JOURNAL OF MATERIALS SCIENCE **34** (1999) 621 – 623

Thermoelectric power studies of Sn/Nb substituted Mn-Zn ferrites

A. D. P. RAO*, B. RAMESH†, P. R. M. RAO‡, S. B. RAJU†
*Department of *Nuclear Physics, †Physics and ‡Inorg. & Anal. Chemistry, Andhra University, Visakhapatnam - 530 003, India*

Thermoelectric power studies of polycrystalline materials of Sn/Nb substituted Mn-Zn ferrites have been carried out. The Seebeck coefficient, carrier concentration and drift mobility were evaluated. The Seebeck coefficient increases up to 420 K and 400 K for Nb and Sn substituted ferrites respectively. All the ferrites exhibited n-type conduction over the range of temperature studied. At high temperatures, a non-degenerate type of semiconductor behaviour has been observed. The conduction of these materials is explained by hopping of electrons from Fe^{2+} to Fe^{3+}, in addition to the existence of narrow bands and localized levels. The variation of drift mobility is explained by wavy bands [1, 2].

1. Introduction

Mn-Zn ferrites are widely used for high frequency applications. Though several studies on these ferrites had been carried out earlier, studies towards an understanding of the conduction mechanism in detail are very limited. Hall effect and thermoelectric power studies are two important experimental methods for understanding the conduction mechanism. A survey of the literature reveals that studies of thermoelectric power in Mn-Zn ferrites are very limited. However some studies were reported [3–5] for Li-Zn, Li-Cd and Li-Co ferrites.

By substitution [3, 4] of non-magnetic ions like Zn or Cd in the matrix of lithium ferrite, a minimum value of thermoelectric power (Q) was found at dopant concentrations of 0.6 and 0.4 respectively. At higher dopant concentrations Q was increased. Contrary to this, recent studies of Co substituted lithium ferrite reported [5] that Q was found to increase with the increase in substituent concentration. Substitution [6] of Zn in Mn-Zn ferrite resulted in a continuous decrease of thermoelectric power (Q) with the increase in Zn concentration. The effect of Zn^{4+} on Q in copper ferrite was reported [7] concluding that the Q value would increase with the increase of dopant concentration. But in Sn^{4+} substituted [8] copper ferrite the Q was found to increase initially and later decrease at a higher concentration of tin. The aim of the present work is to understand the effect of high valence cations, Sn^{4+}/Nb^{5+}, on the thermoelectric power of Mn-Zn ferrites.

2. Experiment

Polycrystalline materials of mixed Mn-Zn ferrites with the chemical formula $Mn_{0.58-x/2}\,Zn_{0.37-x/2}\,M_xFe_{2.05}\,O_4$ ($M = Sn^{4+}/Nb^{5+}$, $x = 0.00$ to 0.30 in steps of 0.05) were prepared using a conventional ceramic method. A finely ground mixture of these chemicals obtained through ball milling was calcinated at 1000 °C for a solid state reaction to form the ferrite compound. They were again ground for ball milling, then pellets of these materials were prepared and sintering was done at 1380 °C for one hour in air atmosphere. Subsequently the temperature was lowered to 1280 °C and then they were sintered for one hour. Using Cu Kα-radiation, X-ray diffraction studies were carried out and these confirmed the single phase formation of the intended ferrites. Earlier investigators [9] reported in their studies on Mn-Zn ferrites that the formation of high resistivity layers was due to enrichment of Nb atoms in grain boundaries. But the photographs [10] taken by the scanning electron microscope (SEM) on the surfaces of the same specimens indicated dissolution of dopants in the Mn-Zn ferrites. Experimental techniques [11] like electron micro-probe analysis or Energy Dispersive X-ray (EDX) analysis at grain boundaries would give more reliable information, since SEM and X-ray diffraction techniques are not able to detect the low concentration of dopant. With the help of a hot probe technique [12], thermoelectric power studies were done from room temperature to about 560 K. This technique employs a point contact probe, which was kept in contact with the upper surface of a ferrite specimen and acts as the hot junction. The specimen was placed on a metal base which acts as the cold junction. The temperature of the probe was raised with the help of an electric heater wound around it.

