Journal of the Indian Institute of Science Vol. 55, No. 2, April 1973

EFFECT OF ADDITION OF GLASS AND SILVER POWDERS IN THERMISTER MATERIALS

D. B. GHARE

(Indian Institute of Science, Bangalore-12, India)

[Revised manscript received: March 21, 1973]

ABSTRACT

Small percentages of glass and silver powders were added to a manganite based thermister material. It was noted that such composites show slightly improved B values for lower room temperature resistivity values. Further, such composites can be sintered at much lower temperatures and hence have obvious technological advantage.

INTRODUCTION

Oxidic semiconductors are generally used as the basic materials in the manufacture of thermisters. The high temperature coefficient of resistence (or the B value) of thermisters is due to the high thermal activation energy for electrical conduction in these materials. But in these materials the energy of activation is a function of the impurity concentration and it decreases with the increasing impurity content^{1,2,3,4,5,6}. Therefore as the resistivity of the material decreases with the increasing impurity content^{1,2,3,4,5,6}. Therefore as the resistivity of the material decreases with the increasing impurity concentration, the temperature coefficient or the B value of the thermisters decreases. The only method to decrease the resistivity without subsequent decrease in the B value is to reduce the thickness and increase the electrode dimension. This however has obvious practical limitation.

An attempt was therefore made to embed a small percentage of fine silver particles within the sintered mass, so that these particles short circuit some of the grains and the effective thickness of the pellets is largely reduced, thus reducing the room temperature resistivity of the material, without affecting its B value. The percentage of silver particles was not increased above 10 per cent because at higher percentages, the silver particles may from continuous parallel paths and thus affect the B values. The results of such attempts are reported in this article.

EXPERIMENTAL DETAILS

A manganite based spinel (nickel manganite) was chosen as the basic moterial for this work because it has high B value (3500), high stability of electrical resistivity and it is also a common basic material used in the manufacture of thermisters. The sintering temperature of this basic material is quite high (1100 °C), and hence if any silver is added and the material sintered at 1100 °C, the silver will melt and can even go into solid solution with the material. This was not intended. A small proportion of glass was therefore added to the compositions, in order to achieve high binding strengths at lower temperatures (800 °C), so that any reaction between the silver and the manganite is minimised. In some compositions only glass powder was added, in order to investigate the effect of addition of glass as the binder material. The glass powder used in this work was obtained by melting a lead glass composition in a platinum crusible and the melt quenched in water and crushed to fine particle size. The chemical composition of the glass in weight per cent is Si O₂ 56 per cent, Pb O 30 per cent, Na₂013 per cent and Al₂O₃ | per cent. The resistivity of such a glass is above 10¹² ohm cm, in the range of temperature, employed for the measurement of P-Tcharacteristics reported in this work. The silver and glass powders were sieved through 200 mesh sieve and only the finer grains were used for the purposes of this work.

Pellets were sintered at 800 °C for four hours and then allowed to cool to room temperature inside the furnance. After cooling, contacts were made by acquadag. The resistance measurements were made on a Philips

AC conductivity bridge and the resistance verses temperature characteristics were measured, using a constant temperature oil bath thermostat. The B values were then calculated using the relationship $\rho = \rho_0 \exp B/T$ where $\rho = \text{resistivity}$ of the material at the temperature T°K, ρ_0 and B are constants and T = Temperature in degrees Kelvin.

RESULTS AND DISCUSSION

In all, twelve different compositions consisting of various proportions of the manganite, glass powder and silver powder were prepared and the data obtained has been described in Table 1 and Figs. 1, 2, 3 & 4.

Since glass is an insulating material one would expect that the increase in the glass content would increase the resistivity of the material. But contrary to this expectation it can be seen from Fig. 1 that the resistivity actually decreases with increase in the glass content for all the compositions with and without silver. This decrease in resistivity can be due to better binding and consequent decrease in the grain to grain contact resistance. This view is supported by the fact that even for pure manganite the resistivity decreased when the material was sintered at higher temperature (Table 1).

