

Effect of the Cation Size Disorder at the A-Site on the Structural Properties of SrAFeTiO₆ Double Perovskites (A = La, Pr or Nd)

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Abstract

In this paper, the cation size disorder effect of the A-site on the structural properties of the SrAFe-TiO₆ (A = La, Pr or Nd) was investigated. The compounds were synthesized—as the best of our knowledge—for the first time by conventional and precursor method to get crystalline materials. The results obtained from the experimental measurements carried out on new double perovskite materials were presented. The data of X-ray diffraction (XRD), Fourier Transform Infra Red FTIR were measured at room temperature. From the X-ray diffraction, and by means of standard Rietiveld method, all the samples have the same structure (orthorhombic) with Pnma space group. The difference in the tolerance factor is clearly noticed and refers to the cation size disorder at the A-sites. The Fourier Transform Infra Red FTIR measurement has been done; the results of it confirm the double perovskite structure and the difference between the samples were noticed. The tolerance factors for the samples altered from SrLaFeTiO₆ up to SrNdFeTiO₆ and this difference return to ionic radius and cation size effect.

Keywords

Cation Disorder, Double Perovskite, Tolerance Factor

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1. Introduction

Double perovskite oxides, $A_2BB'O_6$ or AA'BB'O₆, where A and A' are alkaline—earth and/or rare—earth metals and B and B' are transition metals, have been investigated [1]. These materials are especially interesting in view of the possibility that B and B' cations could be ordered at the octahedral sites, giving rise to novel electrical and magnetic properties due to B - O - B' interaction [2]. The study of these oxides was initiated in the 1950s and since then several hundred of these compounds have been produced and studied because they exhibit quite interesting structural, electronic as well as magnetic properties [2]. One can anticipate many more of these types of compounds to be realized given the diversity of the ions that can occupy both the A- and B-sites. The last few years ordered double perovskite oxides have been received an enormous amount of attention because certain members of this family of oxides exhibit spectacular physical phenomena such as colossal magnetoresistance and half metallicity in the ferrimagnetic Sr_2FeMoO_6 [3] and La_2VRuO_6 [4] compounds.

The physical properties of double perovskite DP are generally determined by the cations occupying the B, B' sites. Thus, special attention has been given to the factors that impact the B-sites arrangement, namely the charge, size and electronic configuration of B cations as well as the A/B size ratio. Anderson *et al.* [2] have concluded that an ordered structure is most likely to be formed if the charge difference between B and B' is two or higher. An exception to this condition is the case of LaCaMnCoO₆ [5]; this compound was ordered even though the B - B' charge difference is one. The ideal perovskite has a primitive cubic structure with the formula ABO₃, where the B-ions are at the corners of the cubic cell and the A-ions at the cubic octahedral (12 coordinated) site. There is a variety of ordered structures known in perovskite oxides; among them the double perovskite (A₂BB'O₆) or AA'BB'O₆) and the triple perovskite (A₃BB'₂O₉) structures are the most popular.

These ordered structures can be obtained mainly by substituting other cations at their A or B sites of the ABO₃ structure and occur due to the charge difference. Many of these ordered perovskite cations Ti, Fe and Mn as the B-cations, are interesting due to their optimum dielectric characteristics for applications in electronic industry [6]-[8].

2. Experimental Details

The double perovskite SrAFeTiO₆ samples where A is (La, Pr, Nd) respectively, were prepared.

Most of the chemicals used in the preparation were Alfa Acer of purity 99.9%. The method used for preparation of these double perovskite is in accordance with the well known procedures [9] [10]. The X-ray diffraction and FTIR measurements were carried out for the samples under investigation.

SrLaFeTiO₆, SrPrFeTiO₆ and SrNdFeTiO₆ were synthesized by both conventional and precursor solid state reaction from the compounds SrCO₃, La₂O₃, Fe₂O₃, TiO₂, Pr₇O₁₁ and Nd₂O₃ raw materials with purity more than 99%. The grouped compounds were mixed together and then ground in an agate mortar for 45 minutes at least. After that the compounds were heated into a Carbolite air furnace to 900 degrees of centigrade for 12 hours. Then it was pressed into pellets under 7 MPa pressure for 30 seconds following by preheating in air at 900°C for 24 hours with intermediate grinding and finally it was calcinated at 1200°C for 12 hours. Phase analysis and characterization were carried out by X-ray diffraction (XRD) using Cu K_{α} radiation on both X'Prot Bruker D8 and Schimadzu 6000.

3. Results

Determination of the crystal structure, the lattice parameters and the space group symmetry become of central importance in the study of structural, electrical and magnetic properties of the double perovskite materials [11].

