Study the Oxygen Vacancies and Fe Oxidation States in CaFeO$_3$-δ Perovskite Nanomaterial

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Research Article

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Abstract

In this study, CaFeO$_{3-\delta}$ perovskite nanomaterial has been synthesized by sol-gel method. The oxygen vacancies and Fe oxidation states in CaFeO$_{3-\delta}$ perovskite nanomaterial were investigated by using X-ray diffraction (XRD), Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetry analysis (TG), differential scanning calorimetric (DSC), and vibrating sample magnetometer (VSM). Rietveld analysis of the XRD shows that the sample was crystallized in orthorhombic perovskite structure with space group pcmn. The oxygen vacancies and oxidation states of Fe ions in CaFeO$_{3-\delta}$ sample were determined from Mössbauer spectroscopy. XPS shows the presence of different states of Fe ions and oxygen vacancies in the surface of CaFeO$_{3-\delta}$ sample. The thermal and magnetic properties of this sample have been investigated.

1. Introduction

CaFeO$_{3-\delta}$ perovskite nanomaterials have been extensively attracted much attention as a result of the presence of oxygen vacancies, different electronic states of Fe ions, and the unique physical properties [1-3]. These properties make CaFeO$_{3-\delta}$ suitable for the promising applications such as battery, fuel cells, gas sensors, catalytic and electronic devices [3]. The crystal structure of stoichiometric CaFeO$_3$ is cubic at high temperatures with antiferromagnetic behavior [4, 5]. The presence of oxygen vacancies in CaFeO$_{3-\delta}$ perovskite leads to the distortion in the ideal cubic structure and changes it into tetragonal or orthorhombic structure [4]. Zafar et al. [6] studied the structure of polycrystalline CaFeO$_3$ sample which synthesized by solid state reaction method and they found that the CaFeO$_3$ sample crystallized in orthorhombic structure with space group pcmn. In addition to CaFeO$_{3-\delta}$ has brownmillerite-structure at the high oxygen vacancies content [7, 8], Ceretti et al. [9] investigated the structure of CaFeO$_{2.5}$ and they found that the CaFeO$_{2.5}$ has brownmillerite-structure and G-type antiferomagnetic structure with high Neel temperature. CaFeO$_{3-\delta}$ nanoparticle materials exhibit charge disproportionation and structure transition which is associated with metal-insulator transition [10, 11]. Until now, there are few studies on the relation between the structure and properties such as charge disproportionation and metal-insulator transition in CaFeO$_{3-\delta}$ nanoparticle materials [4]. This relation in CaFeO$_{3-\delta}$ depends on oxygen vacancies content and the valence states of Fe ions which is affected by the different preparation methods [6-9]. The sol-gel method is the appropriate way for synthesis the perovskite materials at low temperatures which have small crystallite size [12]. The purpose of this work is to study the oxygen vacancies and oxidation states of Fe ions in CaFeO$_{3-\delta}$ nanomaterial which synthesized by sol-gel method.

2. Experimental

2.1. Synthesis of the CaFeO$_{3-\delta}$ sample by sol-gel method

CaFeO$_{3-\delta}$ perovskite sample was synthesized by sol-gel method. The synthesis process of CaFeO$_{3-\delta}$ perovskite sample was begun by dissolving separately the stoichiometric amount of the metal salts
(Ca(NO$_3$)$_2$), (Fe(NO$_2$)$_3$·9H$_2$O) and citric acid (C$_6$H$_8$O$_7$) (in the molar ratio 1 : 1 : 4 ratio respectively) in a distilled water. The salt solutions were mixed successively and then stirred. After that, the resultant mixture mixed with citric acid as a complexing agent and to remove the solvent, the gel is heated at 250 °C using hot plate with magnetic stirrer. Moreover, the ethylene glycol (C$_2$H$_6$O$_2$) was added to the mixture drop by drop under stirring. The resulting solution was continuously heated on hot plate with magnetic stirrer to evaporate H$_2$O and polymerization organic compounds and until the gel is formed. The obtained powders were calcined at a temperature of 1000 °C for 12 h in air to produce the required CaFeO$_{3-\delta}$ perovskite.

