Active and Passive Elec. Comp., 1993, Vol. 16, pp. 7–18
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Printed in Malaysia

EFFECT OF THE ADDITION OF DIFFERENT METAL OXIDES IN LEAD BOROSILICATE GLASSES ON THE ELECTRICAL CHARACTERISTICS OF SbSn COMPOSITION-BASED THICK-FILM RESISTORS

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(Received January 17, 1992; in final form January 13, 1993)

The paper reports the effect of addition of metal oxides in lead borosilicate glasses on electrical characteristics of SbSn alloy-based thick-film resistors.

The Sb and Sn powder (1:1 by weight) is taken in two quartz tubes separately, vacuum sealed at 10^{-5} Torr and heated in a resistive furnace at 430°C and 630°C respectively. The conventional glass [1] is modified by using different dopants like tungsten oxide, cobalt oxide, lithium oxide, titanium dioxide, venadium pentoxide, chromium oxide, nickel oxide and manganese dioxide. The resistive pastes are formulated with both powders, 5% glass and conventional organic binder. The firing temperature is optimized for eight glasses.

The sheet resistivity varies from 1600 Ω/□ to 40 Ω/□, with negative temperature co-efficient of resistance varying from 2000 ppm/°C to 800 ppm/°C respectively. Material characterization is carried out using the XRD technique. Aging studies of resistors at room temperature over the period of two months indicate that these resistors stabilize within 15–20 days.

INTRODUCTION

Commercially available thick film pastes are costly because of the use of Ruthenium oxide and Ruthenates. In order to get low cost resistive pastes, S.H. Bhide [1] et al and M.R. Kadam [2] et al tried to formulate SnO_2 pastes. Kattimani [3] et al have reported the effect of loading of an SbSn alloy in SnO_2. In all these low-cost pastes, conventional borosilicate glass is used. The TCR is of the order of few thousands ppm/°C.

In the present paper, a study of the effect of addition of metal oxides in lead borosilicate glasses on electrical characteristics (TCR and ρ_s) of SbSn alloy-based thick-film resistors is reported.

EXPERIMENTAL

The Sb and Sn powders are taken in 1:1 proportion by weight and ball milled for 24 hours to get a homogeneous mixture in an acetone medium. The powder is

taken in two quartz tubes separately. The tubes are vacuum sealed at 10^{-5} Torr and heated in a resistive furnace to 430°C and at 630°C, respectively, for 3 hours. After heating the quartz tube is taken out and broken carefully to get the powder, which is ball milled for 24 hours to get a particle size of about 4–5 microns. The SbSn powders at 430°C (I) and 630°C (II) are used throughout the experimentation. The SbSn resistor paste is formulated by having 95% of SbSn powder and 5% glass as the solid phase and ethyl cellulose and butyl carbitol acetate (BCA) as an organic vehicle used as a temporary binder. The paste is prepared keeping the solid-to-liquid ratio 70:30 by weight. The liquid phase consists of 8% ethyl cellulose and 92% BCA.

The properties of the glass control the film properties to a great extent. Here, lead oxide-based borosilicate glass is selected. The composition [4] of the glass is 70% PbO, 18% SiO_2, 9% Al_2O_3 and 3% B_2O_3 by weight. The ingredient oxides used are chemically 99.9% pure. The component oxides are mixed by wet milling in a ball mill using acetone as a medium. Mixing is carried out for nearly one hour to get uniform mixing of all oxides. The cake is dried and transferred into the platinum or nickel crucible and heated with a mixture of cooking LPG gas + O_2. The molten oxide mixture is quickly poured into distilled water in a process called fritting. The glass lumps and frits are powdered in an agate morter pestle and filtered using a fine mesh (140 mesh) to get fine powder. The powder is ball milled in a stainless steel jar with stainless steel balls for 48 hours.

