Electrical properties of $Mn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticle synthesized via high-energy milling technique

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Abstract. The $Mn_{0.5}Co_{0.5}Fe_2O_4$ sample was produced from high-purity metal oxides by high-energy ball milling method. Single-phase cubic spinel structure and nanoparticle structure of the synthesized sample were confirmed by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The results show that the produced powder of the as-prepared sample has average grain size of about 8 nm. Bulk samples in the form of pellets were also produced from the as-prepared sample for resistivity measurements. The temperature dependence of the electrical resistivity for samples sintered from 600 - 1100 ^{o}C under argon atmosphere were studied using the four-probe method from room temperature to about 110 ^{o}C. Two possible mechanisms for resistivity involving T^{-1} and $T^{-1/2}$ dependences were investigated which we associated with semiconducting and inter-grain conductivity respectively. The $T^{-1/2}$ dependence is found to fit the data better and predicts higher activation energies. The resistivity was observed to be sensitive to the surface of the pellet being probed and the annealing temperature.

1. Introduction

The Spinel ferrites are widely used in several applications due to the combination of electrical and magnetic properties [1]. These properties depend on the chemical composition, cation distribution, grain size and preparation method. The substitution by different magnetic or non-magnetic cations at different sites in ferrite systems can provide different types of electrical and magnetic properties. Ferrite materials have high resistance because the metal ions are isolated by oxygen ions from each other. In general, spinel ferrites behave like semiconductors with high resistivity. The electrical resistivity appears to obey an exponential dependence of the electrical resistivity with temperature. This also depends on the composition of the compound and the cation distribution. The resistivity is expected to be due to the presence of divalent Fe^{2+} and trivalent M^{3+} metal ions. The extra electron from Fe^{2+} or the positive hole from M^{+3} can move through the crystal lattice. The existence of Fe^{2+} results in n-type behaviour and p-type behaviour from M^{3+}. The movement of a charge carrier is described based on a hopping mechanism where the charge carrier jumps from one ionic site to another site as the temperature increases [2]. The hopping depends on the activation energy associated with energy barriers experienced by the electrons during the hopping process. The electrical conductivity can also be described based on a granular tunnelling mechanism in which the charge carriers tunnel between neighbouring ferrite grains that are separated by grain boundaries [3]. In this

report, we investigated the variation of resistivity as a function of T^{-1} and $T^{-1/2}$ respectively for $Mn_{0.5}Co_{0.5}Fe_2O_4$ spinel ferrite.

2. Experimental details

The $Mn_{0.5}Co_{0.5}Fe_2O_4$ compound was synthesized by the high-energy ball milling technique from $MnFe_2O_4$ and $CoFe_2O_4$ single-phase spinel ferrites. The experimental procedure employed here has been discussed elsewhere [4]. Single-phase formation and structure analysis of the samples was based on XRD data obtained at room temperature. The XRD spectra of the samples were obtained using CoK_α radiation with wavelength λ = 1.7903 Å on a Phillips diffractometer type PW1710. The average particle diameters of the powders were also obtained by high-resolution electron microscopy (HRTEM) measurement on a type Jeol_JEM-2100 instrument in order to confirm estimates of average particle size from XRD measurement.

The D C resistivity measurements were carried out in air by the four-point probe method from about 300 to 400 K in a Proportional-Integral-Derivative (PID) controlled micro-oven. The electrical measurements were performed on both faces of the same pelletized sample annealed from 600 to 1100 ^oC under argon atmosphere. The pellet was annealed for 6 hours at each annealing temperature after being initially compacted in an evacuated 13 mm diameter ICL die at a pressure of 1.5×10^8 N m^{-2} for about 2 minutes. In the present four-probe set-up the spacing between the probes was fixed to 0.2 cm. The pelletized sample studied had a thickness of about 0.06 cm. Hence, the relevant equation used to calculate resistivity was based on the formula

$$\rho = t(\pi / \ln 2)(V / I) \qquad (1)$$

where V is the measured voltage across the two inner probes and I is the current through the sample [5].

3. Results and discussion

Figure 1 shows the XRD diffraction patterns of the as-prepared sample and for annealed sample at 400 ^oC for $Mn_{0.5}Co_{0.5}Fe_2O_4$. Typical HRTEM microstructure of the as-prepared sample is shown in figure 2. The grains appear to be nearly cubic in shape. The average crystalline size of 8 nm was estimated from XRD data by using Debye-Scherrer formula [4] which confirmed the HRTEM measurement. The bulk densities of the sample annealed at different temperatures were calculated using physical dimensions of the pellets [4]. Figure 3 shows the effect of the annealing temperature on the bulk density of the pellet.

