factor is usually employed to convert arbitrary intensities to absolute intensities, which raised the number of data sets required to three. Though we have only two sets of diffraction data (XRD and NPD), we first intended