Eleven different glasses are made in addition to the conventional glass as shown in Table I. Fourteen pastes with glasses of set I and 10 pastes from set II are formulated and their electrical characteristics are studied. The thick film resistors are fabricated using the standard technique [2]. The resistors are fired between 450

TABLE I
Composition of various glasses

Ist set of glasses (% composition)					
Glasses	PbO	SiO_2	Al_2O_5	B_2O_3	Metal Oxides
Conventional glass G_{11}	70	18	9	3	—
G_{12}	65	18	9	3	WO_3 - 5%
G_{13}	65	18	9	3	CoO - 5%
G_{14}	65	18	9	3	Li_2O - 5%
G_{15}	65	18	9	3	TiO_2 - 5%
G_{16}	65	18	9	3	V_2O_5 - 5%
G_{17}	65	18	9	3	Cr_2O_3 - 5%
IInd set of glasses (% composition)					
Glasses	PbO	SiO_2	Al_2O_5	B_2O_3	Metal Oxides
G_{21}	64	18	9	3	TiO_2 - 6%
G_{22}	64	18	9	3	WO_3 - 10%
G_{23}	70	18	3	3	TiO_2 - 6%
G_{24}	23.5	18	—	45	NiO - 13.5%
G_{25}	50	10	—	30	MnO_2 - 10%

to 700°C to get good adhesion and stable resistance. At 650°C the TCR and ρ_s is minimum and the adhesion is good as tested by adhesion tape. Therefore, optimized firing temperature is 650°C.

All the resistive pastes are found to have good printability and thixotropic properties. The resistances are measured and the sheet resistivity of each resistor is calculated [3]. TCR measurement is carried out in the range of 30°C to 130°C. The temperatures are measured using Cromel Alumel thermocouple with the help of temperature controller. Material characterization is done for all the samples by XRD in the range of 20 = 20° to 100°, keeping all parameters constant. The peaks observed in X-ray spectra of SbSn I and II powders with various glasses are identified for possible chemical composition with standard X-ray diffraction data [5] (d values agreeing with ±0.003 Å). Aging characteristics are studied over the period of two months at room temperature.

RESULTS

For optimization of firing temperature (Fig. 1 and 2), the pastes having the composition of 95% SbSn powder II (630°C) and 5% glasses are used. Here, 95% SbSn powder II is doped with metal oxide WO_3, TiO_2, Cr_2O_3, NiO and MnO_2. The resistors are fired at 450°C. Since the adhesion is found to be poor in this case, firing is carried out at 500°C, 550°C, 600°C, 650°C and 700°C. At 650°C, good adhesion is obtained as tested with Scotch (tixo tape). Also ρ_s and TCR are minimum, so a firing temperature of 650°C is opted throughout the experiment. Graph of TCR and ρ_s versus firing temperature are given in Fig. 1 and 2. After printing and firing at 650°C, the ρ_s and TCR of the 24 samples are measured as given in Table II.

Aging studies for about 2 months (Fig. 3) at room temperature indicate that the resistors stabilize within 15–20 days.

DISCUSSION OF RESULTS

It has been reported [3] that the firing temperature of 650°C for the powder II with G_{11} gives better adhesion, though not minimum ρ_s and TCR. The composition of the paste was 25% SnO_2, 70% SbSn, and 5% glass, and the firing range was 500–750°C. In the present case the optimized temperature is 650°C.

It has also been reported [1] that the optimum firing temperature is 550°C, for 90% SnO_2 doped by 5% Sb and 5% glass in the range of 450°C to 600°C. M.R. Kadam et al have reported [2] the optimum firing temperatures of 725°C, for the pastes having composition of 45% $SnCl_2$, 45% SnO_2, 5% Sb, and 5% glass in the range of 550–775°C.

In the above two cases, functional material has reacted with the glass, which is obvious from the peaks of $PbSnO_2$ obtained in XRD. In the present case, SbSn and glass are the only functional materials. In conclusion, it could be said that

