

Preparation and Characterization of New 1-2-1-2 Compounds $MA_2RECu_2O_{8-\delta}$ and $Nb_{1-x}Ru_xSr_2RECu_2O_{8-\delta}$ ($M = Nb$ or Ta , $A = Ba$ or Sr , and $RE = Pr$ or Sm)

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New compounds $MA_2RECu_2O_{8-\delta}$ ($M = Nb$ or Ta , $A = Ba$ or Sr , and $RE = Pr$ or Sm) have been prepared and characterized. Structural analysis revealed that they crystallize in a 1-2-1-2 $TaBa_2LaCu_2O_{8-\delta}$ structure type similar to that of $YBa_2Cu_3O_7$. Cations such as Nb^{5+} , Ta^{5+} , and Ru^{4+} are accommodated in the basal plane and the double CuO_2 pyramidal planes are maintained. All the compounds show semiconducting behavior. With Ru substitution the formal copper valence increases from +2 to about +2.14. © 1994 Academic Press, Inc.

INTRODUCTION

All known high- T_c cuprate superconductors contain layers of copper-oxygen squares, pyramids or octahedrons as their electronically active structural components (1, 2). The layers of these structural components are intergrown with oxide layers such as $Ba(Sr)-O$, $Bi-O$, $Tl-O$, or $RE-O$ ($RE =$ rare earth element). These layer compounds can be varied from insulators to semiconductors, metals, or even superconductors by proper doping. $MBa_2LaCu_2O_8$ ($M = Nb, Ta$) compounds show these structural characteristics but do not show superconductivity (3, 4). Nevertheless band properties similar to those of typical cuprate superconductors have been predicted theoretically for $NbBa_2LaCu_2O_8$ and $TiBa_2LaCu_2O_8$ (5). An effort to raise the Cu oxidation state in the Ba containing compounds was not successful (3, 6). However, the substitution of Nb by $3d$ transition metals in the compound $NbSr_2EuCu_2O_8$ has shown a good tendency even though no superconductivity was detected (7). In a previous work we reported the synthesis of new compounds $MA_2RECu_2O_{8-\delta}$, with $M = Nb$ or Ta , $A = Ba$ or Sr , and $RE = Pr$ or Sm (8). All of them show semiconducting behavior with a formal copper valence close to +2. In this paper we report on a further investigation of these new com-

pounds and also of new ruthenium substituted compounds $Nb_{1-x}Ru_xSr_2SmCu_2O_{8-\delta}$ for $x = 0$ to 0.5.

EXPERIMENTAL

The compounds investigated were prepared by conventional solid state reaction method. Stoichiometric amounts of M_2O_5 , RuO_2 , $BaCO_3$, $SrCO_3$, Pr_6O_{11} , Sm_2O_3 , and CuO , all with purity better than 99.9 percent, were ground in an agate ball mill for 1 hr and pressed into pellets at a pressure of 800 MPa. In order to improve homogeneity the calcination was performed in two steps at 1040 and 1050 °C respectively for 20 hr in air with intermediate regrinding and repressing. Structural analysis was carried out by powder X-ray diffraction (XRD) at room temperature using $CuK\alpha$ radiation. The instrument was calibrated with silicon powder. The XRD experiment was performed from 6° to 100° (2θ) at a speed of 0.25 degrees per minute.

The intensities of Bragg peaks were measured by integrating the corresponding areas and subtracting the background. The theoretical calculation for XRD intensity was performed by using the FINAX program (9). The measured XRD intensities were normalized to corresponding total calculated intensities. Lattice parameters were calculated by a least squares refinement. The oxygen content was determined by thermogravimetric analysis (TGA) in H_2/N_2 atmosphere with 10 vol% H_2 . The temperature dependence of the electrical resistivity was measured by employing a standard DC four-point probe technique from room temperature down to 10 K. Room temperature resistivity was determined by using the van der Pauw method (10).

