

Chemical Synthesis of Sub-micrometer- to Nanometer-sized of Antiferromagnetic Sr_2CuO_3 Ceramic

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A modified sol-gel synthesis route has been used to prepare the fine homogeneous powder of Sr_2CuO_3 ceramic. The single phase of Sr_2CuO_3 with high purity obtains at 950 °C. Influence of concentration of citric acid on the structure of prepared materials was investigated by SEM images. Characterization of specimens was performed using scanning electron microscopy and transmission electron microscopy, supported by other techniques including XRD diffraction, energy dispersive X-ray and FT-IR spectrum.

Keywords: Powders-chemical preparation, Sol-gel, Sr_2CuO_3 , Nanoparticle, Citric acid.

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1. INTRODUCTION

It One-dimensional spin system with antiferromagnetic interactions, e.g., Ca_2CuO_3 , Sr_2CuO_3 (spin $S = 1/2$), CsNiCl_3 ($S = 1$), CsVCl_3 ($S = 3/2$) etc, have been investigated eagerly [1] because of possible appearance of superconductivity in the hole-doped systems and pronounced quantum mechanical effects reflecting the low-dimensionality [2]. At ambient pressure, the stoichiometric Sr_2CuO_3 forms an orthorhombic structure. Introducing extra oxygen and applying high pressures leads to the formation of a K_2NiF_4 -type tetragonal structure containing a CuO_2 plane but the apical oxygen sites are partially occupied. On the other hand, the oxygen atoms at the apical sites of a CuO_6 octahedron (apical oxygen) form the nearest-neighbor charge reservoir block (Fig. 1) [3].

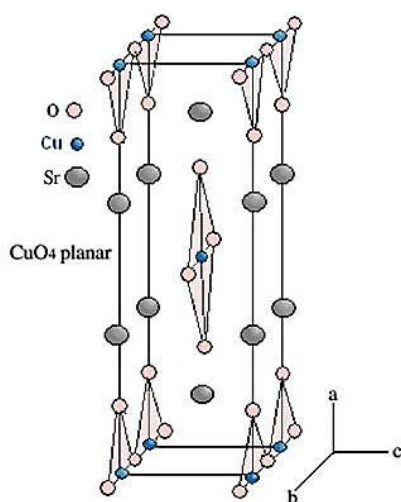


Fig. 1 – Schematic structures of Sr_2CuO_3

A single-phase of $\text{Sr}_2\text{CuO}_{3+\delta}$ with nominal $\delta = 0.4$ ($T_c = 75$ K) was synthesized by using a high-pressure technique [4]. As increasing the annealing temperature to 300 °C, T_c increases monotonically to 95 K [5]. Sr_2CuO_3 particles are commonly prepared by a solid state reaction method [6] but the disadvantages of this method, such as inhomogeneity and high temperature, are improved by using a solution-based method. The sol-gel method is a useful and attractive technique for the preparation single-phase products much more easily than by other processes.

In this article, we synthesized Sr_2CuO_3 fine particles via the modified sol-gel method by adding citric acid and diethylene glycol monobutyl ether and studied the influence of concentration of citric acid on the size and structure of the prepared samples.

2. METHODS OF SAMPLE MANUFACTURING

Strontium and copper nitrate dissolved in diethylene glycol monobutyl ether (DGME) to achieve an overall cation stoichiometry of Sr:Cu = 2:1 using the modified sol-gel method [7]. Then, anhydrous citric acid (CA) was subsequently added to this solution with Sr:Cu:CA = 2:1:(1, 2, 3, 4 and 10) in molar ratio and stirred continuously throughout the process using a magnetic stirrer until a blue viscous gel is obtained. The obtained bluish solutions were heated to remove excess water and further heated to become more viscous and finally form a xerogel. Then, xerogels were placed at 400°C for 1 h. Result powders were calcined in the furnace to 950°C for 1 h in air, followed by cooling to room temperature.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The XRD result of sample heated at 900°C showed that the sample has been constituted from Sr_2CuO_3

