

SYNTHESIS AND STUDIES OF Y-Ba-Cu-O HIGH TEMPERATURE
SUPERCONDUCTOR PREPARED BY SOL-GEL METHOD

S. G. GRIGORYAN, A. L. MANUKYAN, A. G. HAYRAPETYAN,
A. M. ARZUMANYAN, L. H. RASHIDYAN, N. Y. MKRTICHAN,
A. A. MKRTCHYAN, K. A. KURGINYAN,
A. H. TROZIAN AND R. S. VARDANYAN

Armenian Scientific Research Institute of Applied Chemistry "ARIAC", Yerevan

Received 6 V 2002

A new method of preparation of powders of Y-Ba-Cu-O high temperature superconductor by sol-gel processing technique based on new and convenient precursors stable in air, having high compatibility with each other has been developed. Basic scientific and technological issues related to the synthesis of bulk materials, their structure and electrical conductivity are discussed.

Fig. 4, ref. 5.

In literature the methods of preparation of Y-Ba-Cu-O high temperature superconducting (HTSC) materials by sol-gel processing technique both for powders and thin films are described [1]. All these methods are based on using yttrium alkoxides as precursors, which are not ready available reagents, besides the majority of these methods use copper alkoxides, which show low solubility in organic solvents, besides they are very sensitive to hydrolysis in air.

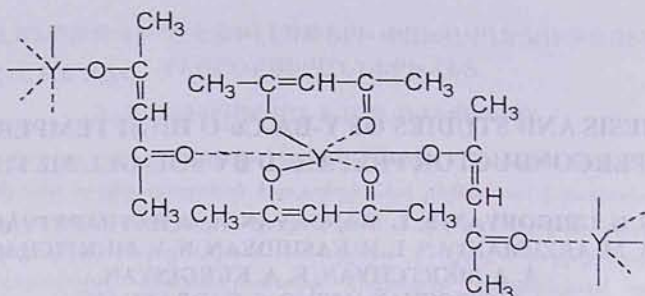
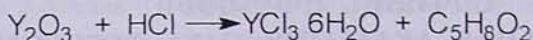
We offer a new method of preparation of Y-Ba-Cu-O ceramic materials by sol-gel processing technique based on new and convenient precursors stable in air, having high compatibility with each other.

Basic scientific and technological issues related to the synthesis of bulk materials, their structure and electrical conductivity are discussed.

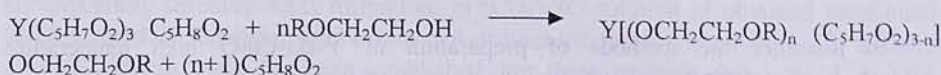
Results and Discussions

1. Yttrium Precursors

We offer to use acetylacetonate complex of yttrium as an active yttrium precursor. It was prepared by the reaction of yttrium trichloride (obtained by dissolving of yttrium oxide in hydrochloric acid) with acetylacetonate in alkaline water solution.



The complex obtained most probably exists in the form of co-ordination polymer. According to IR and elemental analysis data its structure corresponds to that of yttrium chelate. It poorly dissolves in common organic solvents. However at long time heating in bidentate type complex forming solvents, such as 2-alkoxyethanols, it gradually dissolves due to the cleavage of intermolecular coordination bonds and partial substitution of acetylacetonate ligands by 2-alkoxyethanol ones. Color of the complex changes from white to brown. It becomes readily soluble in many organic solvents especially alcohols. According to IR, H^1 NMR spectral as well as elemental analyses data structures of the complexes are as follows:



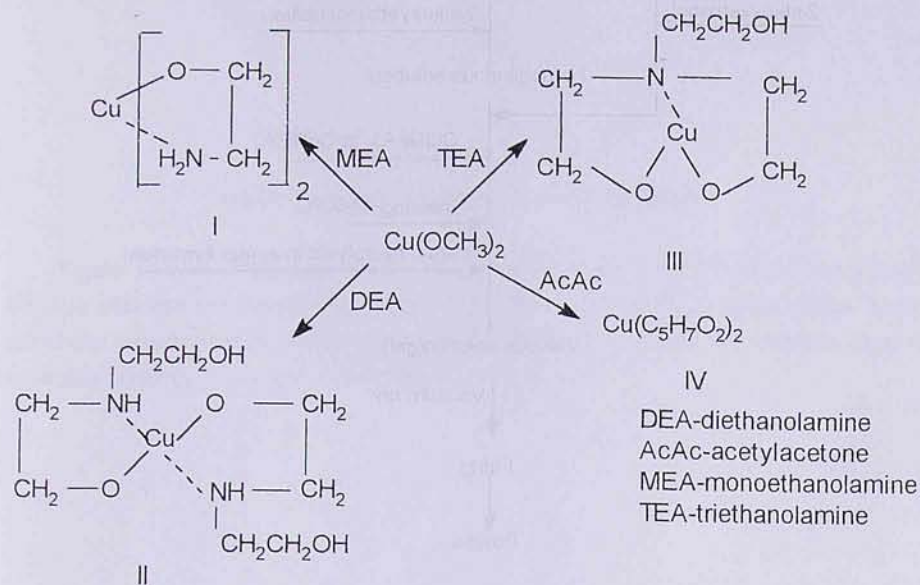
where $R=CH_3$, $n=2$; $R=C_2H_5$, $n=1$

