



Green Synthesis of Tetragonal $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$

ACHALA NAGAR¹ and PRAVEEN MATHUR^{2,*}

¹Department of Chemistry, Government Engineering College Jhalawar, Sunel Road, Jhalawar-326 023, India

²Department of Chemistry, Government P.G. College, Kota-324 001, India

*Corresponding author: E-mail: praveenmathur@fastmail.fm; mathurpraveen7@gmail.com

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The bulk superconducting $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$ compounds have been prepared in a short time of 35 min using a domestic microwave oven operated at 2.45 GHz and 600 W, without any post-heat treatment. Post heat treatment was avoided as the sample was irradiated with microwaves by adjusting long heating cycles. Intermittent regrinding leads to the successful preparation of homogenous tetragonal $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$ which is found to be superconducting at 61.8 K. The analysis is consistent with published data on $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ oxide superconductor.

Key Words: Superconductivity, Ceramics, Microwave heating.

INTRODUCTION

It has been well established^{1,2} now that the synthesis of ceramics in a microwave oven leads to the isolation of a pure product in a fraction of time as compared to conventional heating techniques that typically require 12-24 h or more for such type of synthesis. This suggests that with proper microwave irradiation and on improving the sample environment, superconducting ceramics can be easily synthesized in several minutes. In most of the cases, however, post-heat treatment using an electric furnace after microwave radiation was necessary to form a superconducting sample^{3,4}. But, the most famous $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO-123) superconductor with T_c ca. 90 K could be successfully prepared using only a domestic microwave oven in a short time of 25 min without any post heat treatment⁵. $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ was also prepared by microwave irradiation under different heating cycles with safe expulsion of NO_2 gas and the X-ray diffraction study showed that the final product was not only of high purity but also of high crystallinity⁶. Attempts were made from time to time to form a new material offering higher T_c 's by various methods⁷. The main disadvantage of YBCO (123) compound is the instability of oxygen. So, bulk YBCO (124) compound with stability of oxygen at higher temperatures were synthesized using high-pressure oxygen technique^{8,9}, sol-gel method¹⁰ or by first preparing 123 phase and then its conversion to 124 phase by reaction with CuO using normal heat treatment method¹¹. It has also been reported that addition of Ca enhances the T_c of YBCO (124) phase up to 90 K¹². $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$ with T_c 83.5 K

was prepared at an ordinary pressure of oxygen by conventional solid-state reaction method¹³.

In the present study, we have attempted to prepare $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$ by microwave irradiation of the sample in air without any post heat treatment. The sample was subjected to different heating cycles. The prepared samples were characterized by X-ray diffraction and resistivity measurement.

EXPERIMENTAL

In order to prepare ceramic samples of $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$, acetates of the relevant metals $\text{Y}(\text{CH}_3\text{COO})_3$, $\text{Ca}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$ were used as raw materials. The salts were weighed stoichiometrically in an electronic balance which has an accuracy of 0.01 mg. The reacting acetates were first heated individually in hot air oven at 200 °C for 5-6 h to remove the moisture. These weighed masses were then carefully transferred in an agate mortar without losing any of the powders as far as possible, during the process and mixed thoroughly using the pestle for about 5-6 h till homogeneity and uniform grain size was achieved. Finally, the mixture was transferred to a very good quality, cleaned, microwave safe glass petri-dish and kept on the turn-table of a domestic microwave oven (L.G. Intellrowave) having a frequency of 2.45 GHz and 600 W of power. The first microwave heating cycle was completed in 10 min with the blue-green colour of the mixture of acetates turning black. The product was allowed to cool and then reground to a fine powder. It was again exposed to microwaves for further 25 min when the mixture turned rust brown

in colour. The powder was cooled and carefully transferred to air-tight glass ampoules. The resulting black powder obtained after 10 min and brown powder obtained after 35 min were first subjected to elemental analysis and then to powder XRD (using Rigaku rotating anode with voltage 40 KV, current 100 mA and radiation source as $\text{CuK}\alpha$, courtesy DAE-CSR, Indore, India). The synthesis was carried out by repeating the process 4-5 times till a satisfactory homogenous powder was obtained. The result is the mean of all these findings.

