



Structural, Electric and Thermoelectric Studies of CaFeO₃ System

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ARTICLE INFO

Article history :

Received : 25 November 2014

Revised : 19 March 2015

Accepted : 24 March 2015

Keywords :

Structure

Thermoelectric

Resistivity

VRH

ABSTRACT

Polycrystalline CaFeO₃ samples were synthesized through solid state route at 1000 °C. The sintered samples were analyzed by XRD for crystal structure analysis. Electrical resistivity and seebeck coefficient were also measured for transport properties. The Rietveld analysis performed on the XRD data revealed that the sample is single phase with orthorhombic crystal symmetry. The space group was found to be pcmm. Power factor has been obtained from Seebeck Coefficient and electrical resistivity data. Electrical resistivity showed that conduction in the sample occurred through variable range hopping of the electrons. The negative Sign of Seebeck coefficient revealed that majority charge carriers in these samples are electrons. The properties determined make this material a potential candidate for electric and thermoelectric device applications.

1. Introduction

Thermoelectric effect is a phenomenon in which heat energy is directly converted into electrical energy. This can be a good alternate to the conventional solar and geothermal sources. Waste heat from factories and automobiles can also be converted into useful energy using thermoelectric materials. Ceramic oxides are potential candidates for thermoelectric devices applications because of their thermal and chemical stability [1]. During the last three decades of research on thermoelectric; two fundamental problems were identified, the low efficiency and the high processing cost of thermoelectric materials [2].

Thermoelectric materials are environment friendly and they might be a solution for conversion of waste heat in future if the efficiency of thermoelectric materials can be increased [3]. An ideal thermoelectric material should possess high Seebeck coefficient and electrical conductivity but low thermal conductivity. Figure of merit (ZT) is also another important factor to determine the efficiency of thermoelectric materials. Figure of merit is defined as $ZT = (S^2\sigma / k T)$ where S, σ and k are Seebeck coefficient, electrical conductivity and thermal conductivity respectively. A thermoelectric material has the ability of converting heat into electricity and vice versa. Power factor is defined as $S^2\sigma$. The materials with high power factor are ideal for thermoelectric applications. Seebeck coefficient and electrical conductivity cannot be varied independently because both depend upon carrier concentration [4]. An ideal thermoelectric material should behave as a glass thermally and as crystal electronically [5]. Current research focuses on the fabrication of alloys materials for thermoelectric applications. In this paper we have presented the work which is related to the synthesis of CaFeO₃

ceramic thermoelectric material. This material can be a potential candidate for application in different kinds of thermoelectric modules.

2. Experimental

CaFeO₃ was synthesized by the solid state route. The chemical compounds CaCO₃ and Fe₂O₃ with 99.99% purity (Alfa Aesar) were used as starting materials. Initially the starting materials were weighed in stoichiometric amounts and then mixed in a mortar with pestal for 1 hour to obtain highly uniform mixture. This mixture was then calcined in a furnace at 900 °C for 12 hours. The calcined powders were reground and pressed in the form of pellets under a pressure of 4 ton in a hydraulic press. The pellets were again sintered in a furnace for 24 hours at 1000°C. X-ray diffraction (XRD) data of sintered pellets was obtained on Rigaku XRD Machine in 2 θ range 10-80° with a step size of 0.02°. Thermoelectric measurements were performed on fine bars cut from the sintered pellets and the Seebeck coefficient data was collected using MMR Seebeck Measurement System. Resistivity experiment was performed on the sintered pellets by four probe technique.

3. Results and Discussion

The synthesized samples were characterized by XRD measurements for their structural and thermal atomic parameters beside phase analysis. Rietveld profile method by using "Rietca" software [6] was employed to refine the XRD data. A number of structural and profile parameters were refined. Peak shape was defined by pseudo-Voigt function which is a combination of Gaussian and Lorentzian functions. The background was fitted by sixth order polynomial function. Severe peaks overlap were diminished by taking intensities six times to the full width

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at half maximum (FWHM) for each particular reflection. Refined parameters include unit cell, atomic positions, the instrument zero point, scale factor and individual atomic thermal parameters for the individual atoms. In total 35 structural and profile parameters were varied simultaneously. For initial refinement the structural model was taken from [7] in space group of *pcmn*. During simultaneous refinement of thermal factors of atoms it gave negative values of temperature factors due to surface roughness of the sample [8] for some of the atoms. Therefore instead of considering the isotropic thermal atomic parameters for these atoms, anisotropic thermal factors were varied. Presence of platy crystallites in the sample resulting in the preferred orientation was carried out in the (001) direction according to Dollase [9]. The refined pattern showing observed data along with fitting (red line) is placed in Fig. 1.