2. Copper Precursors

We have shown that intramolecular copper complex alkoxides with diethanolamine and triethanolamine are active precursors for synthesis of Y-Ba-Cu-O ceramic materials. They show high solubility in 2-alkoxyethanols and compatibility with yttrium complexes described above. It is very important that they also show high stability to hydrolysis especially the diethanolamine based complexes.

Detailed studies of different methods of preparation of these complexes show that just these complexes are formed, when diethanolamine or triethanolamine were used as complex forming agents for enhancing solubility of copper alkoxides [2,3], particularly for copper methoxide- the common used precursor for synthesis of HTSC ceramics by sol-gel method. We have shown that triethanolamine and diethanolamine are not only complex forming agents but also active reagents, reacting with copper methoxide at room temperature, resulting in the formation of the intramolecular type complex alkoxides II and III (Scheme).

The compound III was prepared also by thermal treatment (80°C) of the initial $\text{Cu}(\text{OH})_2\text{-N}(\text{CH}_2\text{CH}_2\text{OH})_3$ complex compound, prepared according to Duff and Steer method [4]. The compound II was prepared also by the reaction of copper hydroxide with diethanolamine according to the method [4]. The monoethanolamine complex I was obtained by the reaction of $\text{Cu}(\text{OCH}_3)_2$ with monoethanolamine or by treatment of $\text{CuO} \cdot 2\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ complex with boiling dry isopropyl alcohol [4]. These complex alkoxides are readily soluble in alkoxyethanol type solvents forming dark blue solutions.



Scheme
Reactions of copper methoxide with ethanolamines

Copper methoxide readily reacts with acetylacetonate resulting in the formation of copper bis(acetylacetonate) IV.

According to IR spectral and elemental analysis data structure of complexes I-III obtained by this scheme and that of compounds obtained through copper oxide/hydroxide are identical. The latter method for preparation of these complexes is simple enough and easily reproducible. Thus for the first time we have offered to use readily available intramolecular copper complexes of ethanolamines as active and stable reagents showing high solubility in organic solvents for synthesis of Y-Ba-Cu-O ceramic materials.

Y-Ba-Cu complexed alkoxides were prepared first by multi-hour heating of yttrium acetyl acetonate in 2-methoxyethanol or 2-ethoxyethanol (Figure 1). In case of 2-methoxyethanol the reaction requires milder conditions to carry out otherwise hydrolysis and precipitation of insoluble solid throughout the reaction may take place. After homogenization a solution of barium alkoxide, prepared by dissolving of metallic barium in corresponding 2-alkoxyethanol, is introduced into the solution prepared by dissolving of yttrium acetyl acetonate in 2-alkoxyethanol. After some hours of heating for

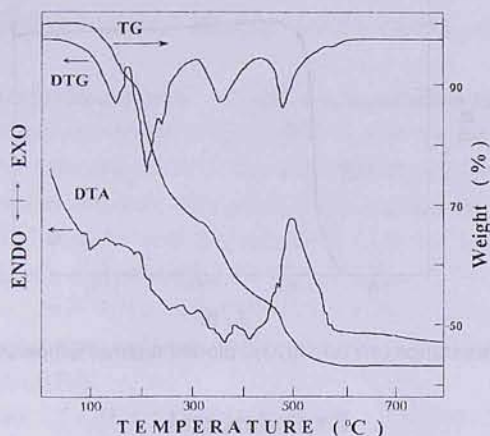


Figure 2. DTA, DTG, TG of Y-Ba-Cu-O gel powder.

