

Sol-Gel Synthesis of Some Rare Earth Cuprates RE_2CuO_4 , (RE = La, Eu and Nd)

MARWA A. SHERIEF

Department of Inorganic Chemistry, National Research Centre, Dokki, Cairo, Egypt

E-mail: gohamora@yahoo.com

Two samples of rare earth cuprates, RE_2CuO_4 (RE = La, Eu, Nd) were prepared by using sol-gel method. The first sample was prepared by mixing RECl_3 and CuCl_2 with molar ratio 1:1 in presence of ethylene oxide gas as gelating agent. The product was dried at 120 °C. The second one was prepared from RECl_3 and CuCl_2 and using citric acid and ethylene glycol for gelation with molar ratio 1:1:10:40. The product was dried at 130 °C to give a gel form of RE_2CuO_4 . The gel was converted to powder by heating at 350 °C. The produced samples were characterized by XRD, IR, thermal analysis and SEM. The results indicate that RE_2CuO_4 in a very fine particle size was formed. The analysis of XRD pattern showed that a single phase of RE_2CuO_4 was formed by using the first method while a residual of the precursor material was appeared on using the second method. The electrical conductivity (σ') of the produced samples were measured between 25-300 °C after sintering at 850 °C for 2 h. The results of measurements indicate that all the produced samples behave as semiconductor materials where the value of electrical conductivity (σ') increased with temperature.

Key Words: Rare earth cuprates, Sol-Gel synthesis, Characterization, Electrical conductivity.

INTRODUCTION

The interest in the properties of rare earth cuprates, RE_2CuO_4 (RE = rare earth) has been high since the discovery their superconductor properties^{1,2}.

The appropriate doping on the RE_2CuO_4 destroys the oxygen atoms from their symmetric positions, where, RE_2CuO_4 crystallizes in tetragonal structures in which RE_2O_2 blocks are separated by CuO_2 plans³. This displacement causes a decrease in the mobility of the charge carriers and affects the semiconductor properties of the cuprates.

Most of the studies on the synthesis and the characterization of the rare earth cuprates were concerned with the Gd_2CuO_4 and a few investigators interested to study of the rare earth cuprates as a series. Gd_2CuO_4 particles were synthesized by sol-gel techniques, using urea as gelating agent, in

order to study the effects of particle size on the magnetic properties⁴⁻⁷. This study showed that Gd_2CuO_4 in pure phase is produced by calcinations of the gel at 650 °C, while the using of the ceramic process, Gd_2CuO_4 is produced after calcinations at 1080 °C. Also, this study indicates that the magnetic properties of Gd_2CuO_4 are strongly depended on the particle size, which in turn is controlled by the method of preparation.

On other hand, Mira *et al.*^{8,9} found a difference in the dynamics behaviour of two ceramic Gd_2CuO_4 samples, depending on the final annealing temperature at which the samples were synthesized. Also, they found that DC and AC magnetic susceptibility measurements give evidence on the effects of the thermal treatment on the magnetic behaviour of Gd_2CuO_4 ceramic samples. A homogeneous series of lanthanum cuprates were synthesized by Cava *et al.*¹⁰ to investigate the dependence of their magnetic properties on the temperature of treatment.

In present work, a series of rare earth cuprates [RE = La, Eu, Nd] were synthesized by using a sol-gel techniques, which have some advantages on the ceramic method. The electrical conductivity of the produced samples was performed to draw some light on the semiconductor properties of the rare earth cuprate compounds.

EXPERIMENTAL

The starting materials for the synthesis were analytical grade salts of chlorides of lanthanum(III), Cu(II), Nd_2O_3 , Eu_2O_3 , citric acid, ethylene oxide gas, ethylene glycol and HCl 3 N.

Method-I: CuCl_2 , 0.1 M was added to $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, 0.1 M in equal volume; the solution was kept at 0 °C, then ethylene oxide gas was passed through the solution with constant shaking until the gel was formed.

For Eu and Nd, a certain weight of Eu_2O_3 and Nd_2O_3 were dissolved in 3 N HCl to form a solution of 0.1 M of EuCl_3 and NdCl_3 , then CuCl_2 0.1 M was added to the EuCl_3 and NdCl_3 , respectively. The mixture was kept at 0 °C and ethylene oxide gas was passed into the solutions with constant shaking until the gel was formed. The produced gel was dried at 130 °C.