2.2. Characterization techniques

XRD pattern of the CaFeO$_{3-\delta}$ sample at room temperature was obtained from SIEMENS D5000 diffractometer using Cu K$_{\alpha}$ radiation between 2θ ranges from 20° to 80°. The XRD pattern of the CaFeO$_{3-\delta}$ sample was analyzed by employing Rietveld refinement using the FULLPROF WinPLOTR software suite. The Mössbauer spectrum of CaFeO$_{3-\delta}$ sample at room temperature was obtained using a conventional $^{57}$Fe constant acceleration spectrometer with $^{57}$Co (embedded in rhodium matrix) radioactive source. The elemental composition and surface electronic states of the CaFeO$_{3-\delta}$ sample were analyzed by X-ray photoelectron spectroscopy (XPS: a Thermo Scientific™ K-Alpha™ USA) using a monochromatic aluminum source (AL-K$_{\alpha}$). A simultaneous thermogravimetry analysis and differential scanning calorimetric (TG-DSC) of the CaFeO$_{3-\delta}$ sample were carried out using TA instruments unpacking the discovery STA model 650 with a heating rate of 20 °C /min in the 45-950 °C temperature range. The magnetic hysteresis M (H) loop measurement for CaFeO$_{3-\delta}$ sample was recorded at room temperature by using vibrating sample magnetometer (VSM), Lakeshore 7410 with magnetic fields from -20 kG to 20 kG.

3. Results And Discussion

3.1. XRD and crystal structure studies

Fig. 1 shows the observed data and Rietveld refined of XRD pattern of the CaFeO$_{3-\delta}$ sample. It can be seen that the sample crystallized in a single phase in orthorhombic perovskite structure with space group pccn [6, 13]. This result is in agreement with the previous reports [6, 13]. The refined structural parameters for CaFeO$_{3-\delta}$ sample including the lattice parameters, atoms, lattice coordinate, and reliability factors are listed in Table 1. From this table, it can be seen that the lattice parameters of CaFeO$_{3-\delta}$ sample is higher than that of CaFeO$_{3-\delta}$ sample which was synthesized by solid state reaction technique at 1273 K [6]. This result may be due to the different amount of oxygen vacancies. The amount of oxygen vacancies in CaFeO$_{3-\delta}$ sample can be determined from Rietveld refined by varying the oxygen occupancies. This result is confirmed by DSC, XPS and Mössbauer results. The decrease of oxygen vacancies in CaFeO$_{3-\delta}$ sample leads to the space reduction around the cations.
Fig. 2 shows the crystal structure obtained from refined parameters of the orthorhombic CaFeO$_{3-δ}$ perovskite sample. This crystal structure was drawn by VESTA software. From this figure, it is clear that the structure of this sample composed of alternating layers of Fe cations in tetrahedral (FeO$_4$) and octahedral (FeO$_6$) coordination which are linked by O(2) [14, 15]. This result is in agreement with Mössbauer results as mentioned below. In octahedral (FeO$_6$), the Fe cations are located at center while the oxygen anions are located at the vertices [16]. The average crystallite size (D) from XRD data of CaFeO$_{3-δ}$ sample has been calculated by using Scherrer equation

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where k =0.9 is the Scherrer constant (depends on the shape of crystallite size), λ=0.15406 nm is the X-ray wavelength of the Cu K$_{α}$ radiation used for the diffraction, θ is the Bragg’s diffraction angle measured and β is the full width at half maximum intensity of the diffraction peaks which has been obtained from Rietveld refinement of XRD patterns [17]. The value of D is 37.5 nm which revealed that average crystallite size of CaFeO$_{3-δ}$ sample in nanometer size.