The results of the XRD for the samples obtained after conventional solid state method is shown in **Figures** 1(a)-(c) for the samples SrLaFeTiO₆, SrPrFeTiO₆ and SrNdFeTiO₆. Clearly, the quality of the samples is poor whatever grinding times and/or heating temperatures are committed.

By following the precursor method, good quality samples are obtained as shown in Figure 2.

A selection range is given in **Figure 3** in order to show the difference in the peak position for each sample. The shift in the reflection positions indicates differences in the lattice parameters and/or the type of the crystal structure.

3.1. The XRD Analysis

For quantitative analysis, the XRD patterns are analyzed by the standard Rietveld refinement method. Three



Figure 1. (a) The XRD results of the SrLaFeTiO₆ sample prepared by the conventional solid state reaction; (b) The XRD results of the SrPrFeTiO₆ sample prepared by the conventional solid state reaction; (c) The XRD results of the SrNdFeTiO₆ sample prepared by the conventional solid state reaction.



Figure 2. The X-ray patterns for the GI series samples. The green colored is SrNdFeTiO₆, the red colored is SrPrFeTiO₆ and the blue one is SrLaFeTiO₆ sample respectively. Shifts in the intensity are clearly seen above $2\theta = 38$ to the end of the scan.



colored is $SrNdFeTiO_6$, the red colored is $SrPrFeTiO_6$ and the blue one is $SrLaFeTiO_6$ sample respectively.

types of the crystal structures commonly observed in the double perovskites were selected for the analysis purpose. They are cubic, tetragonal and orthorhombic structures.

3.1.1. The SrLaFeTiO₆ Structure

For accurately determination of the crystal structure and its lattice parameters commonly observed among the double perovskites are tested. The XRD data of the SrLaFeTiO₆ structure was used along cubic structure with space group Fm3m, Tetragonal with space group I4/m, tetragonal with space group I2/n and orthorhombic with space group Pnma. The criteria used for the judgments are: all peaks must be fitted to certain crystal structure model and if all the peaks are fitted to more than one space group then the lowest Bragg's factor in the better model is obtained. It was worthy to mention here, that the fitting was started by selecting the highest symmetry structure which is cubic, and subsequently going down to the orthorhombic at the end **Figure 4** as well as the corresponding **Table 1**.

3.1.2. The SrPrFeTiO₆ and SrNdFeTiO₆ Structures

Similar investigations are carried out for the SrPr/NdFeTiO₆ samples. The best fit is obtained for the orthorhom-



Figure 4. Refined XRD patterns of the SrLaFeTiO₆ sample. It shows the orthorhombic structure with (Pnma) space group.

Elements	Coordinates	SrLaFeTiO ₆	SrPrFeTiO ₆	SrNdFeTiO ₆
		Pnma	Pnma	Pnma
Sr/(La, Pr, Nd)	x	0.01016	-0.02036	-0.02810
	у	0.25000	0.25000	0.25000
	z	0.00795	0.00908	0.01365
Fe	x	0.00000	0.00000	0.00000
	у	0.00000	0.00000	0.00000
	z	0.50000	0.50000	0.50000
Ti	x	0.00000	0.00000	0.00000
	у	0.00000	0.00000	0.00000
	z	0.50000	0.50000	0.50000
01	x	-0.00176	0.00674	0.00390
	у	0.25000	0.25000	0.25000
	z	0.52003	0.50578	0.50838
02	x	0.25942	0.29040	0.30266
	у	-0.01639	-0.04803	-0.04097
	z	0.26433	0.25343	0.25000
a (Å)		5.55765	5.52728	5.51584
b (Å)		7.82408	7.79671	7.79255
c (Å)		5.53766	5.51395	5.51391
R _{WP}		2.4	2.85	4.56
R _P		3.61	3.28	4.23

Table 1. The atom positions, the space groups, the lattice parameter and the refinement reliability factors for Sr/(La, Pr, Nd) FeTiO₆ samples.

bic structure by adopting the Pnma space group. The data for these two samples are shown in Figure 5 and Figure 6.

In an ideal perovskite, the A-cation is surrounding by 12 oxygen anions in a regular dodecahedral environment and the B-cation is octahedrally coordinated by 6 oxygen ions, giving rise of 180° B-O-B bond angles [12]. By replacing A-cation with smaller one, the BO₆ octahedral would be rotated from the cubic crystallographic axis to release the structural stress. The cooperative rotation of the B'O₆ octahedra consequently, leads to decrease in the B'-O-B angle and reduction in the coordination number of the A cation [13].

All the pervious reasons let the tolerance factor play one of the conventional methods used to compare the elements and compounds which represent the structural parameters. Figure 7 shows the relation between the







Figure 6. Refined XRD patterns of the $SrNdFeTiO_6$ sample. the orthorhombic structure is shown with (pnma) space group.



