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Investigation of magnetic, optical and electrical properties of $La_3Ba_3Cu_6O_{14}$ synthesized by molten flux method

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Abstract: The great deal of novel rare earth based semiconducting lanthanum barium copper oxide $La_3Ba_3Cu_6O_{14}$ (LBC-336) were synthesized by low temperature molten salt synthesis (MSS) due to "dissolution precipitation mechanism". Here, we reported one pot synthesis of product by direct precipitation from a molten KOH-NaOH mixture at 450 ºC and single phase $La_3Ba_3Cu_6O_{14}$ with tetragonal crystal system. The particle size of 140–200 nm were observed in both PXRD pattern and HRSEM micrographs and it showed a cubic morphology. The semiconducting nature was extracted from various parameters like optical band gap (1.8 eV), AC conductivity (0.70 eV), DC conductivity (0.70 eV), and also Hall effect parameters like the charge carrier concentration values n=6.0×10^{26} m^{-3} and it proved as a p-type semiconductor. The electrical phase trasition temperature from ferroelectric to antiferroelectric system (T_m=420 K) and anti-ferroelectric – paraelectric system (depolarization temperature T_d=673 K) which attributed to the space charge polarization contributed to the conduction mechanism. The magnetic phase transitions were from ferromagnetic to ferrimagnetic system (Curie temperature (T_c=70 K)) and it led to soft magnetic material and also held good for superconductor application upto 70 K.

Keywords: molten flux synthesis; band gap; phase transitions; semiconductor; superconductors; rare earths

Lanthanum-barium-copper oxygen deficient pervoskite attracted a great deal of interest in the recent years, due to the unusual metal-insulator transition properties. LBC-336 system has efficient application as transport properties and also acts as a good catalyst for oxidation of carbon monoxide. $La_3Ba_3Cu_6O_{14}$ was first synthesized by solid state method in the air, for 24 h at 1000 ºC[1–3]. The electrical properties depend on structure, composition, oxygen partial pressure and it leads to both metallic, semiconducting behavior of the LBC-336[3,4]. $La_3Ba_3Cu_6O_{14}$ has one sixth of copper atoms in the ideal composition is in trivalent state. Additional oxygen is located at the centre of the unit cell, converting two neighboring Cu(II)O_5 square pyramidal polyhedron into corner linked Cu(III)O_6 octahedron. This may then inhibit movement of electrons along the chains suppressing superconductivity. Wide superconducting transitions may be related with the optimal preparation method[5,6]. Rare earth (RE) lanthanum based ceramic magnetic material has wide industrial applications like aerospace, automotive, electronics, medical, and military. The rare earth magnetic materials are essential ingredients in these high performance magnets. Based on intermetallic behavior is due to the extremely high magneto crystalline anisotropy made possible by unique 3d-4f interactions between transition metals and rare earths. In recent years, the feasibility of a low temperature technique as molten salt synthesis has been investigated. MSS has been considered as a good technological process for preparing inorganic materials as well where the synthetic temperature can be greatly lowered, and the diffusion speeds of reacting constituents can be obviously accelerated due to the incorporation of salt medium. So products generally possess a good crystalline and different morphology[7–14]. In this work, the molten salt technique has been used to synthesize $La_3Ba_3Cu_6O_{14}$ at low temperature using easily available oxide raw materials and optical properties have been studied. To our knowledge $La_3Ba_3Cu_6O_{14}$ powder, prepared by this method has ever been reported. AC-conductivity observed for the function of temperature from room temperature to 673 K indicates that the space charge polarization contributes to the conduction mechanism. The AC conductivity data have been used to estimate the apparent activation energy and minimum hopping length[15]. The important parameters such as activation energy, carrier concentration, ionic mobility, etc., were determined by four probe resistivity and Hall effect measurement. The temperature dependent magnetic study proves the soft ferrimagnetic nature of the material. This molten hydroxide method represents a useful technique for the preparation of rare earth compounds like lanthanum based pervoskite.

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1 Experimental

The high purity analytical-grade starting materials were lanthanum oxide, barium hydroxide, copper oxide, potassium hydroxide, and sodium hydroxide taken in stoichiometric ratio (1.5 mol/L La_2O_3, 6 mol/L CuO and 3 mol/L $Ba(OH)_2{\cdot}8H_2O$) and ground in an agate mortar for 4 h. The mixed fine powders were added into the 1:1 molar ratio of NaOH and KOH flux for reaction recrystallized alumina crucible for 2 h at 170 ºC in a silica carbide furnace (INDFUR furnace heating rate 10 ºC/min). Initially, we observed clear blue solution and future increasing the temperature slowly up to 450 ºC the blue color solution changed into black in color and kept the same environment to 6 h for homogenous reaction. The synthesized black powder was washed with deionized water and dried in a hot air oven at 60 ºC and the process was repeated for 6 times to harvest single phase $La_3Ba_3Cu_6O_{14}$ powder.

