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Preparation, temperature and composition dependence of some physical and electrical properties of mixtures within the NiO–Mn_3O_4 system

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The NiO–Mn_3O_4 mixtures using cryochemically prepared powders have been made. Resitivity of the mixtures in the system with $Ni_{1-x}Mn_{2+x}O_4$ has been measured as a function of temperature and composition. Bulk densities, temperature coefficient of resistance, activation energy, bias voltage and time constant have also been determined. A fairly wide range of composition exists in the system suitable for thermistor application.

1. Introduction

Nickel manganite, $NiMn_2O_4$ has a cubic spinel structure and it is semiconducting in behaviour, like many transition metal oxides containing cations of the same element in two valence states. It is prepared by reacting NiO with Mn_3O_4. NiO is cubic, Mn_3O_4 exists both in tetragonal and cubic forms. All semiconductors have one phenomenon in common, their electrical resistivity decreases with temperature, i.e. they have negative temperature coefficient of resistance. This resistance decreases down to 6%, per degree centigrade, at and around room temperature (300 K). Because of this negative temperature coefficient of resistance, $NiMn_2O_4$, is used to form the basis of ceramic devices, e.g. thermistors, for electronic application. Thermistor circuit elements and infrared detectors are thermally sensitive resistors having negative temperature coefficient of resistance. This investigation has been made essentially from the point of view of nickel manganite being used as a thermistor. Only some of the properties of the system useful for thermistor application have been undertaken for the study.

The aim of the present investigation thus has been to attempt to establish the conditions of formation of stoichiometric $NiMn_2O_4$, or $Ni_{1-x}Mn_{2+x}O_4$ in a single phase, if possible and to study some of the properties, e.g. electrical resistivity and the temperature coefficient of resistance, I–V characteristics and some other related properties, as a function of temperature and/or composition. Activation energy, w, for semiconductor behaviour and bulk densities have also been determined as a function of composition.

2. Experimental procedure

2.1. Sample preparation

NiO and Mn_3O_4 powders used in this investigation for making the samples have been made by the cryochemical method [1] and the spray drying method. Powders made by these techniques have controlled parameters, suitable for being used in making electronic devices. NiO and Mn_3O_4 used in this study have surface area $\simeq 8.0\,m^2\,g^{-1}$. and equivalent spherical diameter $\simeq 150$ nm. A series of mixtures, starting from 95.0 mol % NiO and 5.0 mol % Mn_3O_4 to 95.0 mol % Mn_3O_4 and 5.0 mol % NiO were made by weighing the required quantities of the powders and thoroughly mixing them with acetone and a few drops of 10% PVA solution, as the binder. These powders were pressed in a die under 5000 psi to make circular discs of about 0.5 inch in diameter and 1.0 to 1.5 mm in thickness.

2.2. Sample calcination

The circular discs were heated to various temperatures from 800 to 1300° C and soaked for various lengths of time, but no less than 8.0 h at any temperature in a silicon carbide furnace in air atmosphere. At lower temperatures the samples

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were heated for longer time, about 24.0 h. Samples were repeatedly ground and repressed after heating at a temperature at two to three hours interval to ensure complete reaction between the ingredients. After the heat treatment at a given temperature, the samples were quenched.

2.3. Density determination

Some samples were selected for density determination. Some of the samples were richer in Mn_3O_4 content, some in NiO content and in some both the ingredients were in equimolar proportion. The geometrical densites of the samples were determined from their weight and geometrical volumes.

2.4. X-ray diffraction analysis

The quenched samples were analysed by X-ray diffraction technique at room temperature to identify the various phases present in the samples. A Philip Norelco Diffractometer using Cu*Kα* radiation was used for X-ray analysis.

2.5. Resistivity measurement

Both the surfaces of the samples were ground flat and smooth. Silver paint was applied on both the surfaces for electrical contact and dried in an oven at 120° C. Resistance of the samples was measured at room temperature using a universal L-C-R bridge, TF2700, made by Marconi Instruments. For measuring the resistance of the samples as a function of temperature, a low and high temperature chamber, −17 to 170° C, model No, SK3102 made by Associate Testing Laboratory, with an accuracy of ± 1% was used.

