Study the Oxygen Vacancies and Fe Oxidation States in $\text{CaFeO}_{3-\delta}$ Perovskite Nanomaterial

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Research Article

Keywords: $\text{CaFeO}_{3-\delta}$, crystal structure, X-ray photoelectron spectroscopy, Mössbauer spectroscopy.

Posted Date: March 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-308092/v1>

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Abstract

In this study, $\text{CaFeO}_{3-\delta}$ perovskite nanomaterial has been synthesized by sol-gel method. The oxygen vacancies and Fe oxidation states in $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample were determined from Mössbauer spectroscopy. XPS shows the presence of different states of Fe ions and oxygen vacancies in the surface of $\text{CaFeO}_{3-\delta}$ sample. The thermal and magnetic properties of this sample have been investigated.

1. Introduction

$\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ has brownmillerite-structure at the high oxygen vacancies content [7, 8]. Ceretti et al. [9] investigated the structure of $\text{CaFeO}_{2.5}$ and they found that the $\text{CaFeO}_{2.5}$ has brownmillerite-structure and G-type antiferromagnetic structure with high Neel temperature. $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ nanoparticle materials [4]. This relation in $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ nanomaterial which synthesized by sol-gel method.

2. Experimental

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

$\text{CaFeO}_{3-\delta}$ perovskite sample was synthesized by sol-gel method. The synthesis process of $\text{CaFeO}_{3-\delta}$ perovskite sample was begun by dissolving separately the stoichiometric amount of the metal salts

($\text{Ca}(\text{NO}_3)_2$), ($\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (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 ($\text{C}_2\text{H}_6\text{O}_2$) 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_2O 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 $\text{CaFeO}_{3-\delta}$ perovskite.

2.2. Characterization techniques

XRD pattern of the $\text{CaFeO}_{3-\delta}$ sample at room temperature was obtained from SIEMENS D5000 diffractometer using Cu K_α radiation between 2θ ranges from 20° to 80°. The XRD pattern of the $\text{CaFeO}_{3-\delta}$ sample was analyzed by employing Rietveld refinement using the FULLPROF WinPLOTR software suite. The Mössbauer spectrum of $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample were analyzed by X-ray photoelectron spectroscopy (XPS: a Thermo Scientific™ K-Alpha™ USA) using a monochromatic aluminum source (AL- K_α). A simultaneous thermogravimetry analysis and differential scanning calorimetric (TG-DSC) of the $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample. It can be seen that the sample crystallized in a single phase in orthorhombic perovskite structure with space group pcmn [6, 13]. This result is in agreement with the previous reports [6, 13]. The refined structural parameters for $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample is higher than that of $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample leads to the space reduction around the cations.

Fig. 2 shows the crystal structure obtained from refined parameters of the orthorhombic $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample has been calculated by using Scherrer equation

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

where $k = 0.9$ is the Scherrer constant (depends on the shape of crystallite size), $\lambda = 0.15406$ 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 $\text{CaFeO}_{3-\delta}$ sample in nanometer size.

3.2. Mössbauer and XPS studies

Fig.3. shows the Mössbauer spectrum of $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample lies above the room temperature [18]. This result is in agreement with the previous report for $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ (where $0 \leq x \leq 1$) ceramics [19]. The Mössbauer hyperfine parameters of the $\text{CaFeO}_{3-\delta}$ sample are listed in Table 2. The magnetic sextets in the $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample, oxygen vacancies are created because of the conversion of unstable Fe^{4+} into Fe^{3+} ions [12]. The oxygen vacancies in the $\text{CaFeO}_{3-\delta}$ 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]:

$$(3 - \delta) = 2.5 + 0.5 f_{\text{Fe}^{4+}} \quad (2)$$

where $f_{Fe^{4+}}$ represent the fractions of Fe^{4+} ions in the sample. The oxygen vacancies (δ) value in the $CaFeO_{3-\delta}$ sample is listed in Table 2. From this table, it can be seen that the δ 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_2O_{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 $\text{CaFeO}_{3-\delta}$ sample.

