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NEW MATERIALS FOR THICK-FILM ELECTRONICS

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ABSTRACT

Certain ceramic compounds such as rare-earth perovskites and transition-metal diborides that exhibit metallic conductivity are readily available or can be easily synthesized. Some are stable in air at firing temperatures typical of hybrid-circuit processing. The work described is part of an exploratory program to determine whether these materials can be used as low-cost alternatives to precious metals for thick-film conductor and low-resistor inks or as substitutes for copper in nitrogen-fireable compositions.

1. INTRODUCTION

Hybrid-circuit technology is responsible for much of the miniaturization of consumer and military electronic devices. The advantages of the hybrid approach include high functional density (i.e., more components on a smaller board), automated manufacturing, and improved performance.

A typical hybrid circuit is shown in Fig. 1.1. The circuit conductors are made by screen printing a conductive thick-film ink onto a ceramic substrate. After the conductors are fired in a belt furnace, additional components such as resistors and capacitors are screen printed and fired on. Then, discrete components such as semiconductor devices are attached to the substrate and connected to the circuit lines by soldering or wire bonding. For high-volume devices, the entire process from printing and firing to assembly and testing can be automated.

Commercial thick-film materials fall into three categories.

1. Conductors are generally based on precious-metal systems so they can be fired in air without oxidizing. Commonly used formulations include gold, gold-palladium, gold-platinum, and silver-palladium. Lower cost materials are available, in which copper is substituted for the precious metal; however, these materials must be fired in nitrogen to prevent the copper from oxidizing.

2. Resistors include compositions based on ruthenium oxide, silver-palladium, lanthanum hexaboride, and tin oxide. The first two compositions are air fired for use with conventional gold circuits, whereas the latter two are nitrogen fired for use with copper.

3. Dielectrics include materials for printed capacitors, crossover insulators (for multilayer circuits), and encapsulants.

The current size of the U.S./Canadian thick-film market is $170 million annually, which accounts for more than half the total world market (B. Moody & Associates, Wilmington, Delaware, personal communication to B. S. Hoffheins, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1990). Real dollar growth from 1989 to 1990 was expected to be 7% in both domestic and world markets. Precious metals account for three-fourths of this market. Silver-palladium is commonly used for conductors in commercial hybrids, whereas military hybrids have traditionally used gold—primarily to avoid silver migration in hostile environments (Moody 1989). Because of the high cost of precious metals, the hybrid-circuit industry has devoted much effort to the search for alternative thick-film conductors. However, significant technical difficulties exist with many possible substitute materials. Copper conductors must be fired in an inert atmosphere, making it difficult to remove the organic binders and increasing firing costs. Nevertheless, manufacturers in Asian markets have committed to the use of copper, and U.S. military hybrids now reflect increasing use of copper conductors where maximum reliability is not an issue (Moody 1989). Completely new thick-film systems had to be developed for use with copper conductors because most resistor and dielectric compositions were developed for compatibility with air-firing (gold) conductors and are

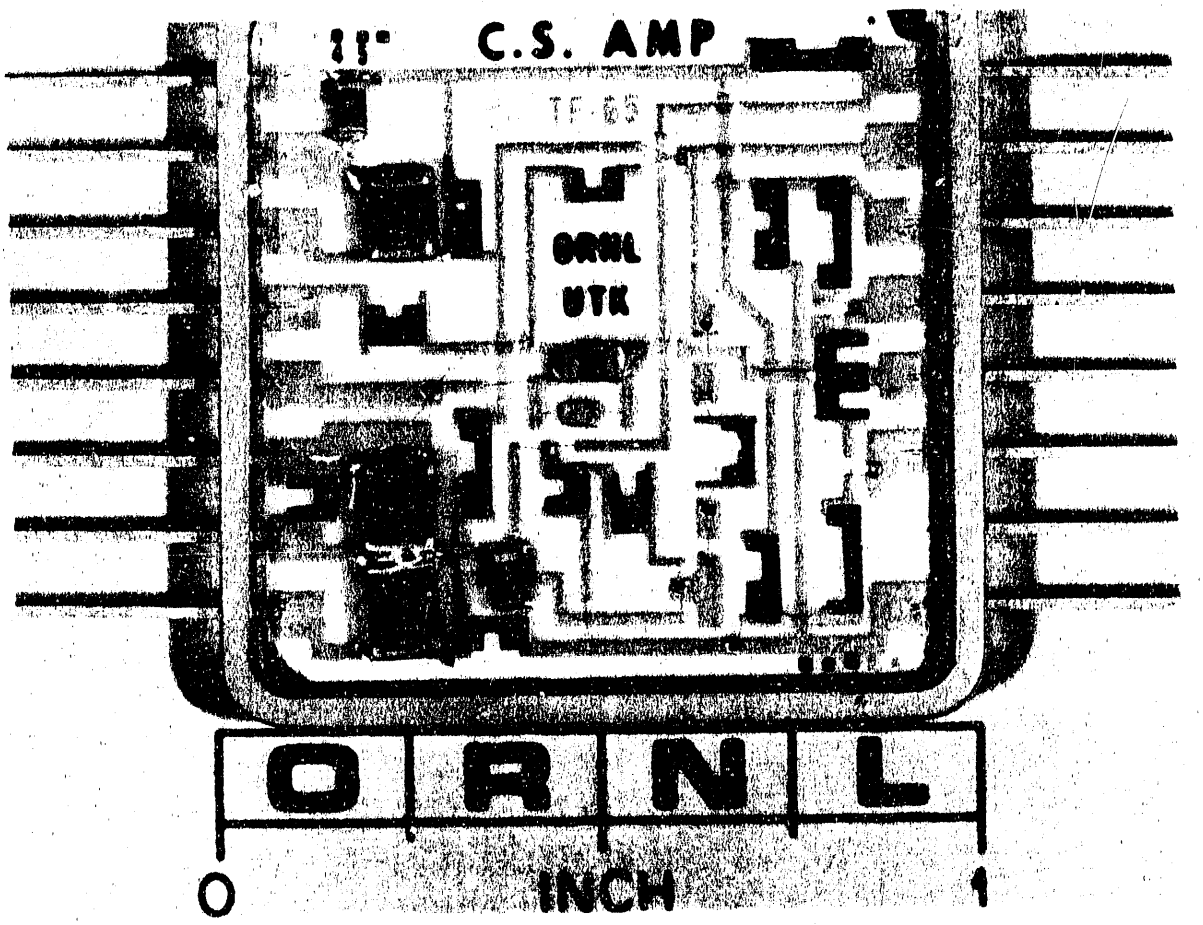


Fig. 1.1. A typical hybrid circuit designed, produced, and packaged at Oak Ridge National Laboratory's hybrid laboratory. Visible in the photo are conductor paths (gold), thick-film resistors (black), chip capacitors (tan), and wire-bonded semiconductor devices (small black squares). Notches in the resistors were made to trim the resistors to specified values. Barely visible are crossover dielectrics (arrow).

not suitable for nitrogen firing. The development of these nitrogen-fired resistors and dielectrics has been slow and costly but now these systems are more readily accepted (Moody 1989). Although the cost of silver-palladium conductors can be reduced by increasing the silver:palladium ratio this increase can lead to silver migration, greater environmental sensitivity, and higher packaging costs.

Certain families of oxide ceramics exhibit metallic conductivity (Vest and Honig 1974). In particular, some rare-earth perovskite compounds such as $La_{.8}Sr_{.2}CrO_3$ exhibit high conductivity because of the overlap of electron orbitals (Table 1.1). Figure 1.2 shows the resistivities for several of these compounds, the best of which are well within the range needed for a practical circuit. They can be synthesized easily from relatively low cost raw materials. Another inexpensive group of materials is the refractory borides. Some borides have been tested as components of thick-film inks and at least one, LaB_6, has been incorporated in a copper-compatible resistor ink, which is fired in nitrogen (Du Pont 1988).

In this study, several examples of these kinds of materials were examined for suitability in thick-film inks. Originally, the project goal was to investigate low-cost alternatives for precious-metal–based conductors and resistor inks. A prospective conductor material should have a sheet resistance of 10 to 70 mΩ/square, and a low-value resistor material should have a sheet resistance of 1 to 100 Ω/square (E. Conrad, Ferro Corp., Santa Barbara, California, personal communication to R. J. Lauf, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1987). We had hoped that some materials might adequately replace palladium in multilayer capacitors.