2.6. *I–V* characteristics

I–V characteristics of some selected samples having the temperature coefficient of resistance between −4% and −6% were determined using a digital multimeter with an accuracy of ± 0.25%.

3. Results and discussion

3.1. Density

The variation of the geometrical bulk density of the samples as a function of the temperature has been shown in Fig. 1. The densities of the samples with 60.0 mol% Mn_3O_4 vary linearly, increasing with increasing temperature. It is almost constant for the samples containing 90 mol% Mn_3O_4 and decreases from a high value to a minimum and then rises again for the samples containing 10% Mn_3O_4. Samples containing 90% Mn_3O_4 are well sintered and there is not any significant variation in the density.

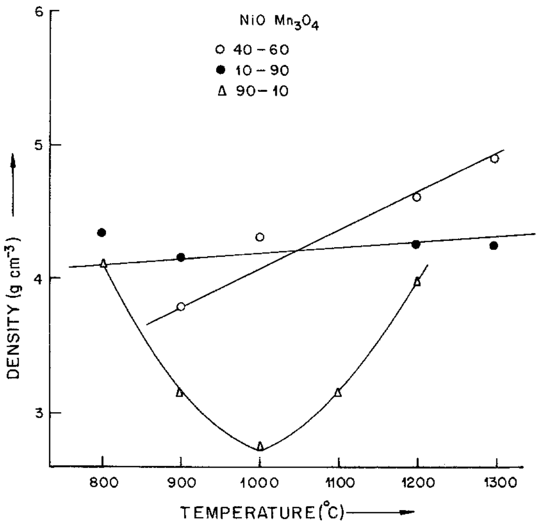

Figure 1 Bulk densities of various $NiO–Mn_3O_4$ samples as a function of temperature.

3.2. X-ray analysis of mixtures in the $NiO–Mn_3O_4$ system

The results inferred from the X-ray analysis of various mixtures heated in the temperature range of 800 to 1300° C have been summarized in Table I. No single phase stoichiometric $NiMn_2O_4$ or $Ni_{1-x}Mn_{2+x}O_4$ has been found. Beyond the region of the composition corresponding to the stoichiometric $NiMn_2O_4$, the cubic spinel nickel manganite represented by $Ni_{1-x}Mn_{2+x}O_4$ is found to exist, from the shift of X-ray diffraction peak positions of the stoichiometric $NiMn_2O_4$ [2]. No systematic variation in the lattice parameters has been calculated. X-ray analysis indicates the presence of nickel manganite in all the samples

TABLE I Results of room temperature X-ray analysis of various mixtures of NiO and Mn_3O_4, calcined at different temperatures

Initial composition of mixtures		Calcination temperatures (° C)	Phases present in the calcined mixtures
NiO	Mn_3O_4		
95–80	5–20	800–1300	NiO, $NiMn_2O_4$
80–55	20–45	800–1300	NiO, $NiMn_2O_4$, Mn_3O_4 (cubic)
55–25	45–75	800–1300	$NiMn_2O_4$, Mn_3O_4 (cubic and tetragonal)
25–5	75–95	800–1300	$NiMn_2O_4$, Mn_3O_4 (tetragonal)