3.3. Thermal and magnetic studies

Fig.7. shows TG and derivative thermogravimetry analysis (DTG) curves of $\text{CaFeO}_{3-\delta}$ 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 $\text{SrFeO}_{3-\delta}$ 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_3O_4 in the presence of oxygen oxide (O_2) and leads to the formation of $\text{CaFeO}_{3-\delta}$ [18]. Beyond this temperature nearly no weight loss is observed which means that the $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample in the temperature range of 45-950 °C. It can be seen that the $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ [34, 40]. The fourth exothermic peak may be attributed to the formation of the expected $\text{CaFeO}_{3-\delta}$ perovskite phase [18, 34].

Fig. 9 shows the hysteresis loop obtained for $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample. This result indicates the presence of amixture 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 ($M_{\max}$), 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 $\text{CaFeO}_{3-\delta}$ sample indicates the presence of antiferromagnetic with weak ferromagnetic [17].

4. Conclusion

$\text{CaFeO}_{3-\delta}$ perovskite nanomaterial has been successfully synthesized by sol-gel method. Rietveld refinement of XRD revealed that the $\text{CaFeO}_{3-\delta}$ sample has a single phase in orthorhombic perovskite structure with space group pcmn . The average crystallite size of $\text{CaFeO}_{3-\delta}$ sample was found to be 37.5 nm. According to Mössbauer results, $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample lead to the presence of weak ferromagnetic. Based on the present results, $\text{CaFeO}_{3-\delta}$ nanoparticle sample could be used as a promising in the electronic applications.

Declarations

Acknowledgements

The authors thank the Academy of Scientific Research and Technology (ASRT), Egypt, for financing and supporting this project. (ASRT) is the 2nd affiliation of this research.

Conflict of interest: The authors declare that they have no conflict of interest.

Funding Information: This project was supported financially by ASRT, Egypt, Grant No 6668.

Author contribution: All listed authors have participated in the research presented in this paper.

Ethical statement: This article does not contain any studies with human participants or animals performed by any of the authors.

References

1. Ghosh, D. K. Mahato, S. Banerjee, Formation of Magnetic Glass By Kinetic Arrest of First Order Magnetic Phase Transition In CaFeO_3 , Materials Today: Proceedings 5 (2018) 15426–15430
2. Morimoto, T. Yamanaka, M. Tanaka, Structure and electron density distribution of CaFeO_3 in the "charge disproportionate" state, Physica B 237-238 (1997) 66-67.