RESULTS AND DISCUSSION

Experimental results for the $MA_2RECu_2O_{8-\delta}$ compounds are given in Table 1. Structural analysis by XRD revealed that all compounds with $A = Sr$ and also the

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TABLE 1
Structural Parameters and Resistivities for $MA_2RECu_2O_{8-\delta}$ at Room Temperature

Compound	δ	a (Å)	c (Å)	ρ ($\Omega \cdot \text{cm}$)
$NbSr_2SmCu_2O_{8-\delta}$ (pure)	0.04	3.877(1)	11.636(1)	0.98
$TaSr_2SmCu_2O_{8-\delta}$ (95%)	—	3.872(1)	11.676(3)	4.79
$NbSr_2PrCu_2O_{8-\delta}$ (pure)	-0.01	3.892(1)	11.681(2)	0.67
$TaSr_2PrCu_2O_{8-\delta}$ (95%)	—	3.890(2)	11.713(5)	0.77
$NbBa_2PrCu_2O_{8-\delta}$ (pure)	0.04	3.950(2)	11.947(4)	544

$NbBa_2PrCu_2O_{8-\delta}$ compound could be prepared. The other Ba-containing materials resulted in phase mixture of CuO and Ba_2REMO_6 , as already reported in a similar work (6). They are, therefore, no longer referred to.

The compounds with $M = Nb$ are single phase, those with $M = Ta$ contain about 5% impurities such as $SrCuO_2$. All compounds have tetragonal crystal structure as shown in Fig. 1 with space group $P4/mmm$. It is the same as that of $TaBa_2LaCu_2O_8$ (3, 4) and quite similar to that of $YBa_2Cu_3O_7$ (Y-123). In this structure the Sr or Ba ions occupy the A site and the unit cell has a tripled c -axis with respect to the perovskite lattice. The M -ions with sixfold oxygen coordination are located between the SrO or BaO layers. The CuO_2 - RE - CuO_2 double pyramidal layers, similar to those in the Y-123 structure, are retained. Lattice constants measured by XRD are given in Table 1. These parameters are smaller than that of $MBa_2LaCu_2O_8$ and very close to those of typical cuprate superconductors ($a \approx 3.8$ - 3.9 Å) (1, 3, 4). A typical powder XRD spectrum for pure $NbSr_2SmCu_2O_{8-\delta}$ with a tetragonal structure is shown in Fig. 2.

The observed and calculated d -values and XRD intensi-

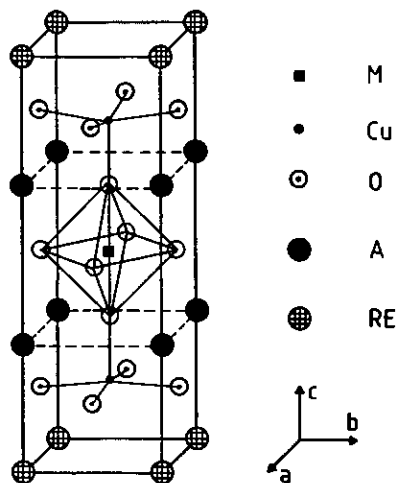


FIG. 1. Crystal structure of $MA_2RECu_2O_8$ with $M = Nb$ or Ta , $A = Sr$ or Ba , and $RE = La, Pr, \text{ or } Sm$.

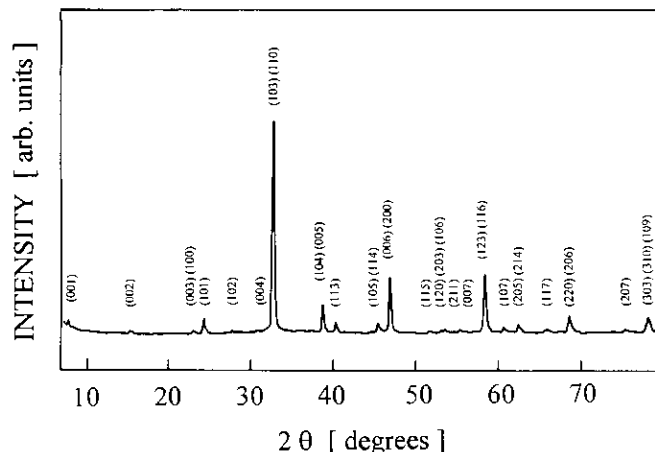


FIG. 2. Powder XRD spectrum for the tetragonal compound $NbSr_2SmCu_2O_{8-\delta}$ obtained with $CuK\alpha$ radiation.