Method-II: Aqueous solutions of reacting materials according to the molar ratios of RE/Cu/citric acid/ethylene glycol = 1:1:10:40 in order to attain the desired molecular formula RE_2CuO_4 were mixed.

RECl_3 , (0.1) M was first dissolved in 4 M of ethylene glycol and 1 M of citric acid as chelating agent was subsequently added to this solution and kept at 50 °C per 1 h. After complete dissolution, 0.1 M $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ was added. The mixture was then stirred for 2 h at 80 °C until the solution become completely clear. The solution was then concentrated by further heating with stirring for about 15 h at 130 °C in an open beaker, covered with a glass dish. The gels were subsequently evaporated in an electric dry

furnace at 350 °C for 3 h in air to remove water and any residual organic compounds. The precursor gel resulted in a black solid mass and was lightly ground into a powder.

For IR studies, Jasco instrument, FT/IR-300E was used in the range 3000-400 cm^{-1} using the KBr pellet technique. For X-ray measurements, the diffraction patterns of the produced samples were obtained by means of a chart recording Philips PW X-ray diffractometer (Holland) using copper ($\text{K}\alpha$) radiation. The instrument was properly calibrated and adjusted with respect to the X-ray source. A high voltage of 40 kV and anode current of 30 mA were chosen. The connected Geiger Muller tube detector was adjusted to the order of one degree/cm, for identification purposes. Thermal decomposition (TG) of the gel was measured on a Perkin-Elmer 7-Series thermal analysis instrument up to 1000 °C, with heating rate 10 °C min^{-1} . Scanning electron microscope (SEM), was performed by Jeol JSM-T20 scanning microscope. The electrical conductivity of the prepared samples (discs of 10 mm diameters and 2~3 mm thickness), was studied as a function of temperature (25-300 °C) using LCR Hioki instrument (Japan). The frequency was adjusted at 50 KHz and 4 volts.

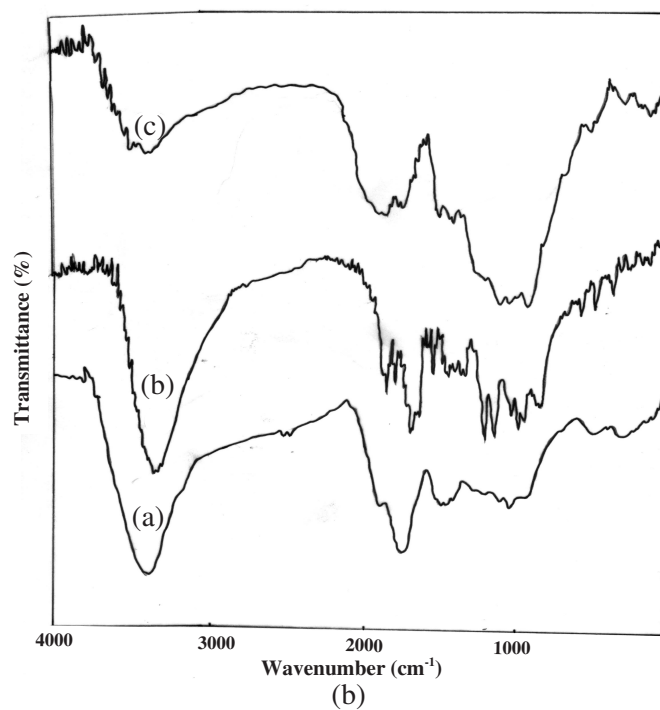
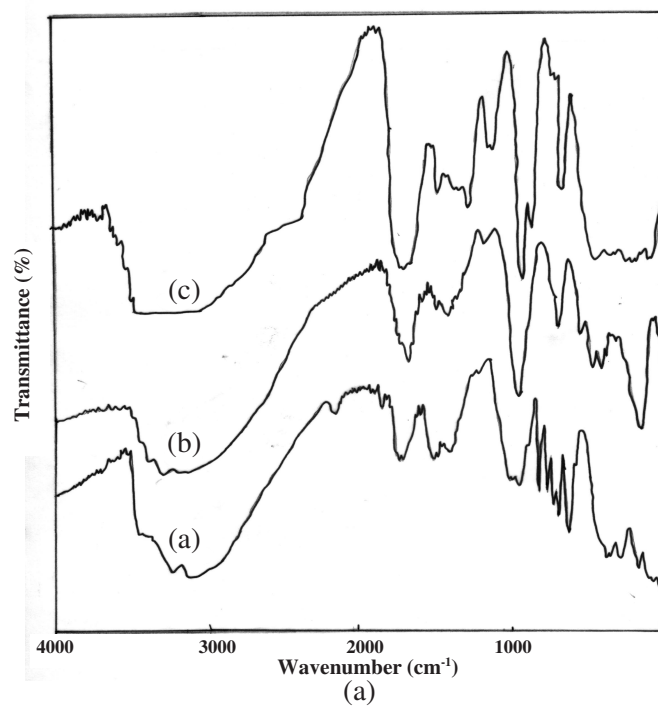
RESULTS AND DISCUSSION