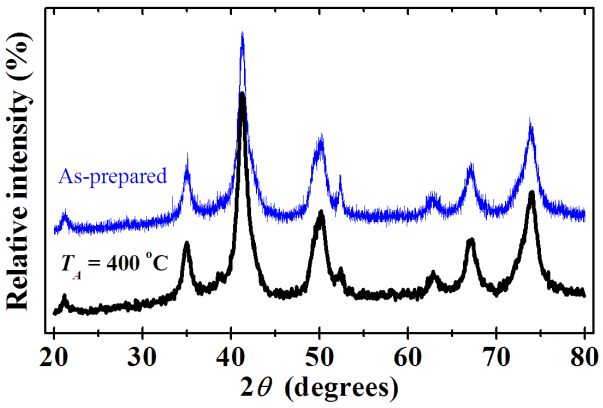


Figure 1. XRD of the as-prepared sample and sample annealed at 400 ^oC of $Mn_{0.5}Co_{0.5}Fe_2O_4$ sample.

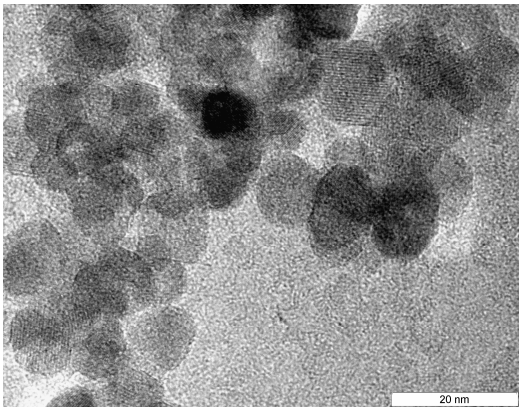


Figure 2. HRTEM image for the as-prepared $Mn_{0.5}Co_{0.5}Fe_2O_4$ compound.

In this study, we have performed systematic measurements of the resistivity on a single pellet following each annealing procedure where we take into account the surface that is being probed. The two surfaces of a pellet slightly differ in appearance. One surface is on the shiny side (face 1) and the other is on the dull side (face 2). Two distinct sets of plots at higher (face 2) and lower (face 1) values of resistivities can be identified. Different characteristics of the two surfaces suggest slight non-uniformity in the compaction of the pellets. This suggests a concentration gradient across the thickness of the pellet.

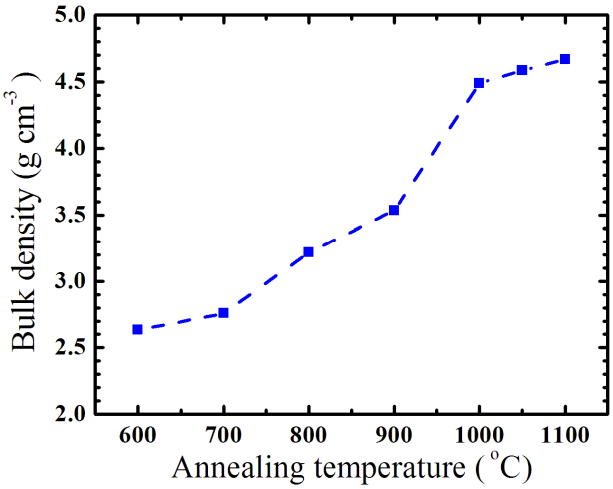


Figure 3. Variations of bulk density as a function of annealing temperature for $Mn_{0.5}Co_{0.5}Fe_2O_4$.

Ferrites have been reported to exhibit semiconductor behaviour based on a hopping mechanism that obeys the Arrhenius equation [6] where the resistivity at a finite temperature varies as

