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Some Resistive Properties of Novel Oxide Conductors $Cu_{28-m}\ Pb_{m-x}\ A_{x-p}\ M_p\ O_y$ (A, M = Ba, Sr, Ag)

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Oxide conductors have been prepared starting from the composition with the unit cell formula $Cu_{24}Pb_4O_{32}$ which corresponds to the compound with NaCl type structure referred to in the literature as mineral murdochite. The Pb^{4+} ions are partly substituted by ions of lower valency like Sr^{2+}, Ba^{2+} and this results in oxidation of copper ($Cu^{2+} \rightarrow Cu^{3+}$) which in turn establishes mixed valency states (MVS). The general unit cell formula $Cu_{28-m}\,Pb_{m-x}\,A_{x-p}\,M_p\,O_y$ can be proposed and variation of parameters m, p, x with permutation of ions A and M results in a pronounced conductivity of samples at room temperature *(RT)*. Some of them exhibit downturn of the electrical resistance (DER) by cooling from 230 K — 350 K. Since the electrical resistance is enhanced by application of higher current densities in the temperature range where the DER occurs, metallic derivatives of murdochite obtained by substitution of Cu and Pb can be used as interesting candidates for the searching of superconductivity (SC) at $T > 200$ K.

INTRODUCTION

The discovery of Bednorz and Müller[1] that the perovskite type compounds Ba—La—Cu—O exhibit superconductivity at 35 K triggered interest throughout the world in the synthesis of new metallic compounds based upon oxides and prepared by the common methods of powder metallurgy. Soon Chu and coworkers[2] reported the SC onset temperature of 93 K in a mixed system $Y_{1.2}Ba_{0.8}CuO_4$. In the next step Cava *et al.*[3] recognized the single phase $YBa_2Cu_3O_7$ in $Y_{1.2}Ba_{0.8}CuO_4$. Recently Maeda *et al.*[4] synthesized $CaSrBiCu_2O_x$ with the SC transition starting at 115 K. A bonus of the Ca—Sr—Bi—O system is the absence of rare earth metals. A common property of these perovskite based superconductors may be 2D conductivity in the Cu—O and Bi—O layers. This has been postulated in a number of models but not yet clearly proved by experiments.

In addition to the possibility of 2D conductivity in CuO planes also the conductivity along the c-axis of Cu—O octahedra may be important. Some hints at the possibility of such conductivity are provided in the work of Warren *et al.*[5] who reported NQR data with two different energies for pair formation associated with two copper sites in the $YBa_2Cu_3O_{7-\delta}$ unit cell. $YBa_2Cu_3O_{7-\delta}$ contains one Cu—O octahedron per unit cell, since there are no oxygen atoms in yttrium planes and uninterrupted slabs of Cu—O octahedra along the c-axis are not possible. Of prospecting materials, containing Cu—O octahedra linked in an uninterrupted array we paid an attention to the mineral murdochite* discovered in 1954, in the Mammoth mine, Arizona, USA,[6] of the unit cell formula $Cu_{24}Pb_4O_{32}$. The X-ray structural analysis by Christ and Clark[7] reveals an ordered NaCl arrangement with cubic unit cell dimension $a_0 = 9.210$ Å. The 24 Cu atoms can be distributed over 28 sites which results in two possible structural features; one of them is disordered structure with statistical distribution of Cu ions, while an alternative possibility offers the ordered arrangement of Cu ions and holes. The ordered structure of murdochite is schematically shown in Figure 1.

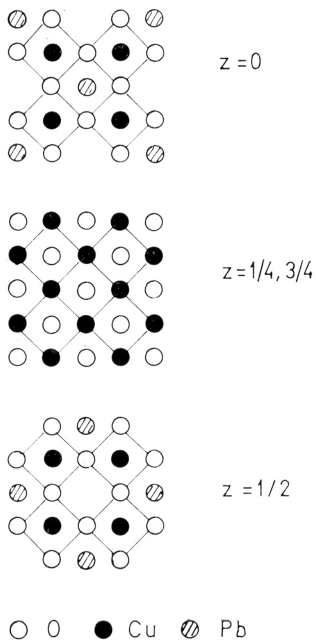

Figure 1. Cross-sections of the unit cell in (a, b) planes of murdochite $Cu_{24}Pb_4O_{32}$ as proposed by Christ and Clark (ref. 7). Note the edge shared slabs of Cu—O octahedra linked along c-axis in an uninterrupted chain.

