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Crystal structure, electronic and magnetic properties of double perovskite Ba_2FeWO_6: A combined experimental–theoretical study

M. Musa Saad H.-E [a,*], N. Rammeh [b]

[a] Department of Physics, College of Science, Qassim University, P.O. 4466, Buraidah 51452, Saudi Arabia
[b] Laboratoire de Physico-Chimie des Matériaux Minéraux et leurs Applications, Centre National de Recherches en Sciences des Matériaux, B. P. 95, Hammam-Lif 2050, Tunisia

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ABSTRACT

Double perovskite oxide Ba_2FeWO_6 has been synthesized in polycrystalline form by the solid-state ceramic method at 950 °C. Structural characterization was performed by using the X-ray powder diffraction (XRD) and neutron powder diffraction (NPD) followed by Rietveld analysis of these patterns. The crystal structure of Ba_2FeWO_6 is cubic; space group Fm-3m with lattice parameter of $a = 8.1351$ Å. Also, a density functional theory (DFT) study of the crystal structure, electronic and magnetic properties of Ba_2FeWO_6 has been carried out using full potential linear muffin-tin orbital (FP-LMTO). We showed that the obtained symmetry lattice parameter agree well with the experimental results. The influence of Fe element on the magnetic and electronic properties of double perovskite oxide Ba_2FeWO_6 is analyzed. Band structure calculations for cubic Ba_2FeWO_6 predict an energy-gap in both spin-up and spin-down. The semiconductor antiferromagnetic (AFM) phase is stabilized by the hybridization of nonmagnetic W^{6+} ($5d^{\circ}$) site positioned in between the magnetic Fe^{2+} ($3d^6$) sites through the O^{2-} anions in a long range O–Fe–O–W–O arrangement. ^{57}Fe Mössbaur spectrum and DFT calculations suggest that the AFM behavior arises since the mixed valence Fe^{2+}–Fe^{3+} effect introduces in Fe^{2+}–O^{2-}–W^{6+} anticoupling.

1. Introduction

Scientific research on double perovskite oxide materials has gained strong interest after detection of room temperature colossal magnetoresistance (CMR) and half-metallic (HM) phenomena in the grand double perovskite oxide Sr_2FeMoO_6 by Kobayashi et al. [1]. The alteration of crystal structure, electronic, magnetic and optical properties by varying the A, B or B' site cations in $A_2BB'O_6$-type double perovskite oxide has also gained attention in order to better understand the mechanism of CMR and other unusual physical properties [2]. The detection of CMR has motivated the research on ferromagnetic (FM) half-metallic double perovskite oxides, as they are functional for the realization spintronics devices, such as used in memory applications. Considerably, higher transition temperatures are required for devices that rely on spin-polarized transport in half-metallic double perovskite oxides if they are supposed to operate in a temperature range around room temperature.

A few 3D-transition metals in double perovskite oxides exhibit co-operative transition between a low-spin (LS) state and high-spin (HS) state. This type of spin-crossover oxide could be used as an active element in memory devices. Therefore, double perovskite oxides $A_2BB'O_6$ with two ordered B-site cations are FM for B=Cr (3d), Fe (3d), Co (3d), etc. and B'=Mo (4d), W (5d), Re (5d), etc., where A-site is an alkaline earth metal (A=Ca, Sr, Ba) [3–6]. Moreover, a variation of the cations in the B-B' sites influences the crystal structure, electronic, and magnetic properties significantly and may contribute to an understanding of the mechanism of the long range super-exchange interaction [–O–B–O– B'–O–] in double perovskite oxides $A_2BB'O_6$.

