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Effect of the internal pressure and the anti-site disorder on the structure and magnetic properties of $ALaFeTiO_6$ (A=Ca, Sr, Ba) double perovskite oxides

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ABSTRACT

Successful preparation of double perovskite oxides of chemical formula $ALaFeTiO_6$ (A=Ba, Sr and Ca) has been achieved by following the precursor method. The samples were studied by means of X-ray diffraction and Mössbauer spectroscopy. The Rietveld analysis of the X-ray diffraction data showed that all the samples have anti-site disorder. The presence of anti-site disorder has altered the electronic environment around the Fe ion sites which creates electric field gradient between two different sites. Observation of quadruple splitting in the ideal cubic perovskite $BaLaFeTiO_6$ (its tolerance factor equals 1) is the evidence of this anti-site generated electric field gradient. The valence state of the Fe atom determined from the measurements of the Mössbauer effect of ^{57}Fe at room temperature and 80 K showed that the iron ion has the Fe^{3+} high spin state as extracted from the values of the isomer shift for all the samples. It is evidenced that the anti-site disorder has no appreciable effect on the spin state of the Fe ion, but alters the charge densities at the Fe sites and influences the hyperfine parameters of the present samples. Weak ferromagnetism is observed in $CaLaFeTiO_6$ and $SrLaFeTiO_6$ and is related to both the internal pressure and the anti-site effect which facilitate the occurrence of the $Fe^{3+}\uparrow-O-Fe^{3+}\downarrow$ antiferromagnetic interaction with canted spin.

1. Introduction

Double perovskite (DP) compounds have attracted considerable research activities in many due to their interesting structural, magnetic and electronic properties. The general chemical formula of double perovskite oxides can be expressed as $A_2BB'O_6$, where A is an alkaline earth element such as Sr, Ca, Ba etc., and B site is occupied by the first row of the 3d magnetic elements in the periodic table. The B′ site is occupied by the 4d non-magnetic elements, with O atom located in between forming alternate BO_6 and $B'O_6$ octahedra and B–O–B′ bonds [1,2]. The wide range of these compounds is due to the variety of the magnetic (B) and non-magnetic B′ elements as well as the A-site cations that can form stable double perovskites structures.

Many double perovskite oxides were prepared, and their crystal structures were found to vary from cubic, tetragonal to monoclinic. Stabilization of these kinds of crystal structures depends on the ionic radii of the A, B and B′ sites and the tolerance factor. For example, when A is small, A=Ca, the obtained crystal structure varies from tetragonal to monoclinic [3]. On the other hand, most of the Sr and Ba based compounds were found to be cubic or tetragonal. Kato et al. studied the crystal structure of A_2MReO_6 (A=Ca, Sr, M=Mg, Sc, Cr, Mn, Fe, Co, Ni and Zn). They found that the lattice with small A-site Ca is monoclinic, and the Sr based compounds are tetragonal or cubic [3]. The crystal structure was found to affect the magnetic properties of the double perovskite oxides.

Tuning the properties of the double perovskites was achieved by in either the A-site or the B-site as reported, e.g. in $Sr_{2-x}La_x$-$FeMoO_6$. This doping leads to formation of Fe^{2+}, and the electrical conductivity was seen to increase [4]. Doping at the B-site was also investigated as reported in $Sr_2FeRe_{1-x}Sb_xO_6$ [4]. The properties of these double perovskites were found to be sensitive to the preparation method [5] and may lead anti-site disorder. The disordered arrangement of the B and the B′ is known as the anti-site effect, which leads to B–O–B, B′–O– B′ and B–O–B′ interactions that by their role affect the magnetic and electrical properties of the DP. Rubi et al. [6] showed by means of magnetization and Mössbauer studies that the anti-site effect introduces near neighbour antiferromagnetic interactions between the Fe ions in Nd-doped Ca_2FeMoO_6 which lead to enhancement of the Curie temperature.

The structures $ALaFeMO_6$ (A=Ba, Sr and Ca; M= Mn, Ru and Co) have been studied by many groups to inspect the B-cation ordering [7,8] where M ion is a magnetic element. Shaheen et al.

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[7] have studied $ALaFeMnO_6$ (A=Ca, Sr, Ba) by means of X-ray, neutron diffraction and Mössbauer spectroscopy. They found that the room-temperature measurements of the Mössbauer spectra are doublets with a quadruple splitting equals 0.43 mm/s for $CaLaFeMnO_6$ and increases to 0.6 mm/s in $BaLaFeMnO_6$. Similarly, $SrLaFeRuO_6$ shows room temperature quadruple splitting equals 0.43 mm/s [8], and the origin of this quadruple splitting was related to the non-cubic crystal structure of the studied materials. The anti-site effect on the MS spectra of these materials was not included.

The cation distribution and the anti-site effect of the Fe containing double perovskites in addition to the chemical pressure effect were investigated by means of the Mössbauer spectroscopy (MS) [9]. Douvalis et al. showed by means of MS that the Fe ion in $Sr_{2-x}Ca_xFeReO_6$ has three chemical environments. Consequently, not all iron ions experience the same first cation neighbour environment [10]. The different Fe environments appear as different components of the Mössbauer spectra due to the influence of their different environments on their hyperfine parameters [10]. Further, they found that the quadruple splitting (QS) increases as the crystal structure changes form cubic structure to monoclinic structure.

In this work, the effect of the anti-site disorder of $ALaFeTiO_6$ (A=Ca, Sr and Ba) will be studied in terms of X-ray diffraction (XRD) and Mössbauer spectroscopy. The cause of the quadruple splitting, in this type of double perovskites, will be discussed. Moreover, the occurrence of weak ferromagnetism due to lattice disorder and anti-site effect is also investigated.