ties for $NbSr_2SmCu_2O_{8-\delta}$ are shown in Table 2. The atomic positions in Ref. (4) for $NbBa_2LaCu_2O_8$ were considered for the calculation of theoretical intensities I_c . The best fit to the experimental results was obtained for the case that cations Nb^{5+} occupy the Cu(1) site of the Y-123 parent structure which yields a residual value of $R = 0.06$. In contrast, the case that cations Nb^{5+} occupy the Cu(2) site of the Y-123 parent structure results in a residual value of $R = 0.21$. So we believe that Nb^{5+} is substituting into Cu(1) site of the Y-123 parent structure. This result is in good agreement with that of Refs. (6, 7).

The TGA for single phase compounds in a reducing atmosphere (10 vol% H_2 in N_2) shows that the reduction of the copper ions starts at about $280^\circ C$, and comes to the end at $650^\circ C$ as shown in Fig. 3. The calculation of the oxygen content per chemical formula is based on the assumption that in these compounds the cations are stable in Nb^{5+} , Ba^{2+} , Sr^{2+} , and Sm^{3+} states, respectively. Indeed the XRD analysis for the reduced $NbSr_2SmCu_2O_{8-\delta}$ sample demonstrates that it is composed of copper metal, $Nb_2Sr_4O_9$ and Sm_2O_3 . The oxygen content per chemical formula calculated from the TGA is very close to 8 as shown in Table 1; therefore, the formal copper valence is close to +2. Fig. 3 shows the corresponding weight loss in percentage.

The substitution of the $4d$ transition element Ru for Nb gives a nearly single-phase solid solution until $x = 0.5$, with estimated impurity less than 5% according to XRD intensities. The lattice constants decrease when x increases from 0 to 0.5 (Fig. 4). Further increase in x results in multiphase materials. The measured and calculated powder XRD intensities for the $x = 0.5$ compound are given in Table 3. The comparison of the observed and calculated results indicates that Ru is substituted for Nb, since for such a substitution the residual value R equals

TABLE 2
Powder XRD Data for $\text{NbSr}_2\text{SmCu}_2\text{O}_{8-\delta}$

hkl	d_o	d_c	I_o	I_c
0 0 1	11.669	11.636	72	142
0 0 2	5.828	5.818	36	51
0 0 3	3.876	3.879	—	5
1 0 0	3.876	3.877	—	26
1 0 1	3.681	3.678	129	140
1 0 2	3.227	3.226	21	29
0 0 4	2.911	2.909	19	19
1 0 3	2.744	2.742	1537	1000
1 1 0	2.744	2.742		527
0 0 5	2.329	2.327	213	49
1 0 4	2.329	2.327		159
1 1 3	2.239	2.239	90	95
1 0 5	1.996	1.995	98	18
1 1 4	1.996	1.995		61
0 0 6	1.939	1.939	445	78
2 0 0	1.939	1.938		363
1 1 5	1.774	1.774	—	16
1 0 6	1.734	1.734	—	2
2 0 3	1.734	1.734	—	4
2 1 0	1.734	1.734	—	7
2 1 1	1.714	1.715	32	10
0 0 7	1.663	1.662	43	22
2 1 2	1.663	1.662		10
1 1 6	1.583	1.583	509	113
2 1 3	1.583	1.583		359
1 0 7	1.529	1.528	59	56
2 0 5	1.490	1.490	94	39
2 1 4	1.490	1.489		66
1 1 7	1.421	1.421	44	43
2 0 6	1.371	1.371	167	88
2 2 0	1.371	1.371		99
3 0 2	1.263	1.262	26	35
3 1 0	1.226	1.226	171	165

Note. d_o and d_c are observed and calculated values for different planes with miller indexes (h, k, l). I_o and I_c are the corresponding intensities. Dashed lines “—” in the I_o column represent that the observed intensity is lower than 15.

