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Thermoelectric power studies of Co–Cr nano ferrites

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ABSTRACT

One of the Electrical transport properties, Thermoelectric power of Cr substituted Cobalt Nano structured Ferrite materials with the formula $CoCr_xFe_{2-x}O_4$ ($0 \leqslant x \leqslant 1$), prepared by Sol–gel process were studied. The measurements were carried out from 320 K to well beyond Curie temperature by the differential method. The results showed a negative value for Seebeck coefficient for $CoFe_2O_4$ ($x = 0$), indicating n-type semiconductor behavior over the entire measured temperature range with the electrons as majority of charge carriers. $CoCr_xFe_{2-x}O_4$ ferrites (with x = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) behave as p-type semiconductors up to 360 K with positive Seebeck Coefficient above which they behave as n-type semiconductor. Ferrite with the composition $CoCrFe_2O_4$ has shown maximum value of Seebeck coefficient at all temperatures. Compositional and temperature dependence of the Seebeck coefficient in the present ferrite system has been discussed. On the basis of these results a conduction mechanism for Co–Cr nano ferrites system is suggested in different temperature regions. The value of thermoelectric power shows maximum value at T_c (K).

1. Introduction

Ferrites are low mobility semiconductors. Electrical transport properties of ferrites provide information suitable for the selection of these materials for specific application. To interpret the conduction mechanism in ferrites, Electrical transport properties such as Hall Effect and thermoelectric properties are widely used. Hall Effect measurement is straightforward and gives precise results. However, in case of ferrites that are low mobility semiconductors, it is somewhat difficult to measure the Hall Effect. In such cases the thermoelectric measurement is the only alternative. Moreover, the measurement of thermo e.m.f or seebeck coefficient is simple, straightforward and its sign gives vital information regarding the type of charge carriers (electrons and holes) responsible for the conduction process in semiconductors, i.e. whether they are n-type or p-type. It enables one to calculate Fermi energy, charge carrier concentration, mobility of charge carriers, etc. [1,2]. Knowledge of Fermi energy gap helps in the determination of various regions namely impurity conduction, impurity exhaustion and intrinsic conduction regions of a semiconductor. The electron jumps between differently charged ions of the same metal present in equivalent crystallographic sites is responsible for the conduction in ferrites.

Cobalt Ferrite possesses an inverse spinel structure which has high resistivity and low eddy current loss. It is an important magnetic material used in audio–video tapes and high density digital recording [3]. The Electrical properties of cobalt ferrites change drastically with composition. Hence, they are frequently used to investigate the conduction mechanism in ferrites. Cobalt ferrite is used as an excellent core material for power transformer in electronic and telecommunication applications due to its high electric resistivity and good magnetic properties [4]. The electrical transport properties of the ferrites are influenced by method of preparation, type of substituent, sintering temperature and duration [5]. Our earlier studies report that substitution of Cr^{3+} in place of Fe^{3+} in cobalt ferrite results in an increase in the resistivity which is desirable for electronic inductors, transformers, electromagnets and telecommunication applications. Electrical and transport phenomena of Cd substituted Cobalt ferrites prepared by double sintering ceramic technique were reported by Abdeen et al. [6]. Gul et al. have reported the magnetic and electrical properties of Zn substituted Co ferrites prepared by the chemical co-precipitation method [7].

During the past 10 years, considerable interest was observed in finding new materials and structures to make use in highly efficient cooling and energy conversion systems [8,9]. To the best

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of author's knowledge no information is available on the high temperature thermoelectric power studies of Chromium substituted Cobalt nano ferrites synthesized by Citrate–gel method. Moreover, with a view to understand the conduction mechanism in Co–Cr nano ferrites system the investigation of thermoelectric power studies of $CoCr_xFe_{2-x}O_4$ (with $x = 0.0$, 0.1, 0.3, 0.5, 0.7 0.9 and 1.0) nano ferrites prepared by Citrate–gel method was undertaken. The present work reports the thermoelectric power and conduction mechanism of chromium substituted Cobalt nano ferrites as a function of composition and temperature.

2. Materials and methods

2.1. Materials and synthesis

$CoCr_xFe_{2-x}O_4$ nano ferrites ($0 \leqslant x \leqslant 1$) were prepared using Citrate–gel auto-combustion method with the metal nitrates and Citric acid as starting materials [10].

2.2. Methods

The X-ray diffraction analysis confirmed the formation of homogeneous single phase cubic spinel structure with a crystallite size ranging from 6 to 12 nm [10]. The Curie temperatures of the samples have been determined using Loria experimental technique [11].

For the thermoelectric power measurements, Circular pellets (diameter – 13 mm and thickness – 2 mm) of the synthesized powders were made using polyvinyl alcohol as binder by exerting a pressure of 5 tons for 1–2 min. These samples were finally sintered at 400 °C for 5 h and then slowly cooled to room temperature. Pellets were then coated with a thin layer of silver paste to have good electrical contact.