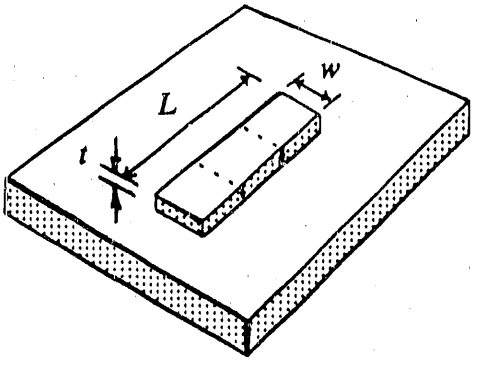
Our research addressed several issues: (1) synthesis or preparation of selected conductive phases, (2) scoping studies to determine compatibility with candidate frit systems, and (3) limited tests of actual screen-printable thick-film formulations.

Table 1.1 Electrical characteristics of selected conductive oxide ceramics

Compound	Room temperature conductivity(σ) $(\Omega\cdot cm)^{-1}$	Calculated minimum sheet resistivity (ρ_s) (Ω/sq)	Reference[a]
$La_{.84}Sr_{.16}MnO_3$	25.6[b]	1.5	1
	190[c]	0.2	1
$La_{.7}Ca_{.3}CoO_3$	1000	0.4	2
$La_{.6}Sr_{.4}CrO_3$	10	3.9	3
$Y_{.85}Ca_{.15}CrO_3$	0.33	120	4
$SrCrO_3$	10^5	0.0004	5
$SrRuO_3$	1000	0.04	5
$SrFeO_3$	500	0.08	5
$La_{.95}Sr_{.05}CoO_3$	50	0.8	5
$La_{.8}Sr_{.2}CrO_3$	25	1.6	5
$La_{.8}Ca_{.2}MnO_3$	20	2.0	6
$YBa_2Cu_3O_x$	1400	0.03	7
$La_{.6}Sr_{.4}VO_3$	2500	0.02	8
$La_{.8}Ba_{.2}VO_3$	100	0.4	8
$Gd_{.5}Sr_{.5}VO_3$	32	12	8

[a,b,c]See footnotes on next page.

Note: Resistance R is given by $R = \rho L/A$, where L is the specimen length and A is the cross-sectional area. By expressing the resistance as $R = \rho L/tw$, one defines sheet resistivity $\rho_s = \rho/t$; then $R = \rho_s(L/w)$. The dimensionless aspect ratio L/w is expressed as that number of squares, and ρ_s is expressed as ohms per square. In the table, we assumed a fired thickness $t = 0.0254$ cm.



[a]*Sources:*

1. M. Kertesz et al., "Structure and Electrical Conductivity of $La_{0.84}Sr_{0.16}MnO_3$," *J. Solid State Chem.* **42**, 125–29 (1982).
2. I. F. Kononyuk et al., "Preparation and Properties of $La_{1-x}Ca_xCoO_3$ ($0.2 \leq x \leq 0.6$), *J. Solid State Chem.* **48**, 209–14 (1983).
3. D. P. Karim and A. T. Aldred, "Localized Level Hopping Transport in $La(Sr)CrO_3$," *Phy. Rev. B* **20**(6), 2255–63 (1979).
4. W. J. Weber, C. W. Griffin, and J. L. Bates, "Electrical and Thermal Transport Properties of the $Y_{1-x}M_xCrO_3$ System," *J Mater. Res.* **1**(5), 675–83, 1986.
5. R. W. Vest and J. M. Honig, "Highly Conducting Ceramics and the Conductor-Insulator Transition," pp. 343–453 in *Electrical Conductivity in Ceramics and Glass,* Part B, ed. N. M. Tallan, Marcel Dekker, Inc., New York, 1974.
6. J. Tanaka et al., "Electrical Conduction of $(La_{0.8}Ca_{0.2})MnO_3$ with Homogeneous Ionic Distribution," Phys. Status Solidi. **A80**, 621–30, 1983.
7. R. K. Williams, Oak Ridge National Laboratory, personal communication to R. J. Lauf, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1987.
8. P. Dougier and A. Casalot, "Sur Quelques Nouvelles Series de Composes Oxygenes du Vanadium et des Lanthanides de Structure Perovskite," *J. Solid State Chem.* **2**, 396–403 (1970).

[b]Measured on sample 80% dense.

[c]Calculated for sample 100% dense.

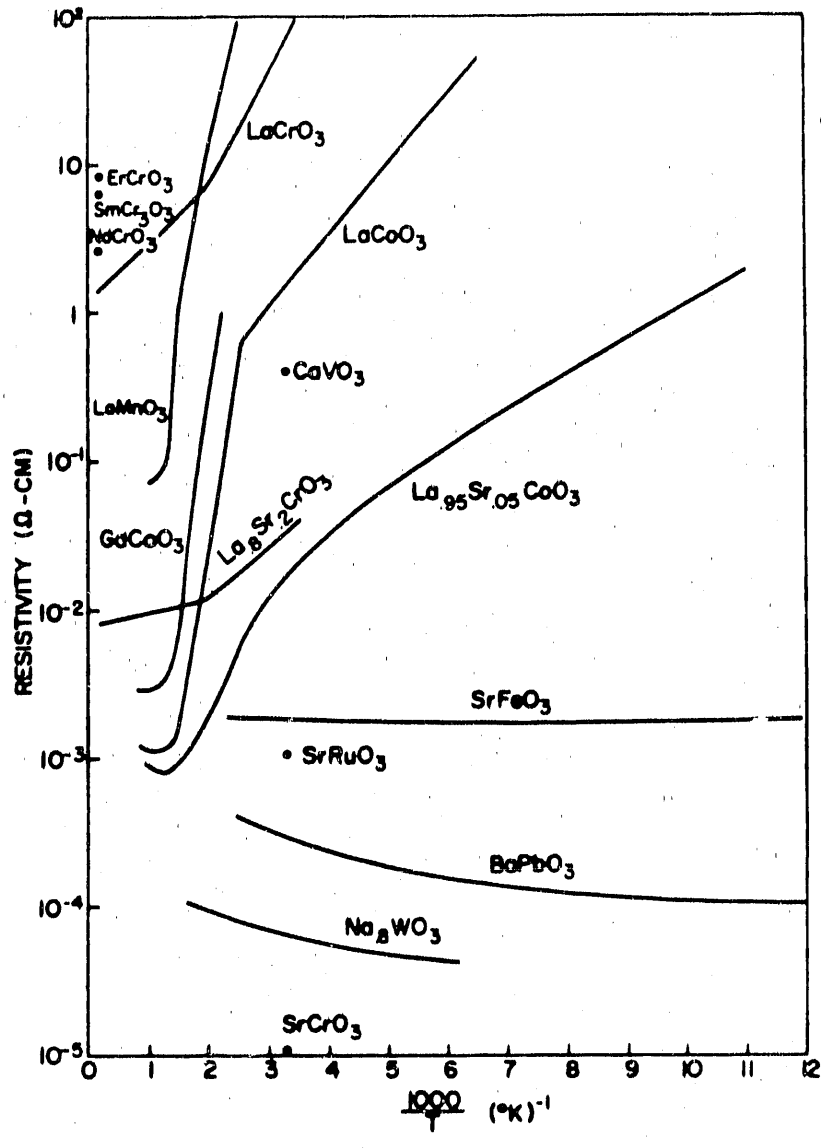


Fig. 1.2. Electrical characteristics of selected conductive oxide ceramics. *Source*: Based on data from R. W. Vest and J. M. Honig, "Highly Conducting, Ceramics and the Conductor-Insulator Transition," pp. 343–453 in *Electrical Conductivity in Ceramics and Glass*, Part B, ed. N. M. Tallan, Marcel Dekker, Inc., 1974.

2. EXPERIMENTAL

2.1 SYNTHESIS OF CONDUCTIVE PHASES

2.1.1 Perovskite Structure

Two compounds were selected for initial tests: $SrFeO_3$ and $La_{.6}Sr_{.4}VO_3$. Interestingly, $SrFeO_3$ attains its highest conductivity when fired at high oxygen pressures (MacChesney, Sherwood, and Potter 1965). Conversely, $La_{.6}Sr_{.4}VO_3$ cannot be synthesized in air, because of the high stability of La_2O_3; therefore, it must be fired in an inert or reducing atmosphere (Reuter and Wollnik 1963).

A third oxide, $La_{1.85}Ba_{.15}CuO_4$, can be synthesized and processed in air. This compound is one of a family of superconducting oxides with the K_2NiF_4 structure originally described by Balz and Plieth (1955). The structure consists of alternating rock salt (AO) and perovskite (ABO_3) layers with separation between layers almost twice the intraplanar distance between two nearest-neighbor copper ions (Fig. 2.1).

The first compound, $SrFeO_3$, was synthesized by mixing strontium acetate and Fe_2O_3 in the correct proportions and ball milling to achieve intimate blending. The milled powder was pressed into pellets and fired for 2 h at 1200°C in air [Fig. 2.2(*a*)]. The resulting material was black and soft enough to be milled easily into fine powder.