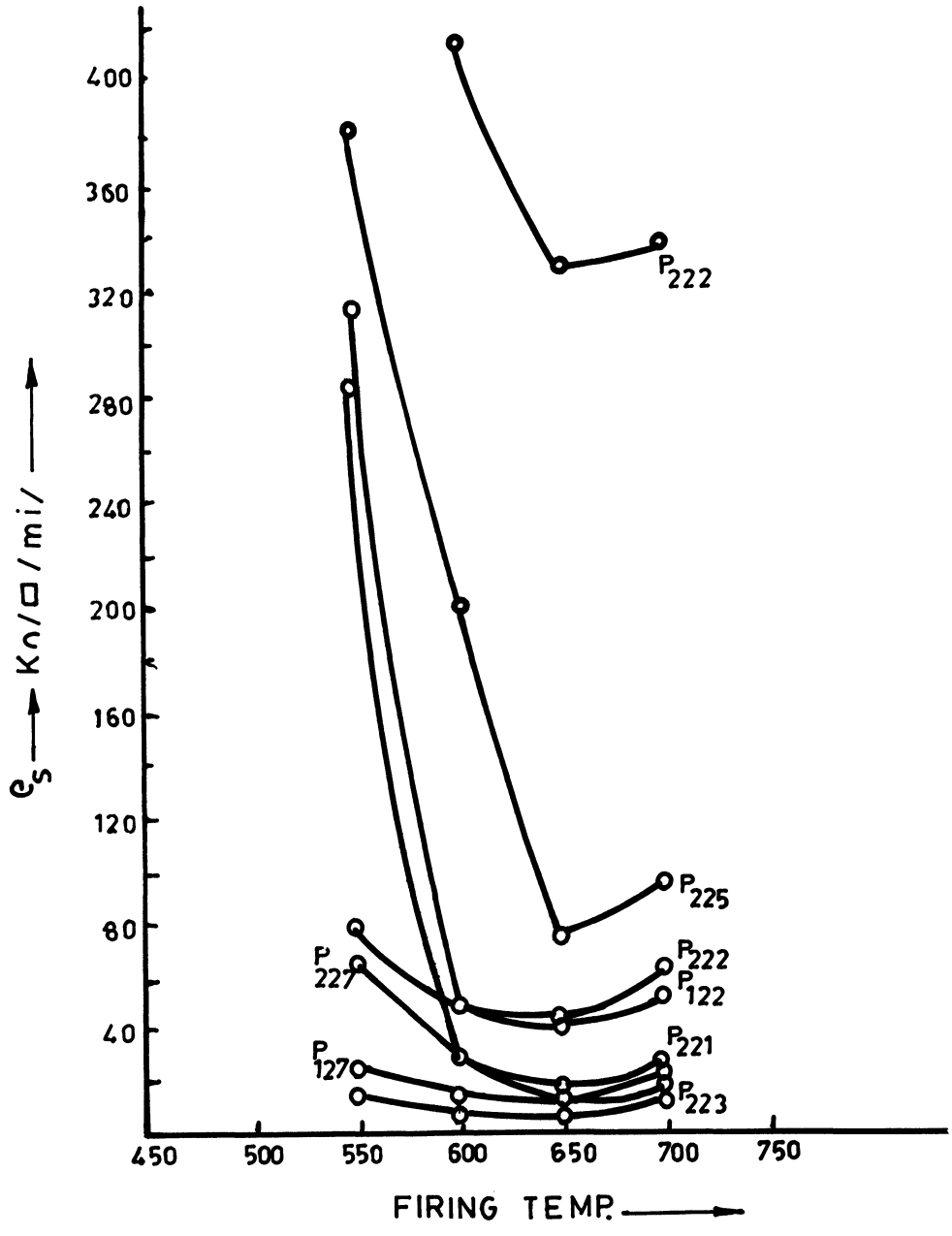

FIGURE 1 Variation of ρ_s with firing temperature.

