

Preparation of Lanthanum Ferrite Substituted with Mg and Ca

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Pervoskite lanthanum ferrite and related compounds have attracted considerably due to their wide applications in fuel cells, catalysts, sensors, and environmental monitoring systems. In this work, lanthanum ferrite and substituted compounds have been prepared by combustion synthesis process using lanthanum nitrate, ferric nitrate, and urea. The parent compound has been substituted with alkaline earth metals like Mg and Ca. The synthesized compounds are characterized using thermal analysis, X-ray diffraction (XRD), UV-visible, Fourier transform infrared spectroscopy, scanning electron microscopy (SEM). From thermal analysis, it is seen that Mg^{2+} and Ca^{2+} ions have pronounced effect on the phase formation process. From XRD spectrum, it is seen that the crystalline lanthanum ferrite possesses an orthorhombic disorder perovskite structure with space group Pbnm with four formula units per unit cell, where La ion is tetragonally coordinated. The UV-visible reflectance spectra of lanthanum ferrite and substituted compounds shows two prominent absorption bands, which are shifted towards the lower wavelength side on substitution. The FTIR spectra of the parent substituted compounds recorded between 400 to 4000 cm^{-1} . The existence of the prominent bands shows the formation of the single-phase crystalline lanthanum ferrite. From the SEM figure, if we compare the morphological features of the electrodes before and after substitution, it could be seen that the surface of the materials are disintegrated on oxygen evolution and weaken the intergrain spots.

Keywords Chemical synthesis; Combustion process; DTA studies; Electrochemical studies; Electrodes; Infrared spectroscopy; Lanthanum ferrite; Morphological features; Organic compound; Orthorhombic disorder; Pervoskite; Pervoskite structure; Scanning electron micrograph (SEM); Substitution of Mg and Ca ions; Thermogravimetric analysis; UV-visible; X-ray diffraction (XRD).

1. INTRODUCTION

Recently much attention has been paid on the preparation of complex perovskite oxides because of their interesting physical and chemical properties. Pervoskite lanthanum ferrite and related compounds with general formula of $La_{1-x}A_xFeO_3$ and $LaFe_{1-x}B_xO_3$, where A is Ce, Sr, Sm, or other rare earth elements, B is Fe, Co, Ni, or the other transition metals are considered as promising materials due to their wide applications in fuel cell technology [1], catalysis [2, 3], sensors [4], and environmental monitoring systems [5]. Due to its stability, sensitivity, and selectivity it is also used as sensors for diagnosis of diseases [6]. Strontium substituted lanthanum ferrite has been synthesized and characterized by solution combustion method [7]. Nanocrystalline lanthanum ferrite has been prepared using a reverse drop coprecipitation method and characterized by DTA, X-ray diffraction (XRD), and scanning electron microscopy (SEM) [8]. Sr doped lanthanum ferrite has been studied as SOFC cathodes in fuel cell technology [9]. The structural and electrical properties of these materials are mainly depending on the methods of preparation including hydrothermal process [10], combustion synthesis [11, 12], sol-gel method [13], co-precipitation [14], and citrate gel process [15]. Highly ordered lanthanum ferrite nanowires have been synthesized with a porous anodic aluminium oxide template by a citrate

sol-gel route [16]. The effect of the catalyst addition in the preparation method have been studied previously [17, 18] comparing the morphological features of the electrodes, before, and after substitution it could be seen that the surface of the materials are disintegrated on oxygen evolution and weaken the intergrain spots. The present investigation elucidates the preparation of fine particle lanthanum ferrite, with the substitution of Mg and Ca by simple combustion synthesis. By this substitution method the temperature of the method is reduced, and pure compounds are obtained.

2. EXPERIMENTAL

Fine crystalline $LaFeO_3$ and substituted compounds were prepared by solution combustion synthesis process. Lanthanum nitrate was obtained by treating grade (AR) lanthanum oxide with concentrated nitric acid. Stoichiometric proportion of AR grade $Fe(NO_3)_3 \cdot 9H_2O$ and the prepared $La(NO_3)_2 \cdot 6H_2O$ solution were mixed with urea and used for the fuel in the combustion process. The mixed solution was kept in a quartz bowl heated to 300°C and ignited at higher temperature until they were completely transformed in to a foamy powder. Similarly, substituted compounds of lanthanum ferrite with Mg and Ca were prepared by changing the stoichiometric ratio with the addition of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 6H_2O$ as reactants. The as-synthesized powders were finely ground, placed in a high alumina crucible and calcined at 100°C for 50h using an electrical resistance furnace. The thermal reactions of the as-dried precursor powder were followed under static air atmosphere by thermogravimetric analyzer Instrument model SDT Q 600. The phase formation and the crystalline features of lanthanum ferrite and the calcined powders were determined by XRD analysis