3. Results and discussion

Due to the one degree temperature difference on the surfaces of the specimen, the induced thermo-emf across the specimen gives the thermoelectric power (Seebeck coefficient, Q). Thus the thermoelectric power can be calculated as

$$Q = \frac{\Delta V}{\Delta T}$$

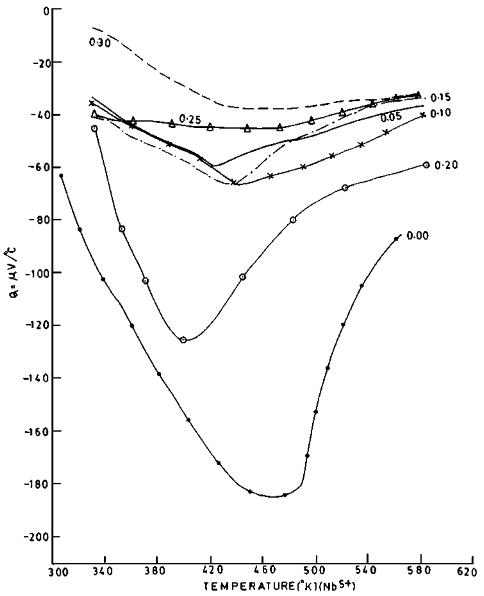

Figure 1 Variation of Seebeck coefficient as a function of temperature for niobium substituted Mn-Zn ferrites.

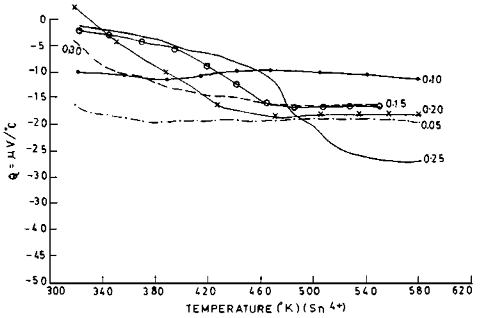

Figure 2 Variation of Seebeck coefficient as a function of temperature for tin substituted Mn-Zn ferrites.

where ΔV is the induced voltage of the thermo-emf across the specimen for a ΔT difference of temperature for the two surfaces of the ferrite pellet.

Figs 1 and 2 show the variation of the Seebeck coefficient (Q) as a function of temperature for Nb/Sn substituted Mn-Zn ferrites respectively. All the materials exhibit n-type conduction over the whole range of studied temperatures. For the Nb^{5+} substituted ferrite, the Seebeck coefficient rapidly increased up to the temperature of 420 K, and decreased beyond 420 K. For $x = 0.25$ and 0.30 concentrations, the Q value remained almost constant at higher temperature. For Sn substituted ferrites also, the increase in Q was observed for higher concentrations (for $x = 0.15$ to 0.30) up to the temperature of 440 K as observed for Nb doped ferrites. Beyond this temperature, the decrease of Q was observed for $x = 0.15$ to 0.30. Above 440 K and for other concentrations of Sn, the Q value remained practically constant. But the variation of Q with temperature is greater for Nb doped ferrites than for Sn doped ferrites.

The n-type conduction reveals that all the materials have electrons as majority carriers. The increase in the Seebeck coefficient (Q) with temperature had been observed in other ferrites [7, 8] also. This is due to the increase of charge carriers, namely electrons, and their movements as the thermal energy of these carriers increases with the increased temperature. The rapid increase of Q up to a certain temperature (approximately 425 K) is confirmed with the similar observation by earlier investigators [13] in $Mn^{2+}Ti^{4+}$ substituted Ni-Zn ferrites. The temperature dependence of Q can be explained [14] by the relation $Q = A + (B/T)$, where A and B are constants. One possible reason for the conduction below certain temperatures (420 K for Nb and 440 K for Sn materials) might be due to the extrinsic behaviour of these ferrites.

The larger variation in Q for Nb doped ferrites than for Sn doped ferrites can be attributed to the 4d orbital contribution for the polaron hopping mechanism. Generally conduction in ferrites is explained either by a hopping mechanism or a band type process [7]. The decrease in Q above a certain temperature can be understood by reference to an observation [15] where the conduction was assumed to be in the intrinsic region. In this region, the contribution to Q from electrons becomes less significant with the decrease in the hopping mechanism. Then Q becomes increasingly influenced by the mobility of holes lying far below the Fermi energy. At higher temperature the plateau of Q versus T shows that the thermoelectric power is independent of temperature. It was reported [13] that Mn-Zn ferrites belong to the degenerate type of semiconductor and that thermo-emf does not depend on temperature. Hence, in the present investigations, the materials exhibit degenerate semiconductor behaviour at higher temperature (intrinsic range) and non-degenerate semiconductor behaviour at lower temperature (extrinsic range).