$$\rho(T) = \rho(0)\exp(E_{a1}/k_BT). \quad (2)$$

E_{a1} is the activation energy which is the minimum energy needed for an electron to jump from one ion to a neighbouring ion and $\rho(0)$ is a constant. The activation energy depends on the magnetic state of a material. In the ordered state in a ferromagnet, the activation energy is lower compared to the value for a paramagnet due to the effect of magnetic spin-disorder. In the paramagnetic state, the sintering temperature decreases the concentration of the current carriers and this changes the conduction mechanism [6]. One way in which the ferrite electrical resistivity can be explained is through the Verwey-de Boer mechanism [7]. In this mechanism, the electrons are exchanged between the ions of different valence states amongst the same element in a compound. Increasing the measuring temperature may also lead to a random distribution of the ions over equivalent crystallographic lattice sites A or B. The B site sublattices are known to be responsible for electrical resistivity in ferrites [8]. Therefore, partial reduction of Fe^{3+} to Fe^{2+}, Mn^{3+} to Mn^{2+} or Co^{3+} to Co^{2+} can be expected to occur in $Mn_{0.5}Co_{0.5}Fe_2O_4$. The variation of the resistivity with composition in ferrites can therefore be explained as an electron exchange transfer between the same elements [9]. The resistivity also depends on the sintering conditions and the number of ions which form during the preparation of such samples [7]. The electrical resistivity can also be explained on the basis of the tunnelling effect of electrons between charge carriers. In this process, the conductivity in granular materials occurs because of the transport of the electrical charge by tunnelling between grains. The charge carriers are generated from the transfer of electrons from neutral to neighbouring charged grains. The possible polaronic conduction process can therefore be written as: $Fe^2 \rightarrow Fe^{3+} + e^-$, $Mn^2 \rightarrow Mn^{3+} + e^-$, and $Co^2 \rightarrow Co^{3+} + e^-$. The variation of the tunnelling resistivity with temperature in granular

metals strongly depends on the electrostatic charge energy which is needed to generate the positive and negative charged grains. In this system, the charge carriers can be thermally activated at high temperature. Sheng et al [10] have suggested that the temperature dependence of resistivity due to the tunnelling between neighbouring grains follows the equation

$$\rho(T) = \rho(0)\exp[2(E_{a2}/k_B T)^{1/2}] \qquad (3)$$

where E_{a2} is the tunnelling activation energy between grains. The temperature variation of resistivity of our sample has therefore be tested against equations (2) and (3). Figures 4 and 5 show the variations of electrical resistivity as a function of T^{-1} and $T^{-1/2}$ respectively for a pellet of a $Mn_{0.5}Co_{0.5}Fe_2O_4$ sample which was annealed at 600, 700, 800, 900, 1000, 1050 and 1100 ^{o}C.