Murdochite provides at least two important advantages of interest for the preparation of new conductors. First, the stability of NaCl structure, as compared to that of perovskites is not governed by the empirical Goldschmidth rule which relates the ionic radii of constituents to a unique tolerance factor,[8] which enables the substitution of a number of different atoms in the unit cell. Second, copper and lead can be introduced in varying ratios without the basic structure being changed.[7]

PREPARATION AND STRUCTURE

Samples are prepared by using a common powder metallurgy route in a solid state reaction from CuO, PbO, $SrCO_3$, $BaCO_3$, $AgNO_3$ (Ag_2CO_3). The powders of the relevant constituents are mixed and pressed under uniaxial stress between two anvils made of polished steel. Together with the powder, gold wires (80 microns in diameter) are inpressed to ensure contacts for measurements of electrical resistance during the fusion stage and the subsequent annealing procedure. The method has been published elsewhere[9] and it provides a sensitive tool for the control of different physical and chemical processes in the material during preparation. The inpressed gold wires serve also for the measurement of electrical resistance on cooling to liquid nitrogen (LN_2) temperatures. Since the contact resistance between the sample and the wires is less than a few milliohms, such contacts are much superior to those made of silver paint, especially for the measurements with high current densities. Typical dimensions of the samples are $5 \times 5 \times \times 0.015$ mm^3. The comparatively small thickness is favorable option for measurements in high current densities since the self heating of the sample is prevented by fast removal of heat from the sample glued onto a copper substrate. For different selections of parameters m, p, x and A, M the reaction temperatures and preparation conditions differ and in this paper we present several representative preparations with the corresponding properties of prepared materials.

a) $m = 4,\ p = 0$

The proposed unit cell formula $Cu_{24}Pb_{4-x}A_xO_y$ resembles the perovskite compound $La_{2-x}A_xCuO_4$ (A = Sr, Ba) and it is reasonable to believe that the valency state Cu^{2+} can be increased in murdochite by substitution of Pb^{4+} with ions of lower valency like Sr^{2+} and Ba^{2+} as it is the case in La_2CuO_4. We varied the parameter x in the samples $Cu_{24}Pb_{4-x}A_xO_y$ (A = Sr, Ba) prepared in a solid state reaction at 730 °C for 24 hours in air. For $x = 0$ the samples are insulators at $T < 300$ K. Substitution of Pb^{4+} by Sr^{2+} and Ba^{2+} gradually decreases the resistivity and in Figure 2 the logarithm of resistivity $\rho(x)$ at *RT* is plotted. It is evident an abrupt decrease of ρ takes place by increasing x from $x = 0$ to $x = 0.8$ (A = Ba). In a rather narrow range $0.76 < x < 0.80$ the resistivity is of the order of 1 mΩ cm. By increasing x from $x \sim 0.80$ to $x \sim 1.20$, an increase of ρ takes place. For $1.2 < x < 2.0$, the samples are simply metallic with the positive slope of electrical resistance plotted *versus T*. Similar properties appear for A = Sr but characteristic values of parameter x are different from those for A = Ba. The lowest resistivities at *RT* are recorded for $x \sim 1.6$ and are an order of magnitude higher than for A = Ba at $x \sim 0.80$.

The temperature dependence of the electrical resistance at $T < 400$ K (A = Ba) is shown in Figure 3 for different values of x. For $x < 0.72$, semiconducting dependence is obeyed while for $0.72 < x < 0.80$ DER occurs in the temperature range $220\ K < T < 320$ K. The lowest resistivity recorded in the temperature interval $77\ K < T < 300$ K was 45 μΩ cm for $x = 0.780$. Again, it is worthy to note the similarity with $La_{2-x}A_xCuO_4$ (A = Sr, Ba) when the semiconducting properties are gradually deteriorated for $0 < x < 0.2$ and superconductivity sets on.