RESULTS AND DISCUSSION

It is observed that the reaction in the microwave oven starts after 1 min of exposure of the mixture with the radiation. The mixture of acetates starts decomposing with the evolution of CO_2 . After 5 min of microwave irradiation, the door of the oven is opened slightly to expel the evolved CO_2 . About 40 % weight loss was observed. The reaction takes place in a smooth manner as compared to the nitrates in which the reaction is highly exothermic with orange glow. Further exposure of the material for 5 min causes the material to turn into a black powder (Fig. 1). During the course of reaction, the temperature in the oven reaches as high as 1100 °C. In our study, it was observed that the complete decomposition of 123 stoichiometric mixture of acetates occurred within 10 min. After irradiation for further 25 min, CaO, CuO and Y_2O_3 phases disappear with the formation of $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$. The XRD patterns obtained after irradiation for 10 and 35 min are indexed by means of rigorous calculations and are represented in Figs. 2 and 3, respectively. Various values of hkl were identified for the peaks at various 2θ values using standard XRD data reported for tetragonal $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$. These are presented in Tables 1 and 2. The lattice parameters were calculated from hkl planes. The sample was found to be single phase tetragonal unit cell with lattice parameters $a = 11.82 \text{ \AA}$, $c = 6.21 \text{ \AA}$. Fig. 4 shows the temperature dependence of the electrical resistivity ρ for the powder of $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$. The superconducting transition curve has a single step and is rather sharp. T_c is found to be 61.8 K. Above T_c , the compound shows semiconducting behaviour. It has been reported in literature¹⁴⁻¹⁶ that $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ in tetragonal phase goes superconducting with T_c ca. 50-60 K. Our work is parallel to the similar findings. However, the method followed in our study is different in the manner that it involves the use of microwave energy with reactions occurring in fraction of time, thereby indicating its utility as a green synthetic tool.



Fig. 1. Black powder of Y-Ca-Cu-O prepared after exposing to microwave for 10 min

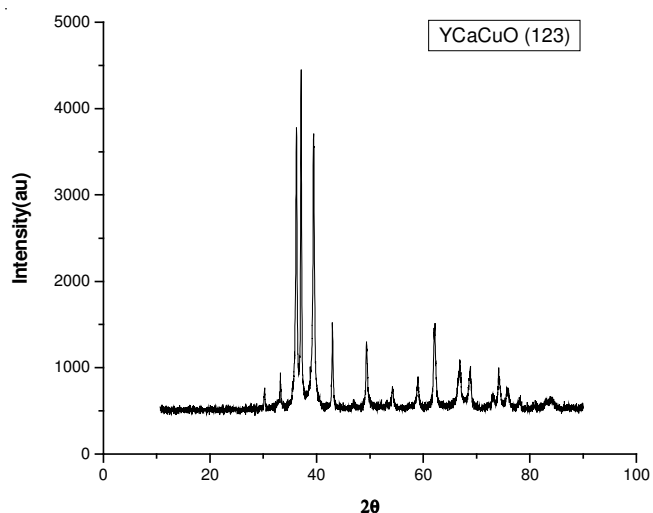


Fig. 2. XRD patterns of the mixture of acetates of Y, Ca and Cu after exposing to microwave for 10 min

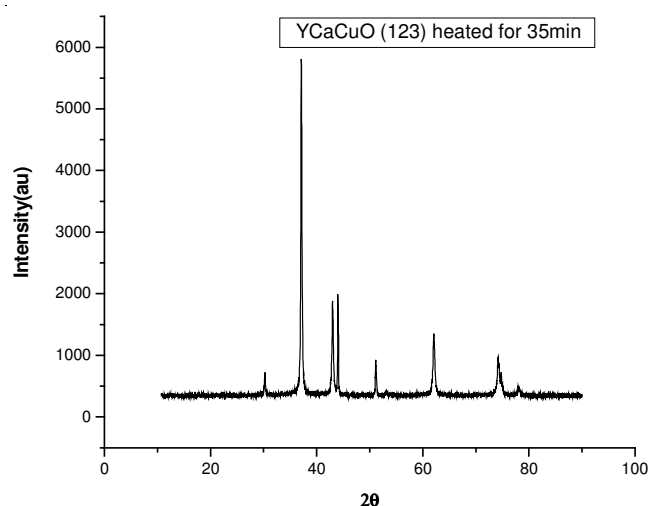


Fig. 3. XRD patterns of the mixture of acetates of Y, Ca and Cu after exposing to microwave for 35 min

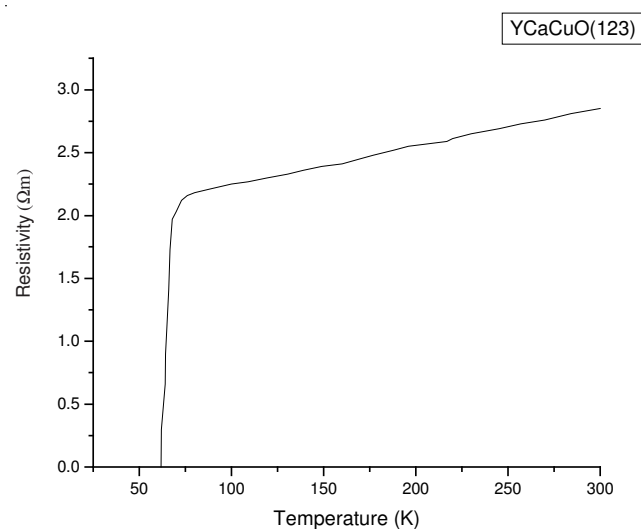


Fig. 4. Variation of electrical resistivity with temperature for $\text{YCa}_2\text{Cu}_3\text{O}_{7.8}$