3.2. Mössbauer and XPS studies

Fig.3 shows the Mössbauer spectrum of CaFeO$_{3-δ}$ sample at room temperature. It is clear from this figure that the spectrum consists of two sextets, and one doublet. The existence of magnetic sextets in Mössbauer spectrum indicated that the Néel temperature (T$_N$) of CaFeO$_{3-δ}$ sample lies above the room temperature [18]. This result is in agreement with the previous report for Bi$_{1-x}$Ca$_x$FeO$_3$ (where 0 ≤ x ≤ 1) ceramics [19]. The Mössbauer hyperfine parameters of the CaFeO$_{3-δ}$ sample are listed in Table 2. The magnetic sextets in the CaFeO$_{3-δ}$ sample have magnitudes of the hyperfine magnetic fields of 51.0 T and 43.6 T and isomer shift values of 0.357 and 0.177 mm/s. The magnetic sextet having larger hyperfine magnetic field and isomer shift is assigned to a disordered Fe$^{3+}$ in octahedral coordination to oxygen [15, 20]. While the smaller hyperfine magnetic field and isomer shift is assigned to the magnetic relaxation Fe$^{4+}$ ions in tetrahedral coordination to oxygen [15, 20]. In addition to, the sextet with smaller isomer shift and higher quadrupole shift indicates the higher distortions in the environment around Fe$^{4+}$ ions [19]. The doublet with IS (0.427 mms$^{-1}$) and QS (0.585 mms$^{-1}$) values are assigned to Fe$^{3+}$ ions in octahedral coordination to oxygen [12, 18]. For electroneutrality in the CaFeO$_{3-δ}$ sample, oxygen vacancies are created because of the conversion of unstable Fe$^{4+}$ into Fe$^{3+}$ ions [12]. The oxygen vacancies in the CaFeO$_{3-δ}$ sample can be estimated from Mössbauer data by using the following electroneutrality equation, starting from usual valance states of calcium (Ca$^{2+}$) and oxygen (O$^{2-}$) [12]:

$$(3 - δ) = 2.5 + 0.5 f_{Fe^{4+}}$$  \hspace{1cm} (2)
where \( \int_{Fe^{4+}} \) represent the fractions of \( Fe^{4+} \) ions in the sample. The oxygen vacancies (\( \delta \)) value in the CaFeO\(_{3-\delta}\) sample is listed in Table 2. From this table, it can be seen that the \( \delta \) value is 0.262. The presence of oxygen vacancies in CaFeO\(_{3-\delta}\) sample may be leads to the coordination number of \( Fe^{3+} \) ions less than six which is in agreement with the crystal structure (Fig. 2) of the orthorhombic CaFeO\(_{3-\delta}\) sample perovskite [19]. Based on the Mössbauer results, we concluded the presence of the new magnetic species at room temperature in CaFeO\(_{3-\delta}\) sample perovskite.