3. Huang, Y. Wang, H. Li, M. Wang, Y. Lyu, S. Shen, N. Lu, Q. He, P. Yu, Tuning the electronic properties of epitaxial strained $\text{CaFeO}_{3-\delta}$ thin films, *Appl. Phys. Lett.* 114 (2019) 221907.
4. M. Woodward, D. E. Cox, E. Moshopoulou, A. W. Sleight, S. Morimoto, Structural studies of charge disproportionation and magnetic order in CaFeO_3 , *Phys. Rev. B* 62 (2000) 844 -855.
5. Ghosh, K. Bagani, M. K. Ray, M. Sardar, S. Banerjee, Re-entrant Magnetic Phases In CaFeO_3 Nanoparticle, *AIP Conference Proceedings* 1536 (2013) 943-944.
6. Zafar, M. N. Khan, Structural, Electric and Thermoelectric Studies of CaFeO_3 System, *The Nucleus* 52 (2015) 25-28.
7. T. Hung, N. H. Lam, A. D. Nguyen, L. H. Bac, N. N. Trung, D. D. Dung, Y. S. Kim, N. Tsogbadrakh, T. Ochirkhuyag, D. Odkhuu Intrinsic and tunable ferromagnetism in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ through $\text{CaFeO}_{3-\delta}$ modification, *Scientific Reports* 10 (2020) 6189.
8. Shin, Oxygen stoichiometry in the system $(\text{Ca}_x\text{Sr}_{1-x})\text{FeO}_{3-y}$, Its effect on crystallographic and thermodynamic properties, *Mat. Res. Bull.*, 16 (1981) 299-312.
9. Ceretti, A. Piovano, A. Cousson, T. Berthier, M. Meven, G. Agostini, J. Schefer, O. Hernandez, C. Lamberti, W. Paulus, Growth and characterization of large high quality brownmillerite $\text{CaFeO}_{2.5}$ single crystals. *Cryst. Eng. Comm.* 14 (2012) 5771–5776.
10. Yao, P. Yoo, P. Liao, A computational study of hydrogen doping induced metal-to-insulator transition in CaFeO_3 , SrFeO_3 , BaFeO_3 and SmMnO_3 , *Phys. Chem. Chem. Phys.*, 21 (2019) 25397-25405
11. X. Zhang, H. L. Xia, H. Liu, Y. M. Dai, B. Xu, R. Yang, Z. Y. Qiu, Q. T. Sui, Y. W. Long, S. Meng, X. G. Qiu, Infrared spectroscopic study on lattice dynamics in CaFeO_3 , *Phys. Rev. B* 95 (2017) 064104.
12. K. Abdel-Khalek, D. A Rayan, A. A Askar, M. I. A. Abdel Maksoud, H. H El-Bahnasawy, Synthesis and characterization of $\text{SrFeO}_{3-\delta}$ nanoparticles as antimicrobial agent, *J Sol-Gel Sci Technol* 97 (2021) 27-38.
13. D. Zhou, J. B. Goodenough, Electronic behavior of three oxygen non-stoichiometric $\text{Fe}^{4+}/\text{Fe}^{3+}$ oxoperovskites, *J. Solid State Chem.* 178 (2005) 3679–3685.
14. Berastegui, S. G. Eriksson, S. Hull, A neutron diffraction study of the temperature dependence of $\text{Ca}_2\text{Fe}_2\text{O}_5$, *Materials Research Bulletin* 34 (1999) 303.
15. D. Battle, T. C. Gibb, S. Nixon, A study of the ordering of oxygen vacancies in the nonstoichiometric perovskite $\text{Sr}_2\text{LaFe}_3\text{O}_{8+y}$ by Mössbauer spectroscopy and a comparison with SrFeO_{3-y} , *J. Solid State Chem* 79 (1989) 75-85.
16. P. Hodges, S. Short, J. D. Jorgensen, X. Xiong, B. Dabrowski, S. M. Mini, C. W. Kimball and, Evolution of Oxygen-Vacancy Ordered Crystal Structures in the Perovskite Series $\text{Sr}_n\text{Fe}_n\text{O}_{3n-1}$ ($n=2, 4, 8$, and ∞), and the Relationship to Electronic and Magnetic Properties, , *Journal of Solid State Chemistry* 151, 190}209 (2000)
17. Kumar, C. Panda, M. Kar, Effect of rhombohedral to orthorhombic transition on magnetic and dielectric properties of La and Ti co-substituted BiFeO_3 , *Smart Mater Struct.* 24 (2015) 045028.