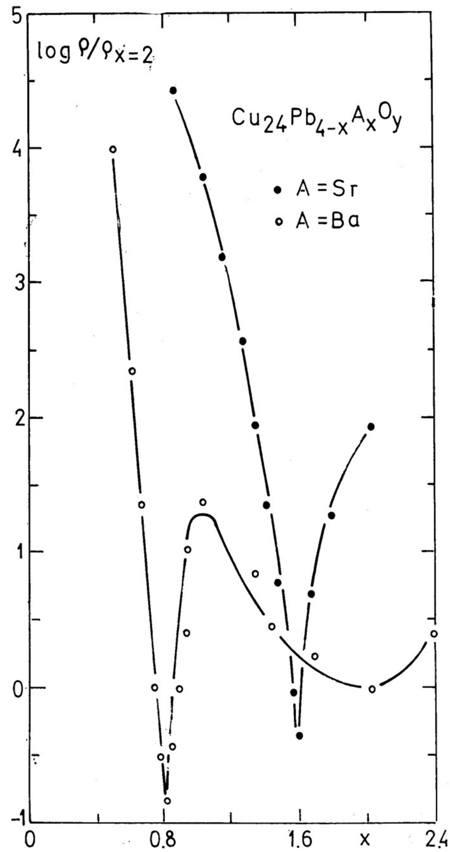

Figure 2. Electrical resistivity of murdochite when Pb^{4+} ions are partly substituted by Ba^{2+} and Sr^{2+}.

b) m = 4, A, M = Sr, Ag

The mixed system with 2 Sr atoms added to the unit cell formula of the nominal composition $Cu_{24}Pb_2Ag_2Sr_4O_y$ (CAPS 24—2—2—4) was prepared from powders of CuO, PbO, $SrCO_3$ and $AgNO_3$ (Ag_2CO_3) and pressed under uniaxial stress between steel anvils. In the first step the heating in air to 340 °C resulted in an abrupt decrease of electrical resistance of compacted powders from the few megaohms at *RT* to ~ 20 ohms at 340 °C. After annealing at 340 °C for 16 hours, we additionally annealed the samples for 1/2 hour under vacuum which is maintained during cooling to 240 °C when the samples were quenched in air, being removed from the furnace. The cooling to LN_2 temperatures resulted in the temperature dependence of resistance for two different samples as it is shown on Figure 4. At 77 K, the resistivity was 20 μΩ cm which should be compared to 12 mΩ cm (sample b) at *RT*. The stability of samples prepared in the described way was poor and after several heating-cooling cycles DER deteriorated. After exposure of sample (a) to dry air for 48 hours, the resistance dependence

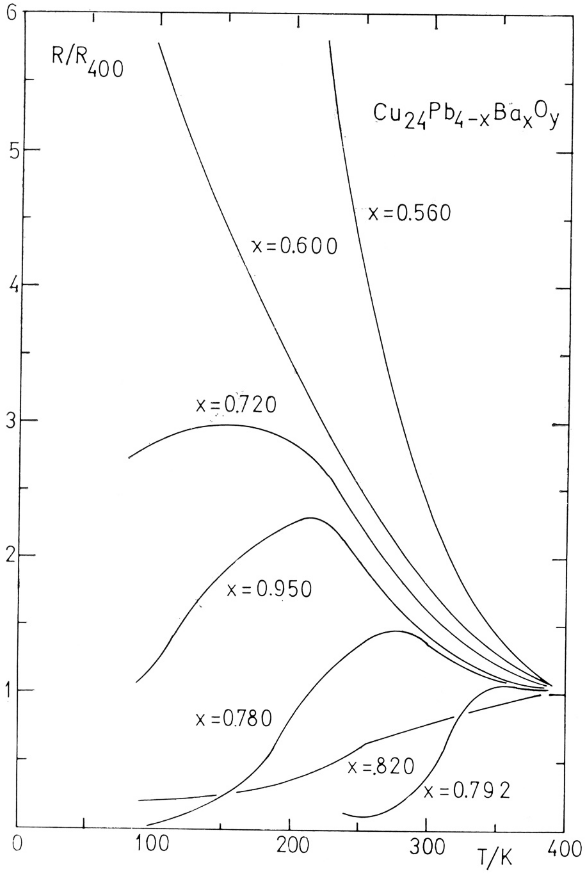

Figure 3. Temperature dependence of electrical resistance of $Cu_{24}Pb_{4-x}Ba_xO_y$ recorded by cooling below 400 K.