TABLE-1
XRD DATA OF $YCa_2Cu_3O_{7-\delta}$ AFTER EXPOSING
TO MICROWAVES FOR 10 min

Observed 2θ	$\sin \theta$	$d = \frac{\lambda}{2\sin\theta}$	$1/d^2$	Intensity I/I_0	hkl
30.24	0.2608	2.9559	0.1144	17	400
33.2	0.2856	2.6992	0.1372	21	212
36.22	0.3108	2.4804	0.1625	85	222
37.08	0.3179	2.4250	0.1700	100	430
39.44	0.3374	2.2848	0.1915	83	431
42.96	0.3661	2.1057	0.2255	34	332
46.94	0.3982	1.9360	0.2668	14	–
49.34	0.4173	1.8473	0.2930	29	–
54.24	0.4558	1.6913	0.3496	17	550
59.02	0.4925	1.5653	0.4081	20	513

TABLE-2
XRD DATA OF $YCa_2Cu_3O_{7-\delta}$ AFTER EXPOSING
TO MICROWAVES FOR 35 min

Observed 2θ	$\sin \theta$	$d = \frac{\lambda}{2\sin\theta}$	$1/d^2$	Intensity I/I_0	hkl
30.22	0.26067	2.9574	0.1143	12	400
37.10	0.31813	2.4232	0.1703	100	430
43.00	0.36650	2.1034	0.2260	32	332
44.00	0.37460	2.0579	0.2361	34	521
51.12	0.43145	1.7868	0.3132	16	323

Conclusion

The present investigation has shown that microwaves from a domestic oven can be effectively and economically utilized to prepare tetragonal superconducting $YCa_2Cu_3O_{7-\delta}$ compounds with Tc 61.8 K. The compound crystallizes to tetragonal system with single phase within the short time of 35 min which is much lower than the conventional methods. The observation leads to the fact that it is the chemical composition which affects superconductivity and not the geometry of the crystal. The present method has considerable advantages and is quite suitable for the preparation of ceramics.

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REFERENCES

1. D.K. Agrawal, *Curr. Opin. Solid State Mater. Sci.*, **3**, 480 (1998).
2. S. Das, A.K. Mukhopadhyay, S. Datta and D. Basu, *Bull. Mater. Sci.*, **32**, 1 (2009).
3. K.G.K. Warriar, H.K. Varma, T.V. Mani and A.D. Damodaran, *J. Am. Ceram. Soc.*, **75**, 1990 (1992).
4. H.K. Varma, K.G. K. Warriar, A. Kumar, T.V. Mani, S.G.K. Pillai and A.D. Damodaran, *J. Appl. Phys. (Japan)*, **31**, L543 (1992).
5. M. Kato, K. Sakakibara and Y. Koike, *J. Appl. Phys. (Japan)*, **36**, L1291 (1997).
6. D.R. Baghurst, A.M. Chippindale and D.M.P. Mingos, *Nature*, **332**, 311 (1988).
7. E.R. Vance, *Ceram. Int.*, **16**, 361 (1990).
8. J. Karpinaski, E. Kaldis, E. Jilek, S. Rusiecki and B. Bucher, *Nature*, **336**, 660 (1988).
9. D.E. Morris, J.H. Nickel, J.Y.T. Wei, N.G. Asmar, J.S. Scott, U.M. Scheven, C.T. Hultgren and A.G. Markelz, *Phys. Rev.*, **39**, 7347 (1989).
10. H. Murakami, S. Yaegashi and J. Nishino, *J. Appl. Phys. (Japan)*, **29**, L445 (1990).
11. S. Jin, H.M. O'Bryan, P.K. Gallagher, T.H. Tiefel, R.J. Cava, R.A. Fastnacht and G.W. Kammlott, *Physica C*, **165**, 415 (1990).
12. T. Miyatake, S. Gotoch, N. Koshizuka and S. Tanaka, *Nature*, **341**, 41 (1989).
13. D.S. Choudhary, M.Y. Salunkhe and D.K. Kulkarni, *Solid State Sci.*, **6**, 1337 (2004).
14. T. Iwazumi, R. Yoshizaki, M. Inoue, H. Sawada, H. Hayashi, H. Ikeda and E. Matsuura, *J. Appl. Phys. (Japan)*, **26**, L621 (1987).
15. T. Kajitani, K. Oh-Ishi, H. Kikuchi, Y. Syono and M. Hirabayashi, *J. Appl. Phys. (Japan)*, **26**, L1144 (1987).
16. V.N. Topnikov, V.I. Simonov, L.A. Muradyan, V.N. Molchanov, A.V. Zvarykina, V.N. Laukhin, L.P. Rozenberg, R.P. Shibaeva and E.B. Yagubskii, *J. Exp. Theor. Phys. Lett.*, **46**, 577 (1987).