Fig. 1a,b represents the infrared spectra of the prepared rare earth cuprates using ethylene oxide gas at room temperature or ethylene glycol and citric acid as gelating agents¹¹.

From this figure, it is observed that for the three rare earth metals (La, Eu, Nd), the infrared spectra have nearly the same trend, where three main peaks were observed. The first one appears at *ca.* 600 cm^{-1} corresponding to the absorption band of Cu-O, the second one appears between 1490-1400 cm^{-1} and attributed to the CH_3/CH_2 stretching which produced from the presence of residual traces of the gelating organic agent. The last absorption peak appears at *ca.* 3400-3300 cm^{-1} and specified the H_2O molecules beside other one at 1640 cm^{-1} corresponding to OH/ H_2O vibration. The band at 1000 cm^{-1} in the Fig. 1a of method (I) may be due to the chlorate anion¹².

For comparison between the IR charts of the three rare earth cuprates (La, Eu, Nd), it is clear that there are some shifts in the position, sharpness and the strength of the specified bands. This may be attributed to the change in the particle size of the produced samples, where the three rare earth cations having nearly the same charges and the ionic radii.

X-Ray diffraction: The results obtained by X-ray diffraction for the samples synthesized using ethylene oxide, or ethylene glycol with citric acid, Fig. 2, indicate that a single phase of RE_2CuO_4 in amorphous state was obtained^{11,13,14}. In the case of using ethylene oxide, X-ray pattern shows peaks characterizing the unreacted.