on temperature exhibited weak anomaly, as shown by curve c. In second step we heated the compacted powder in air to ~ 340 °C, annealed it at this temperature for half an hour in flowing oxygen of 5 bars, cooled to 240 °C and quenched in air to *RT*. The resistive properties of the sample are shown in Figure 5. Figure 6 shows the temperature dependence of electrical resistance for a sample prepared in the same way. The stability of this sample exposed to dry air lasted for 24 hours, and then the DER smeared.

c) m = 4, x = 2

Figure 7 shows the temperature dependent resistance of sample $Cu_{24}Pb_2Sr_2Ag_2O_y$ (24—2—2—2) with 2 Ag atoms added to the unit cell formula prepared in the same way as described for the samples whose resistance dependence is shown in Figures 5 and 6. Resistivity measured at *RT* for 1 mA was less than 0.5 μΩ cm. Heating above *RT* resulted in an abrupt

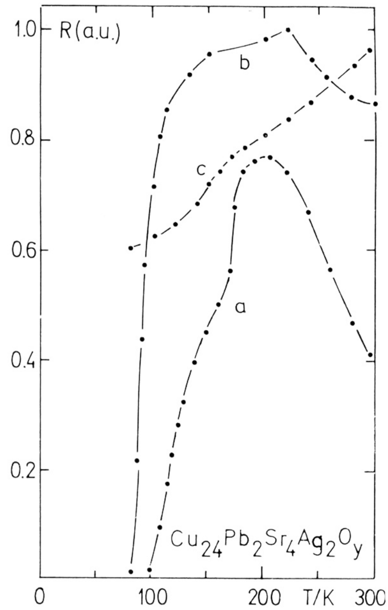

Figure 4. Downturn of electrical resistance (DER) for (2Sr + 2Ag) doped $Cu_{24}Pb_2Sr_2O_y$. Samples were heated in air up to 340 °C and annealed under vacuum at this temperature for half an hour, cooled to 240 °C an quenched to *RT* in air. Curve c) shows the temperature dependence of electrical resistance of sample a) after 48 hours of exposure to dry air.

increase of the resistance at 340—360 K. Repeated cooling to LN_2 temperatures with measuring current of 50 mA resulted in slightly different temperature dependence. The shape of this curve indicates the possibility of transformation to another type of phase than that responsible for the transition at 340—360 K. We believe that higher current densities switch the material from one phase to another. The stability as well as the reproducibility of samples prefired in air is poor in 24—2—2—2 compounds too.

The X-ray diffractograms are indispensable in investigation of substituted murdochite. We tried to obtain Cu_6PbO_8 by solid state reaction and record the X-ray diffractograms in order to compare them with those reported by Christ and Clark[7] for natural mineral Cu_6PbO_8. The most abundant mixtures seem to be obtained by the reaction of CuO and PbO in air at ~ 740 °C for 24 hours. After cooling to *RT*, regrounding and repeated heating to 740 °C with subsequent annealing for 24 hours resulted in diffractogram (Figure 8) which reveals the presence of several diffractions characteristic of murdochite reported in ref. 7 (2Θ = 17.3°, 21.3°, 30.3°, 38.7°, 43.2°, 44.3°, 52.7°). A considerable fraction of unreacted CuO and PbO is present in this mixed system. The diffractograms recorded for $Cu_{24}Pb_2Sr_2O_x$ (Figure 9) and $Cu_{24}Pb_2Ag_2Sr_4O_x$ (Figure 10) point to similarity with that obtained for Cu_6PbO_x (Figure 8) although a considerable fractions of unreacted CuO and Ag are still present.