It can also be seen from Fig. 3 that the B value (and the temperature co-efficient also) decreases as the glass content increases and for compositions containing only glass and manganite it tends to become constant at a value very much near to the B value of pure manganite sintered at higher temperatures. This indicates that the glass-manganite composites sintered at lower temperatures exhibit same electrical properties as those of the pure manganites sintered at higher temperatures. This can lead to a great technological advantage in the manufacture of thermisters.

SI. No.	Composition					Recietivity	
	Basic material in per cent	Glass in per cent	Silver in per cent	Sintering Temp.	Sintering Time	at R.T. in in ohm cm	В
1	100	-	-	1100°C	4 Hrs.	4750	3550
2	100	-	-	900°C	do	5890	3750
3	95	5	-	800°C	do	10000	3900
4	90	5	5	do	do	4300	3600
5	85	5	10	do	do	3230	3400
6	90	10	-	do	do	6700	3400
7	85	10	5	do	do	3250	3400
8	80	10	10	do	do	2700	3300
9	80	20	_`	do	do	4500	3300
10	75	20	5	do	do	2000	3050
11	70	25	5	do	do	1600	2700
12	65	25	10	do	do	960	2500

TABLE 1



Variation of Resistivity as a function of Glass Content in Various Compositions

When silver is added to the copositions, it can be seen from Fig. 1 and and 2 that the resistivity of the compositions sharply decrease as expected. At a constant glass content the resistivity decreases with increasing silver content, and at a constant silver content the resistivity decreases with increasing glass content. This decrease in the conductivity at constant silver content can only be ascribed to better binding between grains of the manganite.

It can be seen from Fig. 3 that at low glass and silver contents the B value of the material is higher than that of pure manganite or glassmanganite composites. But at higher glass and silver contents the B value sharply decreases. The decrease in B value at higher silver contents may be explained by visualising a paraellel continuous conducting path being provided by silver grains. But this is most unlikely in our copounds because the silver content is kept at a maximum of only 10 per cent. For composition Nos. 4 and 11 the silver content is only 5 per cent but still the B value has sharply fallen to a value of 2700 from 3600 as the glass content increases



FIG. 2

Variation in Resistivity with the Silver Content in Various Compositions

from 5 per cent to 25 per cent. Therefore at a constant silver content, B value decreases with increase in the glass content. It therefore seems that the B value or the energy of activation for electrical conduction is also associated with the grain-grain contacts. An alternative explanation can be that the glass having a higher thermal expansion coefficient shrinks much more than the manganite and hence exerts tremendous binding pressure on the manganite grains. This pressure distorts the energy band structure of the material and hence the energy of activation also changes. The data presented in this article is however not sufficient to draw any justifiable conclusions in this aspect.

CONCLUSIONS

If a small percentage of glass powder is added to the thermister materials, the composites can be sintered at considerably lower temperatures without any sacrifice in their electrical properties. Composites with small amounts of glass and silver exhibit slightly higher B values at same R.T. resistivities, as compared with the pure materials.

D. B. GHARE



33

Variation in B value as A Functson of Resistivity in Different Compositions



. . . .

Triaxial Diagram showing the area covered in this work

ACKNOWLEDGEMENT

The author is thankful to Prof. H. V. Gopalakrishna and Prof. A. R. Vasudevamurthy for their constant encouragement during the course of this development project on thermister materials.

REFERENCES

- 1. Morin, F. J. ... Phys. Rev. 1954, 93, 1199.
- 2. Heikes, R. R. and Johnston, W. D. ...
- 3. Yamashita, J. and Kurosawa, T. ...
- 4. Yamashita, J. and Kurosawa, T. ...
- 5. Larson, E. G., Arnot, R J. and Wickham, D. G., ...
- 6 Ghare, D. B. and Sinha, A. P. B. ...
- J. Chem. Phys. 1957, 26, 582.
- J. Phys. Chem. Solids, 1958, 5, 34.
- J. Phys. Soc. Japan, 1960, 15. 802.
- J. Phys. Chem. Solids, 1962, 23, 1771.
- (Ibids.), 1968, 29, 885.