Figure 3 shows X-ray diffraction analysis of the Y-Ba-Cu-O powders. According to the data obtained the samples have perovskite structure with P_{mmm} space group. Lattice parameter measurements ($a=3,8051\text{\AA}$, $b=3,8666\text{\AA}$, $c=11,5998\text{\AA}$) indicate that the crystalline structure obtained has orthorhombic symmetry.

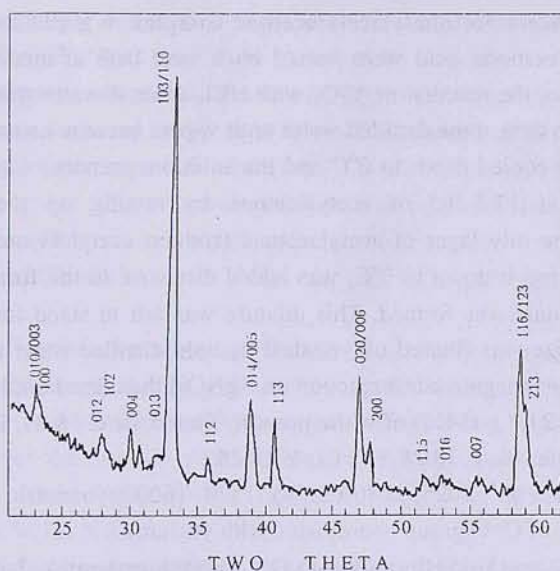


Figure 3. XRD traces of YBCO HTSC powder.

The temperature dependence of electrical resistance $R(T)$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bulk ceramics ranging from 77 to 300K was measured by four-probe method. The results are given in Figure 4. Temperature of transition to the superconducting state $T(0)_c$ and temperature interval of this transition ΔT have been determined. These values have been found to be $T(0)_c=84\text{K}$ and $\Delta T=4\text{K}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bulk ceramics.

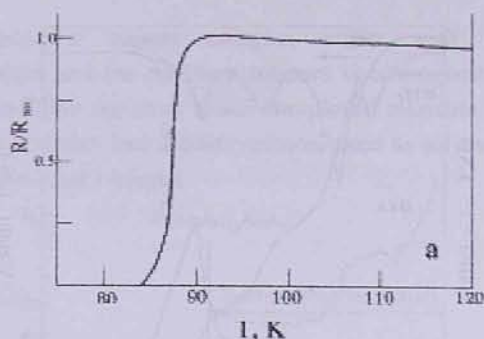


Figure 4. Electric resistance of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ plotted against temperature for powder

Experimental

Reagent grade Y_2O_3 , acetylacetone, other reagents were used in syntheses. Copper methoxide has been obtained according to method [5].

IR spectra measurements were made with "Specord IR-75" spectrometer in Nujol. ^1H NMR spectral measurements were carried out with "Varian-300" spectrometer, using d -DMSO as solvent and HMDS as a standard. XRD analyses of crystalline samples were made with "Dron-2($\lambda\text{CuK}_{\alpha}$)" spectrometer.

Yttrium tris(acetylacetonate)acetylacetone complex. 6 g (0.0265 mol) of Y_2O_3 and 50 ml of hydrochloric acid were heated on a sand bath at mixing until YCl_3 is formed as a result of the reaction of Y_2O_3 with HCl. After it water was evaporated, on adding from time to time some distilled water until vapors become neutral. The resultant 40 ml solution was cooled down to 0°C and the solution, prepared from 15 g Na_2CO_3 (10% solution) and 17.5 ml of acetylacetone by mixing up the mixture until disappearance of the oily layer of acetylacetone (sodium acetylacetonate is formed at this) and after cooling it down to 0°C , was added dropwise to the former one. 10 min later a solid precipitate was formed. This mixture was left to stand for 1 hour at 0°C , after it the precipitate was filtered off, washed by cold distilled water until wastewater was free from Cl ions (negative test reaction on AgNO_3) then dried until constant weight was reached. Yield 21.7 g (84%) of white powder. Found %: C 18.03, H 6.09, Y 18.03. $\text{YC}_{20}\text{H}_{29}\text{O}_8$. Calculated %: C 18.28, H 6.01, Y 18.28.

IR spectrum, ν , cm^{-1} : 1025, 1280 (C-O-), 1520, 1600 (symmetric and asymmetric valence frequencies of C=O group coordinated with yttrium).