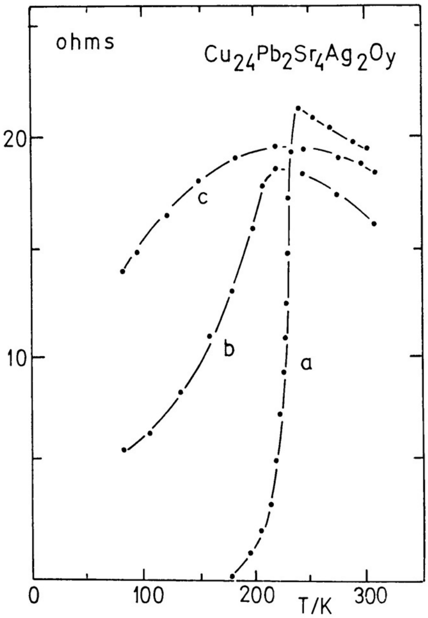

Figure 5. Temperature dependence of electrical resistance of (2Sr + 2Ag) doped $Cu_{24}Pb_2Sr_2O_y$. Sample was heated to 340 °C in air and annealed at this temperature for half an hour in 6 bars of flowing O_2, cooled in O_2 to 240 °C and quenched to *RT* in air. Measurements were taken a) just after quenching, b) after 24 hours of exposure in dry air, c) after 3 days of exposure in dry air.

DISCUSSION

Two important reasons must be considered for possibility of attribution the DER phenomena on boundaries between two phases. Firstly, silver can be segregated on phase boundaries and by cooling below 250—350 K two states of conductivity as a result of disaccommodation between phases may be involved in resistive measurements. Although segregation of metallic silver is indicated by X-ray diffractograms its influence on DER phenomena is less certain since these phenomena are also visible in systems which don't contain silver ($Cu_{24}Pb_{1-x}Ba_xO_y$ and $Cu_{24}Pb_{1-x}Sr_xO_y$). The second serious difficulty is connected with possible transition within Cu_2O which may be obtained by reduction of CuO during heat treatment. In some diffractograms traces of Cu_2O were indicated together with those of CuO. Cu_2O may ressemble the MVS between Cu^{1+} and Cu^{2+} ions (ref. 10) and involve numerous transitions on phase boundaries. We tried to clarify this possibility by studying the model system $Cu_{1-x}Ag_xO_y$ prepared from Cu_2O and Ag_2CO_3 by firing at 350 °C for 24 hours in air. For $x = 0.08$, low resistivity ($\rho \sim 90$ μΩ cm) at *RT* was recorded. For $0.09 < x < 0.07$, resistivity is > 40 mΩ cm. Although X-ray diffractograms reveal the presence of Cu_2O and CuO, no DER phenomena have been observed so far. The role of possible transitions $2CuO \leftrightarrow Cu_2O + O$ in our system is still under serious consideration.

We list also several reasons why the DER phenomena in metallic derivatives of murdochite can be considered as an occurrence of supercon-

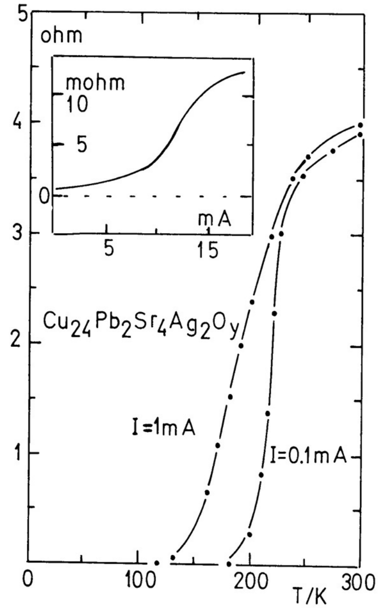

Figure 6. Temperature dependence of electrical resistance for two currents of the sample prepared in the same way as in Figure 5. Inset shows the dependence of electrical resistance on the current at 77 K.