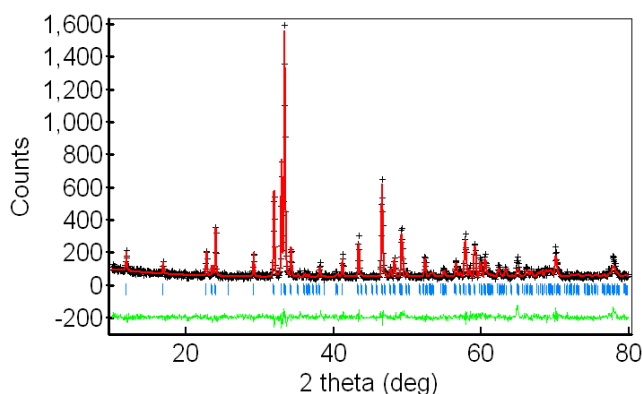


Fig. 1: Rietveld refinement pattern of CaFeO_3 sample showing orthorhombic crystal symmetry with space group *pcmn*. (+ measured data — fitted data | reflection — difference in intensity of observed and fitting)

The XRD results showed that CaFeO_3 has orthorhombic structure with space group *pcmn*. The sample is slightly oxygen deficient as determined through Rietveld refinement by varying the oxygen occupancies. The refined lattice parameters and atomic coordinates are listed in Table.1. The crystal structure obtained from these refined parameters is displayed in Fig. 2.

The Seebeck measurements were carried out in the temperature range of 70-350K as shown in Fig. 3 revealed semiconducting type behavior with a peak at temperature above 290K which may be some sort of phase transition or charge ordering occurring in this system and needs further detailed investigations. The seebeck coefficient showed a negative sign which is an indicator that the majority charge carriers responsible for conduction in this material are electrons rather than holes expected due to the deficiency of oxygen in this material. The Seebeck coefficient has a significant magnitude at the low temperature, showing the

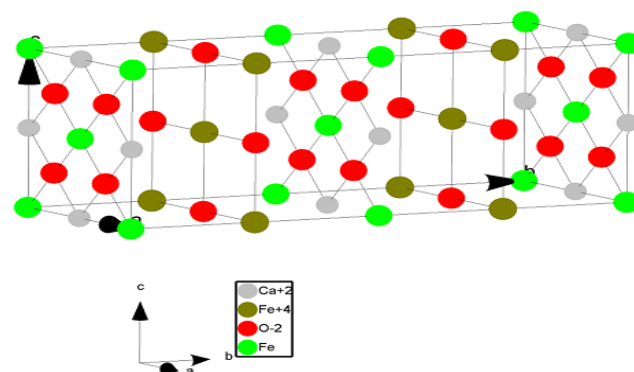


Fig. 2: Unit cell demonstration of CaFeO_3 obtained from Rietveld refined parameters

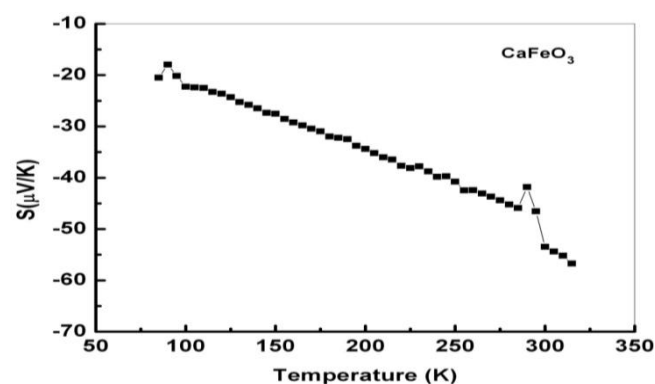


Fig. 3: Temperature dependence of Seebeck coefficient for CaFeO_3 sample

potential of this material for industrial and technological applications.

The electrical resistivity data measured in the temperature 77K-300K and shown in Fig. 4 revealed semiconducting like behavior with no sign of transition in the range 290K. In order to investigate what kind of conduction mechanism is occurring we fitted the low temperature dependence of resistivity data at low temperature using different models such as conduction band and variable range hopping conduction. The best fit