18. Abd El-Naser, E. K. Abdel-Khalek, E. Nabhan, D.A. Rayan, M. S. Gaafar & N. S. Abd El-Aal, Study the influence of oxygen-deficient ($\delta = 0.135$) in $\text{SrFeO}_{3-\delta}$ nanoparticles perovskite on structural, electrical and magnetic properties, *Philos. Mag* 101 (2021) 710–728.
19. T. Kozakov, A.G. Kochur, V.I. Torgashev, K.A. Googlev, S.P. Kubrin, V.G. Trotsenko, A.A. Bush, A.V. Nikolskii, $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ ($0 \leq x \leq 1$) ceramics: crystal structure, phase and elemental composition, and chemical bonding from X-ray diffraction, Raman scattering, Mössbauer, and X-ray photoelectron spectra, *J. Alloys and Compounds*. 664 (2016) 392-405.
20. Nasu, T. Abe, K. Yamamoto, S. Endo, M. Takano, Y. Takeda, Mössbauer study of CaFeO_3 under external high—Pressure, *Hyperfine Interact.* 70 (1992) 1063–1066.
21. Ahmed, S. T Wang, J. Sun, J. Wang, T. Y Li, Y. Yu, Q. J Li, C. C Wang, Colossal dielectric behavior in $\text{BaFeO}_{3-\delta}$ ceramics, *Ceramics International* 45 (2019) 13484–13487.
22. Wang, K. Y Lam, M. Saccoccio, Y. Gao, D. Chen, F. Ciucci, Ca and In co-doped $\text{BaFeO}_{3-\delta}$ as a cobalt-free cathode material for intermediate-temperature solid oxide fuel cells, *J. Power Sources* 324 (2016) 224-232.
23. Chen, Y. Zhang, T. Lv, K. Li, Z. Zhu, J. Zhang, R. Zhang, Q. Liu, Ag- LaFeO_3 nanoparticles using molecular imprinting technique for selective detection of xylene, *Nanomaterials Research Bulletin* 107 (2018) 271–279.
24. H. Kan, M. Chen, J-S Bae, B-H Kim, V. Thangadurai, Determination of Fe oxidation states in the B-site ordered perovskite-type $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{6-\delta}$ at the surface (nano-scale) and bulk by variable temperature XPS and TGA and their impact on electrochemical catalysis, *J. Mater. Chem. A*, 2 (2014), 8736-8741.
25. Benes, A. Molinari, R. Witte, R. Kruk, J. Brötz, R. Chellali, H. Hahn, O. Clemens, Proton Conduction in Grain-Boundary-Free Oxygen-Deficient $\text{BaFeO}_{2.5+\delta}$ Thin Films, *Nanomaterials* 11 (2018) 52.
26. Ghosh, A. Dutta, S. Shannigrahi, T. P. Sinha, Combined XPS and first principles study of double perovskite $\text{Ca}_2\text{GdTaO}_6$, *J Mater Sci* 49(2014) 819–826.
27. A. Abreu-Sepúlveda, Investigation of Electrode Materials Based on Perovskite and Pyrochlore Structures for the Oxygen Evolution Reaction, Ph.D. thesis, University of Rochester, New York 2016.
28. Sezer, İ. Öztoprak, A. Ş. Ahsen, A. Y. Oral, A. Büyükkaksoy, Correlation of Phase, Microstructure and Surface Chemistry Evolution to the Long-term Performance Stability of Thin Film $(\text{La}, \text{Ca})\text{CoO}_3$ SOFC Electrodes *J. Electrochem. Soc.* 167 (2020) 124508
29. W. Han, J. D. Lee and K. H. Kim, H. Song, W. J. Kim and S. J. Kwon, H. G. Lee and C. Hwang, J. I. Jeong, J.-S. Kang, Electronic Structures of the CMR Perovskites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R} = \text{La}, \text{Pr}$; $\text{A} = \text{Ca}, \text{Sr}, \text{Ce}$) Using Photoelectron Spectroscopy, *Journal of the Korean Physical Society*, 40 (2002) 501-510.
30. D Sedykh, O. G Rybchenko, A. N Nekrasov, I. E Koneva, V. I Kulakov, [Effect of the Oxygen Content on the Local Environment of Fe Atoms in Anion-Deficient \$\text{SrFeO}_{3-\delta}\$](#) , *Phys. Solid State*, 61(6) (2019) 1099-1106.