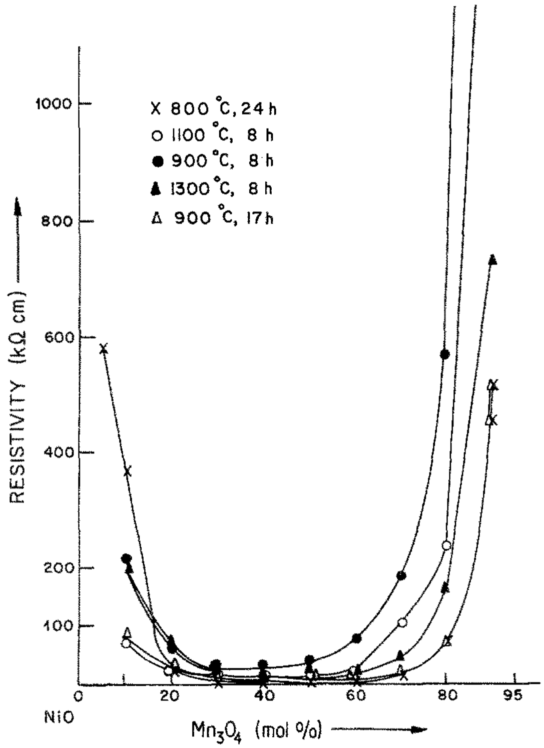

Figure 2 Room temperature resistivity of NiO–Mn_3O_4 samples as a function of composition.

heated in the temperature range of 800 to 1300° C, without any sign of complete decomposition to NiO and Mn_3O_4, as reported by Larson *et al.* [2]. Tetragonal spinel. Mn_3O_4, was prepared by the calcination of cryochemically prepared $MnSO_4$, around 800° C in air and it was found to be stable at room temperature and no Mn_2O_3 was found to be formed [2].

The existence of Mn_3O_4 in the cubic form along with nickel manganite and Mn_3O_4 tetragonal phase in the composition range of 20 to 75 mol% Mn_3O_4, needs further investigation.

3.3. Resistivity measurement as a function of temperature

At room temperature, the resistivity as a function of composition is shown in Fig. 2. It starts from a high value, decreases to a minimum and then increases again. The region where the resistivity is minimum corresponds to the region of stoichiometric $NiMn_2O_4$ and low values of x, in $Ni_{1-x}Mn_{2+x}O_4$. Resistivity of various samples, as a function of temperature (−10 to 170° C) is shown in Figs. 3, 4 and 5.

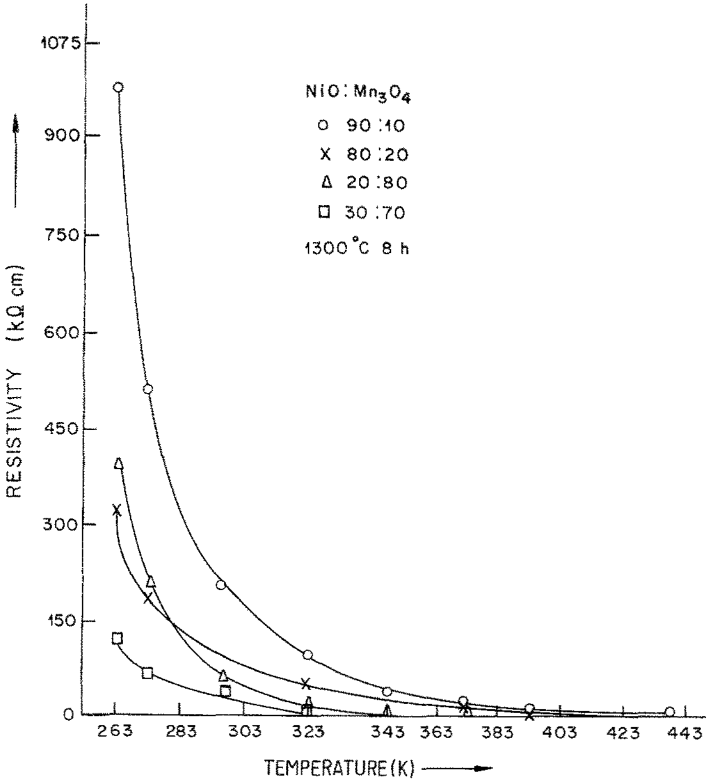

Figure 3 Resistivity of some NiO–Mn_3O_4 samples as a function of temperature.