Thermo electric power studies on circular pellets of $CoCr_xFe_{2-x}O_4$ nano ferrites were measured by a differential method [12] from 320 K to well beyond the Curie temperature. The sample was kept between the hot and cold junctions of the method in the form of pellet. The temperature difference between two ends of the sample was kept at 10 K throughout the measured temperature range. A temperature difference maintained between the hot and cold surfaces of a sample results in the motion of electrons or holes. This leads to the development of a thermo e.m.f. across the sample which is measured by using a digital micro voltmeter.

The thermo electric power or Seebeck coefficient (S or α) was calculated using the relation

$$S = \alpha = \frac{\Delta E}{\Delta T}$$

Where ΔE is the thermo e.m.f. produced across the sample as the charge carriers diffused from the hot to the cold surface due to a temperature difference ΔT in degree Kelvin across the sample.

3. Results and discussions

3.1. Composition dependence of Seebeck coefficient

The approximate Curie temperatures for the samples of the present ferrite system under investigation were measured using Loria technique and were tabulated in Table 1. Based on these values, Seebeck coefficient of the ferrite samples was measured from 320 K to 800 K (beyond Curie temperature). The values of Seebeck coefficient at 340 K for the ferrite samples calculated from the measured values of thermo emf were reported in Table 1.

It can be seen from the table that the sign of Seebeck coefficient for pure Cobalt Ferrite (without Cr content) is negative and that for all the Cr substituted Cobalt ferrites under investigation is positive. Based on it, Cobalt ferrites have been classified as n-type semiconductors and Chromium substituted Cobalt ferrites fall under p-type semiconductors at 340 K.

It is clear from the table that with increase in Cr composition from $x = 0.0$ to 1.0, the value of Seebeck Coefficient increased from −242 to 724 μV/K at 340 K. This indicates that more and more p-type carriers are generated with Cr content at lower temperature.

Table 1
Thermoelectric power data on Co–Cr ferrites.

Ferrite composition	Seebeck coefficient (α) (μV/K) at 340 K	p–n transition temperature (K)	Seebeck coefficient transition temperature T_s (K)	Curie temperature from Loria technique (T_c) K
$CoFe_2O_4$	−242	–	730	740
$CoCr_{0.1}Fe_{1.9}O_4$	285	360	725	722
$CoCr_{0.3}Fe_{1.7}O_4$	399	376	718	716
$CoCr_{0.5}Fe_{1.5}O_4$	444	388	710	700
$CoCr_{0.7}Fe_{1.3}O_4$	546	391	697	695
$CoCr_{0.9}Fe_{1.1}O_4$	652	399	680	678
$CoCrFeO_4$	724	401	668	661

3.2. Temperature dependence of Seebeck coefficient

The variation of Seebeck coefficient (α) with hot junction temperature (T) for the different compositions of $CoCr_xFe_{2-x}O_4$ ferrite system (with $x = 0.0$, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) compositions were shown in Figs. 1–7.

Fig. 1 corresponds to pure $CoFe_2O_4$ where $x = 0$. It can be seen from the figure that the sign of the Seebeck coefficient is negative in the measured temperature range indicating the n-type of semiconducting nature throughout this range. This means that the majority of charge carriers are electrons.

Figs. 2–7 correspond to chromium substituted cobalt nano ferrites ($CoCr_xFe_{2-x}O_4$ ferrite system with $x = 0.1$, 0.3, 0.5, 0.7, 0.9 and 1.0). It is clear that at lower temperature these ferrites show p-type behavior and at about 360–400 K p–n transition occurs. Beyond this temperature range, n-type conduction is dominant in these ferrites showing that majority of charge carriers are electrons. Similar behavior of variation of Seebeck coefficient with temperature was observed in Ni–Cr ferrites [13].

With increase in temperature it is observed that magnitude of Seebeck coefficient increases in the ferromagnetic region and reaches a maximum at certain temperature, denoted as Seebeck coefficient transition temperature. However, beyond this transition temperature the value of Seebeck coefficient was found to decrease with further increase in temperature which is due to the magnetic transition where the material becomes paramagnetic. The transition temperatures of the ferrite samples measured from these

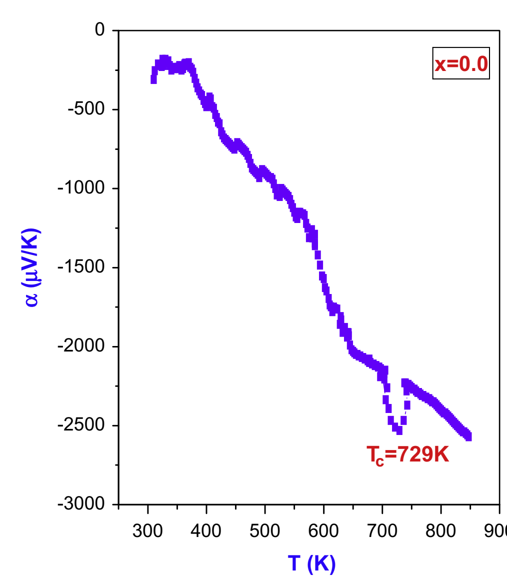

Fig. 1. Plots of Seebeck Coefficient (α) versus temperature of $CoFe_2O_4$.