The second compound, $La_{.6}Sr_{.4}VO_3$, was made from lanthanum oxalate, strontium acetate, and vanadium pentoxide (V_2O_5). These powders were blended and milled as before and pressed into pellets. The pellets were fired for 16 h at 1200°C in N_2–4%H_2 for the first 2 h and in vacuum for the other 14 h. Firing turned the pellets black. The measured density was ~2.11 g/cm^3. Even at this low density, the conductivity was quite high (resistivity ~ 0.1 Ω·cm) and the pellets were porous and quite soft; light ball milling created a fine powder.

The third compound, $La_{1.85}Ba_{.15}CuO_4$, was synthesized by thermal denitration. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3) \cdot 2½\ H_2O$ were mixed with a large excess of NH_4NO_3 (6 moles of ammonium nitrate per mole of copper) and dissolved in deionized water. The solution was heated until it was dry with constant stirring to create a homogeneous mixed nitrate. The mixture was fired for 2 h at 1000°C in air, lightly ground, and pressed into pellets. The pellets were then fired for 3 h at 1200°C in air [Fig. 2.2(*b*)]. Densities of these fired pellets were typically 6.3 g/cm^3, and the pellets were metallic copper-brown and had moderate conductivity (resistivity ~ 0.1 Ω·cm) at ambient temperature.

2.1.2 Refractory Borides

Many binary metal borides, particularly transition metal diborides and rare-earth hexaborides are good metallic conductors. Much attention has been devoted to LaB_6 because its low work function and good thermal stability make it suitable as a thermionic electron emitter for such uses as electron microscope sources.

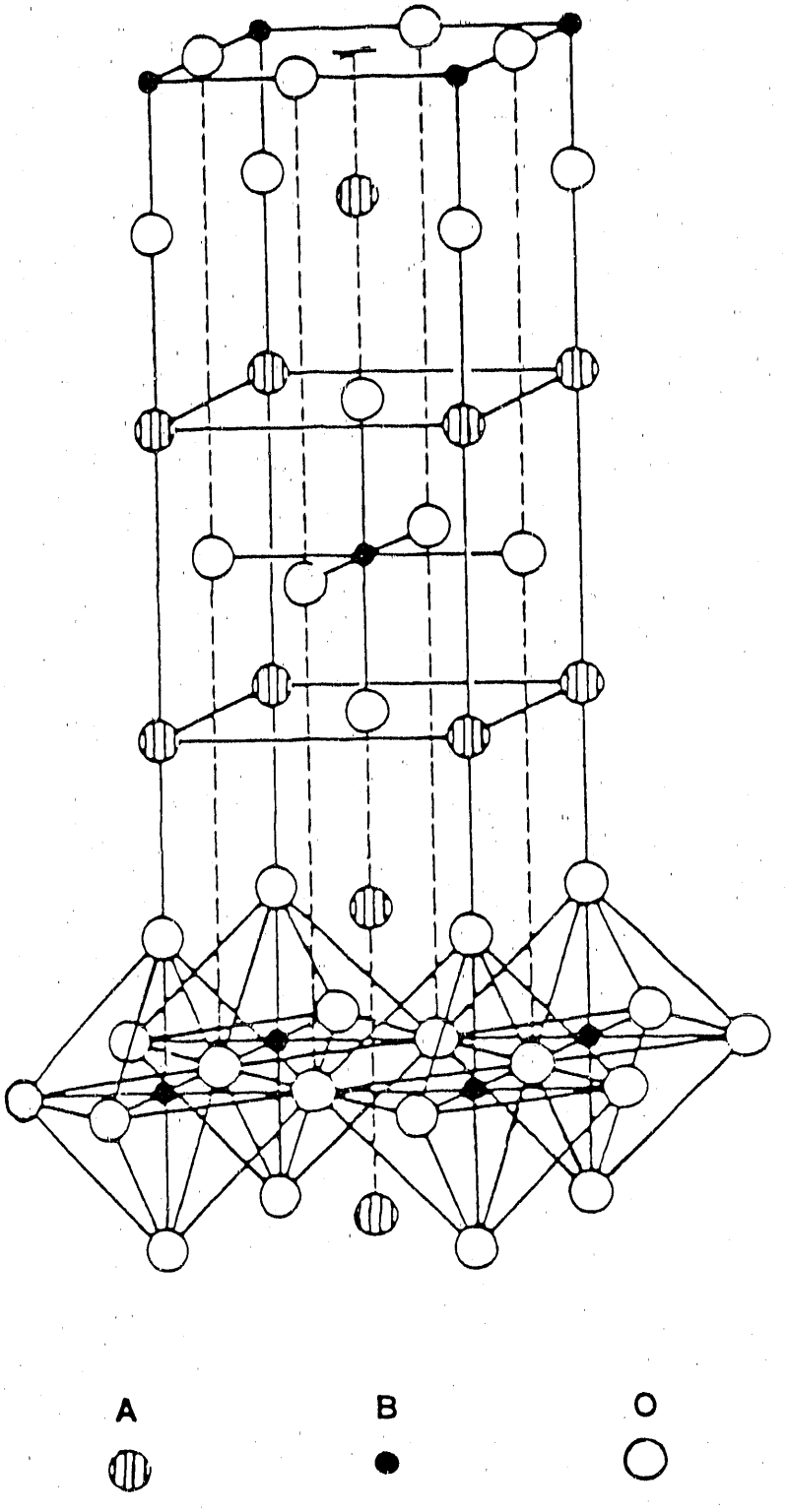
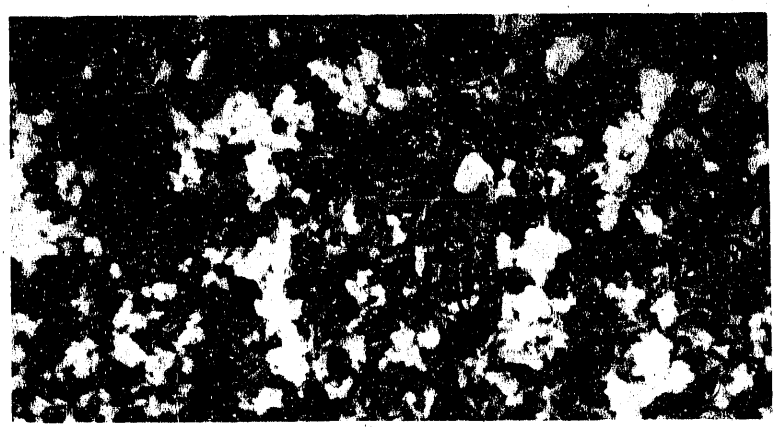


Fig. 2.1. The K_2NiF_4 structure. For $La_{1.85}Ba_{.15}CuO_4$, the A atoms correspond to lanthanum or barium, the B atoms to copper, and the O atoms to oxygen.



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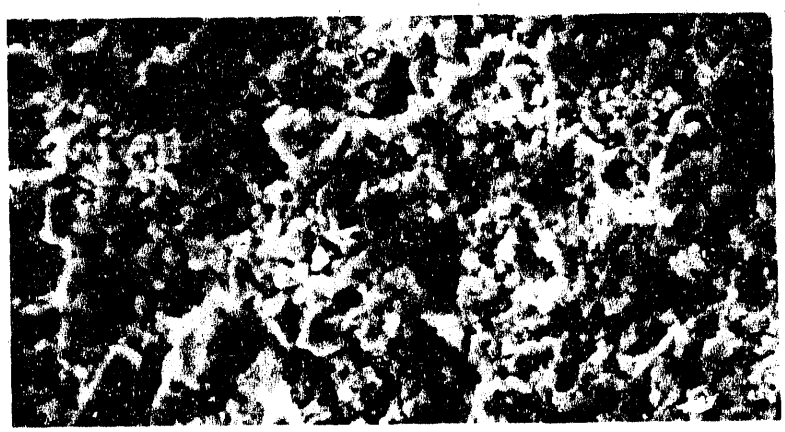
b



c

Fig. 2.2. Pellets pressed from milled powder. (*a*) $SrFeO_3$ at 1000×, (*b*) $La_{.6}Sr_{.4}VO_3$ at 1000×, and (*c*) $La_{1.85}Ba_{.15}CuO_4$ at 1000×. All materials appear to be porous and friable.

Commercial thick-film resistor compositions containing lanthanum hexaboride (LaB_6) as the conductive phase have recently been introduced (Du Pont™ 1988). Because lanthanum is readily oxidized in air, these formulations are limited to nitrogen-fired resistors that are compatible with copper thick-film conductors.

Electrical properties of several metal borides are given in Table 2.1. Note that TiB_2 has one of the lowest resistivities (9–15 mΩ·cm), which compares favorably to that of LaB_6. In addition, the standard free energy of formation of TiO_2 is less negative than that of La_2O_3, so TiB_2 would be more tolerant of traces of oxygen in the firing atmosphere. The cost of TiB_2 is about one-fifth that of LaB_6.