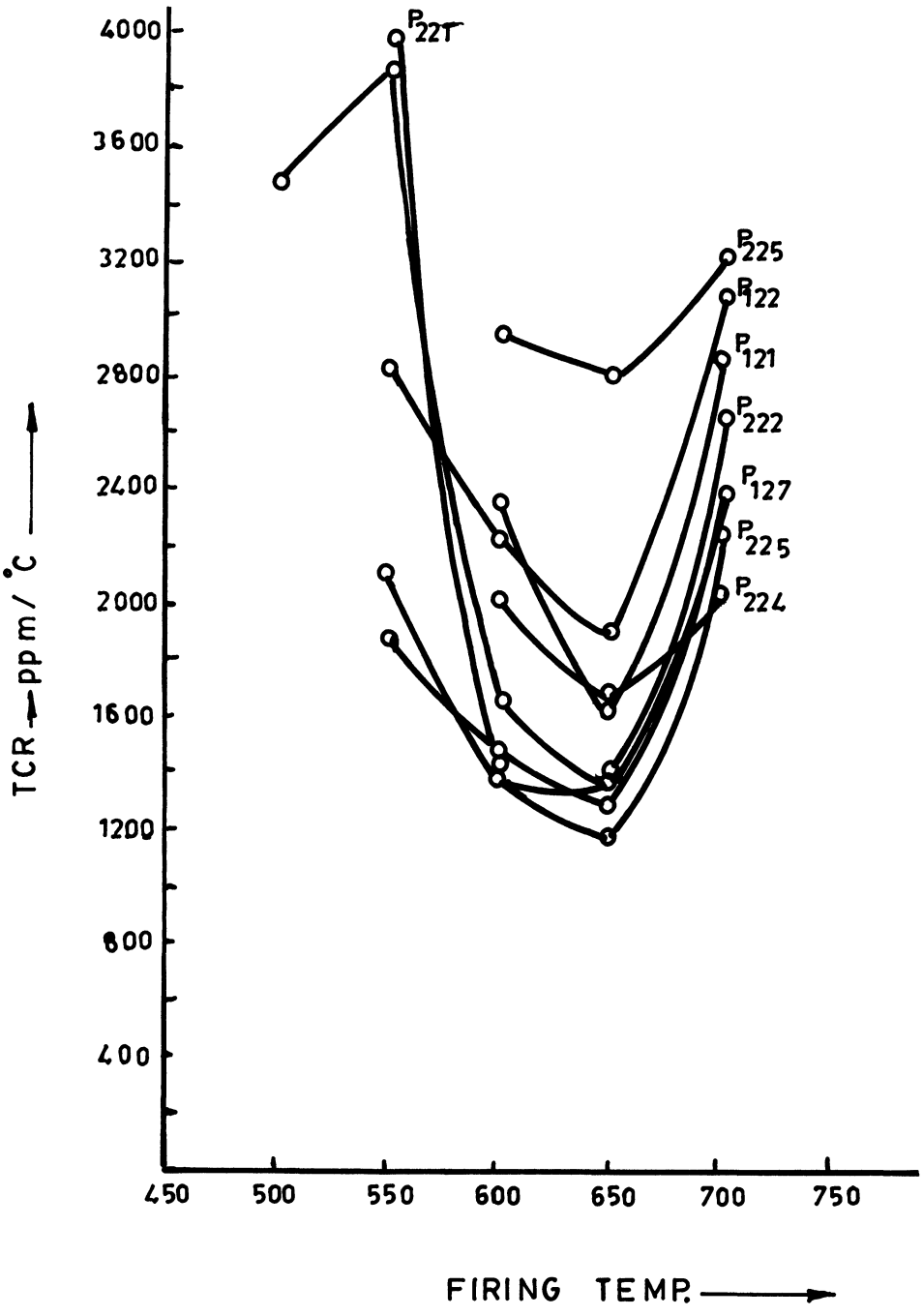

FIGURE 2 Variation of TCR with firing temperature.

TABLE II
Optimisation of firing temperature of 95% SbSn (II) with various glasses (5%)

Firing Temp °C	5% g c G_{11}		5% g with G_{22}		5% g with G_{23}		5% g with G_{21}		5% g with G_{12}		5% g with G_{17}		5% g with G_{24}		5% g with G_{25}	
	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s	TCR	ρ_s
550	—	—	3895	312	2108	14	3975	282	2824	78	1819	25	4934	65	5458	381
600	2151	413	1568	48	1395	6	1489	21	2236	48	1478	13	2007	28	2944	200
650	1610	3285	1390	43	1187	6	1345	19	1881	40	1284	13	1669	15	2809	15
700	2852	337	2663	63	2645	10	2395	27	3073	52	2244	16	2320	20	3223	94