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using JEOL-8030 with Cu K- α radiation ($\lambda = 1.541\text{\AA}$). UV-Visible and FTIR spectra of the as-synthesized and calcined powders were measured using Jasco-7800, UV-visible spectrometer and Perkin Elmer UK pragon-500 spectrophotometer ranging from 400 to 4000 cm^{-1} . The microstructural features of the as-synthesized and calcined powders before and after the electrochemical studies were examined by SEM using JOEL (JSM-3.5 CF).

3. RESULTS AND DISCUSSION

TGA/DTA curve for the as-synthesized lanthanum ferrite and substituted compounds are shown in Fig. 1. It is revealed that the compounds exhibit weight loss when they are thermally activated from room temperature to 700°C due to the dissociation of water molecules and nitrate compounds. Three endothermic peaks can be seen at various temperatures namely 50.5, 303.5, and 377.5°C. The first two peaks are attributed to the dissociation of water molecules, and the remaining one is for the dissociation of nitrate compounds. Beyond 377.5°C, the DTA curve doesn't show any peaks, which indicates the formation of the single-phase lanthanum ferrite compound. Similar observations have also been noticed in the case of substituted compounds except a small difference in the initiation of the reaction temperature. From the above observations, it is seen that Mg^{2+} and Ca^{2+} ions have pronounced effect on the phase formation process.

The XRD pattern for the green and calcined samples of the parent and substituted compounds are shown in Fig. 2. The as-synthesized powder has shown only the amorphous peaks, which indicates that an incomplete phase formation. After calcination at 1000°C the XRD spectrum exhibits very sharp peaks at 32.24° and 57.45° representing the presence of single-phase lanthanum ferrite. This observation is consistent with the reported data for pure LaFeO_3 (JCPDS powder diffraction file No: 37-1493) [19, 20].

On substitution of Mg and Ca ions, the compound shows prominent peaks, which have been altered due to their

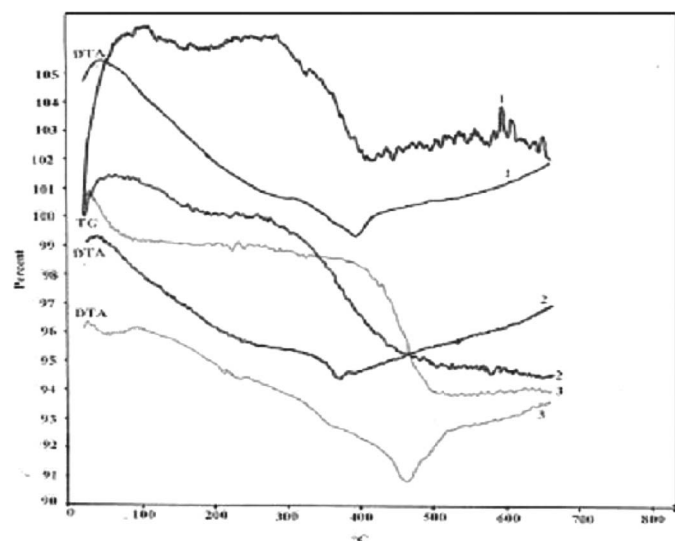


FIGURE 1.—TG-DTA curve for sintered (1) LaFeO_3 ; (2) $\text{La}_{0.5}\text{Mg}_{0.5}\text{FeO}_3$; and (3) $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