For this study, metal diborides were obtained as fine powders. Figure 2.3 shows the particle size and morphology for some of these powders.

2.2 BULK PROPERTIES OF FRITTED SYSTEMS

2.2.1 Frit Requirements

Glass frits serve to bind the particles of the functional material (conductor, resistor, or dielectric) to each other and to the substrate (Licari and Enlow 1988). They typically comprise 10–15% of the volume of a thick-film paste and are composed of mixed oxide glasses chosen for their electrical properties and compatibility with the selected conductive phase and firing atmosphere. During firing, the frit melts and wets the conductive particles. The mixture fuses to the substrate and solidifies on cooldown to ambient. Some newer conductor pastes do not contain glass because (1) the frit tends to form a nonhomogeneous, insulating layer on the top of the metallization, which interferes with wire bonding and soldering; and (2) the conductive phase can be formulated to adhere chemically to the substrate without the addition of glass. The requirements of screen printing dictate that the glass frit particles be typically <200 mesh.

The glass frit selected for this work, based on vanadium oxide glass (Ferro RM4770-1), can be fired in air or nitrogen. The air-fired frit is a semiconductor, 13 kΩ/sq at room temperature, decreasing to 3 kΩ/sq at 150°C. Nitrogen-fired samples have lower resistivities. This glass was supplied by the manufacturer in the form of large, thin flakes, which we ball milled to a standard -325 mesh.

2.2.2 Pellets

To evaluate the compatibility and bulk electrical properties of various fired compositions and reject unsuitable combinations, many materials were first pressed into pellets and fired either in air, argon–4% hydrogen, or nitrogen. This approach allowed us to identify the most promising candidates before time-consuming ink formulations were attempted. The conductive powders, usually with small amounts of glass frit, were pressed to 138 MPa (20,000 psi) in steel dies. Firing was done in air using a belt furnace or in an inert atmosphere.

Table 2.1. Electrical properties of selected metal borides

Compound	Resistivity $\rho(\mu\Omega\cdot cm)$	Cost ($/kg)[a]
	Diborides	
TiB_2	9–15[b]	115
ZrB_2	7–10[b]	180
HfB_2	10–12[b]	900
VB_2	16–38[b]	250
CrB_2	21–56[b]	200
	Hexaborides	
LaB_6	15[d]–27[c]	700
PrB_6	20[c]	
NdB_6	20[c]	
ThB_6	15[c]	

[a]Approximate cost in 1–5 kg quantities. *Sources*: Catalog, Johnson Matthey, Seabrook, N.H.; and catalog, Atlantic Equipment Engineers, Bergenfield, N.J.

[b]*Source*: Value from Y. B. Paderno and G. V. Samsonov, "Electrical Properties of Hexaborides of Alkaline Earth and Rare Earth Metals and Thorium," *Dokl. Akad. Nauk* SSSR **137**, 646–47 (1960).

[c]*Source*: Data from B. Aronsson, "Borides," *Modern Materials*, Vol. 2, ed. H. Hauser, Academic Press, New York, 1960.

[d]Value obtained by extrapolation to zero porosity. *Source*: Y. B. Paderno et al., "The Electrical Properties of Lanthanum Boride," *Fiz. Met. Metalloved.* **10**, 143–45 (1960).

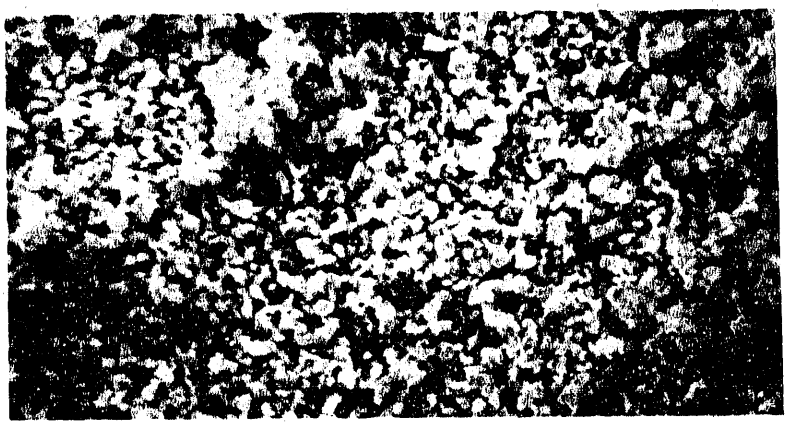
[e]*Source:* Value from J. M. Lafferty, "Boride Cathodes," *J. Appl. Phys.* **22**, 299–309 (1951).

Fired pellets were painted at both ends with a silver-based conductive paint so that the resistance measurement could be taken (Fig. 2.4). (All experiments of solder wetting on pellets failed.) The physical dimensions were measured and the resistivity (ρ) was calculated.

2.3 INK FORMULATIONS

Inks were formulated in two ways. The first type of ink was made by adding the selected powders to a commercial ink, Du Pont™ QP601 or 6403D, which are LaB_6-based compositions. This ink is nominally 10 Ω/sq. We reasoned that if our powder was more conductive than the LaB_6 in the Du Pont ink, then the fired ink resistance would be lower than 10 Ω/sq. In this procedure, we did not attempt to adjust glass and vehicle proportions to maintain original concentrations. The TiB_2/QP601, ZrB_2/QP601, HfB_2/QP601, VB_2/QP601, and CrB_2/QP601 inks were made in this way.

a



b

c

Fig. 2.3. Scanning electron micrograph of metal diboride powders (1000×). (*a*) TiB_2, (*b*) HfB_2, (*c*) ZrB_2.

