Preparation of $La_{1.29}Ca_{0.43}Ba_{1.29}Cu_3O_y$ Powder with Different Organic Acids Containing OH or NH_2

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Abstract—More than ten organic acids containing hydroxyl or amino groups were selected as a medium to prepare sub-micrometer superconducting powder of $La_{1.29}Ca_{0.43}Ba_{1.29}Cu_3O_y$ by using a polymeric precursor method. Heat treated samples were analyzed by IR spectrometer for the degree of polymerization, by ICP and EDS for the homogeneity, by SEM for the particle size determination. T_c measurement and the purity examination were obtained by resistivity and X-ray diffraction, respectively. Organic acids containing three carboxyl groups are highly recommended for preparing high-T_c superconductor. It donates electron pairs for chelating with metal ions and also for the polyesterification with ethylene glycol. On the other hand, organic acids containing amino group along with two or less carboxyl acid groups are not recommended for this purpose.

Index Term—$La_{1.29}Ca_{0.43}Ba_{1.29}Cu_3O_y$, oxide, polymeric precursor method, superconductor.

1. INTRODUCTION

$La_{1.29}Ca_{0.43}Ba_{1.29}Cu_3O_y$ has a tetragonal triple-perovskite unit-cell with a T_c of 80 K [1], which is also known as La-3137 with a formula of $La_3CaBa_3Cu_7O_y$. Due to the absence of the twinning planes, the temperature dependence of J_c of La-3137 is larger, and the slope of B_{irr}-T lines is smaller than that of $YBa_2Cu_3O_y$ (Y-123) [2]. We have investigated La-Ca-Ba-Cu-O system thoroughly and find that T_c is increased by the amount of Ca ion occupying the center position of the unit-cell and decreased by the amount of La ion occupying the Ba site [3]. In general, high-T_c superconductors are prepared by the conventional solid state reaction method, in which starting materials are ground thoroughly and then heat treated at high temperature. Repeating of the grinding and the heat treatment process are required for making materials containing three or more oxides. Extensive grinding increases the homogeneity of the material, but the minimal obtainable particle size of the starting oxides (ea. 1 μm) severely hampers the solid state reaction. On the other hand, by using solution method, starting materials are dissolved in water. Mixing of the constituent ions to the atomic level greatly increases the homogeneity of the resulting powder. In addition, particle size [4] of the final product and the heating time required for making superconductor are reduced [5]. One of the solution methods, called polymeric precursor method is used by us to prepare a record high-T_c of 95 K $Bi_2Sr_2CaCu_2O_{8+\delta}$ [6], $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_2O_y$ [5] and $Pb_2Sr_{0.8}La_{1.2}Cu_2O_{6.1+\delta}$ [7]. We have also studied this method by using different polyprotic acids, such as, oxalic acid, succinic acid, 1,6-adipicacid, malic acid, tartaric acid and citric acid to prepare La-3137. Each acid selected contains at least two carboxyl groups. Some of them also contain hydroxyl group, for example, malic acid, tartaric acid and citric acid. They have one, two and one hydroxyl groups, respectively. Among them, citric acid is the only one that has three carboxyl groups. In this study, more organic acids containing amino group as well as other polyprotic acids were selected for making La-3137 in order to investigate the role played by different functional groups in this solution method.

2. EXPERIMENTAL

Thirteen acids containing one to four carboxyl acid groups, one to two hydroxyl groups or one to two amino groups were selected for this study. The name of these acids and the number of their functional groups are listed in Table I. The appropriate amount of reagent grade chemicals of the constituent nitrate salts, such as, $La(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Ba(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, were dissolved in deionized water. Organic acid (OA) and ethylene glycol (EG) were then added into the aqueous solution. Mole ratio of the Acid/TMI (total metal ions) and EG/TMI was 1.5 and 2.5, respectively. pH of the solution was then adjusted by triethylamine to 6.8. The mixture was dried at 90 °C for about 2 h until it became viscous, indicating that the condensation of the OA with EG took place. Metal cations were supposed to chelate with OA in the organic matrix. The solution was heated at 250 °C to pyrolyse the organic materials. The gray residue obtained was heated at 500 °C for 2 h in order to complete the pyrolysis. Resulting powder was calcined at 800 °C for 3 h and then heat treated at 900 °C for 30 h, annealed at 400 °C in the flowing oxygen atmosphere with a flow rate of 25 mL/min. for 12 h and then followed by furnace cooling to room temperature.