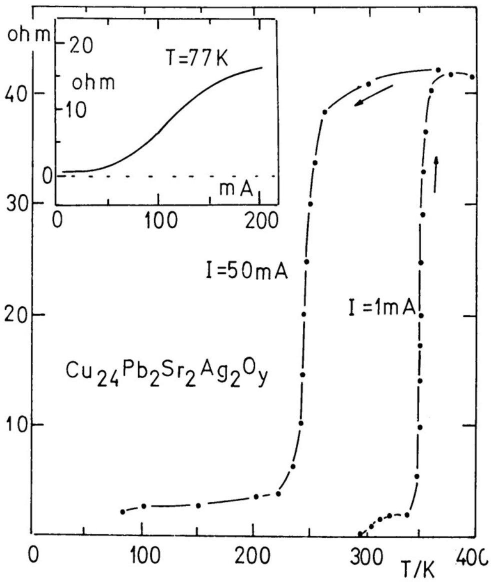

Figure 7. Temperature dependence of electrical resistance of (2Ag) doped $Cu_{24}Pb_2Sr_2O_y$ (24—2—2—2). Sample was prepared in the same way as in Figure 5. Inset shows the dependence of electrical resistance on the current at 77 K.

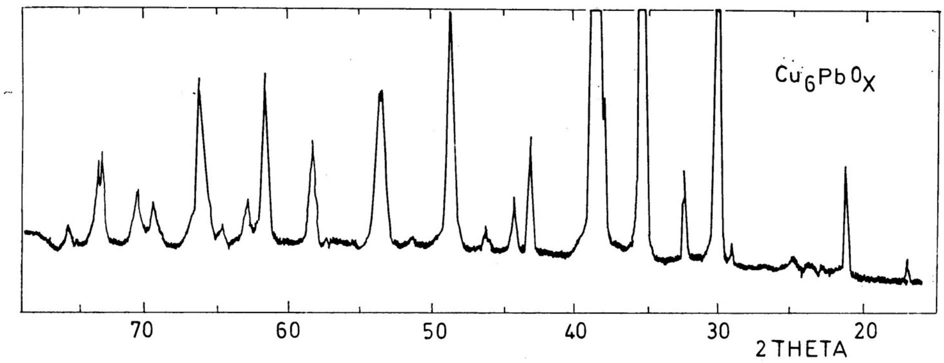

Figure 8. X-ray diffractogram of the system with nominal composition Cu_6PbO_x fused at 740 °C in air.

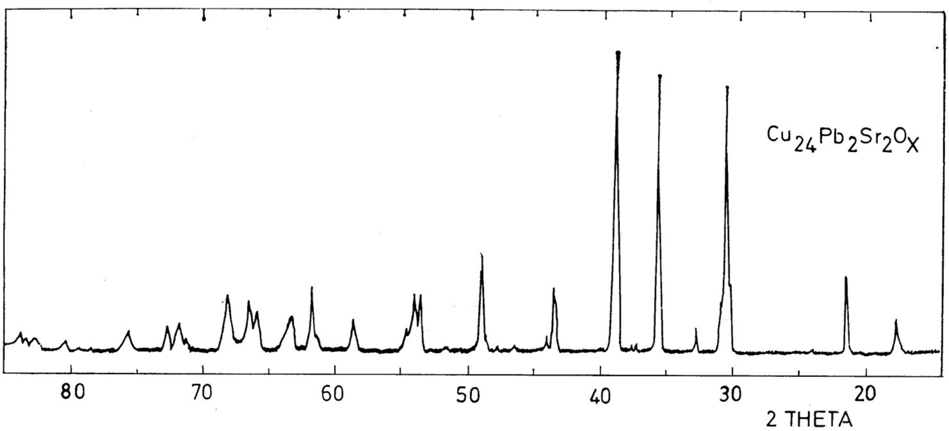

Figure 9. X-ray diffractogram of nominal $Cu_{24}Pb_2Sr_2O_x$ fused af 740 °C in air.