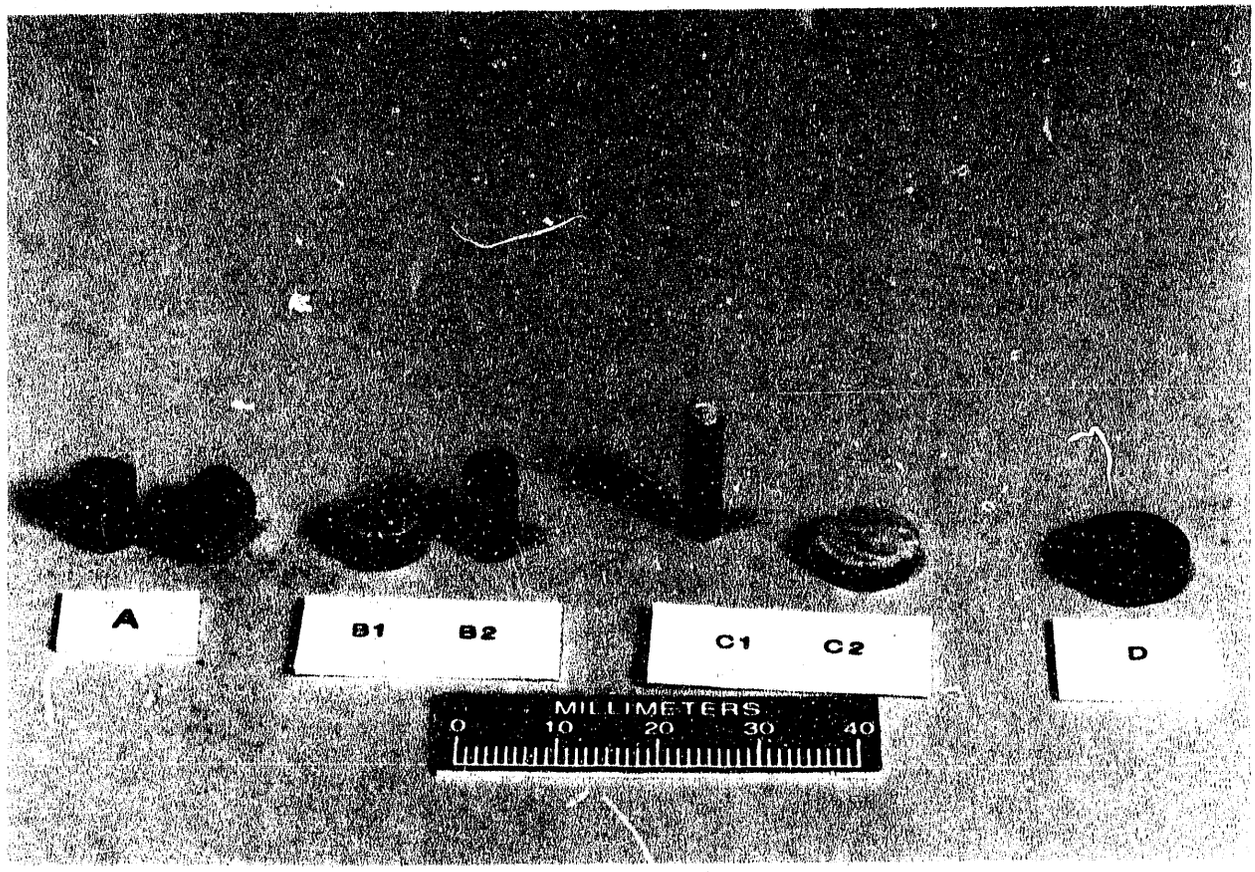


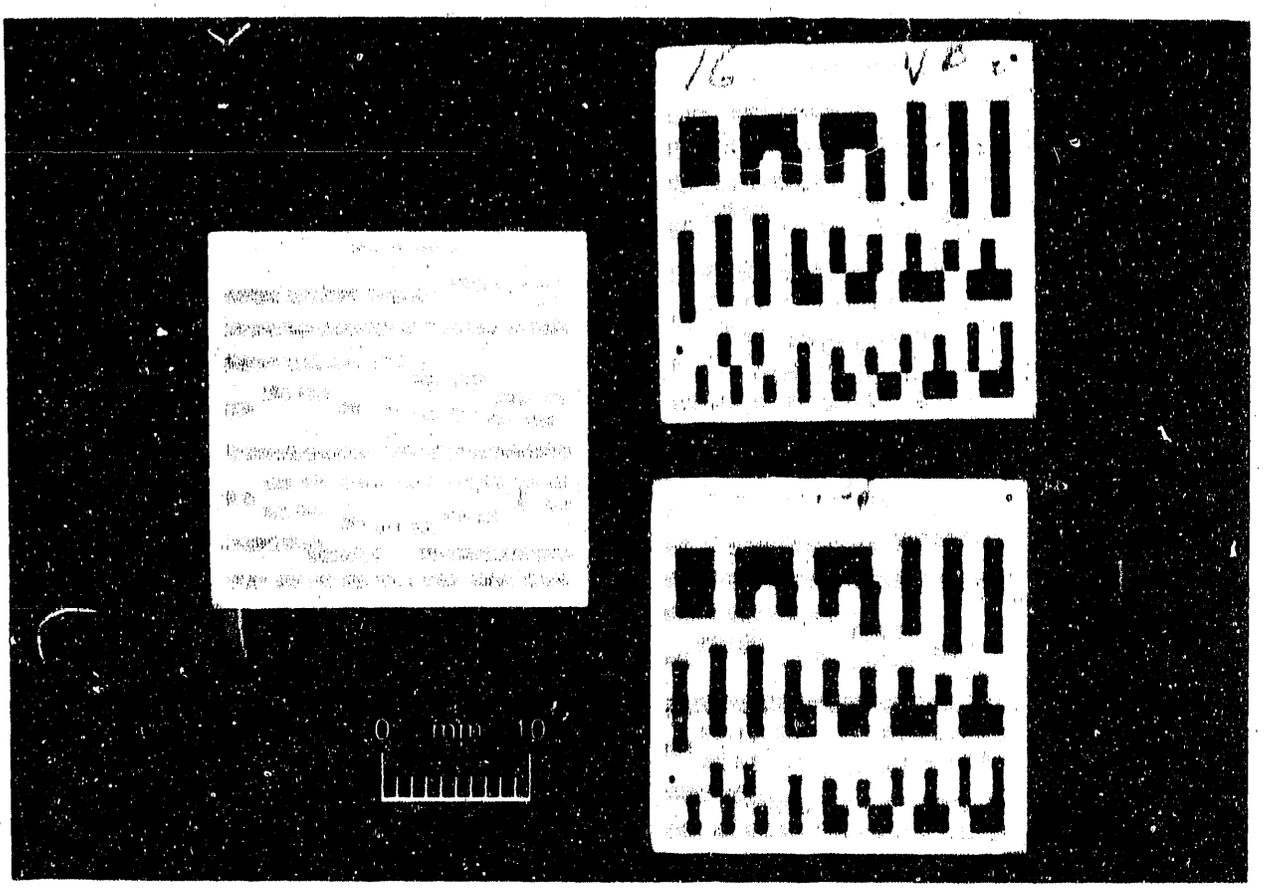
Fig. 2.4. Examples of fired pellets. (*a*) $SrFeO_3$, (*b*) $La_{1.85}Ba_{.15}CuO_4$ freshly pressed and sintered, (*c*) $La_{1.85}Ba_{.15}CuO_4$ exposed to air for six months after sintering, and (*d*) $La_{.8}Sr_{.2}CrO_3$.

The second type of ink was formulated from the basic ink ingredients Ferro™ 4770 glass frit, Du Pont™ 9180 electronic thinner, and Elvacite™ acrylic resin. Solperse™, an organic dispersant, was added in small quantities to aid in mixing the dry powder with the other ingredients. The conductor/glass ratio was 10:1 by weight, and the solvent/resin ratio was 5:1 by weight. The components were intermixed and placed overnight in a 60°C oven to dissolve the resin. More solvent was added where needed to obtain a printable consistency. Two inks made in this way used VB_2 and $La_{1.85}Ba_{.15}CuO_4$ as the conductive phase.

Inks were screen printed on a resistor-test substrate (Fig. 2.5). Screen hole size was 200 mesh. The test substrate was first printed with a conductor layer (Du Pont™ 9910, a gold formulation) to provide measurement contacts for the resistors. Several resistor geometries were printed on one substrate, so that ink characteristics and edge effects could be examined. The substrates were fired either in air in a belt furnace, set at typical hybrid circuit settings, or in nitrogen in a programmable furnace that simulated the temperature-time profile of a belt furnace.

2.4 ELECTRICAL TESTING

Resistances of pellets and thick-film resistors were measured by a two-point technique. Silver paint electrodes were applied to the pellets (Fig. 2.4); the thick-film specimens were measured directly on the preprinted gold metallizations (Fig. 2.5).



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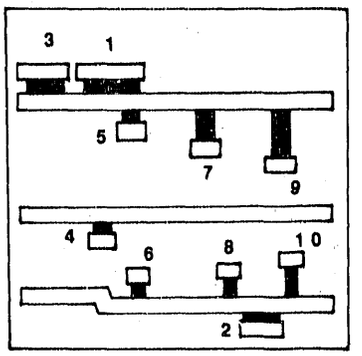


b

Fig. 2.5. Resistor-test substrates. (*a*) A gold electrode layer is deposited and fired first (left). The test ink is then printed and fired (right). The different resistor widths and lengths help explain edge effects and other ink properties. (*b*) Map showing the location of the resistors measured for the indicated sample point. Aspect ratios from one-third square to three squares were measured for two sizes of resistors.

3. RESULTS

3.1 PELLETS

Bulk resistivities of several $SrFeO_3$ compositions are given in Table 3.1. We observed that the bulk resistivities of these compositions are too high for practical use in thick-film systems.

Pellets of $La_{.6}Sr_{.4}VO_3$ and varying amounts of Ferro™ glass frit were fired in air in the belt furnace at several temperature cycles (Fig. 3.1). Reducing the glass and increasing the temperature improved conductivity, but conductivity levels were still much lower than desired. Many pellets with <10% glass cracked, which adversely affected the resistance value. As indicated in the micrograph [Fig. 2.2(*b*)], the fired material did not appear fully dense. Firing temperatures, which were lower than usual for many thick-film materials, were suggested by the manufacturer to achieve the maximum conductivity of the glass frit. The data of Fig. 3.1 suggest that higher firing temperatures should be attempted.

Pellets with the highest conductivity were those of the $La_{1.85}Ba_{.15}CuO_4$ composition. Pellets fired in nitrogen gas disintegrated soon after cooling. Pellets fired in air (as part of an earlier project on superconductivity) exhibit excellent stability in air. Pellets more recently pressed and fired had a conductivity of 1.5 Ω·cm. This material was therefore used as the basis of a thick-film ink.

Table 3.1. Resistances of $SrFeO_3$ pellets fired in air

Glass (%)	Firing temperature (°C)	Firing time (min)	Resistivity (Ω·cm)
2	525	10	5.2×10^5
5	525	10	4.3×10^5
2	580	10	4.7×10^4
5	580	10	2.9×10^5

3.2 THICK-FILM INKS

Because of the results of bulk resistivity measurements and its good long-term stability, $La_{1.85}Ba_{.15}CuO_4$ was selected for the first ink formulations. This ink was mixed as described previously. The ink consistency was not optimized for screen printing, but its rheological properties were adequate for the screen used for the test pattern. Resistor test specimens were printed and fired at several schedules in the belt furnace.