31. Nomura, Y. Sugawara, H. L. Li, Y. Ujihira, Mössbauer spectroscopic study of nonstoichiometric perovskite, $\text{Ba}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$, *Hypcrfirm Interactions* 69 (1991) 879-882.
32. Song, Y. Zhu, Z. Yang, C. Wang, X. Lu, Oxidase-mimicking activity of perovskite $\text{LaMnO}_{3+\delta}$ nanofibers and their application for colorimetric sensing, *J. Mater. Chem. B*, 6 (2018) 5931-5939.
33. Abidov, B. Allabergenov, J. Lee, H-W. Jeon, S-W. Jeong, S. Kim, X-Ray Photoelectron Spectroscopy Characterization of Fe Doped TiO_2 Photocatalyst, *International Journal of Materials, Mechanics and Manufacturing*, 1(2013) 294-296.
34. Theingi, T. T. Hlaing, Preparation and characterization of CaFeO_3 powder and its coagulation activity in terms of reducing turbidity, *J. Myanmar Acad. Arts Sci. A1* (2019) 355-371.
35. O. Augustin, L. J. Berchmans and R. K. Selvan, Structural, electrical and electrochemical properties of co-precipitated $\text{SrFeO}_{3-\delta}$. *Mater. Lett.* 58 (2004) 1260–1266.
36. R. Kumar, W.-T. Ma, H.-C. Lu, L.-W. Teng, H.-C. Hsu, C.-M. Shih, C.-C. Yang and S.J. Lue, Surfactant-assisted perovskite nanofillers incorporated in quaternized poly (vinyl alcohol) composite membrane as an effective hydroxide-conducting electrolyte. *Energies* 10 (2017) 615.
37. Damljanovic. Raman scattering, magnetization and magnetotransport study of $\text{SrFeO}_{3-\delta}$, $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ and $\text{CaFeO}_{3-\delta}$, Ph.D. thesis, University of Stuttgart, 2008.
38. I. Selah, Synthesis and Formation Mechanism of Calcium Ferrite Compounds. *J. Mater. Sci. Technol.*, 20 (5) (2004) 530-534
39. Labii, M. Ceretti, A. Boubertakh, W. Paulus, S. Hamamda, Dilatometric study of $\text{CaFeO}_{2.5}$ single crystal, *J Therm Anal Calorim* 112 (2013) 865–870.
40. Shen, T. Xue, Y. Wang, G. Cao, Y. Lu and G. Fang, Photocatalytic property of perovskite LaFeO_3 synthesized by sol-gel process and vacuum microwave calcination. *Mater. Res. Bull* 84 (2016) 15–24.
41. Khanna, N.K. Verma, Size-dependent magnetic properties of calcium ferrite nanoparticles, *J. Magn. Magn. Mater* 336 (2013) 1–7
42. V. K. Mangalam, N. Ray, U. V. Waghmare, A. Sundaresan and C. N. R. Rao, Multiferroic properties of nanocrystalline BaTiO_3 . *Solid State Commun.* 149 (2009)1–5.
43. T Hung, L. H Bac, N. T Hoang, P. V Vinh, N. N Trung, D. D Dung, [Structural, optical, and magnetic properties of \$\text{SrFeO}_{3-\delta}\$ -modified \$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\$ nanomaterials](#), *Physica B: Condensed Matter*, 53(115) (2018) 75-78.
44. Ghosh, K. Bagani, M. K. Ray, M. Sardar, and S. Banerjee, Re-entrant magnetic phases in CaFeO_3 nanoparticle, *AIP Conference Proceedings* 1536 (2013) 943-944.

Tables

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

Figures

Figure 1

Rietveld refinement of XRD pattern of $\text{CaFeO}_{3-\delta}$ 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 $\text{CaFeO}_{3-\delta}$ sample perovskite.

Figure 3

The Mössbauer spectrum of $\text{CaFeO}_{3-\delta}$ sample at room temperature.

Figure 4

The deconvoluted XPS spectrum of the Fe 2p in $\text{CaFeO}_{3-\delta}$ sample.

Figure 5

The XPS spectrum of Ca 2p peaks in $\text{CaFeO}_{3-\delta}$ sample.

Figure 6

The deconvolution XPS spectrum of the oxygen O 1s peak in CaFeO_{3-δ} sample.

Figure 7

Thermogravimetry (TG) and derivative thermogravimetry analysis (DTG) curves of $\text{CaFeO}_{3-\delta}$ sample.

Figure 8

Figure 9

The magnetic hysteresis M (H) loop of CaFeO_{3-δ} sample at room temperature.

Supplementary Files

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