Double perovskite oxide Ba_2FeWO_6 was studied early by Fresia et al. and T. Nakagawa et al. and reported as a cubic with ($a = 8.133$ Å) [7,8]. More recently the crystal structure of Ba_2FeWO_6 has been refined by Azad et al. in a tetragonal structure, space group $I4/m$ no. 87, with an antiferromagnetic (AFM) magnetic phase below 30 K temperature [9]. To our best knowledge, there is no experimental-theoretical combined studies have yet been performed to investigate the crystal structure, electronic, and magnetic properties of double perovskite oxide Ba_2FeWO_6. Therefore, the current paper describes the detailed study of the crystal structure, electronic, and magnetic properties of Ba_2FeWO_6 by using XRD, NPD, SQUID and ^{57}Fe Mössbaur experimental techniques. Besides, the DFT theoretical calculations by the full potential

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[*] Corresponding author.
E-mail address: musa.1964@gmail.com (M.M. Saad H.-E).

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linear muffin-tin orbital (FP-LMTO) method are performed. This paper is organized as follows: the brief of the details of the experimental techniques and employed computational methods for the calculations are described in Section 2. Section 3 presents and discusses the main obtained results of the crystal structure, electronic and magnetic properties of Ba_2FeWO_6, and a summary of concludes the paper in Section 4.

2. Experimental and computational methods

2.1. Preparation and measurements of Ba_2FeWO_6 sample

The polycrystalline sample of double perovskite oxide Ba_2FeWO_6 was synthesized via the standard solid-state ceramic method. Firstly, the precursor oxide of composition Ba_2WO_5 was prepared by the reaction of stoichiometric amounts of $BaCO_3$, WO_3 oxides (Strem Chemicals, 99.9%) at 900 °C in air for four days; $2BaCO_3+WO_3 \rightarrow Ba_2WO_5+2CO_2$. Secondly, the resultant oxide was mixed with an amount of Fe_2O_3 oxide (Strem Chemicals, 99.9%) to obtain the Ba_2FeWO_6 sample. Finally, the resultant powder was pressed into a pellet and heated in an evacuated sealed silica tube (10^{-4} mbar), at 950 °C for 24 h with intermediate grindings.

Structural characterization was performed by the X-ray powder diffraction (XRD) by means of a STOE STADI-P diffractometer with MoKα radiation. In addition, the high-flux diffractometer D20 at the Institute Laue–Langevin (Grenoble) was used for neutron powder diffraction (NPD). Beam-line B2 at the Hamburger Synchrotron Strahlungslabor HASYLAB (Germany) was used for high-resolution synchrotron powder diffraction in order to check the actual homogeneity of the Fe/W composition in the different crystallites. Diffraction patterns for Ba2FeWO6 have been measured in the range $13^\circ \leq 2\theta \leq 78^\circ$ in steps of 0.006° with a wavelength of $\lambda=1.11957(1)$ Å, selected by a Ge (1 1 1) double-crystal monochromator. A pneumatically bent mirror was used to reduce vertical divergence and, hereby instrumental resolution was optimized so that sample effects are more clearly detectable. Rietveld refinement of the diffraction pattern was made by using the Fullprof software package [10].

2.2. Computational details for Ba_2FeWO_6 compound

Density functional theory (DFT) [11] calculations were performed within the localized spin density approximation (LSDA) [12,13] implemented in the LMTART computational code [14]. The full potential linear muffin-tin orbital (FP-LMTO) method was employed to represent the semi core and valance states in an energy system in transition metal oxides. The spin orbital coupling effect is also taken into account. All calculations were converged with respect to Brillouin zone (BZ) sampling and the size of the basis set. BZ integrations within the self-consistent cycles were performed via a tetrahedron method by using $(8\times8\times8)$ special k-points mesh [15]. The convergence parameter $R_{MT}K_{max}$ was set to 8.0 which controls the size of the basis sets, where K_{max} is the plane wave cutoff and R_{MT} is the smallest of all atomic sphere radii. The G_{max} parameter was taken to be 12 $Bohr^{-1}$. The muffin-tin radii in Ba_2FeWO_6 were set at 2.50, 1.80, 2.0 and 1.60 (in atomic unit) in the FP-LMTO calculations for Ba, Fe, W and O, respectively. Careful convergence tests show that with these parameters relative energy converged to better than 10^{-5} Ry per unit cell.