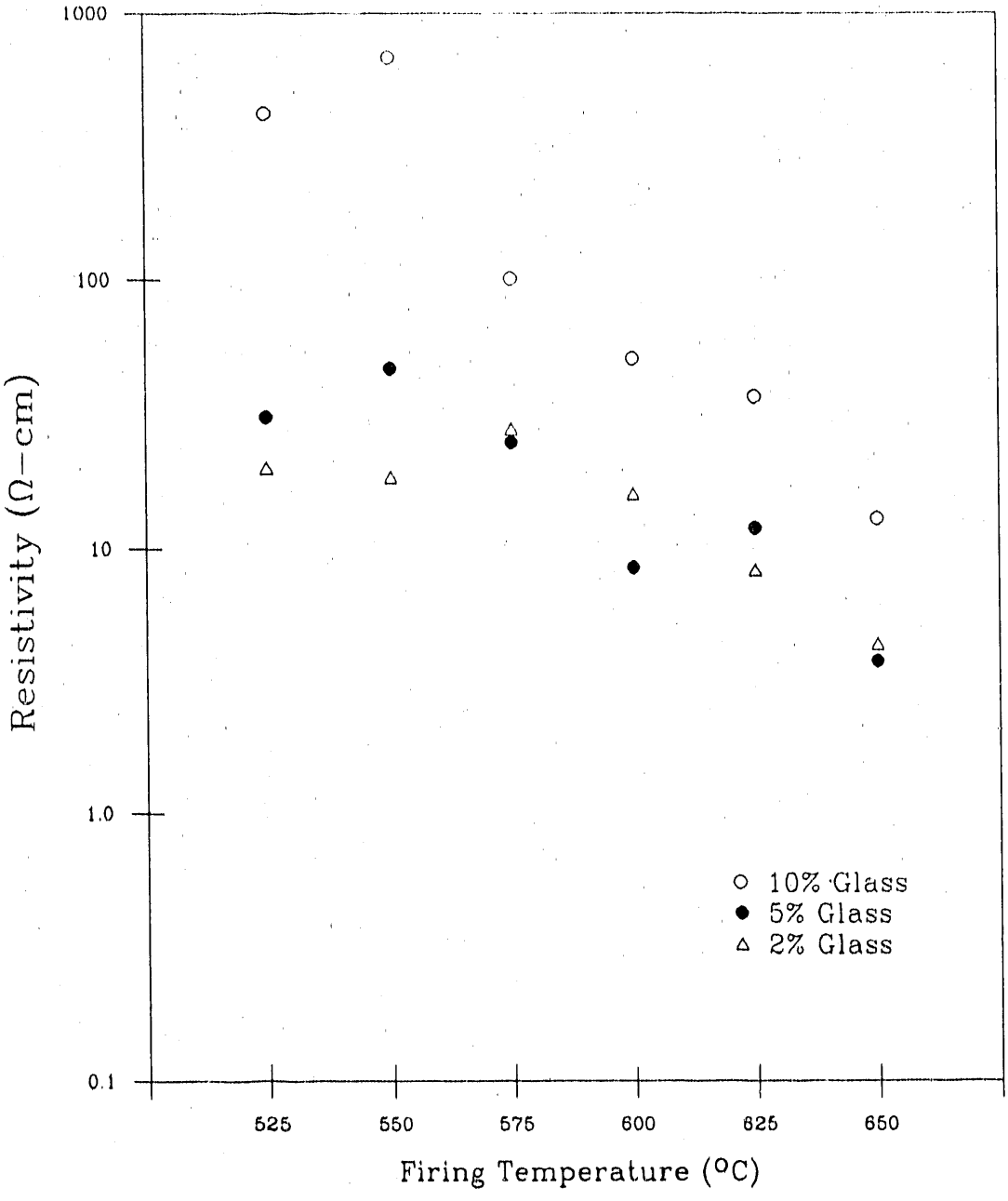


Fig. 3.1. Resistivity of $La_{.6}Sr_{.4}VO_3$/glass pellets fired in nitrogen gas for 15 min at indicated temperatures.

As seen in Fig. 3.2, samples fired at 700° C had inconsistent measurements and high resistances. At medium belt speeds and higher temperatures, resistances decreased and measurements became more consistent. The lowest resistance values were observed at a 900° C firing temperature; unfortunately, the resistance measurements were still several orders of magnitude away from desirable conductor ranges.

Of the inks formulated with the Du Pont™ ink (Fig. 3.3), the TiB_2, VB_2, and CrB_2 apparently lowered the nominal resistance of the pure QP601—but not to any significant amount. On the bases of this effect of the VB_2 powder in the QP601 ink and the inherent compatibility of the powder with our glass frit sample containing vanadium oxide, we formulated VB_2-based thick-film inks.

One of the most common problems with all of these materials is that density was difficult to control in the ink or pellet form. For any material, the highest conductivity is possible at only relatively high densities. Higher densities are easier to obtain in pellets because they can be pressed. Much industrial development work with the ink formulations is devoted to particle size and vehicle chemistry in an effort to maximize the density of the printed film. In our exploratory project, it was obviously not possible to do such optimization, and the results of printing and firing serve only to illustrate general trends. Some experimentation was done with particle size because a smaller particle size enhances surface forces that tend to draw the particles into more intimate contact. A close up comparison between a gold conductor layer and a VB_2-based ink formulation reveals that the gold layer, although porous, is continuous through a layer of fused gold plates [Fig. 3.4(*a*)]. The VB_2 layer shown in Fig. 3.4(*b*), composed of angular particles, is porous but continuous and less conductive than gold by several magnitudes. The VB_2 layer shown in Fig. 3.4(*c*) contains particles 10 times smaller than those in the VB_2 layer shown in Fig. 3.4(*b*). This layer is porous also but is 10 to 15 times less conductive than the VB_2 layer with larger particles. We postulate that the surface area of the smaller particles was much higher and therefore might necessitate the use of more glass frit. Micrographs of fired resistors from two commercially available inks [Fig. 3.4(*d*) based on ruthenium oxide (Du Pont™ 1711) and Fig. 3.4(*e*) based on lanthanum hexaboride (Du Pont™ QP601)] are provided for comparison. Both inks are designed for a 10-Ω/sq resistance. In Fig. 3.5, various mixtures of VB_2-based ink with 10% glass are plotted. Ink mix 3 contains the smaller VB_2 particles, and ink mixes 1 and 2 contain the larger VB_2 particles. When fired at 900° C, mix 2 has the lowest resistance of all other compositions and is within the guidelines set for low-value thick-film resistors. Larger resistors generally had lower sheet resistivities than those of smaller resistors of the same aspect ratio; such end effects are not unusual and are related to chemical interactions between the resistor layer and the underlying gold metallization.

Ink compositions made with less glass had a higher conductivity but poorer adhesion to the substrate. The fired inks were powdery and could be rubbed off the substrate. Inks fired at higher temperatures had better conductivity but appeared to approach the low limit at 900° C. Figure 3.6 gives measurements for several compositions of VB_2 ink with varying amounts of glass. The 95/5 and the 98/2 compositions exhibit the lowest resistances, but these measurements are much greater than desired values for either conductors or low-value resistors.