Following the theory reported [15] earlier, the carrier concentration (n) for all the materials have been evaluated at different temperatures. The values of n are on the order of 10^{20} per cm^3. For semiconductors like ferrites with low mobility, having narrow bands or localized levels the n value would be on the order of 10^{20} per cm^3. This was observed earlier [3–5] in several other ferrites. The increase in charge carrier concentration (n) with temperature is linear for both Nb as well as Sn doped ferrites. The linear dependence of n on temperature had also been observed in other mixed ferrites like Li-Zn and Li-Cd ferrites [3, 4].

The drift mobility (μ) was calculated [16] at different temperatures (using conductivity results published earlier [17]) and carrier concentrations. The value of μ increased exponentially with increase in temperature as reported by earlier investigators [7, 8] in Sn or Zr substituted Cu ferrites. The increase of μ was caused by the decrease of resistivity with temperature. Movement of electrons increases with temperature and hence the mobility of electrons is more significant than holes having lower mobility. In the present studies the activation energy (E_d) values due to mobility were calculated [7]. The values are less than the activation energies obtained from resistivity studies [17]. The estimated activation energies for thermoelectric power and resistivity variations in the extrinsic region are nearly equal, suggesting that the conduction mechanism is only due to polaron hopping [19]. The importance of mobility studies was also reported earlier [15, 16]. The idea of wavy bands gives [1, 2] the importance of activation energies due to mobility. Potential fluctuations arise from an inhomogeneous distribution of dopants and imperfections of the crystal. These fluctuations give rise to activation energies for the motion of holes and electrons when the potential wells are filled with the charge carriers due to trapping. If the potential fluctuations are smoothed out, the mobility activation energies decrease.

4. Conclusions

On the basis of the results and discussion the following conclusions are drawn:

1. The structure of the mixed ferrites reveals no formation of a separate phase which could affect the thermoelectric power of Sn/Nb substituted Mn-Zn ferrites.
2. No region of the variation in thermoelectric power with temperature suggests formation of a new phase along with the cubic spinel phase of the Nb/Sn substituted ferrites.
3. The majority carriers are electrons over the temperature range studied, from room temperature to 560 K.
4. The Seebeck coefficient increased rapidly up to a certain temperature (420 K for Nb and 440 K for Sn doped materials).
5. Non-degenerate semiconductor behaviour was observed at higher temperatures.
6. The dependence of Q, n and order of n value on temperature suggest that the materials have narrow bands or localized levels.
7. The significance of drift mobility is explained by wavy bands.

References

1. G. H. WANNIER, *Phys. Rev.* **76** (1949) 254.
2. H. M. JAMES, *Science* **110** (1949) 254.
3. D. RAVINDER, *Cryst. Res. Technol.* **27**(4) (1992) 545.
4. D. RAVINDER and T. SESHAGIRI RAO, *Cryst. Res. Technol.* **25**(8) (1990) 963.
5. J. M. SONG and J. G. KOH, *J. Mag. & Mater.* **152** (1996) 383.
6. D. RAVINDER and K. LATHA, *J. Appl. Phys.* **75**(10) (1994) 6118.
7. S. A. PATIL, B. L. PATIL, S. R. SAWANT, A. S. JAMBHALE and R. N. PATIL, *Ind. J. Pure & Appl. Phys.* **31** (1993) 904.
8. B. L. PATIL, S. R. SAWANT, S. S. S. VANSHI and S. A. PATIL, *Bull. Mater. Sci.* **16**(4) (1993) 267.
9. H. INABA, T. ABE, Y. KITANO and J. SHIMOMURA, *J. Sol. State Chem.* **121** (1996) 117.
10. A. D. P. RAO, Ph.D. Thesis, Andhra University, India (1995).
11. H. INABA, T. ABE, Y. KITANO and J. SHIMOMURA, *J. Mag. & Mag. Mater.* **133** (1994) 487.
12. D. RAVINDER, Ph.D. Thesis, Osmania University, India (1988).
13. B. V. BHISE, V. C. MAHAJAN, M. G. PATIL, S. D. LOKTE and S. A. PATIL, *Ind. J. Pure & Appl. Phys.* **33** (1995) 459.
14. R. S. NARAYANA and S. R. MURTHY, *Crystl. Res. Technol.* **20** (1985) 701.
15. F. J. MORIN, *Phys. Rev*. **93**(6) (1954) 1195.
16. F. J. MORIN, *Phys. Rev*. **83**(5) (1951) 1005.
17. A. D. P. RAO, B. RAMESH, P. R. M. RAO, and S. B. RAJU, *Proc. V National Seminar of Crystal Growth,* ed. C. Subramanian, Madras (1993), 303.

Received 22 April 1997
and accepted 20 August 1998