Yttrium bis(2-methoxyethanolato-O,O') (acetylacetonate) 2-methoxyethanol complex was prepared by dissolving 0.95 g (0.0019 mol) of $\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3 \cdot \text{C}_5\text{H}_8\text{O}_2$ in 10 ml of 2-methoxyethanol by refluxing at 115°C for 8 h. After cooling the mixture was filtered off from small amount of sediment. The solvent was distilled off in vacuum 40 Torr at 70 - 80°C and dried for 2 h at 50°C and 20 Torr. Yield 0.65 g (81%). Found %: Y 21.80, C 40.11, H 7.37. $\text{YC}_{14}\text{H}_{29}\text{O}_8$. Calculated %: Y 21.46, C 40.59, H 7.05.

IR spectrum, ν , cm^{-1} : 1020, 1270 (C-O-H), 1080, 1130 (C-O-C), 1520, 1580 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium), 3300-3500 (OH).

^1H NMR (δ , ppm): 1.7 (6H, s, CH_3CO), 3.2-3.5 (7H, m, $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-}$), 5.2(H, s, $=\text{CH-}$).

Yttrium bis(acetylacetonate) (2-ethoxyethanolato-O,O') **2-ethoxyethanol complex** was prepared by dissolving 1.0 g (0.0021 mol) of $\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3$ $\text{C}_5\text{H}_8\text{O}_2$ in 10 ml of 2-ethoxyethanol by refluxing at 130°C for 8 h. After cooling the mixture was filtered off from small amount of sediment. The solvent was distilled off in vacuum 40 Torr at $70\text{-}80^\circ\text{C}$ and dried for 2 h at 50° and 20 Torr. Yield 1.0 g (96%). Found %: Y 19.85, C 46.17, H 7.12. $\text{YC}_{18}\text{H}_{33}\text{O}_8$. Calculated %: Y 19.06, C 46.36, H 7.13.

IR spectrum, ν , cm^{-1} : 1015, 1260 (C-O-H), 1080, 1120 (C-O-C), 1520, 1590 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium), 3350-3550 (OH).

^1H NMR (δ , ppm): 1.1 (3H, t, $\text{CH}_3\text{-CH}_2$) 1.8 (6H, s, CH_3CO), 3.3-3.45 (6H, m, $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-}$), 5.2(H, s, $=\text{CH-}$).

Copper monoethanolamine complex (I). 0.35 g (0.0028 mol) of copper methoxide was added to the solution of 0.4 g (0.006 mol) of monoethanolamine in 10 ml of dry benzene. The mixture was heated slowly up to $70\text{-}80^\circ\text{C}$ for two hours after it benzene was removed by distillation. The residue – violet crystals – were washed up by ethyl alcohol and dried. The crystals were refluxed in 5-7 ml of dry isopropyl alcohol for 20-30 min. The resultant brown crystals were washed at first by isobutyl alcohol and after it by dry ethyl alcohol and collected on a glass filter. Yield 0.2 g (38%). Found %: Cu 34.15, N 15.40. $\text{CuC}_4\text{H}_{12}\text{N}_2\text{O}_2$. Calculated %: Cu 34.59, N 15.25.

Copper diethanolamine complex (II). 0.25 g (0.0019 mol) of copper methoxide was added to the solution of 0.4 g (0.0038 mol) of diethanolamine in 15 ml of dry benzene. The mixture was heated slowly up to $70\text{-}80^\circ\text{C}$ for two hours until original blue colour changed to green, after it benzene was removed by distillation. The crystals were collected on a glass filter, were washed up by minimal amount of ethyl alcohol. Yield 0.4 g (78%). Found %: Cu 23.65, N 10.18. $\text{CuC}_8\text{H}_{20}\text{N}_2\text{O}_4$. Calculated %: Cu 23.38, N 10.31.

Copper triethanolamine complex (III). 0.3 g (0.0024 mol) of copper methoxide was added to the solution of 0.36 g (0.0024 mol) of triethanolamine in 15 ml of dry benzene. After one hour formation of blue crystals was observed. After standing for 24 h at room temperature the crystals were collected on a glass filter and dried in vacuum 40 Torr at 40°C . Yield 0.38 g (76%). Found %: Cu 29.90, N 6.98. $\text{CuC}_6\text{H}_{13}\text{NO}_3$. Calculated %: Cu 30.15, N 6.65.

Copper bis(acetylacetonate) (IV). 0.3 g (0.0024 mol) of copper methoxide was added to the solution of 0.24 g (0.0024 mol) of acetylacetonate in 15 ml of dry benzene. After one hour of standing formation of crystals of copper bis(acetylacetonate) was observed. Yield 0.28 g (93%).