Samples were characterized after each heat treatment. Polymerization was checked by an IR spectrometer. Homogeneity was determined by an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) or by an Energy Dispersive Spectrometer (EDS). The L lines of the La and Ba atoms and K_α lines of the Ca and Cu atoms were selected for analysis. Particle size was determined by a Scanning Electron Microscope (SEM) on the gold coated powder sample. T_c was measured by a 4-probe resistivity method on a sintered sample. Organic residue, such as, C, H and N, was determined by elemental analysis. Crystalline

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TABLE I
Number of functional groups in each organic acid

acid	-COOH	-OH	-N<
4-aminobutyric acid	1	0	1
malonic acid	2	0	0
malic acid	2	1	0
l (+)tartaric acid	2	2	0
l-aspartic acid	2	0	1
iminodiacetic acid	2	0	1
ethylenddiamine-N,N'-diacetic acid (EDDA)	2	0	2
β-methyltricarballylic acid	3	0	0
citric acid	3	1	0
tricarballylic acid	3	0	1
nitrilotriacetic acid	3	0	1
1,2,3,4-butanetetracarboxylic acid	4	0	0
ethylenediamine-N,N'-tetraacetic acid (EDTA)	4	0	2

TABLE II
Homogeneity of the samples after heat treated at 250 °C

acid	La ± RSD	Ca ± RSD	Ba ± RSD	Cu ± RSD
4-aminobutyric acid	2.7±21.0%	0.9±30.0%	3.2±43.4%	7.0±23.5%
malonic acid	3.0±6.3	1.1±12.4%	3.0±5.7%	7.0±4.9%
malic acid	2.7±5.9%	1.1±4.2%	2.9±3.9%	7.0±3.2%
l (+)tartaric acid	2.8±2.8%	1.1±1.9%	3.1±2.9%	7.0±7.1%
l-aspartic acid	2.7±8.0%	0.8±2.5%	2.8±5.8%	7.0±2.1%
iminodiacetic acid	2.7±6.8%	1.0±4.0%	3.0±3.7%	7.0±3.1%
EDDA	2.9±3.6%	1.0±6.1%	3.1±3.7%	7.0±4.0%
β-methyltricarballylic acid	2.9±1.7%	1.2±5.8%	3.1±6.2%	7.0±1.0%
citric acid	2.9±0.5%	1.0±0.4%	2.9±0.7%	7.0±1.8%
tricarballylic acid	2.9±5.7%	0.9±1.7%	2.9±3.2%	7.0±3.0%
nitrilotriacetic acid	3.1±5.1%	1.0±3.4%	3.0±3.3%	7.0±8.5%
butanetetracarboxylic acid	2.7±3.0%	0.9±3.7%	2.9±3.5%	7.0±4.4%
EDTA	2.8±2.4%	1.0±3.6%	3.0±3.8%	7.0±3.5%