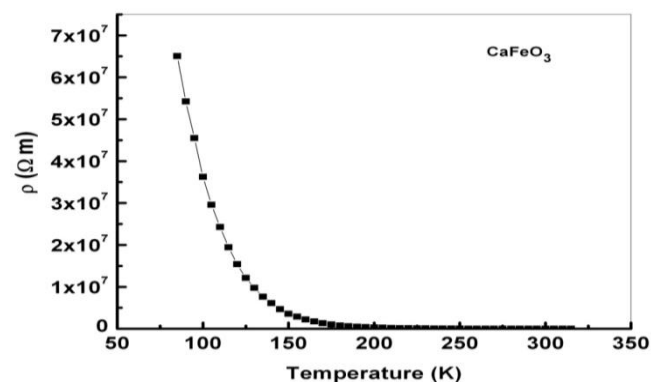


Fig. 4: Temperature dependence of electrical resistivity of the CaFeO_3 sample

Table 1: Rietveld Refined parameters of CaFeO₃

Atoms	x	y	z	B	N(occupancy)
Ca	0.0195(1)	0.1095(3)	0.4754(1)	0.49 (2)	1.0
Fe1	0.0	0.0	0.0	1.06(3)	0.5
Fe2	-0.0703(1)	0.25	-0.0495(1)	1.06(30)	0.5
O1	0.25	-0.0166(8)	0.25	0.76(2)	1.0
O2	0.0834(2)	0.1438(9)	0.0	2.15(1)	1.0
O3	-0.0985(1)	0.25	0.5941(4)	0.64(1)	0.56

Lattice Parameters : $a = 5.5968(5) \text{ \AA}$ $b = 14.7882(2) \text{ \AA}$ $c = 5.4267(5) \text{ \AA}$

$V = 449.15(\text{\AA})^3$

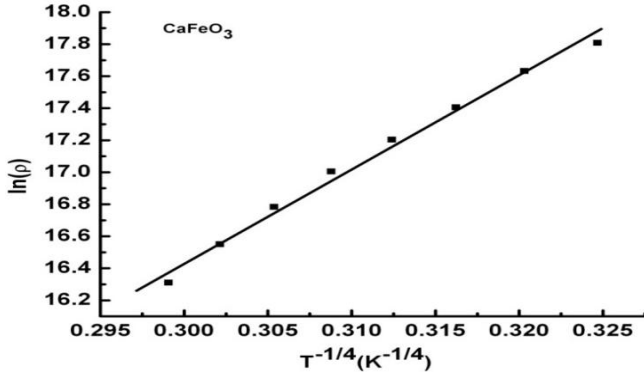


Fig. 5: $\ln \rho$ Vs $T^{-1/4}$ for CaFeO₃ sample showing variable range hopping conduction at low temperature. (Black symbol experimental data; line shows VRH model fitting)

to the data comes with the $T^{-1/4}$ which is variable range hopping conduction (Fig. 5). Using Seebeck and resistivity data the power factor has been calculated as a function of temperature and is demonstrated in Fig. 6. The power factor calculated also showed a sharp increase with increase in the temperature showing the capacity of this material as thermoelectric.

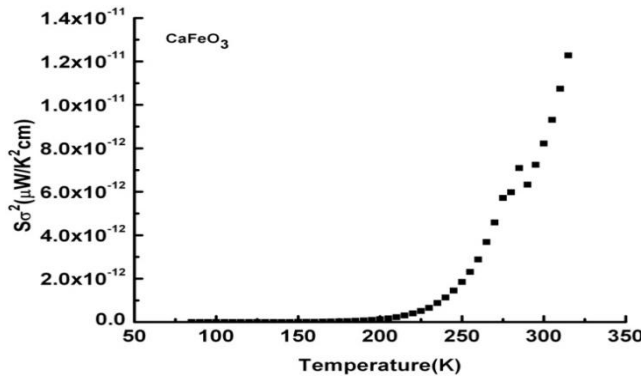


Fig. 6: Temperature dependence of thermoelectric power factor for CaFeO₃ sample

The Seebeck data clearly indicate that a phase transition occurs in the material at 289.72K. This transition is a metal-insulator transition, at this critical point the material shows metallic behavior as the magnitude of the Seebeck coefficient decreases and on other sides of this transition temperature the material behaves as an insulator. The transition is smooth and a type-II transition. It means it is not an abrupt one point critical transition. It is most probably due to gradual charge disproportionate where $2\text{Fe}^{+4} \rightarrow \text{Fe}^{5+} + \text{Fe}^{3+}$, as there exist a subtle interplay between electron – electron interaction, magnetic interaction and electron lattice interaction in realizing charge ordering or charge in homogeneity and charge fluctuations in transition metal oxides [10]. Furthermore no observation of this transition in resistivity measurements while its observation in Seebeck measurements is that seebeck measurements scans the whole Fermi level as a whole. While the resistivity only shows the picture of charge carriers in the vicinity of the Fermi level, where most of the carriers are localized as observed by variable range hopping conduction observed in this system.

4. Conclusion

Single phase ceramics CaFeO₃ has been successfully prepared by the solid state reaction technique at 1000 °C. The Rietveld analysis of XRD data revealed that material possesses orthorhombic structure with space group pcmm. The majority chare carriers in this material are electrons and conduction occurs through variable range hopping of electrons. The material has shown a large thermo power factor and can be consider as a potential material for thermoelectric devices.

Acknowledgement

We are thankful to all the staff members at Central Diagnostic Laboratory (CDL), PINSTECH for their help in different measurements.

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