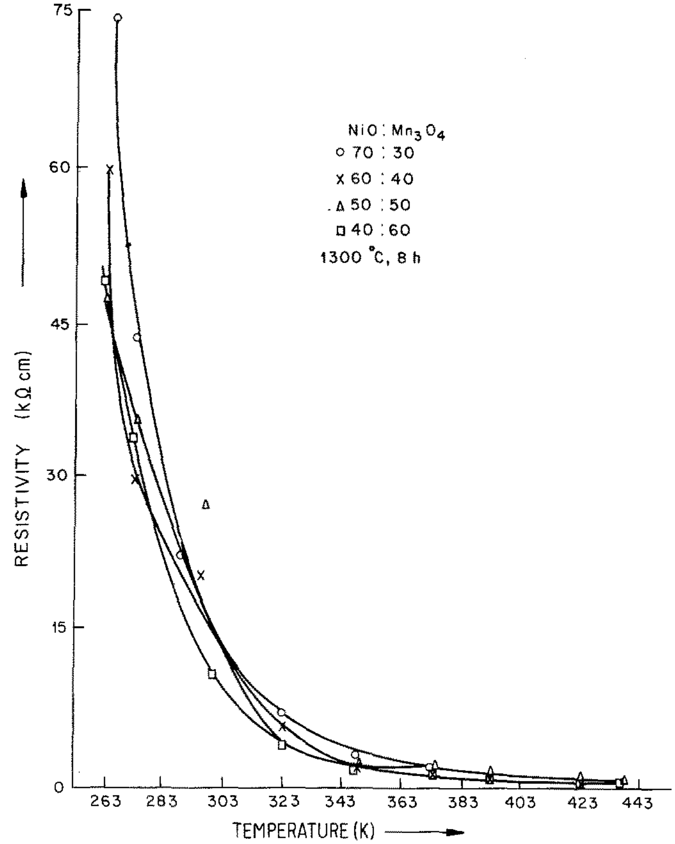

Figure 4 Resistivity of some NiO–Mn_3O_4 samples as a function of temperature.

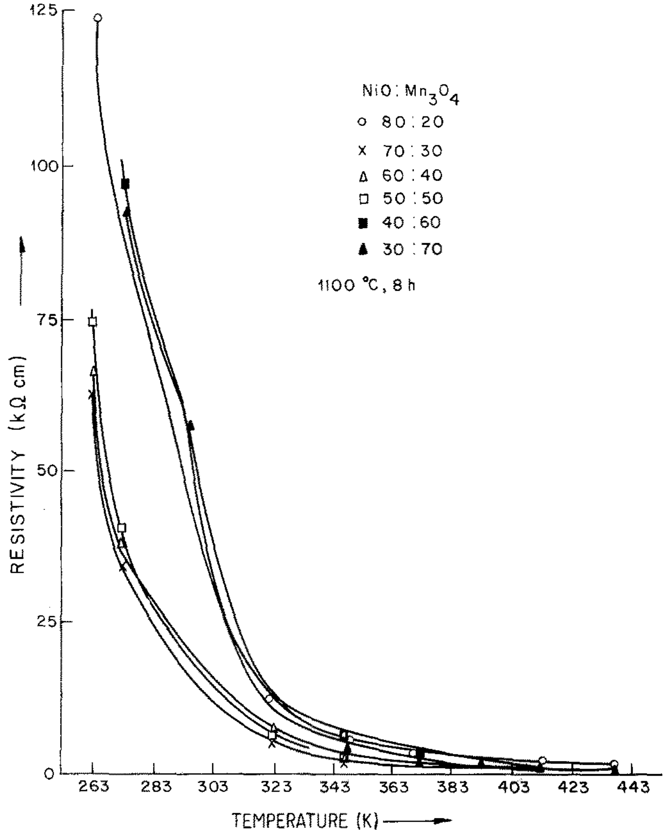

Figure 5 Resistivity of some NiO–Mn_3O_4 samples as a function of temperature.