TCR values are in ppm/°C
ρ_s values are in KΩ/□/mil

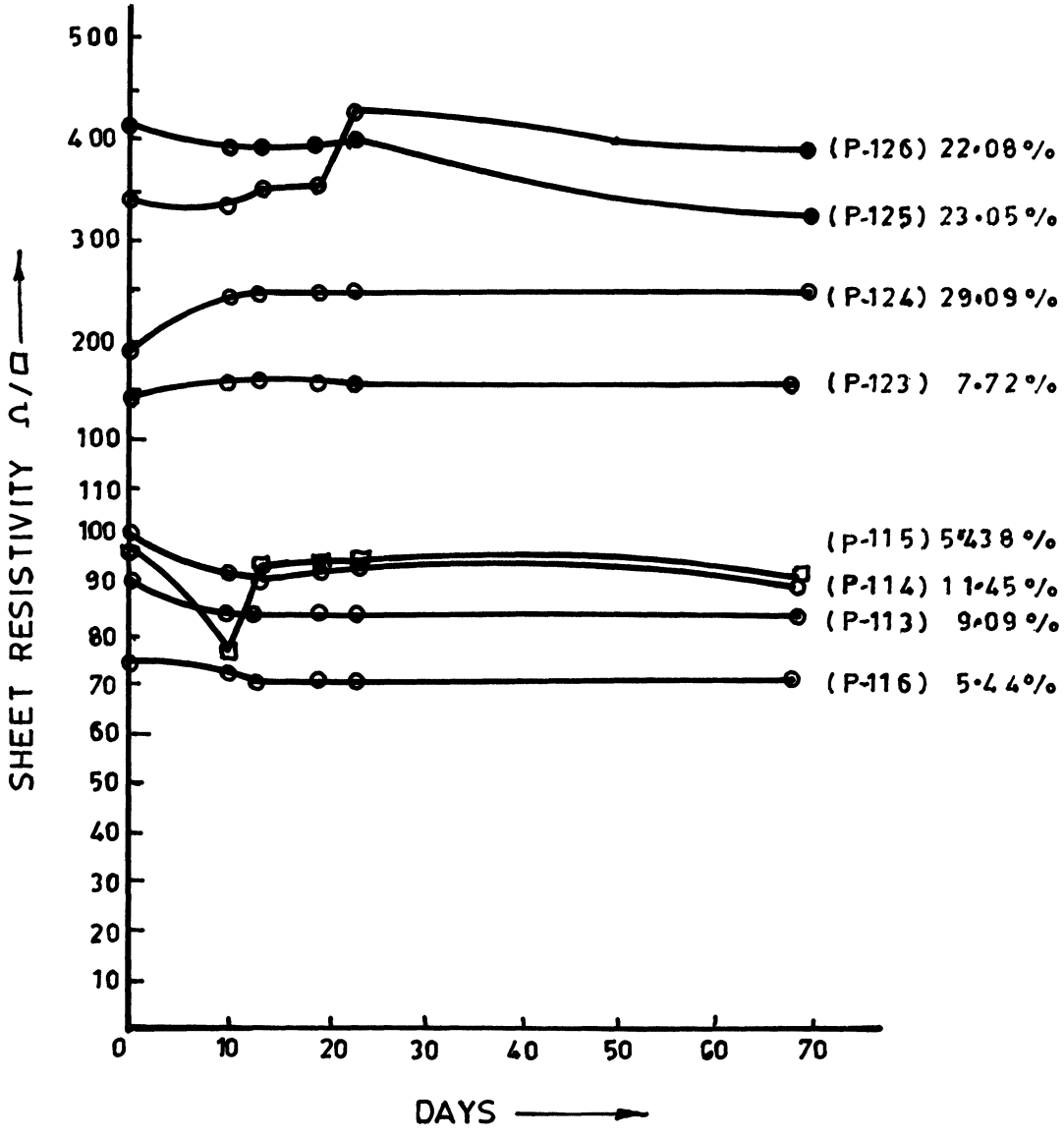

FIGURE 3 Aging characteristics.

functional material plays an important role in determining the optimized firing temperature even if the same glass is used.

Table III shows that glass is playing an important role in determining the ρ_s and TCR of the thick film resistors, though glass is not reacting with the functional material. When glasses are doped with 5% metal oxide as a replacement of PbO, which is the base material for the glass, it affects ρ_s and TCR. For SbSn powder no. II, the trend of ρ_s and TCR for the same glasses is towards the higher side.

TABLE III
Average TCR sheet resistivity of various samples (95% SbSn alloy powder + 5% various glasses)