Fig. 1a,b. IR spectrum bands of RE_2CuO_4 methods I & II

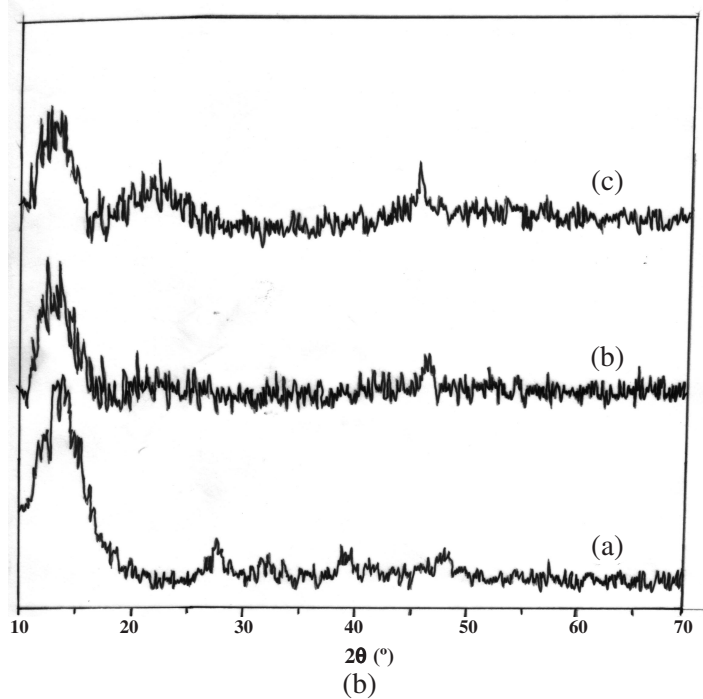
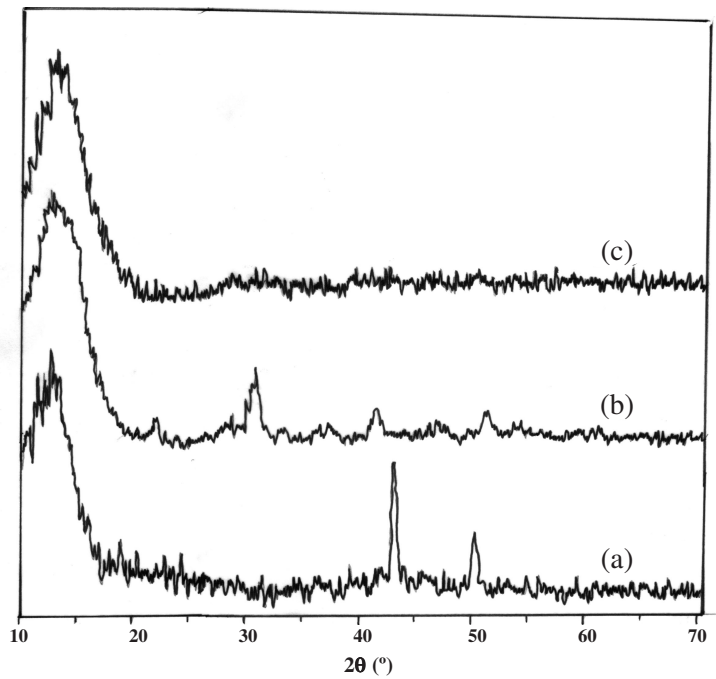
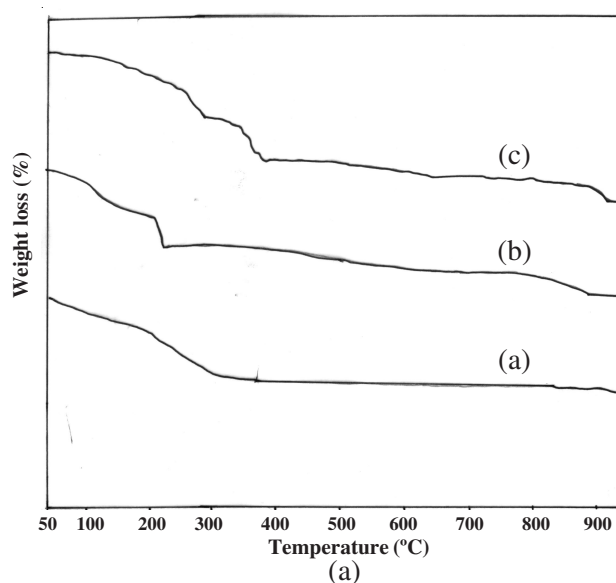


Fig. 2a,b. X-Ray diffraction of RE_2CuO_4 methods I & II

CuCl_2 and also copper metal or the formation of chlorates, which may be due to the low reaction temperature used (Fig. 2a). The advantages of using these methods for preparation are the producing amorphous phase of RE_2CuO_4 at low temperatures up to about *ca.* 350 °C. It is noteworthy that this technique has an advantage to the method processed by Mira *et al.*⁸ for preparation crystalline Gd_2CuO_4 in presence of urea as a gelating agent and calcinate the produced gel at high temperature with long time.

Thermal analysis: Fig. 3 represents the thermogravimetric analysis of the prepared samples. In the case of using ethylene oxide, three stages of the thermal decomposition were observed (Fig. 3a). The first stage ending at *ca.* 120 °C corresponds to the physical water content and the second one up to 300 °C, may be due to the decomposition of the gel. The third stage was observed above 300 °C and it is accompanied by slight weight losses. It may be due to the transition of the amorphous gel to crystalline one. This finding is in agreement with the literature, where the amorphous state converted to crystalline form by calcination¹⁵.

Fig. 3b represents the thermal behaviour of the RE_2CuO_4 prepared by using ethylene glycol and citric acid as a gelating agent. Also, three stages can be specified in the TG curves. The first one at about *ca.* 300 °C may correspond to the evolution of the physical water and volatile organic materials produced from the presence of some traces of the gelating agent. The second stage at about *ca.* 500-600 °C may be due to complete decomposition of the gel, the formation and combination of the representing oxide. The last one from 600-1000 °C represents transformation to the desired formula^{11,15}.



