

Effect of Ca-substitution on Structural and Electrical Properties of YFeO₃ Ceramic

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Abstract: In the present work conventional high temperature solid state reaction route has been used for the synthesis of Ca-doped Yttrium ferrite (Y_{0.99}Ca_{0.01}FeO₃). This product was analyzed by X-ray diffraction (with Rietveld fitting) followed by electrical measurement techniques (I-V characteristics and DC conductivity). X-ray diffraction analysis concludes that Y_{0.99}Ca_{0.01}FeO₃ has orthorhombic structure with Pnma space group which is same for YFeO₃. The calculated activation energy of the prepared ceramic is 0.31eV which reflects that the material shows semiconducting behavior.

Key words:- X-Ray Diffraction, Semiconductor, Rietveld Refinement, I-V Characteristics

INTRODUCTION

YFeO₃ is a member of the Perovskite family having the general formula ABO₃, where A is the rare earth element and B is the transition metal. The Perovskites in which the transition metal site (B-site) is occupied with iron component are extremely important due to their novel magnetic, optical, catalytic, electrical, mechanical and thermal properties like ferrimagnetisms, high thermal conductivity, high electrical resistivity, energy transfer efficiency etc. [1-2]. There are many examples of such type of materials in which Fe is situated at B-cation site i.e. BiFeO₃, NdFeO₃, SmFeO₃, CaFeO₃ and YFeO₃ [3]. Yttrium ferrite (YFeO₃) possesses distorted Perovskite structure and the thermally stable phase which adopts the orthorhombic symmetry with space group Pnma. The YFeO₃ displays ferro-electricity and weak ferromagnetism simultaneously at room temperature. It has high value of resistivity [4-5] and hence its conductivity is not good enough for practical applications. The conductivity of YFeO₃ increases by addition of small amount (~1%) of Ca on Y cation site and also Y_{1-x}Ca_xFeO₃ have high thermal stability which is useful for the cathode materials in high temperature solid oxide fuel cells [6-7]. There are a few reports available on Y_{1-x}Ca_xFeO₃ compound, which are favoring the enhancement in conductivity by substitution of Ca-atom on A-site [8]. But, there is no systematic report available on its structural and electrical properties. The present work is a small effort in this way and we hope it will be helpful for scientific community.

EXPERIMENTAL

Materials synthesis- The ceramic sample of Calcium substituted (for yttrium) Yttrium Ferrite has been synthesized in accordance to solid state reaction mechanism. The raw materials Y₂O₃, CaO and Fe₂O₃ with high purity were premixed according the chemical equation $Y_2O_3 + 2CaO + Fe_2O_3 \rightarrow 2YCaFeO_3 + O_2 \uparrow$. This mixture was grinded manually for 5-6 hours with Agate mortar and pestle in the presence of liquid medium, acetone (a binding agent), which reduce its particle size and improve its homogeneity. Now this fine powder was put in Alumina Crucible and calcined in a muffle furnace. This process of grinding and calcination was repeated for a several number of times in between 973K to 1373K for 2-12 hours. Finally, the calcined powder was again grinded

and palatized using a Die of 10mm diameter with effective pressure of 5tons/cm². This pellet was sintered at 1448K for 2 hours in the same furnace. Now the sintered pellet was ready for characterization.

Characterization- The Rigaku (Ultima-IV) X-ray diffractometer with CuK α radiation was used to get XRD profile of this sample in 2 θ range from 20 to 90 with the scan speed of 40/minute. The I-V measurement was also carried out at various temperature(up to 573K) for this sample to check the response of current in negative to positive (-5 volt to +5volt) voltage region using Source Meter (Agilent B2901A). The behavior of dc conductivity with respect to temperature was measured by applying 8 volt supply using lab made two probe sample holder and vertical furnace.

RESULTS AND DISCUSSION

Structural Analysis- Figure 1(a) shows the comparative XRD patterns with their miller indices of pure YFeO₃ and 1% Ca doped YFeO₃. It is clear from figure that there are three minor impurity peaks occurring in both profiles which is indicated by * and + sign. From review it is clear that the peaks denoted by * and + are due to non reacted amount of Y₂O₃ and Y₃Fe₅O₁₂ respectively [3, 9]. The impurity peaks are so small that these are not affecting the overall structure. From the Rietveld refinement fitting as shown in Figure 1(b) of this XRD profile, the prepared sample was identified in orthorhombic structure with space group Pnma.