Ist set					
	SbSn Powder I			SbSn Powder II	
Name of the sample	TCR ppm/°C	Ω/□/mil	Name of the sample	TCR ppm/°C	Ω/□/mil
P_{111}	1413.2 ± 316	265± 12	P_{121}	1703.5 ± 57	849 ± 376
P_{112}	843.3 ± 82	435.2 ± 16	P_{122}	852.4 ± 8	423 ± 197
P_{113}	1153.5 ± 17	91.3 ± 20	P_{123}	1161.0 ± 17	141 ± 25
P_{114}	1208.5 ± 96	101.4 ± 21	P_{124}	1395.3 ± 50	186 ± 27
P_{115}	1153.9 ± 21	98.7 ± 22	P_{125}	1564.1 ± 15	419 ± 88
P_{116}	1025.5 ± 75	74.8 ± 14	P_{126}	1362.9 ± 34	340 ± 70
P_{117}	3267	1624	P_{127}	1513.4 ± 19	171 ± 34
IInd set					
	SbSn Powder I			SbSn Powder II	
Name of the sample	TCR ppm/°C	Ω/□/mil	Name of the sample	TCR ppm/°C	Ω/□/mil
P_{211}	1678.7 ± 178	212.5 ± 41	P_{221}	2055.71 ± 119	275 ± 65
P_{212}	1424.5 ± 189	243.5 ± 29	P_{222}	1243.61 ± 229	393.29 ± 160
P_{213}	1058.3 ± 128	560.0 ± 114	P_{223}	1207.41 ± 122.8	402.78 ± 130
P_{214}	907.2 ± 28	290.1 ± 101	P_{224}	1444.1 ± 146.	607.6 ± 202
P_{215}	1772.8 ± 68	333.1 ± 57	P_{225}	2845.4	1667

This can be explained with the help of XRD patterns of the pastes in set I. For powder II, conduction is dominated by SnO. One of the reasons for having the lower resistivity for first SbSn powder is the decreasing trend of Sb_2O_5 intensities. Zero intensities in XRD patterns can be attributed to the distructive interference [6].

The possible chemical reactions for the SbSn-based pastes can be explained on the basis of retention of carbon in the thick film resistors. The retention of carbon is observed in XRD patterns, which is not due to the improper firing. The liquid phase of the temporary binder EC and BCA are the long chain compounds. When they are heated up to 650°C, the carbon is retained, which can also be revealed by the thermogravimetric analysis of the pastes. The TGA shows the actual loss to be less than the expected loss [7]. The XRD of the alloys show the dominant phase of Sb_2O_5 (100%) intensity. The retention of carbon supports the reduction of SnO_2 when subjected to the firing cycle.

$$SnO_2 + C \xrightarrow{650°C} SnO + CO \uparrow$$

It is found from the XRD results that during the firing process, part of SbSn gets decomposed into Sb and Sn. Part of Sb gets converted into Sb_2O_3 and Sb_2O_5 and Sn gets converted into SnO and SnO_2. The possible reaction mechanism during the firing cycle can be written as

$$SbSn \xrightarrow[\text{in open atmosphere}]{650°C} Sb_x + Sn_x + SbSn_{x-y}$$

$$Sb_2 + O_2 \xrightarrow{O_2} (Sb_2O_3 + Sb_2O_5)_y + Sb_{x-y}$$

$$Sn_x \xrightarrow{O_2} (SnO + Sb_2 + SnO_2)_X + Sn_{x-z}$$

$$2Sb_2O_4 + O_2 \xrightarrow{650°C} 2Sb_2O_5$$

Dominant phases of SnO_2 are shown by the XRD's of SbSn I. SnO_2 is reduced to SnO as explained above. In case of powder II, dominant peaks are of Sb_xO_y. In the process of firing, Sb oxides (Sb_2O_3 and Sb_2O_5) are formed. For SbSn powder I, Sb_2O_5 is showing a sharp decrease with increasing conductivity, which is not that sharp for powder II. This may be the probable reason for increased conductivity for powder I in set I against powder II. Conduction in SbSn powder II is dominated by SnO. For SbSn powder I, conduction is governed by free Sb and SnO (Figure 4 and 5).

In conclusion, one can say that even if dopant metal oxides are of a lower proportion (0.25%) in the total solid, it affects both the resistivity and TCR of the pastes.

Aging characteristics (Fig. 3) show that resistors having a low value of sheet resistivity stabilize very soon. The percentage of aging ranges from 8 to 11% in the case of SbSn powder no. I. In the case of powder no. II, resistors having a low value of sheet resistivity stabilize within 10 days. The resistors having a high value of sheet resistivity stabilize within 22 days. The percentage of aging in this case