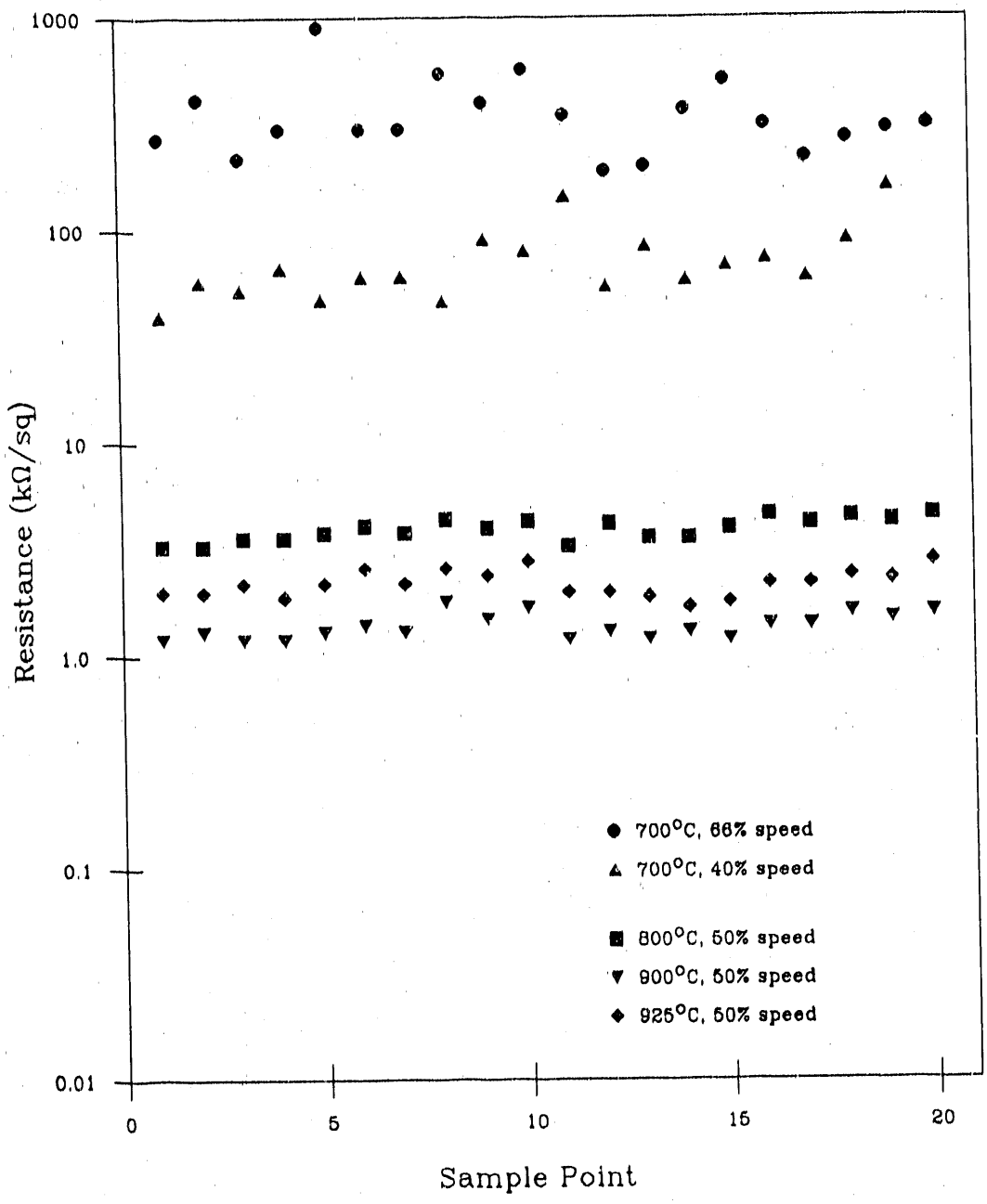


Fig. 3.2. Resistances of thick-film ink based on $La_{1.85}Ba_{.15}CuO_4$ powder. Mixtures contained 10% glass frit. Note that the highest conductivity was reached at a firing temperature of 900° C. Sample points 1 through 10 were on one substrate, points 11 through 20 on another.

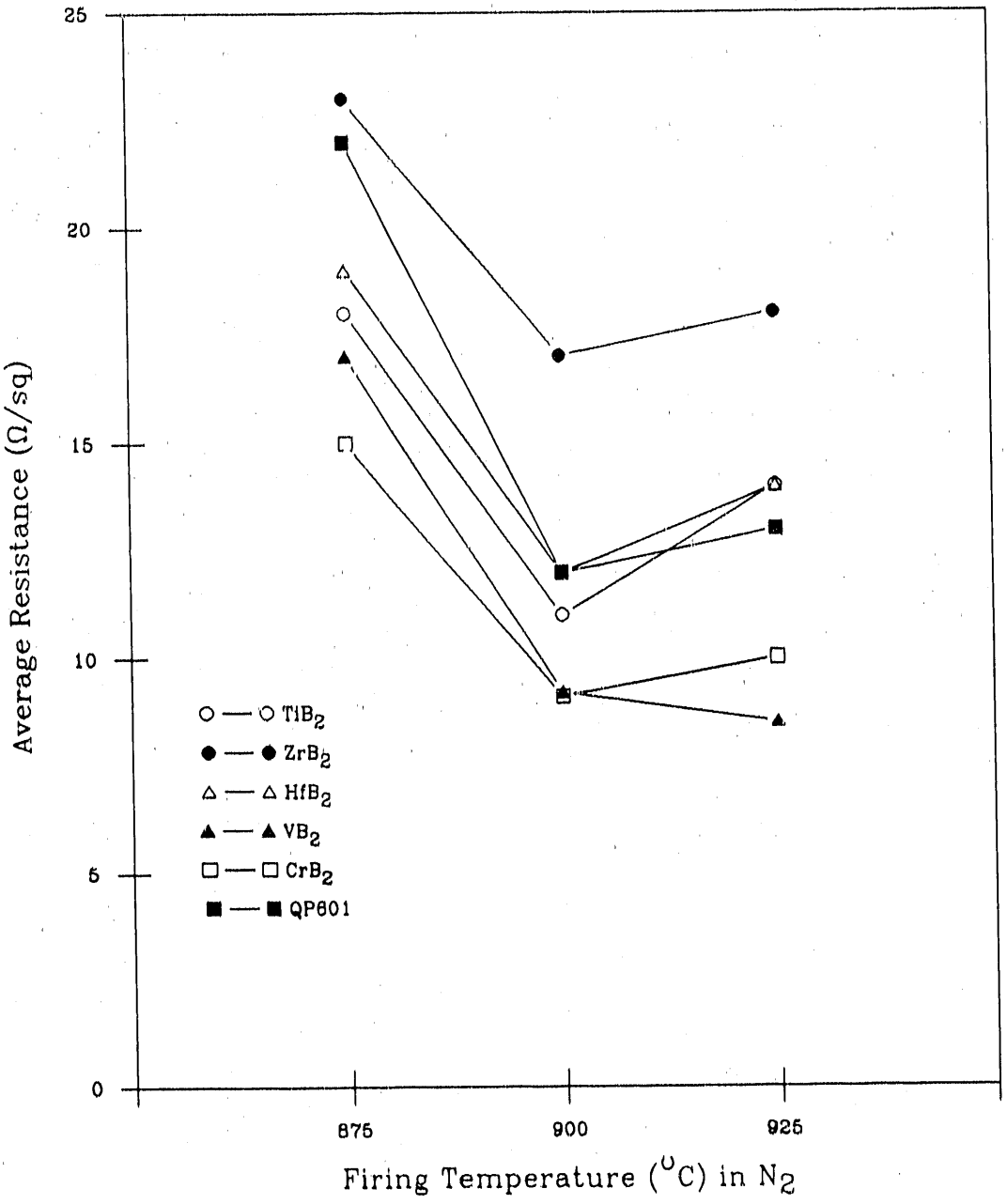
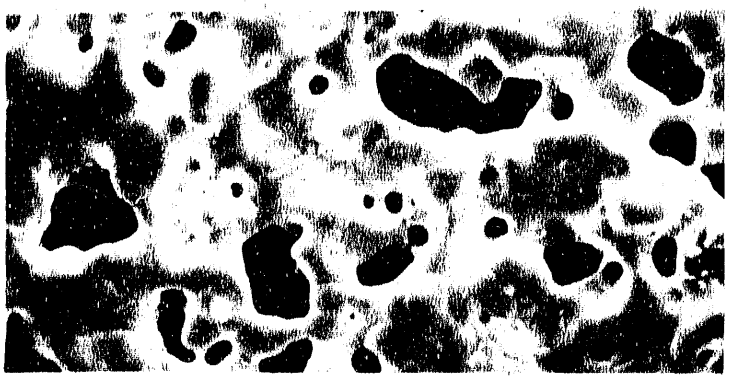
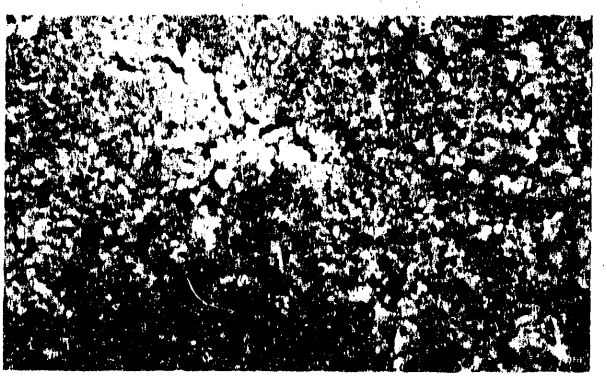


Fig. 3.3. Resistances of Du Pont™ QP601 ink containing several added conductive diboride powders. Additions of significant quantities of TiB_2, VB_2, and CrB_2 slightly lowered the nominal resistance of the pure QP601 ink.



a

b



c

d

e

Fig. 3.4. Micrographs (1000×) comparing fired thick-film materials. (*a*) gold conductor, (*b*) VB_2 plus vanadium oxide glass frit, (*c*) VB_2 plus vanadium oxide glass frit (using finer VB_2), (*d*) ruthenium oxide resistor, and (*e*) lanthanum hexaboride resistor.