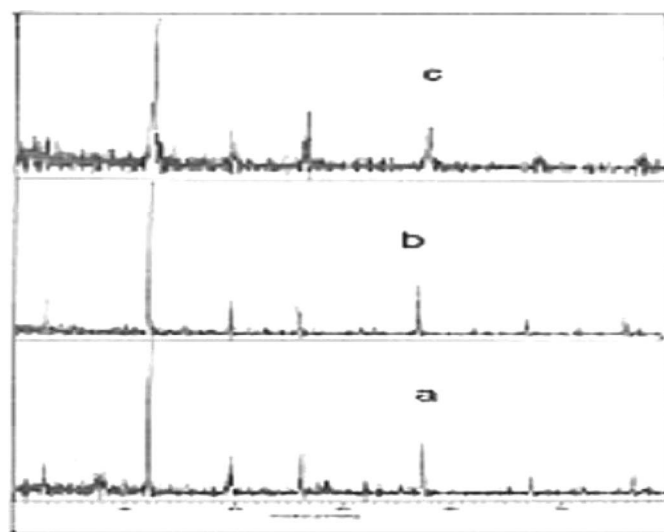


FIGURE 2.—XRD pattern of sintered (a) LaFeO_3 ; (b) $\text{La}_{0.5}\text{Mg}_{0.5}\text{FeO}_3$; and (c) $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

presence in the parent compound. The crystalline lanthanum ferrite possesses an orthorhombic disorder perovskite structure with space group Pbnm with four formula units per unit cell where La ion is tetragonally coordinated while Me ions are octahedrally coordinated. The line broadening is estimated by the standard Scherrer method [21]. The crystalline size for all the compositions were estimated using the formula

$$\Delta x 2\theta = \frac{0.89\lambda}{L \cos \theta}$$

The average crystalline size of the particle, L , using the $\Delta x 2\theta$ values of the (111) peaks was estimated using the above equation, where λ is the wavelength of the X-rays. The average crystallite size is found to be 50–80 nm. For substituted compounds the values are found to be 40 nm for Mg and 20 nm for Ca. The average crystallite size is slightly increased when the compounds are calcined at 1000°C. Similar observations have been reported in the case of perovskite compounds synthesized by polymeric complex method [22].

The UV-Visible reflectance spectra of lanthanum ferrite and substituted compounds after sintering at 1000°C are presented in Fig. 3. The parent compound shows two prominent absorption bands, which are shifted towards the lower wavelength side on substitution. This may be due to calcination and obvious quantum size effect as reported [23].

On substitution with Mg and Ca ions the prominent absorption bands are seen at 350 cm^{-1} and 700 cm^{-1} , and the small bands are obscured. The addition of Mg^{2+} and Ca^{2+} ions are responsible for the metal-to-metal transition occurrence in the compound. In fact, the metal-to-metal transition is that the lighted Fe^{2+} ion is excited to put into the conduction band yields a localized positive charge Fe^{2+} ion which is resulted by the band at 700 cm^{-1} . At lower wavelength side, the appearance of bands between 300 cm^{-1}

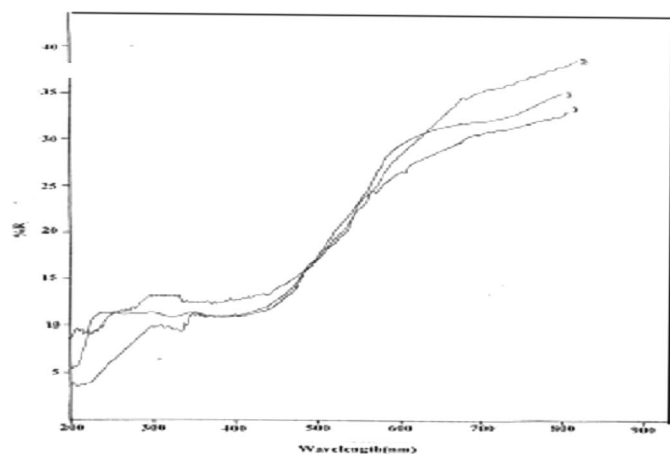


FIGURE 3.—UV-Vis spectrum of calcined (1) LaFeO_3 ; (2) $\text{La}_{0.5}\text{Mg}_{0.5}\text{FeO}_3$; and (3) $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

to 400 cm^{-1} is mainly due to the band-band transition that the valence band O^{2-} ion transits into the conduction band of Fe^{3+} ion. A free electron is produced in the conduction band, and an unlocalized electric hole remains in the valence band [24]. As far as polycrystalline lanthanum ferrite is concerned, it keeps the octahedral structure of $\alpha\text{-Fe}_2\text{O}_3$ except that Fe^{3+} is partially replaced by La^{3+} ion [25]. Lanthanum ferrite has shown a stranger p-type character, which is weakened with increasing the particle size by different processes [26].