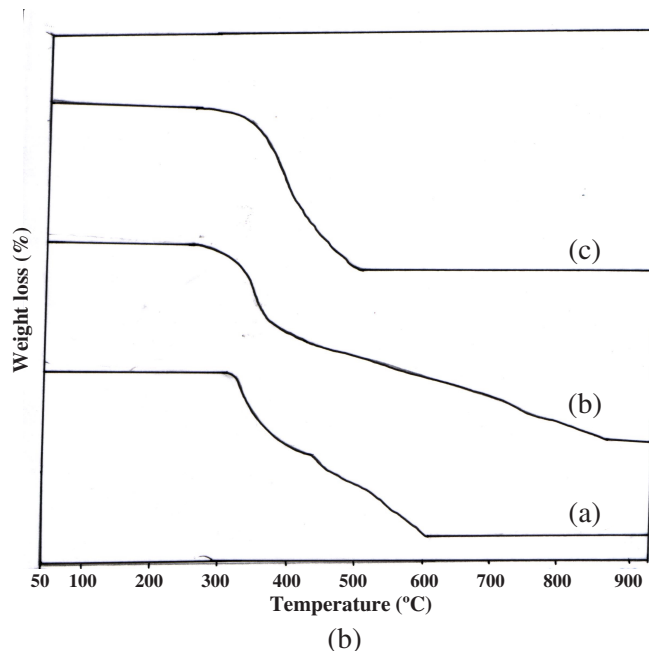


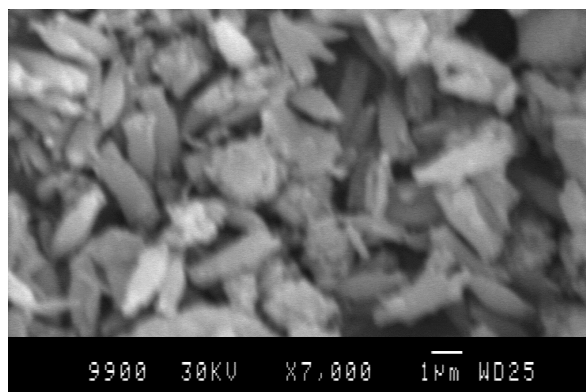
Fig. 3a,b. TG curves of RE_2CuO_4 methods I & II

In all cases the boundary of the three specified stages slightly changes from one rare earth element to another. Also, it is observed that the three stages of the samples prepared by method (II) is more defined than that of the samples prepared by method (I). This may be due to the rate of formation of the gel beside the water and the volatile materials in the produced samples.

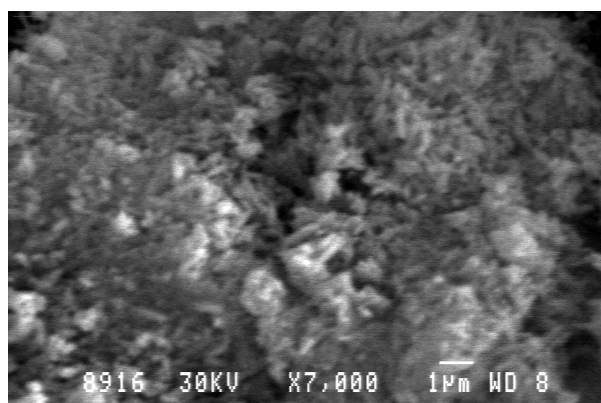
Scanning electron microscope: The morphology of the different samples prepared by two methods (I & II) are represented in Fig. 4a,b. Sample I of La_2CuO_4 shows that the product has octahedral crystal shape¹⁶ that may be due to presence of unreacted CuCl_2 crystals or the formation of chlorate as indicated by X-ray diffraction. Sample I of EuCuO_4 shows the needle shape of some crystal growth. The SEM graph of Nd_2CuO_4 , shows its amorphous nature with the formation of few very fine crystals.

For sample II, the SEM graphs show that the formation of an amorphous glassy state for the all rare earth element with clearness the layered structure in the case of La_2CuO_4 .