In order to obtain better results of electronic and magnetic properties, the correlation parameters, Coulomb energy (U) and Hund's exchange energy (J) [16,17] were utilized for correlated 3d and 5d states in double perovskite oxide Ba_2FeWO_6. Therefore, the spin-dependent total and partial densities of states were obtained from the LSDA plus correlation energy, (LSDA+U) method, resolving spin-up and spin-down states in the calculations. The correlation parameters ($U=5.0$ eV, $J=0.90$ eV) and ($U=1.0$ eV, $J=0.90$ eV) [17,18] are used for strongly Fe (3d) and weakly W (5d) states, respectively.

3. Results and discussion

3.1. Crystal structure of Ba_2FeWO_6

The crystal structure has been investigated by means of high-resolution synchrotron XRD patterns. Fig. 1 shows the XRD pattern of the powdered sample. In double perovskite oxide Ba_2FeWO_6 compound, the Bragg reflections were indexed with a face centered cubic unit cell and refined in space group of Fm-3m with $a=2a_p=8.1351$ Å, where a_p is the parameter of the ideal perovskite. The Rietveld profiles analysis of spectra revealed that the compound is essentially single phase with a secondary phase of $BaWO_4$ with 3.0% impurity. In addition, Fig. 2 shows the neutron powder diffraction (NPD) profiles for Ba_2FeWO_6 measured at two different temperatures $T=5$ K and $T=310$ K. It seen that from the results of NPD measurements, there is no phase transition at low temperature in agreement with the XRD results. Both of XRD and NPD measurements show that Ba_2FeWO_6 compound crystallizes in face centered cubic structure with Fm-3m space group. The obtained unit cell parameters and the space group used in the refinements are displayed in Table 1. The values of experiments are in very good agreement with the calculation results.

Ba_2FeWO_6 adopts cubic crystal structure characterized in the face centered cubic with space group Fm-3m (No. 225) and $O_h{}^5$ octahedral symmetry. Therefore, in rock-salt arrangement, the crystal structure of Ba_2FeWO_6 can be described by the (Fm-3m) space group with Wyckoff's positions of ions Ba in 8 c at (¼,¼,¼); Fe in 4a at (0,0,0); W in 4b at (½,½,½); and O in 24e at (x,0,0). All the equivalent positions are obtained from those indicated by the transitions of the face centered cubic unit cell; (0,0,0), (½,0,0), (0,½,0) and (0,0,½). This result is in contrast to the tetragonal crystal structure of Ba_2FeWO_6 [20]; in this description, it is necessary to consider two different positions for O (1) and O (2) atoms and one position for Fe atom. As no evidence for tetragonal distortion was found in high-resolution synchrotron diffraction, the reported tetragonal model is critically reviewed. In ordered cubic double perovskite oxide Ba_2FeWO_6, the Fe^{2+} and

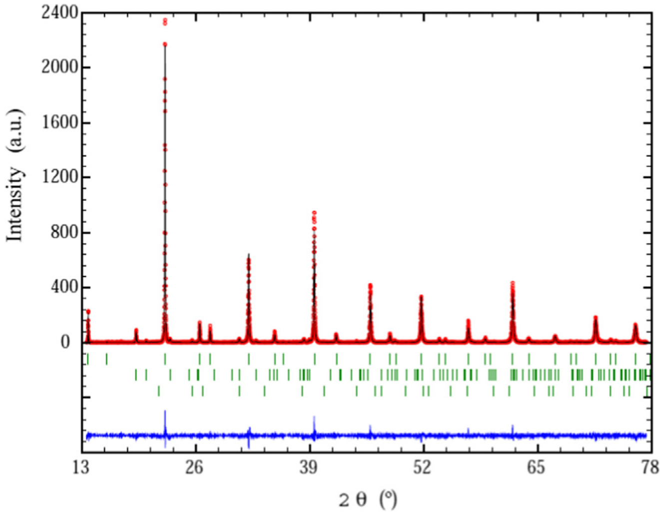

Fig. 1. XRD pattern of double perovskite oxide Ba_2FeWO_6 by high-resolution synchrotron powder diffraction ($\lambda=1.11957(1)$ Å). The red symbols, black line and blue line represent the observed, calculated and difference XRD intensity profiles.