0.06 while the corresponding value for substitution into Cu(2) site equals 0.13.

In order to determine the formal copper valence the reduction of $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ and RuO_2 was performed by TGA. As shown in Fig. 3, RuO_2 was reduced at relative low temperatures starting at 160°C and ending at 240°C. Combination of the TGA and the XRD analysis reveals that in $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ the copper ions are reduced in the temperature range of 280 to 450°C while the ruthenium ions are reduced in the range of 500 to 580°C. It is also noted that the oxygen loss connected with Ru is about 10% less than what we expected from Ru^{4+} in the compound. This is probably caused by the existence of Ru^{3+} and impurities. The total oxygen content estimated from above analysis for the compound

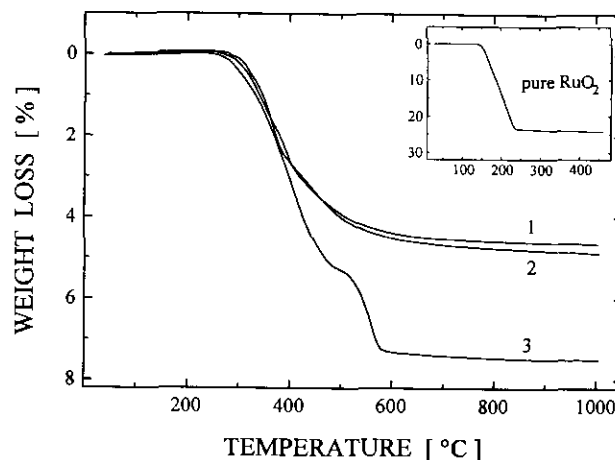


FIG. 3. TGA for compounds (1) $\text{NbSr}_2\text{SmCu}_2\text{O}_{8-\delta}$, (2) $\text{NbSr}_2\text{PrCu}_2\text{O}_{8-\delta}$, and (3) $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ in mixed gas of $\text{H}_2:\text{N}_2 = 10:90$, the same analysis for RuO_2 is shown in the inset.

$\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ equals to 7.88. As shown in Fig. 3, the oxygen content connected with copper is clearly higher for $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ than for $\text{NbSr}_2\text{SmCu}_2\text{O}_{8-\delta}$. The formal copper valence in $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ is about +2.14.

The TGA in air for all these compounds shows no significant oxygen desorption up to 1000°C. This may be connected with the fact that unstable oxygen in the crystal lattice is normally found in single Cu–O chains (11).

The room temperature resistivities for all of the compounds are given in Table 1. We noticed that the compounds with $A = \text{Sr}$ show smaller room temperature resistivities in comparison with $A = \text{Ba}$ such as $\text{NbBa}_2\text{PrCu}_2\text{O}_{8-\delta}$ or $\text{NbBa}_2\text{LaCu}_2\text{O}_{8-\delta}$ (3, 4). This observation is correlated with smaller lattice parameters for compounds with $A = \text{Sr}$, which allow an enhanced orbital

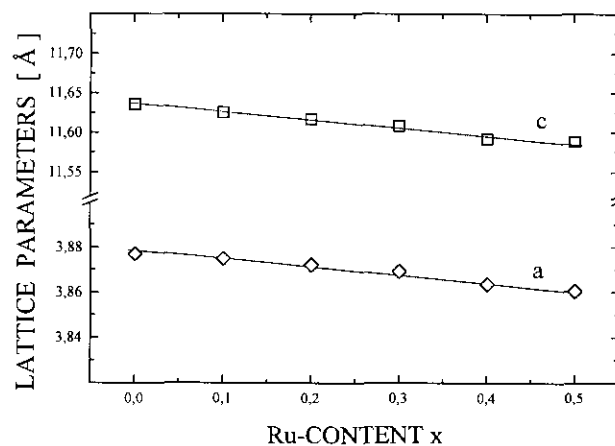


FIG. 4. The lattice parameters a and c for $\text{Nb}_{1-x}\text{Ru}_x\text{Sr}_2\text{SmCu}_2\text{O}_{8-\delta}$ as a function of Ru content x . Lines serve as guides to the eye.