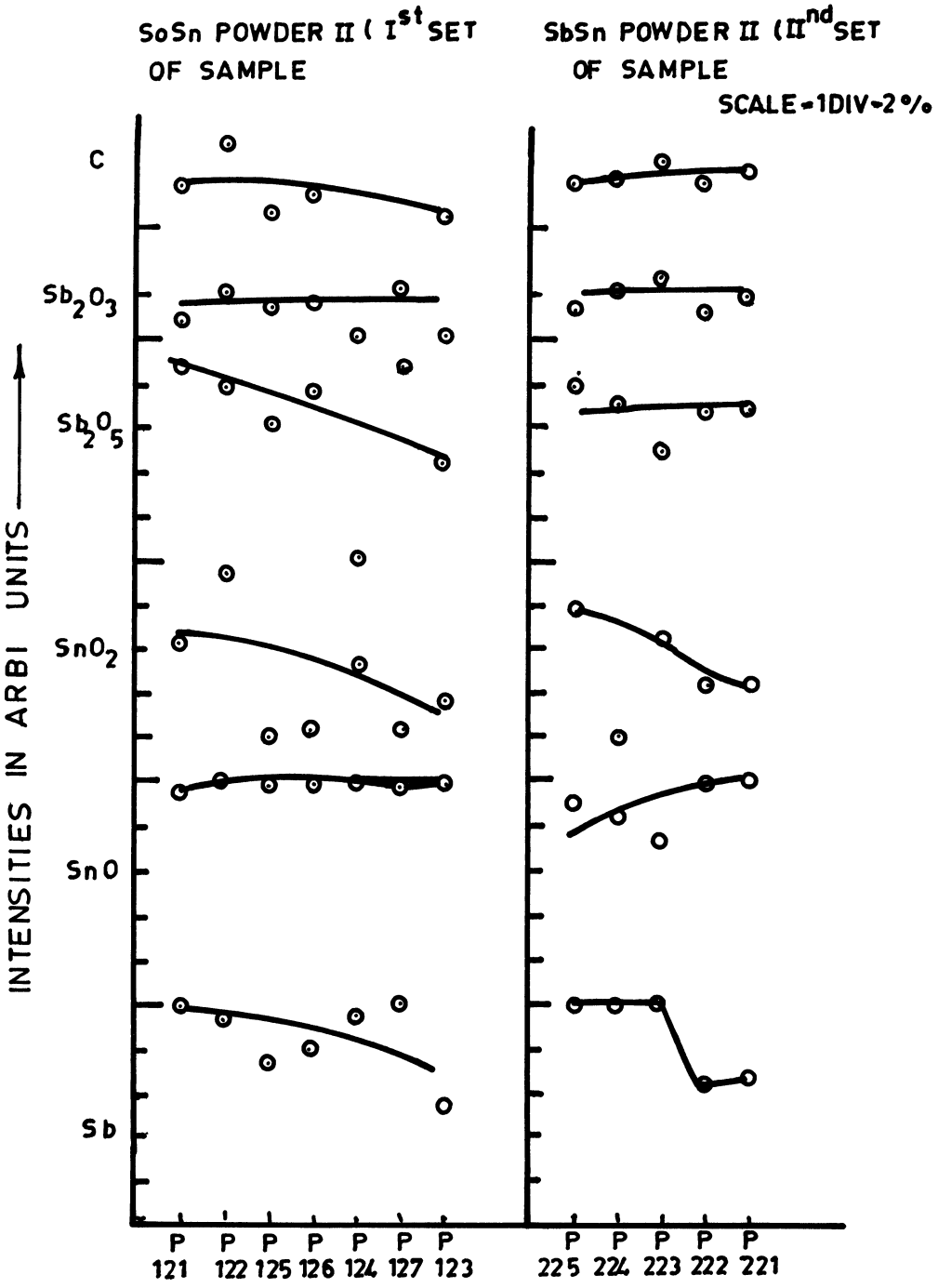

FIGURE 4 XRD intensities of SbSn powder [I and II].