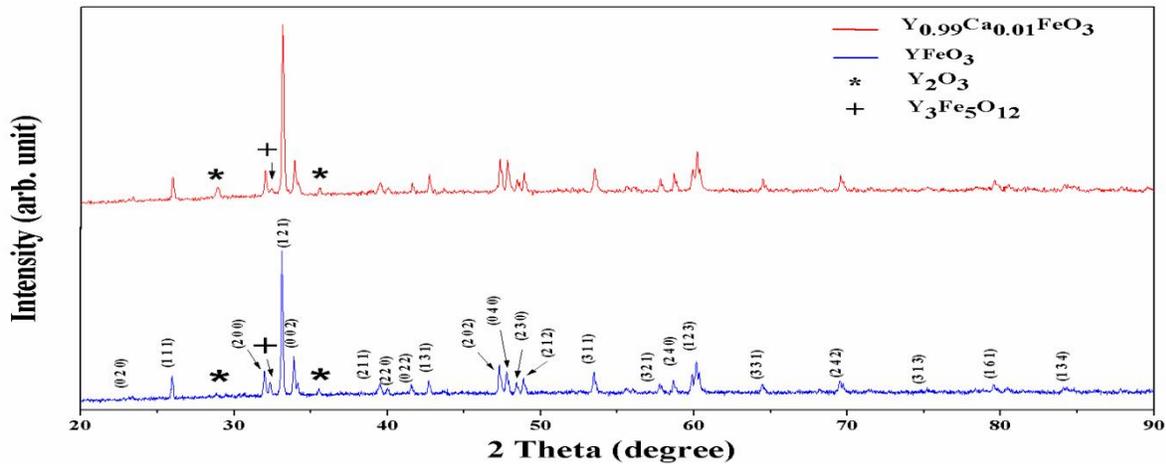


FIGURE 1(a). XRD profile of Y_{0.99}Ca_{0.01}FeO₃ compared with YFeO₃

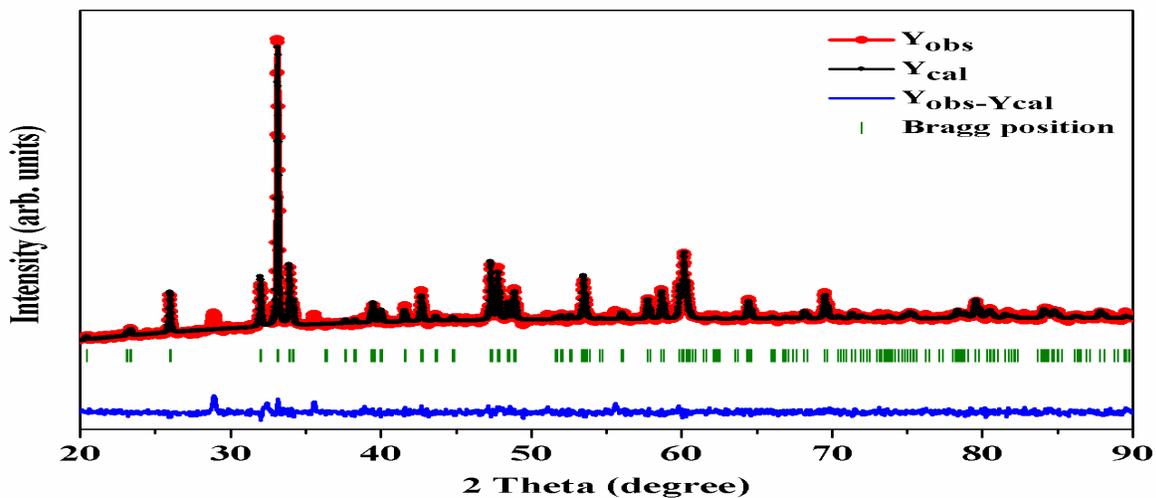


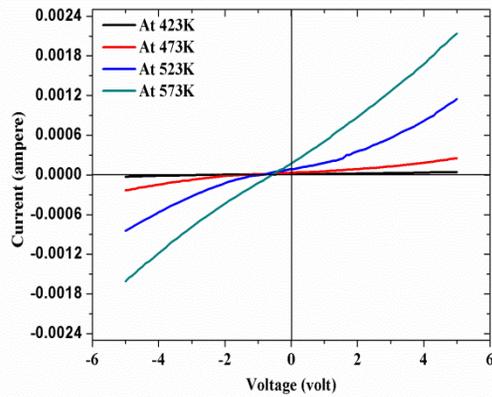
FIGURE 1(b). Rietveld refinement profile of Y_{0.99}Ca_{0.01}FeO₃

The detailed structural parameters of $Y_{0.99}Ca_{0.01}FeO_3$ obtained from Rietveld analysis are shown in Table 1 along with the structural parameters of $YFeO_3$ (our previous study) which are well matching and comparable. Hence it is clear that the substitution of 1% Ca on Yttrium site is not affecting its overall structure.