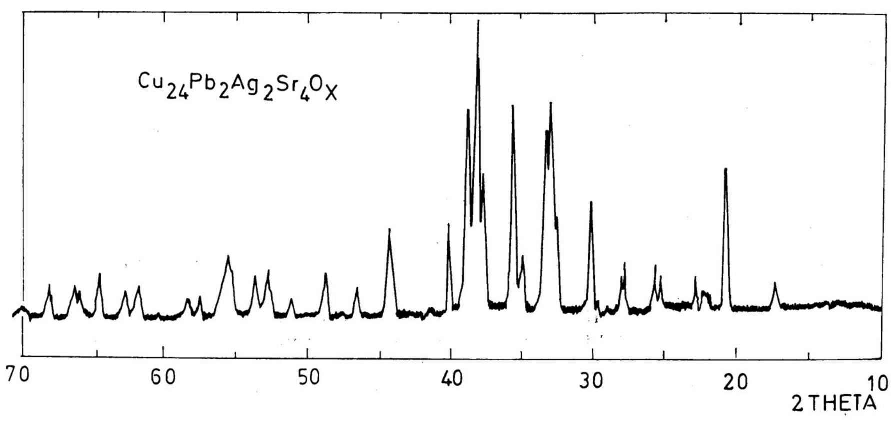

Figure 10. X-ray diffractogram of nominal $Cu_{24}Pb_2Ag_2Sr_4O_x$ having resistive properties as shown in Figure 6.

ductivity. First, it is unlikely that conductivity higher than that of silver ($\rho < 0.5$ μΩ cm) can be explained in defect rich ceramic material by any standard model of electron scattering known so far. Second, the enhancement of electrical resistance by application of higher current densities, although it must be considered with precaution due to possible current driven instabilities in inhomogenous material, favours the assumption that we are not dealing with a simple semiconductor-metal or metal-metal transition. Third, the DER phenomena are produced in a very similar way as superconductivity in the Y—Ba—Cu—O and La—Sr—Cu—O systems after the treatement by oxygen and annealing stage. Fourth, disappearance of the insulating state and stimulation of the well known methods for the preparation of La—Sr—Cu—O superconductors. Fifth, the DER phenomena compete with the insulating or semiconducting states. These states can be related to the existance of antiferromagnetism. Competition of superconductivity and antiferromagnetism is well corroborated phenomenon in a number of systems, like La—Sr—Cu—O and organic superconductors. The possibility of antiferromagnetism in murdochite has ben reported so far[11] in connection with a high negative Curie temperature (—700 K) and value of the magnetic moment ($\mu = 1.75 +/- 0.02$ μB) which is close to complete orbital quenching. In conclusion we have prepared classes of oxide conductors with the general formula $Cu_{28-m}Pb_{m-x}A_{x-p}M_pO_y$ (A, M = Sr, Ba, Ag) which are different from perovskites and preliminary investigations of resistivity appear as promising for the synthesis of new high T_c superconductors.

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SAŽETAK

Neka svojstva otpora novih oksidnih vodiča Cu_{28-m} Pb_{m-x} A_{x-p} M_pO_y (A, M = Ba, Sr, Ag)

D. Djurek i V. Manojlović

Pripravljeni su oksidni vodiči polazeći od sastava formule jedinične ćelije $Cu_{24}Pb_4O_{32}$ koja odgovara spoju strukture tipa NaCl citirane u literaturi kao mineral murdokit (murdochite). Ioni Pb^{4+} djelomično su supstituirani ionima niže valencije (Sr^{2+}, Ba^{2+}), što dovodi do oksidacije bakra ($Cu^{2+} \rightarrow Cu^{3+}$) i stanja miješovite valencije (MVS). Predložena je opća formula jedinične ćelije $Cu_{28-m}Pb_{m-x}$ $A_{x-p}M_pO_y$ i varijacija parametara m, p i x s permutacijom iona A i M rezultiraju naglašenom vodljivosti uzoraka pri sobnoj temperaturi. Neki od njih pokazuju pad električnog otpora pri hlađenju od 230 K—350 K. Budući da se električni otpor povećava primjenom većih gustoća struje u području gdje se javlja DER, metalni derivati murdokita dobiveni supstitucijom Cu i Pb mogu biti zanimljivi kandidati za traženje supravodljivosti u području $T > 200$ K.