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phase along with SrCO_3 peaks as a minor phase. The single phase of Sr_2CuO_3 without impurity peak with preferential orientation of (611) and (321) is observed after heating to 950°C , as shown in Fig. 3. The XRD investigation revealed that the prepared sample has an orthorhombic structure, space group Immm , with lattice parameters $a = 12.6840 \text{ \AA}$, $b = 3.9064 \text{ \AA}$ and $c = 3.4957 \text{ \AA}$ (JCPDS No: 84-1968). Particle size 'D' was calculated 35.5 nm at 950°C using Debye-Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$ where λ is the wavelength of Cu-K α radiations (1.54 \AA), β full width at half maximum of the maximum intensity peak and θ is the angle obtained from 2θ value corresponding to this peak in XRD pattern.

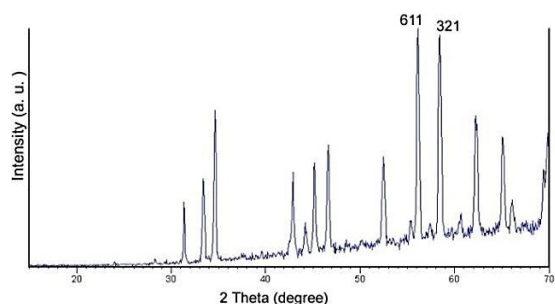


Fig. 2 – XRD pattern of the prepared sample at 950°C

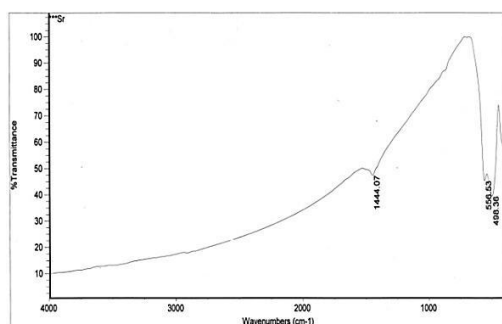


Fig. 3 – FT-IR spectra of Sr_2CuO_3 at 950°C

FT-IR measurement (Fig. 3) was used to identify and characterize the resulting Sr_2CuO_3 at 950°C . It can be seen no any segregation of the carbonate salts in the spectrum. The stretching frequencies appeared in the range of $490 - 700 \text{ cm}^{-1}$, associated with the vibrations of Cu-O, Sr-O, and Cu-O-Cu bonds [8]. So, as the temperature was increased further from 900°C to 950°C , decomposition of SrCO_3 occurred gradually as Sr_2CuO_3 phase was formed in agreement with XRD pattern. Also, EDX spectrum of the prepared sample indicated a purity Sr_2CuO_3 phase.

3.2 Effect of Concentration of Citric Acid

The TEM image of the sample prepared with low molar ratio of CA (see Fig. 4) calcined at 950°C showed a nano-structure with small and tiny grains ($70-90 \text{ nm}$). The nanocrystalline Sr_2CuO_3 particles show close to spherical shaped aggregated particles with a few hundreds of nanometer in diameter in agreement with the analysis result of XRD. When the molar ratio of citric acid increases, particles stick together and are aggregated in a sub-micrometer range (Fig. 5a and b).

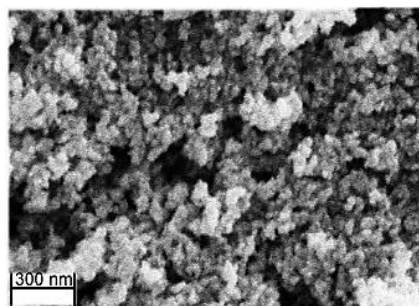


Fig. 4 – TEM images of the sample with molar ratio: Sr:Cu:CA = 2:1:1

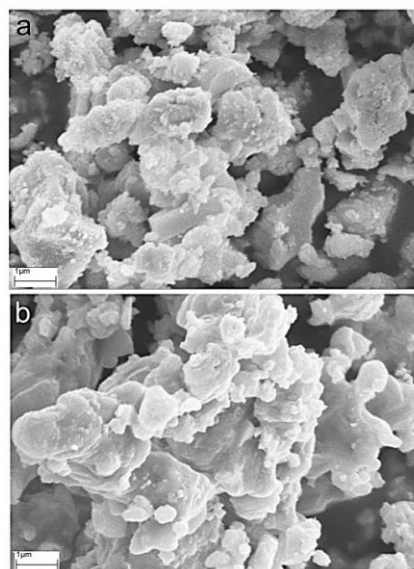


Fig. 5 – SEM images of the samples with molar ratio: Sr:Cu:CA = (a) 2:1:2, (b) 2:1:3 (the scale bar is $1 \mu\text{m}$)