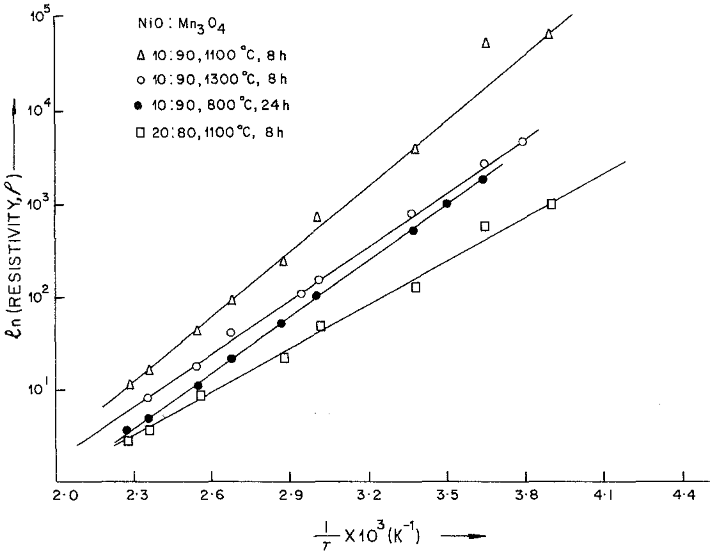

Figure 6 ln resistivity against $1/T$ for some NiO–Mn_3O_4 samples for determining activation energy and the temperature coefficient of resistance.

3.4. Activation energy (w) and the temperature coefficient of resistivity (TCR), α_T

The temperature dependence of the resistivity is given by the expression $\rho = \rho_0 \exp(w/kT)$, where w is the activation energy, k, the Boltzman's constant and T the absolute temperature. From the slope of a plot of $\ln \rho$ against $1/T$, the activation energy w is calculated. The slope of the plot is w/k.

A plot of $\ln \rho$ against $1/T \times 10^3$ is shown in Fig. 6.

Variation of the activation energy as a function of the composition is shown in Fig. 7. The change in activation energy is very slow in the composition range of 10 to 75 mol% Mn_3O_4, thereafter it rises rather sharply to 0.45 eV, the maximum value, corresponding to 90 mol% Mn_3O_4. This activation energy w is probably the activation energy for the "hopping" from a cation M^{n+} to $M^{(n+1)+}$. M is manganese in this case. This activation energy is for the mobility of the cations. α_T, the temperature coefficient of resistivity (TCR) is given by

$$\alpha_T = \frac{1}{\rho}\frac{d\rho}{dT} = -\frac{B}{T^2} \qquad (1)$$

where B is a material constant. The constant B is equal to w/k in the expression $\rho = \rho_0 \exp(w/kT)$ and it has the dimension of K. The slope of the plot of $\ln \rho$ against $1/T$ is equal to $w/k = B$, knowing B, α_T can be calculated.

The variation of α_T as a function of composition is shown in the Fig. 8. The variation of α_T with composition is similar in nature to that

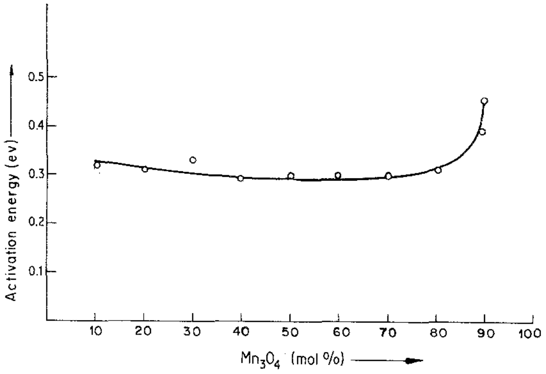

Figure 7 Variation of activation energy as a function of the composition of NiO–Mn_3O_4 system.