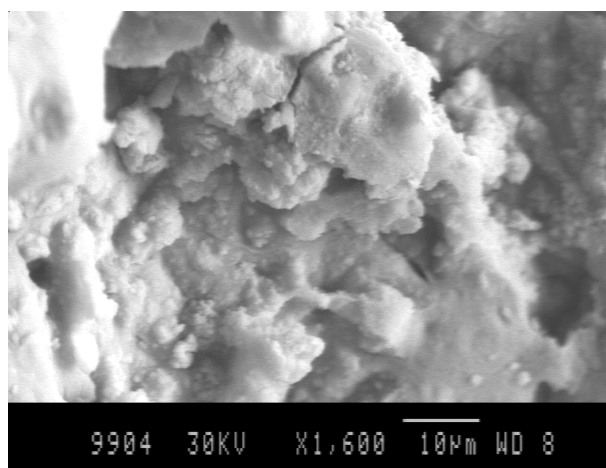
Electrical conductivity (σ'): The electrical conductivity of the RE_2CuO_4 samples measured at different temperatures are shown as a function of reciprocal temperatures (Fig. 5a,b). In general, all the prepared samples exhibit semiconductor properties, where the value of σ' increases as the temperature increase^{11,17}.



La_2CuO_4

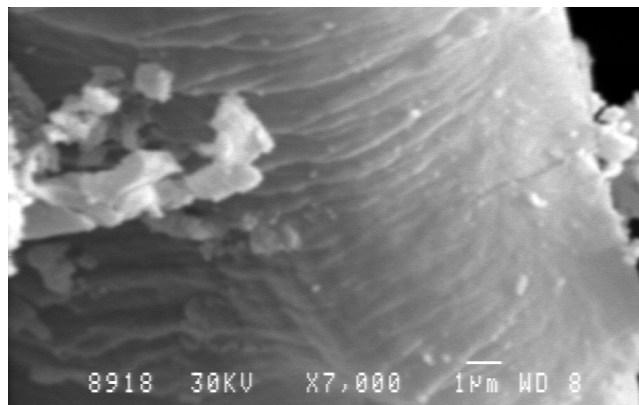


Eu_2CuO_4

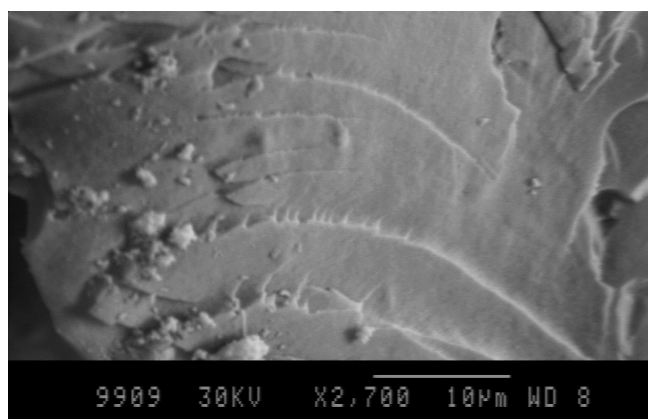


Nd_2CuO_4

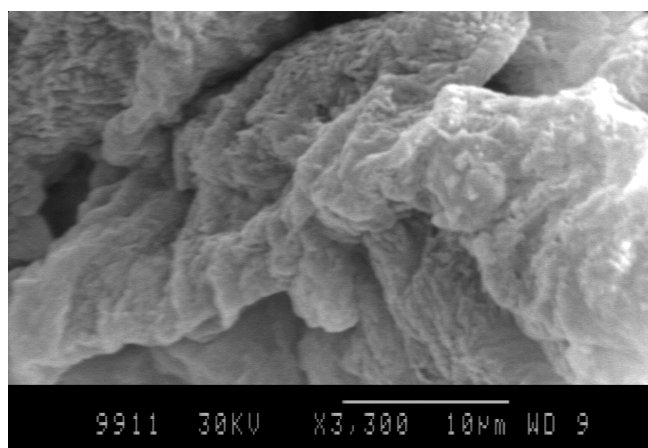
Fig. 4a. SEM of RE_2CuO_4 (method I)