In the sample prepared with a high molar ratio (Fig. 6a and b), material is more compact with fused together grains and size of particles becomes significantly larger.

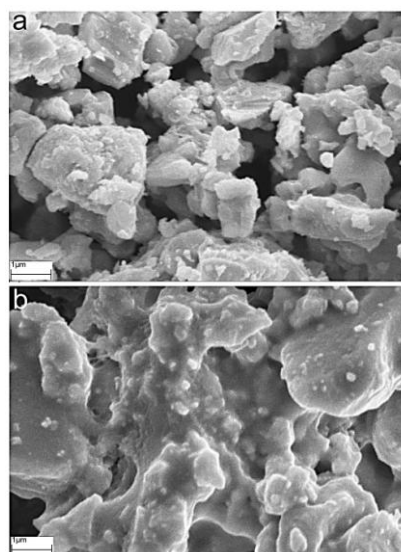


Fig. 6 – SEM images of the samples with molar ratio: Sr:Cu:CA = (a) 2:1:4, (b) 2:1:15 (the scale bar is $1 \mu\text{m}$)

Grains begin to melt; some grain edges and boundaries are indistinct and zone of partial melting can be seen in the sample image. Citric acid was added to the solution as the complexing agent in order to quantitatively complex with the cations. The dehydration and pyrolysis of the prepared citrate gel show that at 433 K the first step of dehydration and decomposition of the citric acid occur [9]. Upon continued heating, citric acid polymerizes and swells up with the decarboxylation process releasing CO₂ that in this process, nano-dispersed precursors were prepared. So, the suitable concentration of citric acid is effective for achieve to highly fine homogeneous powder of Sr₂CuO₃ ceramic.

4. CONCLUSIONS

In summery, we describe the synthesis of the Sr₂CuO₃ particles from micro- to nano-meter by the

modified sol-gel technique. It was demonstrated by SEM images that in samples prepared with low molar ratio of citric acid, nano-structure materials with small and tiny grains were obtained. The XRD result showed that the single phase of Sr₂CuO₃ sample without any impurity peak is formed at 950 °C.

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REFERENCES

1. S. Eggert, *Phys. Rev. B* **53**, 5116 (1996).
2. J. Sirker, N. Laflorencie, *EPL* **86**, 1 (2009).
3. Q.Q. Liu, H. Yang, X.M. Qin, Y. Yu, L.X. Yang, F. Y. Li, R.C. Yu, C.Q. Jin, *Phys. Rev. B* **74**, 1 (2006).
4. H. Yang, Q.Q. Liu, F.Y. Li, C.Q. Jin, R.C. Yu, *Supercond. Sci. Technol.* **19**, 934 (2006).
5. Q.Q. Liu, H. Yang, X.M. Qin, L.X. Yang, F.Y. Li, Y. Yu, R.C. Yu, C.Q. Jin, S. Uchida, *Physica C* **460-462**, 56 (2007).
6. M.A. Augustyniak Jablokow, Y.V. Yablokov, T.A. Ivanova, I. Jacyna Onyszkiewicz, V.A. Shustov, *Acta Physica Polonica A* **108**, 345 (2004).
7. M. Salavati-Niasari, F. Davar, M. Farhadi, *J. Sol-Gel Sci. Technol.* **51**, 48 (2009).
8. M. Salavati-Niasari, F. Davar, M.R. Loghman-Estarki, *J. Alloys Compd.* **494**, 199 (2010).
9. L.C. Pathak, S. K.Mishra, *Supercond. Sci. Technol.* **18**, R67 (2005).