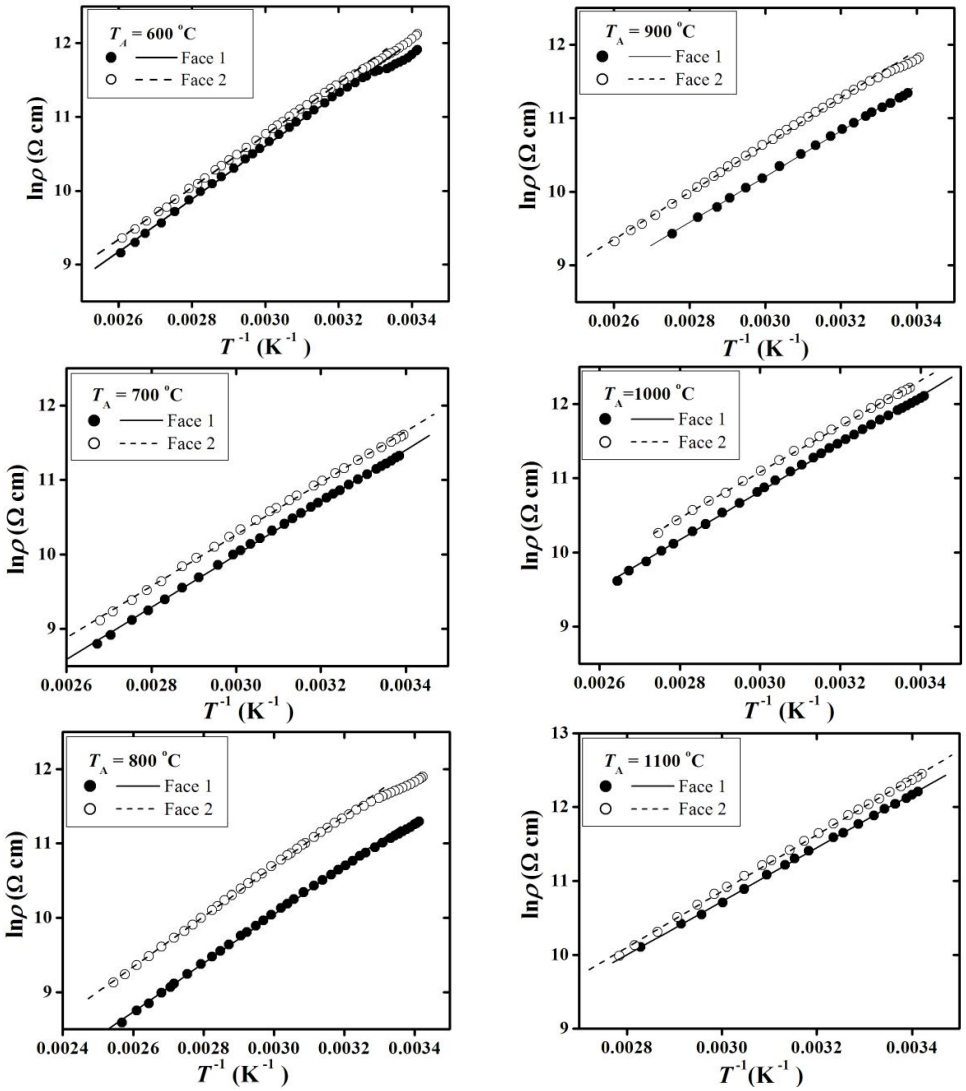


Figure 4 ln ρ versus T^{-1} for $Mn_{0.5}Co_{0.5}Fe_2O_4$ pellet samples annealed at 600, 700, 800, 900, 1000 and 1100 ^{o}C.

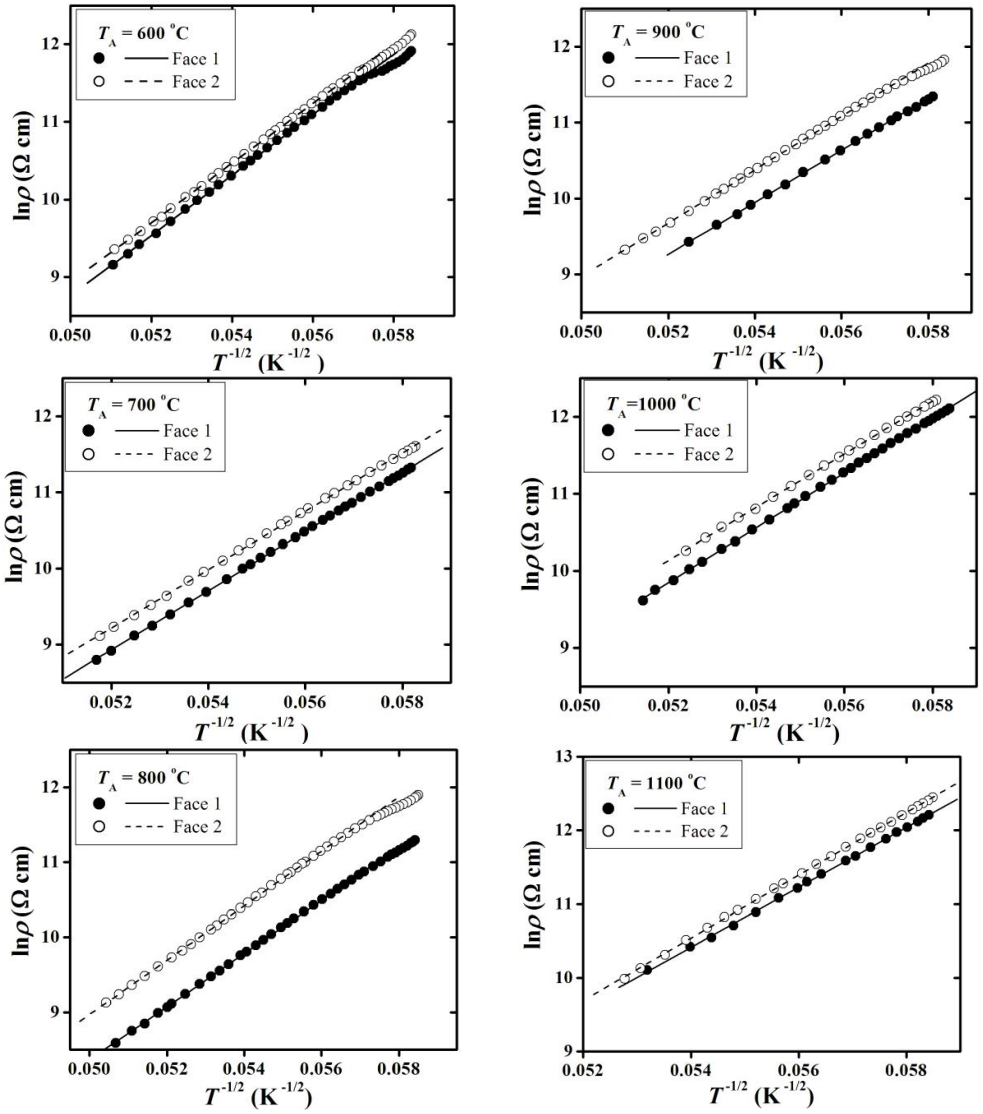
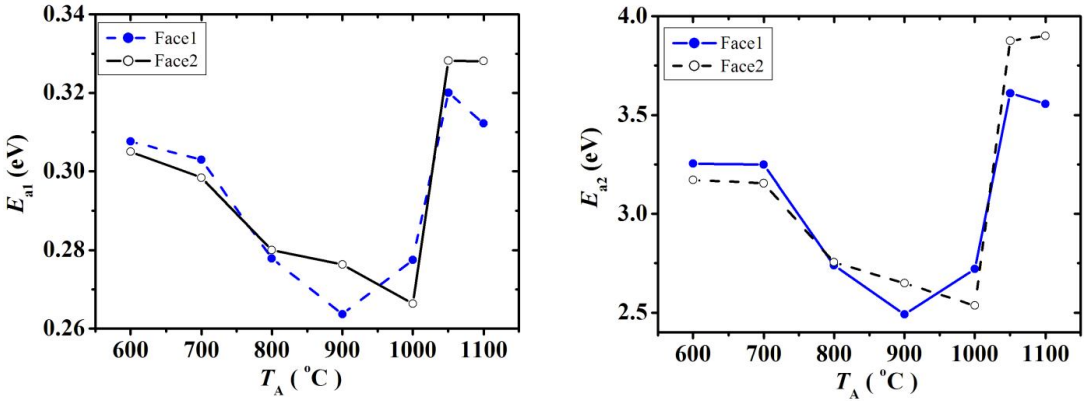