Found %: Cu 24.45 $\text{CuC}_{10}\text{H}_{14}\text{O}_4$. Calculated %: Cu 24.28.

Copper complexes I, II, III have been directly synthesized according to the method described in [4].

Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Complexed Alkoxide. 0.75 g (0.0015 mol) of yttrium acetyl acetonate was refluxed in 6ml of dry 2-methoxyethanol or 2-

ethoxyethanol for 8 h. After homogenization a solution of barium alkoxide, prepared by dissolving of 0.4224 g (0.0031 g-atom) of metallic barium in 2 ml of corresponding 2-alkoxyethanol, was introduced into the solution prepared by dissolving of yttrium acetyl acetonate in 2-alkoxyethanol. After 1h of heating for homogenization purposes a copper complex either with 0.97 g (0.0046 mol) of triethanolamine or 1.26 g (0.0046 mol) of diethanolamine was added and the resultant mixture was heated at 40-60°C for 2 h until it became homogeneous. These solutions were used for preparation of bulk ceramic materials, which were obtained by evaporation of solvent at 100°C in vacuum 20 Torr and drying until reaching the constant weight.

ACKNOWLEDGEMENT

This work was supported by the International Science and Technology Center under grant N^o022-96.

ԲԱՐՉՐ ՋԵՐՄԱՍՏԻՃԱՆԱՅԻՆ ԳԵՐՀԱՂՈՐԴԻՉ Y-Ba-Cu-O ՄԻՆԹԵԶԸ ԶՕԼ-ԳԵԼ ՄԵԹՈՂՈՎ ԵՎ ՆՐԱ ՈՒՍՈՒՄՆԱՍԻՐՈՒՄԸ

Ս. Գ. ԳՐԻԳՈՐՅԱՆ, Ա. Լ. ՄԱՆՈՒԿՅԱՆ, Ա. Գ. ՀԱՅՐԱՊԵՏՅԱՆ, Ա. Մ. ԱՐԶՈՒՄԱՆՅԱՆ,
Լ. Հ. ՌԱՇԻԴՅԱՆ, Ն. Ե. ՄԿՐՏԻՉԱՆ, Ա. Ա. ՄԿՐՏՉԱՆ, Կ. Ա. ԿՈՒՐԴԻՆՅԱՆ,
Ա. Հ. ՏՐՈՅԱՆ և Ռ. Ս. ՎԱՐԴԱՆՅԱՆ

Մշակված է Y-Ba-Cu-O բարձր ջերմաստիճանային գերհաղորդիչի փոշիների ստացումը նոր և հարմար պրեկուրսորների հիման վրա, որոնք կայուն են օդում և ունեն բարձր համատեղելիություն: Ուսումնասիրված են փոշիների ստացման տեխնոլոգիան, նրանց կառուցվածքը և էլեկտրահաղորդականությունը:

СИНТЕЗ И ИССЛЕДОВАНИЕ Y-BA-CU-O ВЫСОКОТЕМПЕРАТУРНОГО СВЕРХПРОВОДНИКА, ПОЛУЧЕННОГО ЗОЛЬ-ГЕЛЬ МЕТОДОМ

С. Г. ГРИГОРЯН, А. Л. МАНУКЯН, А. Г. АЙРАПЕТЯН, А. М. АРЗУМАНЯН,
Л. Г. РАШИДЯН, Н. Е. МКРТЫЧАН, А. А. МКРТЧЯН, К. А. КУРГИНЯН,
А. А. ТРОЗЯН и Р. С. ВАРДАНЫ

Разработан новый метод получения порошков высокотемпературного сверхпроводника Y-Ba-Cu-O на основе новых и удобных прекурсоров, стабильных на воздухе и имеющих высокую совместимость. Исследованы технология получения порошков, их структура и электрическая проводимость.

REFERENCES

- [1] Hirano Sh., Hayashi T., Miura M., Miura H., Tomonaga H. // Bull. Chem. Soc. Jpn., 1989, v. 62, p. 888.
- [2] Monde T., Kozuka H., Sakka S. // Chemistry Letters, 1988, p. 287.
- [3] European Patent N^o 0 292 967 A2.
- [4] Artemenko M. // Ukrainski Khim. Zh., 1967, v. 19, p. 571.
- [5] Singh J.V., Baranwal B.P., Mehrotra R.C. // Z. anorg. allg. Chem., 1981, v. 477, p. 235.