FTIR spectra of calcined powders are presented in Fig. 4. The spectra have shown narrow and broadbands, with some shoulders. Figure 4(a) shows the FTIR spectra of the parent substituted compounds recorded between 400 to 4000 cm^{-1} . The existence of the prominent bands shows the formation of the single-phase crystalline lanthanum ferrite. The spectrum shows only two prominent bands, one at 111.8 cm^{-1} , and another at 1383.9 cm^{-1} . On substitution of Mg^{2+} and Ca^{2+} ions, similar observations are noticed

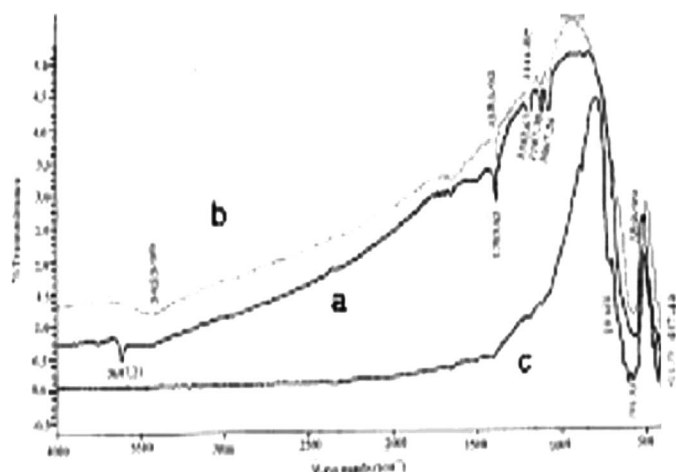


FIGURE 4.—FTIR spectra of sintered (a) LaFeO_3 ; (b) $\text{La}_{0.5}\text{Mg}_{0.5}\text{FeO}_3$; and (c) $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

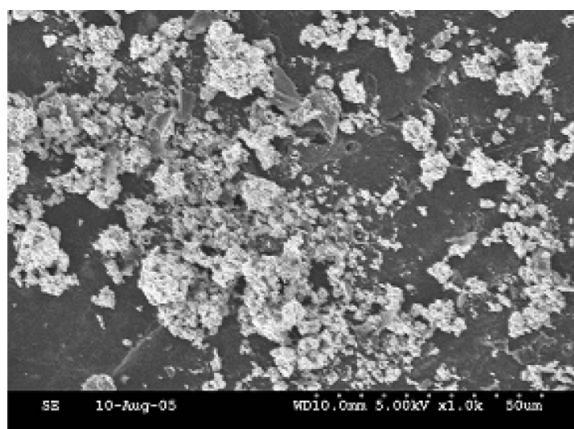


FIGURE 5.—SEM image of coated $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

where the prominent bands are shifted towards the lower wavelength side.

The scanning electron micrographs of the electrode materials ($\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$) are shown in Figs. 5 and 6. On comparing the morphological features of the electrodes, it could be seen that the surface of the materials are disintegrated on oxygen evolution and weaken the intergrain spots.

4. CONCLUSION

Combustion synthesis is found to be one of the convenient method for the preparation of nanocrystalline LaFeO_3 and substituted compounds. TGA/DTA studies reveal the dissociation temperature for water and nitrate molecules and the minimum temperature required for the formation of single phase LaFeO_3 . The XRD analysis confirms the orthorhombic structure, and the effect of substitution of Mg and Ca on the compound formation. UV-visible and FTIR spectra depict the phase formation and the effect of Mg^{2+} and Ca^{2+} ions on the compound formation. From the above studies, it has been concluded that LaFeO_3 with substituted compounds can be prepared by simple combustion process.

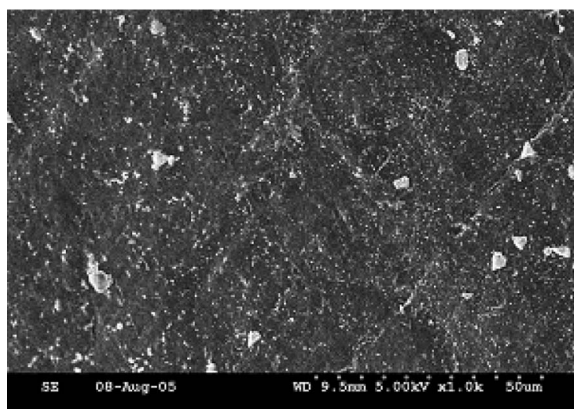


FIGURE 6.—SEM image of coated $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$.

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