Figure 7. The tolerance factor versus the ionic radius for the three samples SrLaFeTiO₆, SrPrFeTiO₆ and SrNdFeTiO₆ respectively.



Figure 8. The IR spectra of the three samples $SrNdFeTiO_6$, $SrPrFeTiO_6$ and $SrLaFeTiO_6$ respectively. The depth of the stretching frequencies ~600 cm⁻¹, were increased from $SrNdFeTiO_6$ to $SrLaFeTiO_6$ with broadening in the peak of the $SrLaFeTiO_6$ sample.

ionic radius R and the tolerance factor. Obviously the tolerance factor increase with R.

3.2. The IR Spectroscopy Results

Since every type of bond has a different natural frequency of vibration, and two of the equivalent types of bond in two unusual compounds are in two slightly diverse environments, no two molecules of dissimilar structure have exactly the same infrared absorption pattern, or spectrum. Although some of the frequencies absorbed in the two cases might be the similar, in no case of two special molecules with their spectra be identical. Thus, the infrared spectrum can be used for molecules such as fingerprint for humans [14].

It is well known that vibrational spectroscopy is very useful in studying crystal structure of ordered perovskite [15]. The BO₆ octahedra present in ABO₃ perovskites can be considered as molecules. They have 15 normal modes of vibrations ($A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$) when they are in octahedral symmetry [15]. Deviation from this symmetry will result in broadening of lines or even splitting [16].

4. Discussion and Conclusions

X-ray diffraction patterns measured at room temperature for the samples SrAFeTiO₆ (A = La, Pr or Nd) using

two different methods and the precursor method gives better pattern than that the conventional method which gives a multi phase (**Figures 1(a)-(c)**). The best fitting of these compounds could be const as their structure, and the closed ionic radius for all samples illustrated that, they have an orthorhombic structure with a Pnma space group. There are also some differences in the lattice parameter where differ from SrLaFeTiO₆ up to SrNdFeTiO₆ as follows: $a = 5.557654 \text{ A}^\circ$, $b = 7.824075 \text{ A}^\circ$, $c = 5.537659 \text{ A}^\circ$ for La, and $a = 5.52728 \text{ A}^\circ$, $b = 7.79671 \text{ A}^\circ$, $c = 5.51395 \text{ A}^\circ$ for Pr, and $a = 5.51584 \text{ A}^\circ$, $b = 7.79255 \text{ A}^\circ$, $c = 5.51391 \text{ A}^\circ$ for the Nd. The patterns were subjected to careful analysis by means of the standard Reitveld methods using the FullProf suite [17]. Three structural models were selected instead of the refinement processes for accurate determination of the best crystal structure 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 are achieved when the anti-site disorder is considered in all the samples. The obtained lattice parameters, atoms positions as well as the reliability factors are shown in **Table 1**.

The tolerance factor is a measure of the internal pressure for perovskite structures. It is given by [18]

$$t = \frac{\left(r(A) + r(X)\right)}{\sqrt{2}\left(r(B) + r(X)\right)} \tag{1}$$

where *t* represents the tolerance factor, r(A), r(B) and r(X) are the ionic radius for A-site, B-site and oxygen respectively. The values of the tolerance factor for SrLaFeTiO₆, SrPrFeTiO₆, SrNdFeTiO₆, are calculated using the SPuDS program [19] and found to be 0.971, 0.965 and 0.959, respectively. The reduction of symmetry in the compounds is related to the small values of the A-site radius (r_A) in order to accommodate empty spaces, which by its role leads to tilting the octahedral of the Fe and Ti atoms. A guide for this behavior is a plot of the tolerance factor and the ionic radii of the La, Pr and Nd ions against the tolerance factor. Tilting of the octahedral in SrLaFeTiO₆, SrPrFeTiO₆ and SrNdFeTiO₆ leads to different electronic environment around the Fe ions and impose magnetic moments miss alignment. Therefore, the magnetic properties of these compounds might be influenced by the internal pressure [20].

Successful preparation of double perovskite oxides of chemical formula $SrAFeTiO_6$ (A = La, Pr or Nd) has been achieved by following the precursor method. The structural characterization analysis proved that it has similar crystal structure (orthorhombic) with a Pnma space group, which found to be consistent with its tolerance factor. The substitution in the A-site has been seen to alter the crystal structure from higher symmetry to lower symmetry as the size of the A-site decreases.

Distortion in the TiO₆ octahedra may result from Jahn-Teller splitting due to the ion existence of Ti⁴⁺ or Fe³⁺ or internal chemical pressure. That belongs to the cation size mismatch (σ^2) which depends on the average radius of the cations in A-site of the perovskite structure. The FTIR spectra results of the samples under study are given in the **Figure 8**. This FTIR spectrum resembles the general appearance of the double perovskite structure. A shift in the peak positions in going from La up to Nd sample in the group has been noticed.

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