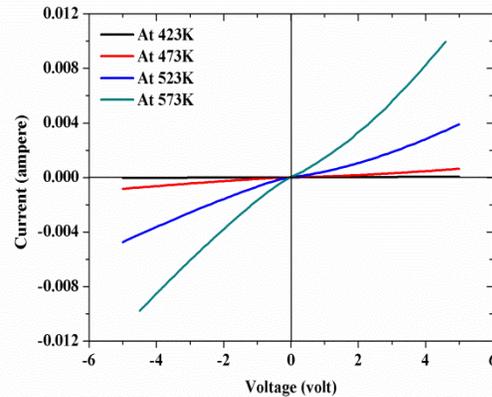
TABLE 1: Structural parameters of $YFeO_3$ and $Y_{0.99}Ca_{0.01}FeO_3$

Sample	Crystal system	Space group	Cell parameters (Å)			Unit cell volume (Å ³)	χ^2	GOF
			a	b	c			
$YFeO_3$ [5]	Orthorhombic	Pnma	5.5907	7.6082	5.2849	224.79	4.53	2.1
$Y_{0.99}Ca_{0.01}FeO_3$	Orthorhombic	Pnma	5.5892	7.6059	5.2841	224.63	2.22	1.5

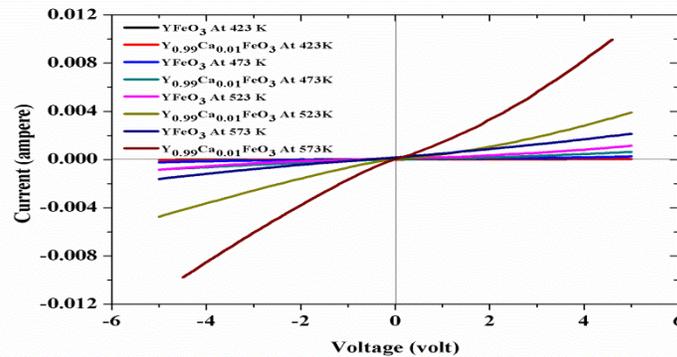
Electrical Analysis: The I-V characteristics of pure and Ca-substituted $YFeO_3$ at different temperature in the voltage range from -5 volt to $+5$ volt are shown in Figure 2(a & b). It is noticed from Figure 2(a) that the highest value of current for $YFeO_3$ at 573K is ~ 0.0019 amp and that for $Y_{0.99}Ca_{0.01}FeO_3$ at 573K is ~ 0.011 amp (fig. 2(b)) which is approximately 6 times higher than the value of current for pure $YFeO_3$ which indicates that the conductivity is increasing drastically with substitution of 1% Calcium for Yttrium in $YFeO_3$. Figure 2(c) shows the combined I-V characteristics of both the compounds at different temperature. Also it is observed from Figure 2(c) that conductivity is increasing with temperature for both cases.



(a) I-V characteristic of $YFeO_3$



(b) I-V characteristic of $Y_{0.99}Ca_{0.01}FeO_3$



(c) Combined I-V characteristics curve

FIGURE 2 (a, b & c). I-V characteristics curves at various temperatures

Figure 3 shows the response of dc conductivity as a function of temperature. It is observed from the figure that the dc conductivity is increasing with increase in temperature. The activation energy has been calculated using the slope of the curve (0.31eV) which is very low in comparison to activation energy of pure YFeO₃ which is 2.12 eV [5].

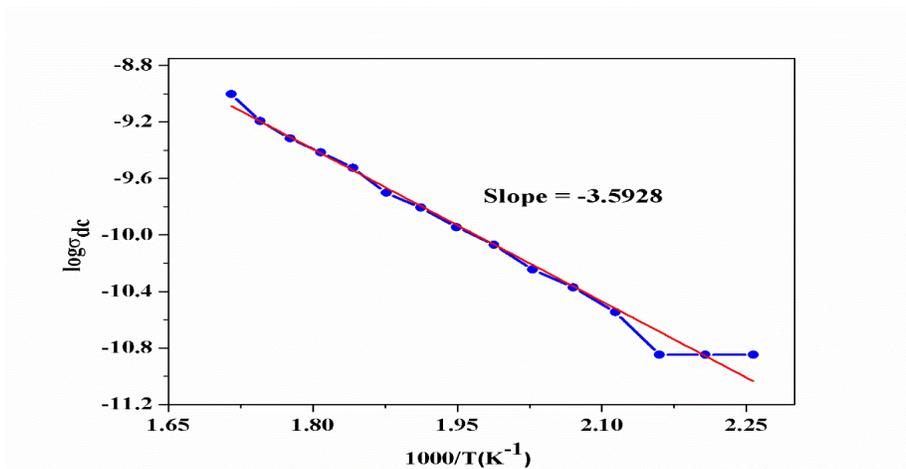


FIGURE 3. $\log\sigma_{dc}$ vs. $1000/T$ curve of Ca-substituted YFeO₃

CONCLUSION

We observed from the above study that the structural parameters of Ca-substituted YFeO₃ obtained from Rietveld refinement technique are consistent with the structural parameters of pure YFeO₃ and hence it is clear that 1% Calcium substitution does not affect the structural parameters of YFeO₃. The I-V characteristics curves show that the values of current are increasing with respect to temperature as well as with substitution of Calcium, which is the solution of the high resistance problem in YFeO₃ for electronics appliances. Also the dc conductivity curve shows the enhancement in the dc conductivity with respect to temperature. The calculated value of the activation energy is 0.31eV for 1% Ca substituted YFeO₃ which is a significant factor for a good conductor.

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