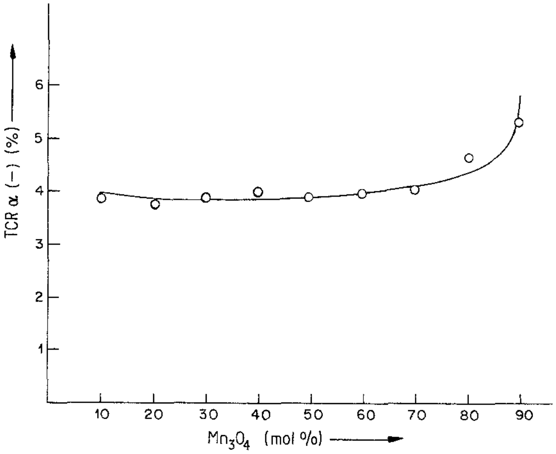

Figure 8 Variation of the temperature coefficient of resistance as a function of composition of NiO–Mn_3O_4 system.

of activation energy with the composition. The change is very slow in the composition range of 10 to 75 mol% Mn_3O_4, and thereafter it rises to the maximum value of −5.8% rather sharply, corresponding to 90 mol% Mn_3O_4. The composition range of 75 to 90 mol% Mn_3O_4 is more sensitive to the variation of temperature and should be more suitable for thermistor application.

3.5. I–V characteristics and the bias voltage (V_B)

For a thermistor application, α_T is desired to be between −4% to −6%. For the samples having α_T in this range, I–V characteristics were determined. A typical I–V characteristic is shown in Fig. 9. Up to the peak voltage of 358 V, the plot is linear, with the increase in current the voltage increases, thereafter the plot becomes nonlinear, with the increase in the current the voltage decreases. Bias voltage, V_B, is taken to be 60% of the peak voltage, V_P, because of the perfect linearity of the I–V plot in this range. For the particular sample in question (90 mol% Mn_3O_4) the bias voltage is 215 V and is the maximum value found in the present investigation. The variation of bias voltage as a function of composition is shown in the Fig. 10. The bias voltage decreases linearly from the maximum value of 215 V corresponding to 90 mol% Mn_3O_4 to about 50 V corresponding to 50 mol% Mn_3O_4. In thermistor applications it is desirable to apply as large a biasing voltage as possible, since the signal to noise ratio is protional to the bias voltage [3]. The limiting noise of a thermistor is the Johnson noise of its resistance. For a bias voltage, 0.6 V_P, current noise is small compared to Johnson noise. The noise of the thermistor is determined by its resistance while the signal is a function of the resistance and the bias voltage [3]. From Fig. 10, it becomes obvious that the sample with 90 mol% Mn_3O_4 is the most suitable for thermistor application, as indicated by α_T in Fig. 8. It is this composition which has the maximum resistivity at room temperature as shown in the Fig. 2.

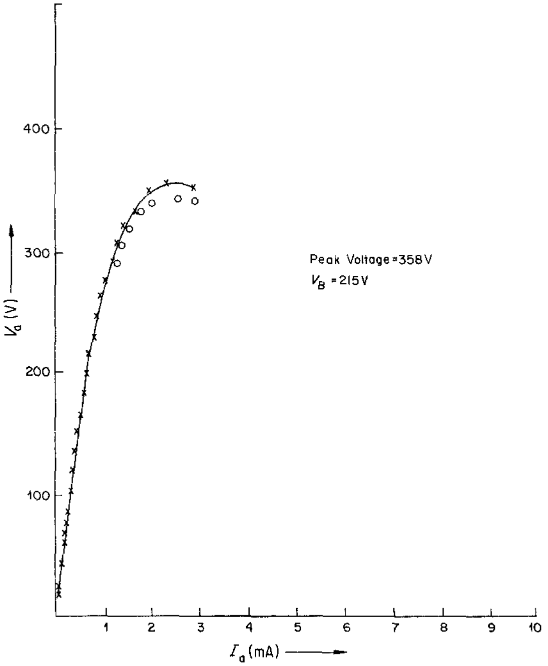

Figure 9 I–V characteristic for a given composition in the $NiO–Mn_3O_4$ system.