TABLE III
Homogeneity of the samples after heat treated at 800 °C

acid	La ± RSD	Ca ± RSD	Ba ± RSD	Cu ± RSD
4-aminobutyric acid	21.9±12.2%	8.1±26.4%	20.0±37.7%	50.0±11.0%
malonic acid	22.9±20.9%	8.2±14.6%	19.7±15.0%	49.2±7.5%
malic acid	21.3±11.5%	7.3±8.8%	22.6±6.6%	48.8±7.6%
l (+)tartaric acid	22.3±11.0%	7.8±9.6%	21.9±8.0%	48.0±5.0%
l-aspartic acid	24.9±17.3%	6.8±28.4%	21.6±11.2%	46.6±2.7%
iminodiacetic acid	23.4±16.5%	7.7±11.0%	23.0±7.2%	45.9±9.5%
EDDA	23.1±16.6%	7.5±5.0%	21.0±7.0%	48.4±5.5%
β-methyltricarballylic acid	22.0±7.1%	7.4±7.2%	21.4±9.6%	49.3±6.9%
citric acid	21.5±3.8%	7.3±4.5%	22.2±3.2%	48.9±2.9%
tricarballylic acid	22.8±6.3%	7.5±10.7%	22.6±6.6%	47.1±3.2%
nitrilotriacetic acid	22.1±9.3%	7.7±14.0%	22.8±10.0%	47.4±3.6%
butanetetracarboxylic acid	22.6±3.5%	7.7±17.6%	21.4±4.1%	48.4±3.8%
EDTA	22.0±6.4%	7.8±8.0%	23.2±14.0%	47.0±5.0%

phase of the final product was examined by an X-ray Diffractometer.

3. RESULTS AND DISCUSSION

After heat treatments at 90 and 250 °C, samples were examined by an IR spectrometer to investigate the degree of polyesterification between the organic acid and the ethylene glycol. From the absorption at 1734 cm^{-1} for the ester C=O bond and a broad absorption near 1240 cm^{-1} for the ester C-O bond, we found that the powders obtained from seven acids, such as, malic acid, β-methyltricarballylic acid, citric acid, tricarballylic acid, nitrilotriacetic acid, butanetetracarboxyl acid and EDTA have the characteristic absorptions of ester. Except malic acid, which contains only two carboxyl acid and one hydroxyl group, the rest of them contain three or more carboxyl acid groups. In the polymerization, it needs carboxyl and hydroxyl groups to form polyester. In addition, metal ions are chelated by the rest of the ligands to be homogeneously distributed in the organic matrix and avoid segregation. At least three ligands in each organic acid are required for making homogenous precursor. If the acids contain amino groups and also two carboxyl acid group only, such as, aspartic acid, iminodiacetic acid and EDDA, they have strong chelating ability with metal ions, as a result, no sufficient carboxyl acid group for polymerization to take place. Therefore, no ester C=O and C-O bonds is observed.

Homogeneity observed by ICP-AES in the sample prepared after 250 °C heat treatment was listed in Table II. Three samples at different locations on the bottom of the beaker from each reaction batch were investigated. Average and the relative standard deviation (RSD) of the mole ratio of the metal ions obtained from each organic acid is listed. Ideal mole ratio of La: Ca: Ba: Cu is 3: 1: 3: 7. From the relative standard deviation, we can easily find that 4-aminobutyric acid is the worst and citric acid is the best for making La-3137 superconductor. 4-Aminobutyric acid contains one carboxyl and one amino group, which has insufficient carboxyl acid to form polyester. It is the only acid studied in this paper that contains only one carboxyl acid group. Therefore, its relative standard deviation is extremely high compared with the rest of the acids.

In measuring the concentration of the metal ion by ICP-AES, sample should be dissolved in water. The measurement is done on the whole solution. It does not give us a microscopic result. In order to know the homogeneity in a smaller area, we check it by EDS after the powder is heat treated by 800 °C for 3 h. Ten data were obtained from different locations of each sample under an SEM. Results are listed in Table III. Theoretical mole ratio of La: Ca: Ba: Cu is 21.4: 7.1: 21.4: 50.0. Again, samples obtained from 4-aminobutyric acid has the largest relative standard deviation and that obtained from citric acid has the smallest figures. If we want to rank the rest of the acids, their order is not obvious from Tables II and III. Therefore, they were treated further by summing the four relative standard deviations to give a total relative standard deviation in Table IV and then used it as a guideline to look for the effect of the organic acid in the preparation of La-3137.