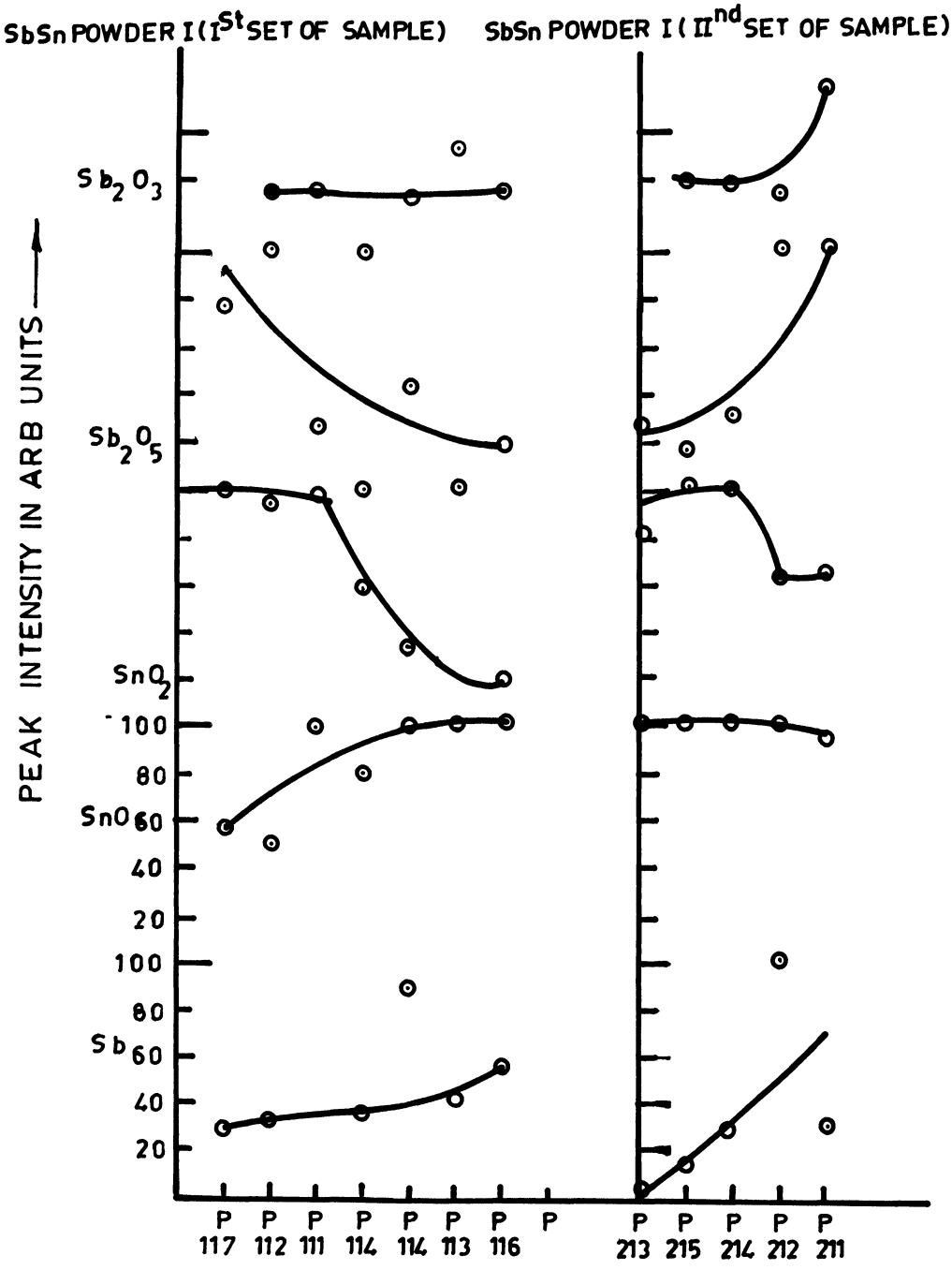

FIGURE 5 XRD intensities of SbSn powder [I and II].

ranges from 7 to 30%. This is less than previously reported for low values and matches well for higher values [2].

CONCLUSIONS

Commercially available thick-film pastes use ruthenium oxide and ruthenates as a functional material. The functional material is very costly and its availability in the market is uncertain. The pastes available in the market have sheet resistivities of 10Ω/□ to 10MΩ/□ with TCR of ±250 ppm/°C. Although TCR is a little higher in the present paste, it can be improved by varying the percentage of metal oxides present in the glass. By this, various values of TCR and ρ_s can be achieved. Although the metal oxide in the glass is very low (0.25%), it affects both the resistivity and TCR of the pastes. The lowest value of ρ_s and TCR obtained for SbSn powder I when glass is doped with V_2O_5 is 74 Ω/□ mil and 1000 ppm/°C, respectively.

The minimum TCR of 850 ppm/°C is obtained for SbSn powder II when glass is doped with WO_3. This is very much lower compared to the previously reported values [1, 2, 3]. If the same composition is loaded with glass containing WO_3, a much lower TCR can be obtained. Resistivity can be made lower by addition of Ag, as reported by M.R. Kadam [8] and S.H. Bhide [1].

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