Fig. 4 shows the XPS spectrum of the Fe 2p in CaFeO\(_{3-\delta}\) sample. It can be seen that the peaks of Fe 2p are very broad which may arise from spin orbit coupling between unpaired 3d electron and 2p core of Fe ions [12, 18]. The spin-orbit of Fe 2p peaks were deconvoluted into six peaks of 2p\(_{3/2}\) and 2p\(_{1/2}\) as well as weak satellite peak. The asymmetric of 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks means the presence of Fe ions in different valance states [21]. This result is the same as that reported by Ahmed et al. [21]. The presence of Fe ions in different valance states are responsible for the oxygen vacancies in CaFeO\(_{3-\delta}\) perovskite nanomaterials which are in agreement with Mössbauer results, as mentioned above [22]. The peaks of 2p\(_{3/2}\) and 2p\(_{1/2}\) at 710.32 and 723.95 eV respectively may be attributed to the existence of \( Fe^{3+} \) in the surface of CaFeO\(_{3-\delta}\) sample [23]. The satellite peak of Fe 2p\(_{3/2}\) at 719.5 eV may be attributed to the presence of \( Fe^{3+} \) ions with oxygen vacancies in the surface of CaFeO\(_{3-\delta}\) sample [21, 23]. The peak of 2p\(_{3/2}\) at higher binding energy 712.79 eV may be attributed to the existence of \( Fe^{3+} \) in the surface of CaFeO\(_{3-\delta}\) sample [24]. The peaks of 2p\(_{3/2}\) and 2p\(_{1/2}\) at higher binding energy at 716.5, and 727.61 eV can be attributed to the existence of \( Fe^{4+} \) ions in the surface of CaFeO\(_{3-\delta}\) sample [12, 18]. The peak of Fe 2p\(_{1/2}\) at higher binding energy at 731.87 eV is characteristic of satellite structure which in agreement with the previous results [25]. The higher binding energy in CaFeO\(_{3-\delta}\) sample is due the increase of the coulombic interaction between the Fe ion core and the electron [22]. Fig. 5 shows the XPS spectrum of Ca 2p peaks in CaFeO\(_{3-\delta}\) sample. It can be seen that the XPS spectrum of Ca 2p for CaFeO\(_{3-\delta}\) sample was splitted into two peaks of spin-orbital components 2p\(_{3/2}\) and 3p\(_{1/2}\) as well as weak satellite loss peak [26, 27]. In the spectrum of CaFeO\(_{3-\delta}\) sample, the peak of Ca 2p\(_{3/2}\) at low binding energy 346 eV may be attributed to Ca lattice (Ca\(_{latt}\)) in CaFeO\(_{3-\delta}\) perovskite which indicated the presence of oxygen vacancies in CaFeO\(_{3-\delta}\) structure [19, 26, 28]. The peak of Ca 3p\(_{1/2}\) at higher binding energy 350 eV may be attributed to surface bound Ca non-lattice (Ca\(_{non-latt}\)) [19, 26, 28]. The presence of weak satellite loss peaks in Ca region may be arised from plasmon energy loss [29]. Fig. 6 shows the deconvolution analysis of the oxygen O 1s peak in CaFeO\(_{3-\delta}\) sample. It can be seen that the XPS spectrum of O 1s for CaFeO\(_{3-\delta}\) sample was deconvoluted into four individual peaks located at 529.29, 530.21, 531.6 and 534.17 eV. These peaks indicate the presence of four kinds of O states at the surface [30]. The peak at 529.29 eV can be attributed to the oxygen lattice (O\(_{latt}\): O\(^{2-}\)) of CaFeO\(_{3-\delta}\) sample [21, 31]. The peak of O 1s at 530.21 eV is due to the oxygen ions located at the defect sites which arises from oxygen vacancies [19]. This observation is in agreement with Mössbauer results which mentioned above. The peaks of O 1s at 531.6 and 534.17 eV may be due to the surface adsorbed oxygen (O\(_{ads}\):OH\(^{+}\)) and the oxygen in chemically surface adsorbed water (H\(_2\)O\(_{ads}\)).
respectively [32, 33]. Based on the results of XPS, we concluded the existence of oxygen vacancies and mixed oxidation states of Fe ions on the surface of CaFeO$_{3.5}$ sample.

### 3.3. Thermal and magnetic studies

Fig. 7. shows TG and derivative thermogravimetry analysis (DTG) curves of CaFeO$_{3.5}$ sample in the temperature range of 45-950 °C. It can be seen that the TG curve exhibits four distinct weight loss steps. These weight loss steps are corresponding four peaks in DTG curve which in agreement with the reports for CaFeO$_3$ and SrFeO$_{3.5}$ sample [18, 34]. The first weight loss and the corresponding first peak in DTG curve at 108.18 °C can be attributed to the loss of adsorbed water [35, 36]. The second weight loss and the corresponding second peak in DTG curve at 452.35 °C can be attributed to the loss of oxygen in the lattice which may be due to the reduction of Fe$^{4+}$ into Fe$^{3+}$ [37]. The third weight loss and the corresponding third peak in DTG curve at 623.36 °C may be attributed to the decomposition of calcium nitrate into calcium carbonate [18]. The fourth weight loss and the corresponding fourth peak in DTG curve at 720.73 °C may be attributed to the decomposition of calcium carbonate into calcium oxide (CaO). Thus CaO reacts with Fe$_3$O$_4$ in the presence of oxygen oxide (O$_2$) and leads to the formation of CaFeO$_{3.5}$ [18]. Beyond this temperature nearly no weight loss is observed which means that the CaFeO$_{3.5}$ compound is formed. The slightly change in weight loss on TG curve indicates that the prepared powder was stable [38].

Fig. 8. shows DSC and the derivative DSC curve of CaFeO$_{3.5}$ sample in the temperature range of 45-950 °C. It can be seen that the CaFeO$_{3.5}$ sample exhibits two broad exothermic peaks which represent the presence of phase transitions [18, 39]. The two broad exothermic peaks in the derivative of DSC curve of CaFeO$_{3.5}$ sample exhibit four exothermic peaks. The first exothermic peak may be attributed to the oxygen loss [12, 18]. The second exothermic peak may be due to the decomposition of organic matters and may be due to the antiferromagnetic Néel temperature ($T_N$) which is consistent with above Mössbauer results [18]. The third exothermic peak may be due to the decomposition of nitrates and crystallization of CaFeO$_{3.5}$ [34, 40]. The fourth exothermic peak may be attributed to the formation of the expected CaFeO$_{3.5}$ perovskite phase [18, 34].