Figure 5. ln ρ versus $T^{-1/2}$ for $Mn_{0.5}Co_{0.5}Fe_2O_4$ pellet samples annealed at 600, 700, 800, 900, 1000 and 1100 °C.

The variation of resistivity according to equation (2) is similar to that of semiconductor materials. This is associated with the hopping movements of electrons or holes between divalent and trivalent metal cations. In the present case for $Mn_{0.5}Co_{0.5}Fe_2O_4$ sample, the hopping is suspected to be between Fe^{2+} and Fe^{3+} (or Mn^{2+} and Mn^{3+} or Co^{2+} and Co^{3+}) ions through intervening oxygen anions.

The resistivity measurements appear to distinguish the characteristics of the two surfaces. Higher resistivities were obtained when the dull surface (face 2) was probed. Therefore, any systematic measurements on different pellets must take into account the surfaces of the pellets being probed. Good linear fits are obtained to fits data in figures 4 and 5. Plots of ln ρ versus $T^{-1/2}$ have slightly better correlation coefficients to the plots ln ρ versus T^{-1} than for movements between charged and neutral grains.

The values of E_{a1} and E_{a2} deduced from the slopes in figures 4 and 5 are plotted as a function of annealing temperature in figures 6. Similar trends are observed which indicate similar intrinsic behaviour in the measurements on either faces of the pellets. Minimum values of activation energies are obtained for annealing temperatures around 900 - 1000 ^{o}C. We suspect that for this range of annealing temperature, T_A, values the sample may be transforming from single-domain to multi-domain structure. The activation energies based on equation (2) are consistent with some previous measurements [1, 11]. The resistivity based on tunnelling between grains gives much larger activation energies and better fits to the data than that based on semiconductor behaviour. We suspect that higher activation energies would be required in order to promote conduction by hole or electron.



Figures 6. Variations of activation energy with annealing temperature for $Mn_{0.5}Co_{0.5}Fe_2O_4$, deduced from the best fits of equations (2) and (3).

4. Conclusions

We have made $Mn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticle compounds using high-energy ball milling from $MnFe_2O_4$ and $CoFe_2O_4$ ferrites as starting materials. The temperature dependence of resistivity of $Mn_{0.5}Co_{0.5}Fe_2O_4$ nanosized compacts seems more favourable to the tunnelling effect of charge carriers between grains. Analysis of the resistivity based on tunnelling between grains gives much larger activation energies and better fits to the data. The resistivity and activation energy of a sample has been found to depend on the annealing temperature and the surface of the pellet that being probed. Our results show minimum activation energies at around 900 ^{o}C.

References

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