La_2CuO_4

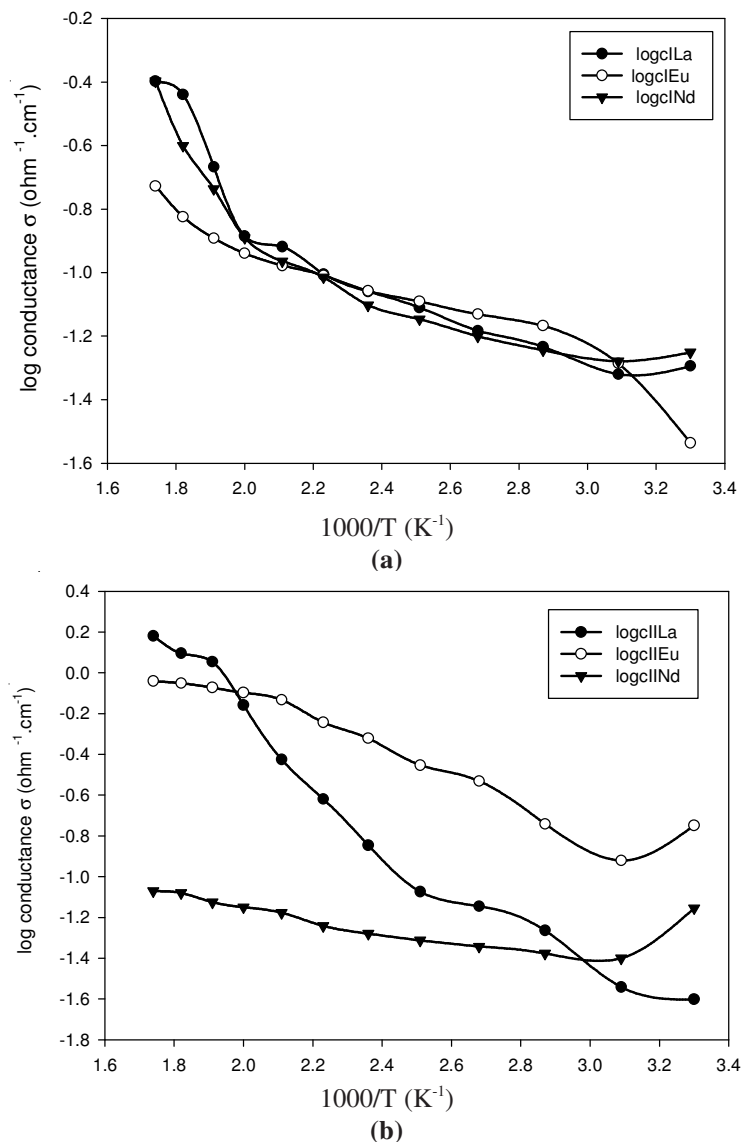


Eu_2CuO_4



Nd_2CuO_4

Fig. 4b. SEM of RE_2CuO_4 (method II)

Fig. 5a,b. Variation of log σ with $1000/T$ for RE_2CuO_4 , process I,II

From the relation between σ and T , it is observed that: (1) At higher temperature, the values of σ and its dependence on temperature are high; which may be attributed to the high mobility of the carriers in comparison with that at low temperature¹⁵. (2) For the samples, RE_2CuO_4 prepared by using ethylene oxide gas as a gelating agent and dried at 130 °C, it is observed that a sudden decrease in σ value was appeared at *ca.* 200 °C and attributed to the water losses as indicated by the TG curve. (3) For the samples, RE_2CuO_4 prepared in presence of ethylene glycol and citric acid and fired

at 350 °C, the values of σ did not exhibit the sudden decrease at *ca.* 200 °C as that observed for the previous samples. This may be due to the absence of physical water as shown from the thermal analysis curves. On other hand, the samples prepared by this method exhibit a decrease in the σ values as temperature increase. This decrease starts about at 275 °C and may be attributed to the decomposition of the gel as shown from the thermal behaviour of these samples (Fig. 3b).

Conclusion

The produced samples of RE₂CuO₄ (RE = La, Eu, Nd) depend on the method of their preparation as well as the conditions of reaction. The three rare earth cuprates behave nearly the same trends when characterized by X-ray diffraction or IR technique with some shifts in position and the broadness of the specified peaks. This may be attributed to the change in the particle size of the produced samples, where the three rare earth captions having nearly the same charges and the ionic radii. The prepared compounds exhibit semiconductor properties where the values of the electrical conductivity increases with temperature increase.

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