2. Experimental details

Polycrystalline samples have been synthesized by the standard solid-state reaction technique. The raw metal carbonates and oxides' material $SrCO_3$, La_2O_3, Fe_2O_3, TiO_2, $BaCO_3$ and $CaCO_3$ are all from Alfa Acer of purity 99.9% was used to prepare the $ALaFeTiO_6$ double perovskite.

A precursor composite was first made by mixing of ferrous and titanium oxides together carefully and ground manually for 45 min continuously on an agate mortar with a little amount of acetone for homogeneity. Then, the mixture was placed in a high density alumina crucible and heated at 900 °C for 12 h. After cooling to room temperature, the alkaline earth carbonate and the rare earth-oxides were added, grind and then pressed into pellets at pressure of 1.9×10^8 N/m^2 and heated at 900 °C. Finally, the samples were ground again and pressed as before and sintered at 1200 °C for 12 h, then cooled to room temperature. All the heating and cooling cycles were set at a rate of 10 °C/min.

Phase analysis and characterization were carried out with X-ray diffraction (XRD) using a Bruker-axs D8-Focus X-ray diffractometer. The data were collected for the 2θ range 20°–80° at a step size of 0.02 and count time of 5 s. The collected data are then fed to the FullProf suite [11] for determination of the lattice parameters, space group and atoms' positions.

Mössbauer spectra were collected at 300 K and 80 K at a constant acceleration. The spectrometer was calibrated with α-Fe foil at room temperature.

3. Results and discussion

3.1. Structural characterization

The XRD patterns measured at room temperature for the samples $CaLaFeTiO_6$, $SrLaFeTiO_6$ and $BaLaFeTiO_6$ along with their best fittings are shown in Fig. 1. These patterns were subjected to careful analysis by means of the standard Rietveld methods using the FullProf suite. Three structural models were selected for the refinement processes for accurate determination of the best crystal structure that matching the data. The anti-site effect of the Fe and Ti atoms is considered by their shared occupation between the B and B′ sites. The XRD characterization showed that all the samples are of single-phase. The best-fitting results were achieved when the anti-site disorder is considered in all the samples. The crystal structures of the samples are found to be monoclinic, tetragonal and cubic structures within the space group P21/n, I4/m and Fm-3 m for $CaLaFeTiO_6$, $SrLaFeTiO_6$ and $BaLaFeTiO_6$ respectively. The obtained lattice parameters, atoms' positions as well as the reliability factors are shown in Table 1.

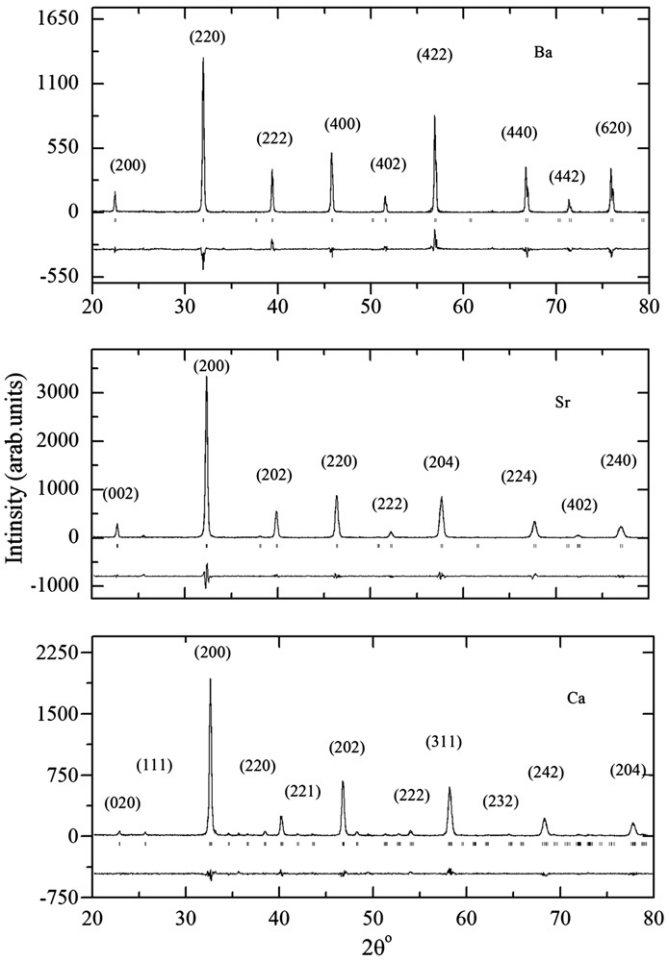

Fig. 1. The results of the Rietveld refinement along with indexing of the main peaks of the compounds $CaLaFeTiO_6$, $SrLaFeTiO_6$ and $BaLaFeTiO_6$.

The tolerance factor is a measure of the internal pressure for perovskite structures. It is given by [12]

$$t=\frac{(r(\mathrm{A})+r(\mathrm{X}))}{\sqrt{2}(r(\mathrm{B})+r(\mathrm{X}))} \quad (1)$$

where t represents the tolerance factor, r(A), r(B) and r(X) are the ionic radii for A-site, B-site and oxygen respectively. The values of the tolerance factor for $CaLaFeTiO_6$, $SrLaFeTiO_6$ and $BaLaFeTiO_6$ are calculated using the SPuDS program [13] and found to be 0.9442, 0.971 and 1.0006 respectively. The value of the tolerance factor for $BaLaFeTiO_6$ is a typical value for an ideal cubic perovskite. This is consistent with the results of the Rietveld analysis of the XRD which shows that $BaLaFeTiO_6$ is a cubic double perovskite. The reduction of symmetry in the other two compounds is related to the small values of the A-site radius (r_A)