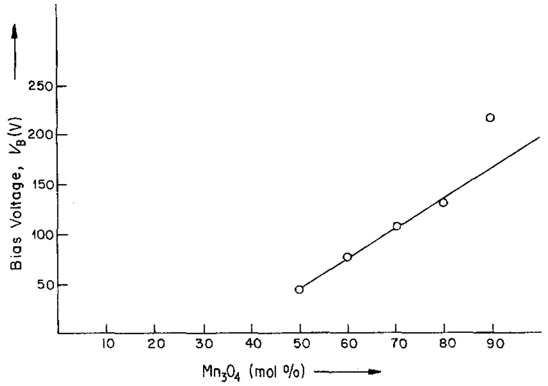

Figure 10 Variation of bias voltage as a function of composition of the $NiO–Mn_3O_4$ system.

3.6. Time constant, τ

It is another characteristic of a thermistor and is a measure of the minimum time required by the thermistor to pick up a given signal. The time constants for the samples satisfying the TCR requirement as mentioned earlier were calculated using the relation

$$\tau = \frac{C}{G} \tag{2}$$

where C is the heat capacity.

$$G = \text{dissipation constant} = \frac{W_m}{T_m - T_A}$$

$$T_A = \text{ambient temperature}, \; W_m = V_m I_m$$

and $V_m = V_P$ in the I–V plot, I_m is the maximum current in the I–V plot.

$$T_m = \frac{B}{2}\left[1 - \left(1 - \frac{4T_A}{B}\right)^{1/2}\right] \tag{3}$$

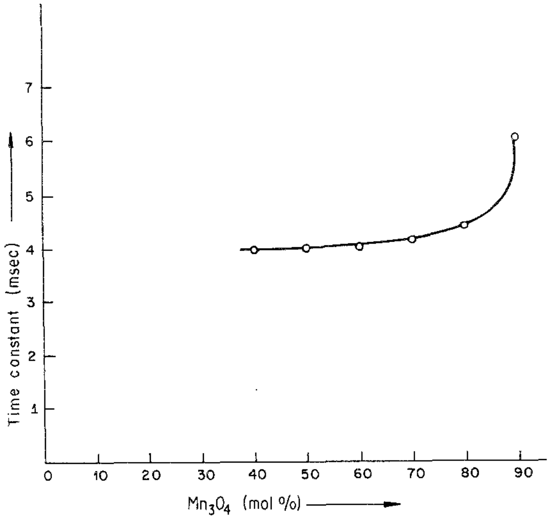

Figure 11 Variation of time constant as a function of composition of the NiO–Mn_3O_4 system.

where $B = w/k$, as already discussed in connection with α_T.

The variation of the time constant, τ, as a function of composition is shown in Fig. 11. The composition corresponding to 90 mol% Mn_3O_4 has the maximum time constant of 6 msec and then decreases sharply to 4.5 msec corresponding to 80 mol% Mn_3O_4 and then further decreases very slowly to 4 msec corresponding to 30 mol% Mn_3O_4. From this plot even though the 90 mol% Mn_3O_4 composition does not appear to be the best, but the variation in the time constant being so small, it is still this composition (80 to 90 mol% Mn_3O_4) which appears to be the most suitable for thermistor application.

Some thermistor infrared detectors have been made out of the composition range as given in the present study and successfully tried for the detection of hot spots in the axles of fast moving railway trains.

4. Conclusion

No single phase region for the stoichiometric $NiMn_2O_4$ or $Ni_{1-x}Mn_{2+x}O_4$ has been found to exist. $Ni_{1-x}Mn_{2+x}O_4$ exists with Mn_3O_4, both in the cubic and the tetragonal phase. In the temperature range of 800 to 1300° C, nickel manganite is stable and does not decompose into NiO and Mn_3O_4.

At room temperature it is Mn_3O_4 and not Mn_2O_3 which has been found to be formed. Activation energy, temperature coefficient of resistance, bias voltage, time constant are found to increase with the increase Mn_3O_4 content.

There is a fairly wide range of composition from about 90 mol% Mn_3O_4 to 50 mol% Mn_3O_4 in the system which satisfies the requirements for being used as a thermistor infrared detectors, but it is the composition between 80 to 90 mol% Mn_3O_4 which appears to be the best.

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