Seven acids give a total relative standard deviation by EDS measurement under 31.5. They are samples obtained from malic acid, tartaric acid, β-methyltricarballylic acid, citric acid, tricarballylic acid, butanetetracarboxyl acid and

TABLE IV
Total relative standard deviation obtained from ICP and EDS

acid	ICP	EDS
4-aminobutyric acid	117.9	57.3
malonic acid	29.3	44.0
malic acid	17.2	29.0
l (+)tartaric acid	14.7	25.3
l-aspartic acid	18.4	51.9
iminodiacetic acid	17.6	38.3
EDDA	17.4	35.8
β-methyltricarballylic acid	14.7	24.8
citric acid	3.4	18.0
tricarballylic acid	13.6	29.9
nitrilotriacetic acid	20.3	35.5
butanetetracarboxylic acid	14.6	30.1
EDTA	13.3	31.3

EDTA. For six of them, the characteristic ester absorption peaks appeared in the IR spectra. We deduce that the possibility of the polymerization does help the dispersion of the metal ions in the sample. As a result, homogeneity is improved. All the organic acids containing amino groups give the total relative standard deviation higher than 30 no matter whether they have 2, 3 or 4 carboxyl acid groups. Obviously, organic acid containing amino group is not an advantage in this process. Comparing the total relative standard deviation for the tartaric acid, malic acid and malonic acid, we find that hydroxyl group is helpful for improving the homogeneity of the metal ions. The relative standard deviation of these three acids are 25.3, 29.0, 44.0, respectively. Citric acid containing three –COOH and one –OH group, it has the best result. Comparing the three acids containing at least 3 –COOH groups, their relative standard deviation is still higher than that of citric acid. It shows that the organic acid containing –OH group is helpful for making homogeneous superconductor.

Average particle size of the powder is analyzed by an SEM on the materials calcined at 800 °C for 3 h. Most of the particles have a regular round shape and their average diameter is less than 0.2 μm, if they are not prepared by the organic acid containing amino groups. Again, the sample prepared by 4-aminobutyric acid has the largest average particle size. Aspartic acid and iminodiacetic acid are the two acids with two carboxyl groups and also containing amino groups. It is clear that these three acids are not good media for preparing La-3137 superconducting powder by this precursor method.

Checking the residual concentrations of C, H and N left in the sample after it is calcined at 800 °C for 3 h, no hydrogen and nitrogen is found in all the samples, except that one made by 4-iminodiacetic acid. However, all the samples have trace amount of carbon left. That is possible to reduce by further heat treatment. The amount of carbon left in the materials does not depend on the functional groups of the polyprotic acid. However, materials prepared by the amino containing acid seems to have less carbon residue left.

TABLE V
Average particle size, residual C, H and N left in the samples after heat treated at 800 °C

acid	particle size (μm)	C (%)	H (%)	N (%)
4-aminobutyric acid	0.47	0.42	0	0
malonic acid	0.17	0.92	0	0
malic acid	0.17	1.75	0	0
l (+)tartaric acid	0.13	1.12	0	0
l-aspartic acid	0.29	0.49	0	0
iminodiacetic acid	0.33	1.02	0.43	0
EDDA	0.13	0.45	0	0
β-methyltricarballylic acid	0.23	0.53	0	0
citric acid	0.14	0.56	0	0
tricarballylic acid	0.16	0.72	0	0
nitrilotriacetic acid	0.21	0.93	0	0
butanetetracarboxyl acid	0.16	1.26	0	0
EDTA	0.19	0.45	0	0