Fig. 9 shows the hysteresis loop obtained for CaFeO$_{3.5}$ sample at room temperature up to an applied field 20 kOe. It is noticed that the shape of the loop is a small hysteretic and the saturation of magnetization not observed for CaFeO$_{3.5}$ sample. This result indicates the presence of a mixture of weak ferromagnetic and antiferromagnetic ordering of the spins [12, 41]. The presence of small hysteretic for the sample suggests that the Néel temperature ($T_N$) of it lies above the room temperature [18]. This is consistent with Mössbauer results, as mentioned above. The presence of weak ferromagnetic in the sample at room temperature may be due to spin canting and the formation of oxygen vacancies which create magnetic moments at the surface [18, 42]. On the other hand, the presence of antiferromagnetic in the sample at room temperature may be due to the sperexchange interaction between Fe cations [14, 43]. The sperexchange interaction occurs between two Fe cations which have the same number of electrons [44].
The maximum magnetization ($M_{\text{max}}$), remanent magnetization ($M_r$) and coercive force ($H_c$) values are 0.174 emu/g, 0.072 emu/g and 8.80 G, respectively. The small value of remanent magnetization ($M_r$) for CaFeO$_{3-\delta}$ sample indicates the presence of antiferromagnetic with weak ferromagnetic [17].

4. Conclusion

CaFeO$_{3-\delta}$ perovskite nanomaterial has been successfully synthesized by sol-gel method. Rietveld refinement of XRD revealed that the CaFeO$_{3-\delta}$ sample has a single phase in orthorhombic perovskite structure with space group pccn. The average crystallite size of CaFeO$_{3-\delta}$ sample was found to be 37.5 nm. According to Mössbauer results, CaFeO$_{3-\delta}$ sample exhibits oxygen vacancies and new magnetic species at room temperature (Fe$^{3+}$ in octahedral coordination and Fe$^{4+}$ in tetrahedral coordination to oxygen). XPS results showed the existence of oxygen vacancies and mixed valence states of Fe ions (Fe$^{3+}$ and Fe$^{4+}$ species) on the surface of the sample. TG and DSC analysis of the CaFeO$_{3-\delta}$ sample showed the presence of loss oxygen in the lattice and phase transitions. The formation of oxygen vacancies and mixed valence states of Fe ions in CaFeO$_{3-\delta}$ sample lead to the presence of weak ferromagnetic. Based on the present results, CaFeO$_{3-\delta}$ nanoparticle sample could be used as a promising in the electronic applications.

Declarations

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Tables

Due to technical limitations, table 1,2 is only available as a download in the Supplemental Files section.
Figure 1

Rietveld refinement of XRD pattern of CaFeO3-δ sample. Red dots, black line, green vertical lines and blue line denote the observed data, calculated profiles, possible Bragg peaks and the difference between observed and calculated patterns.
Figure 2

The crystal structure obtained from refined parameters of the orthorhombic CaFeO₃-δ sample perovskite.
Figure 3

The Mössbauer spectrum of CaFeO$_3$-$\delta$ sample at room temperature.
Figure 4

The deconvoluted XPS spectrum of the Fe 2p in CaFeO$_3$-$\delta$ sample.
Figure 5

The XPS spectrum of Ca 2p peaks in CaFeO3-δ sample.
Figure 6

The deconvolution XPS spectrum of the oxygen O 1s peak in CaFeO3-δ sample.
Figure 7

Thermogravimetry (TG) and derivative thermogravimetry analysis (DTG) curves of CaFeO3-δ sample.

Figure 8
Differential scanning calorimetric (DSC) and derivative DSC curve of CaFeO$_3$-$\delta$ sample

Figure 9

The magnetic hysteresis $M(H)$ loop of CaFeO$_3$-$\delta$ sample at room temperature.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Table1.jpg
- Table2.jpg