TABLE 3
Powder XRD Data for $NbSr_{0.5}Ru_{0.5}Sr_2SmCu_2O_{8-\delta}$

hkl	d_o	d_c	I_o	I_c
0 0 1	11.572	11.588	72	141
0 0 2	5.813	5.794	36	51
0 0 3	3.864	3.863	—	4
1 0 0	3.864	3.861	—	26
1 0 1	3.667	3.663	118	135
1 0 3	2.733	2.731	1492	1000
1 1 0	2.733	2.730		512
0 0 5	2.319	2.318	166	37
1 0 4	2.319	2.317		111
1 1 3	2.230	2.229	91	87
1 0 5	1.987	1.987	96	14
1 1 4	1.987	1.987		46
0 0 6	1.930	1.931	441	92
2 0 0	1.930	1.930		333
1 1 6	1.577	1.577	519	126
2 1 3	1.577	1.576		356
1 0 7	1.526	1.522	44	44
2 0 5	1.484	1.483	74	30
2 1 4	1.484	1.483		46
1 1 7	1.416	1.416	31	30
2 0 6	1.365	1.365	189	102
2 2 0	1.365	1.365		91

Note. d_o and d_c are observed and calculated values for different planes with miller indexes (h, k, l). I_o and I_c are the corresponding intensities. Dashed lines “—” in the I_o column represent that the observed intensity is lower than 15.

overlap between $Cu(d_{x^2-y^2})$ and $O(p_x, p_y)$. Ruthenium substitution into the niobium site decreases the room temperature resistivity from $0.98 \Omega \cdot \text{cm}$ for $x = 0$ to $0.05 \Omega \cdot \text{cm}$ for $x = 0.5$. All the compounds prepared in this work show semiconducting behavior from room temperature down to 10 K. A typical behavior of resistivity as a function of temperature for $NbSr_2SmCu_2O_{8-\delta}$ and $Nb_{0.5}Ru_{0.5}Sr_2SmCu_2O_{8-\delta}$ is shown in Fig. 5. The activation energy E is estimated for $x = 0$ and 0.5 according to the relation $\rho \propto \exp(E/2k_B T)$. From plots of $\log \rho$ against $1000/T$ in Fig. 5, a clear tendency of decreasing E with increasing Ru content is observed. A relative small E value of 16 meV at 25 K is observed for $x = 0$, and it decreases to about 3.5 meV for $x = 0.5$. This is probably connected with the fact that extra carriers (holes) are introduced into CuO_2 planes by the Ru substitution.

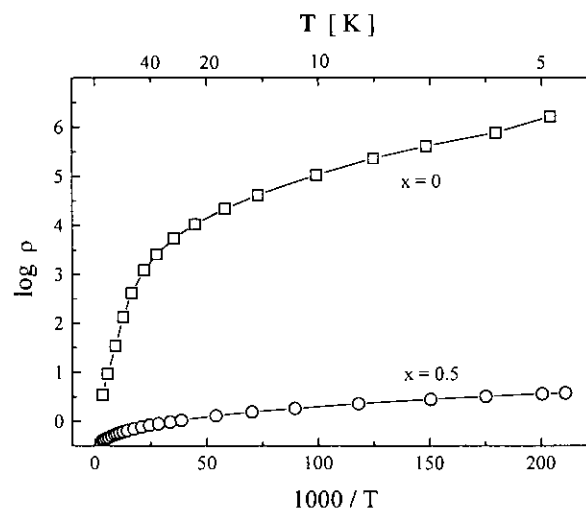


FIG. 5. Logarithm of resistivity as a function of reciprocal temperature for compounds $Nb_{1-x}Ru_xSr_2SmCu_2O_{8-\delta}$, $x = 0$ and 0.5. Lines serve as guides to the eye.

In summary new compounds $MA_2RECu_2O_{8-\delta}$ have been prepared and characterized. Structural analysis revealed that they crystallize in an 1-2-1-2 $TaBa_2LaCu_2O_{8-\delta}$ structure type. Partial substitution of Ru for Nb increases the copper valence from +2 to +2.14 and decreases the room temperature resistivity.

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