TABLE VI
T_c, ΔT_c, ρ_{290K} and $\rho_{290K/120K}$ of the samples prepared

acid	$T_{c(zero)}$ (K)	ΔT_c (K)	ρ_{290K} (mΩ·cm)	$\rho_{290K/120K}$
4-aminobutyric acid	23.8	34.0	3.83	0.97
malonic acid	65.8	9.3	2.02	1.30
malic acid	75.0	4.9	1.58	1.44
l (+)tartaric acid	76.2	3.2	1.17	1.50
l-aspartic acid	66.3	10.0	2.03	1.27
iminodiacetic acid	73.6	5.0	1.64	1.43
EDDA	76.2	3.5	1.36	1.51
β-methyltricarballylic acid	78.5	2.4	0.89	1.55
citric acid	78.4	2.2	0.87	1.50
tricarballylic acid	77.9	2.3	0.93	1.54
nitrilotriacetic acid	75.8	3.2	1.30	1.55
butanetetracarboxylic acid	76.7	2.8	0.95	1.38
EDTA	76.2	2.8	1.02	1.65

$T_{c(zero)}$, ΔT_c, ρ_{290K} and $\rho_{290K/120K}$ obtained in the temperature dependent resistivity measurement on all the samples after they are annealed under oxygen atmosphere are listed in Table VI. From the resistivity ratio, it is found that all the samples have metallic conducting behavior in the normal state, except the one made by 4-aminobutyric acid, which has a semiconducting behavior. Its T_c and ΔT_c are 23.8 K and 34 K, respectively. These results are relatively bad compared with other samples. We believe that its homogeneity is terrible and that segregation of the metal ions probably happened in the precursor powder which prevented the formation of homogeneous La-3137. Most of the samples have T_c higher than 70 K, except the two made by malonic acid and aspartic acid. Both of them contain only two carboxyl groups. The latter contains one amino group, which is not as helpful for making homogeneous sample as the acid containing hydroxyl group. The former has only two ligands, which is not sufficient for polymerization and also for chelating of the metal ions. We deduce that the metal ions are not evenly distributed in the orgainic matrix before it is pyrolysed. Again, the homogeneity is also affected. The highest T_c is found in the β-methyltricarballylic acid and citric acid, both of which have three carboxyl groups, which have the ability of forming ester and also grasping the metal ions into its organic matrix. Homogeneity is improved. Those materials that have ρ_{290K} lower than 1 mΩ· cm are prepared by acids containing three or more carboxyl groups. In addition, they have higher T_c, and smaller ΔT_c.

TABLE VII

T_c and shielding fraction obtained from SQUID of the samples prepared

acid	shielding fraction (%)	$T_{c(onset)}$ (K)
4-aminobutyric acid	1.36	70
malonic acid	13.0	70
malic acid	20.8	79
l (+)tartaric acid	21.2	77
l-aspartic acid	10.9	70
iminodiacetic acid	11.0	76
EDDA	20.4	75
β-methyltricarballylic acid	71.3	79
citric acid	67.7	77
tricarballylic acid	31.3	78
nitrilotriacetic acid	25.2	78
butanetetracarboxylic acid	31.3	79
EDTA	21.5	78

$T_{c(onset)}$ and the shielding fraction (the relative amount of superconducting phase) observed by a SQUID Magnetomer are listed in Table VII for the samples. All of them have a T_c higher than 70 K. T_c measured by susceptibility is about the $T_{c(mid)}$ measured by the resistivity method from our past experience. Therefore, they are higher than the $T_{c(zero)}$ listed in Table VI. These results show that the shielding fraction of the material prepared by 4-aminobutyric acid is very small. In other words, only a small amount of superconducting phase is obtained. Two samples that have relatively high shielding fraction are made by β-methyltricarballylic acid and citric acid. It is clearly shown that organic acids containing three carboxyl groups are highly recommended for making high-T_c superconductor by the polymeric precursor method.

4. CONCLUSION

For the preparation of superconducting La-3137 compound by the polymeric precursor method, it is found that samples prepared by an organic acid containing three carboxyl groups are highly recommended whereas organic acids containing amino group and only two carboxyl groups are not recommended. Organic acids containing hydroxyl and two carboxyl groups are also recommended.

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