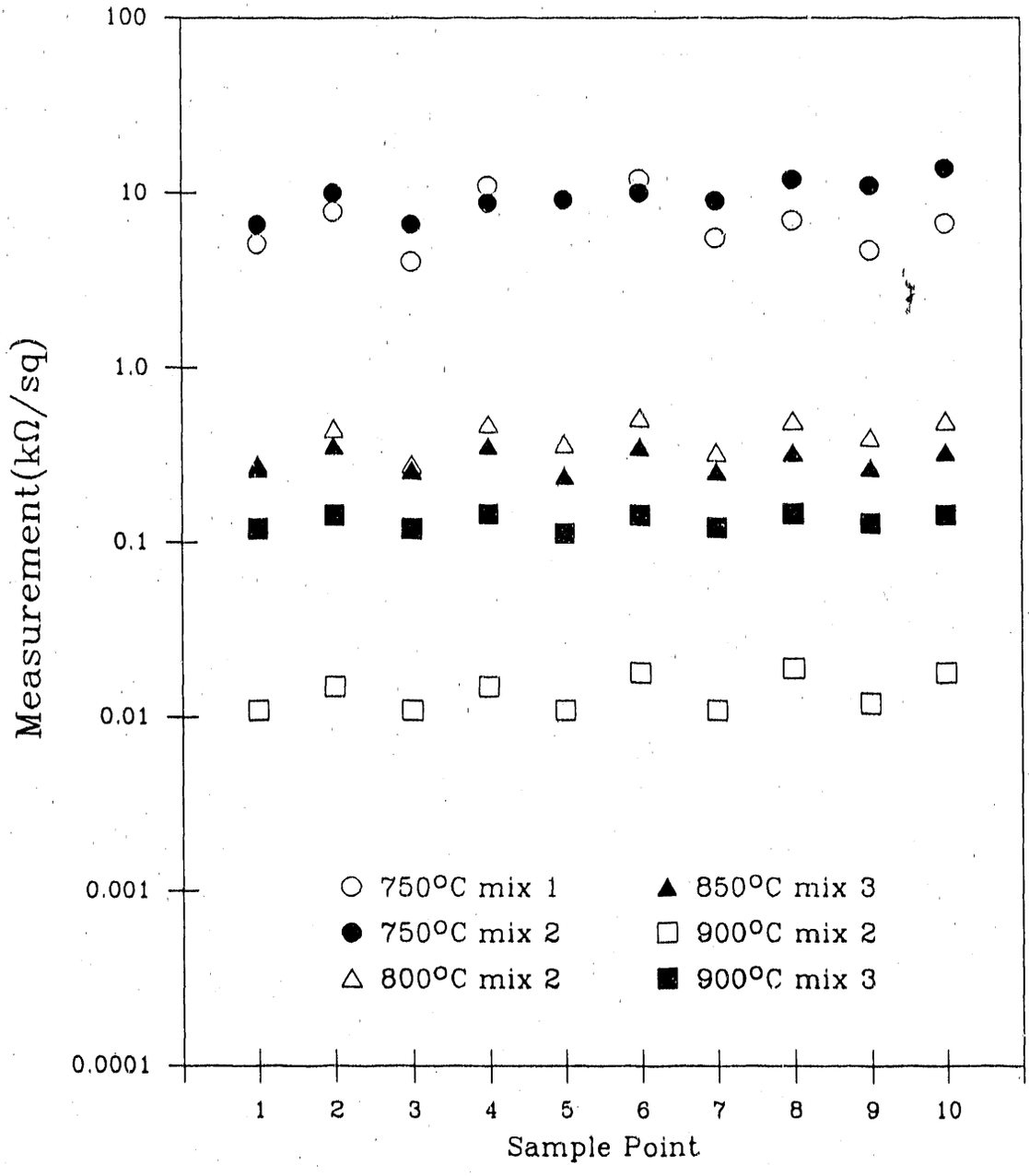


Fig. 3.5. Resistivities of VB_2-based thick-film ink with 10% glass frit. Mixtures 1 and 2 contain VB_2 particles ~ 10 μm in diameter, whereas mixture 3 contains particles ~ 1 μm. Mix 2, fired at a peak temperature of 900° C, had the lowest resistance.

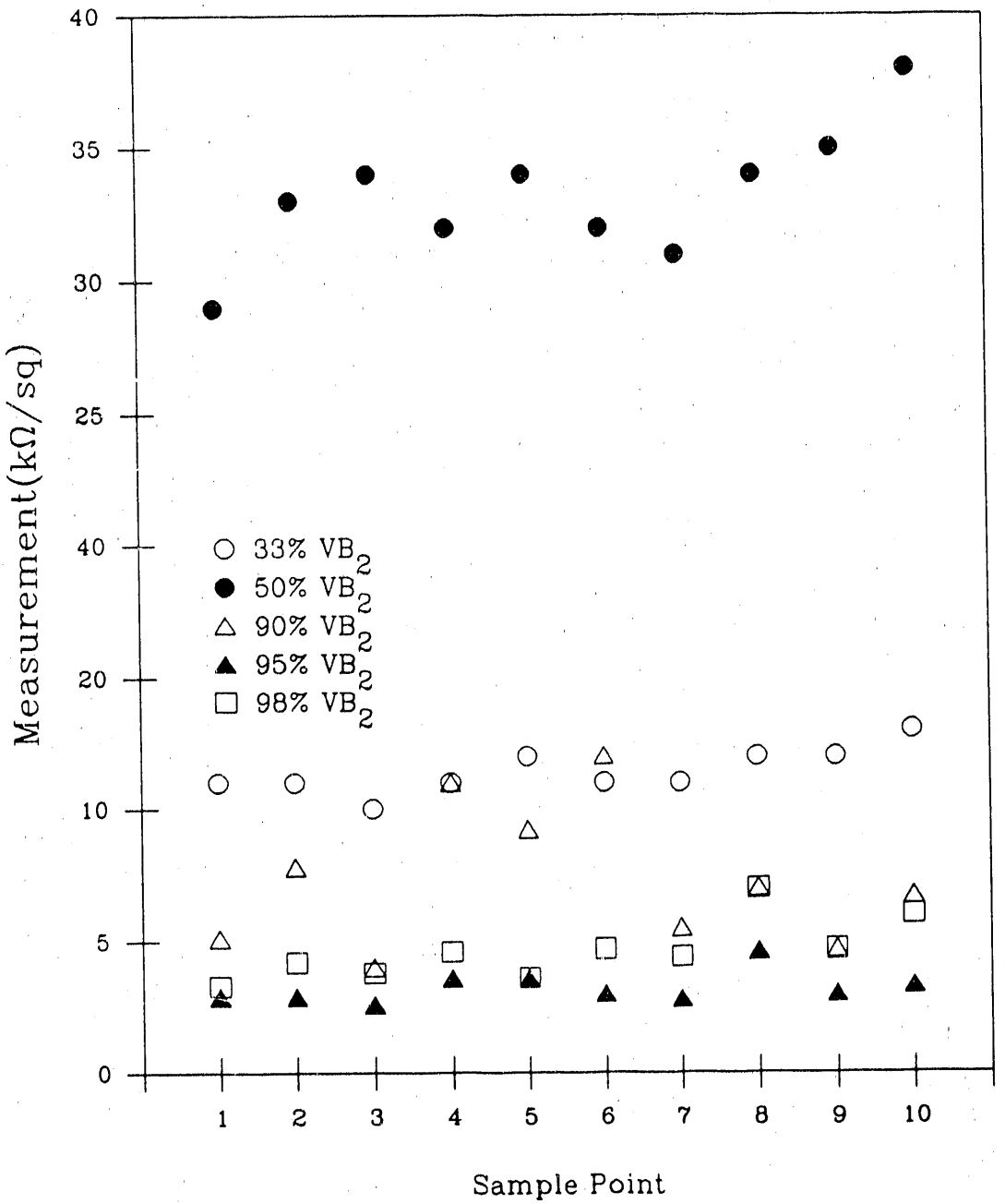


Fig. 3.6. Resistivities of VB_2-based thick-film ink with varying amounts of glass. Lower concentrations of glass increase conductivity but hinder adhesion to the substrate.

4. CONCLUSIONS

From this work to determine which materials can be used as low-cost alternatives to precious metals for thick-film conductor and low-resistor ink or as substitutes for copper in nitrogen-fireable compositions, we reached the following conclusions.

1. $La_{1.85}Ba_{.15}CuO_4$ might be suitable for internal electrodes in multilayer capacitors because it can withstand high firing temperatures, it is stable in air, and its thermal expansion is compatible with that of the perovskite dielectric. This material might be useful also as an inexpensive filler in mid-to-low-range resistor pastes that require air firing.

2. The borides might be useful as inexpensive fillers in nitrogen-fired resistor pastes. Their properties compare favorably to those of lanthanum hexaboride at lower cost.

3. Much work remains before the conductive ceramics studied can be incorporated into commercial products. Development issues include chemical interactions between these phases and existing materials, temperature coefficients of resistivity, thermal expansion coefficients, and other issues.

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