2 Results and discussion

2.1 PXRD analysis

The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 advanced instrument with a scan speed 0.3 s with Cu Kα (λ=1.5406). Fig. 1(a) shows that the PXRD pattern of $La_3Ba_3Cu_6O_{14}$ was obtained as pure single phase without any impurities, and this graph was exactly coincident with early reports. The peaks were indexed, and the sharpness of the diffraction peaks indicates that the materials have good crystalline nature and are in good agreement with that of the JCPDS file (74-0761). The PXRD pattern reveals that the crystal system belongs to tetragonal crystal system and its lattice parameters are a=b=0.55257 nm, c=1.17462 nm consistent with those reported in JCPDS (card No. 74-0761) as shown in Fig. 1(b). Hence, the $La_3Ba_3Cu_6O_{14}$ compound was successfully formed at low temperature compared to early reports.

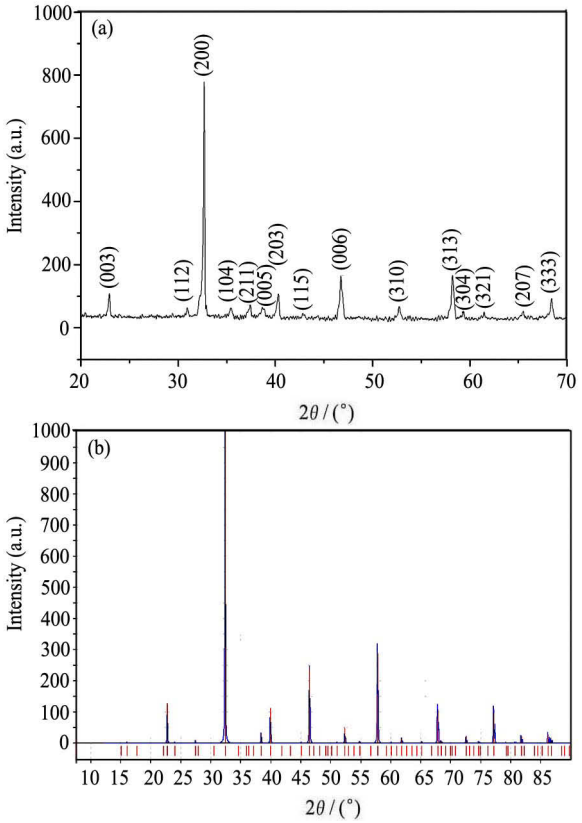

Fig. 1 XRD patterns of $La_3Ba_3Cu_6O_{14}$ (a) and $La_3Ba_3Cu_6O_{14}$ (b) compared with standard JCPDS data

The synthesized powder particle size was estimated using the Scherrer Eq. (1) through PXRD diffraction pattern.

$$D=K\lambda/\beta\cos\theta \quad (1)$$

Where, D–crystalline size (nm); K–shape factor (K=0.9 constant value), λ–wavelength of X-ray, β–full width at half maximum (FWHM). The calculated average particle size lies between 140–200 nm.

2.2 FTIR studies

Since the inorganic compound has board and stretched peaks behaviour and it is strongly relates to the particle size, phase and morphology of the compounds. So, we study through the recorded FTIR spectrum, as shown in the Fig. 2. The synthesized compound was mixed with KBr powder in the 1.5:0.5 molar ratio and made into 12 mm circular pellet which were subjected to Fourier transform infra red (FTIR) analysis in range 400–4000 cm^{-1} using JASCO 400 spectrometer. The FTIR spectrum of $La_3Ba_3Cu_6O_{14}$ possesses two board and strong bands at 3493 and 3149 cm^{-1} assigned to the stretching vibrations of the bulk OH− ions group due to the presence of a small amount of water adsorbed on the surface. The small band at 1625 cm^{-1} is due to the OH bending of water in the surface and compensates the oxygen deficiency of synthesized compound. A sharp peak was observed near 1400 cm^{-1}. It indicates that lanthanum (La^{2+}) compounds are exposed to ambient condition and the process of carbonation occurs. It leads to be the formation of carbonates on the surface. The small intensity peak at 571 cm^{-1} reveals that group of La–O, Cu–O

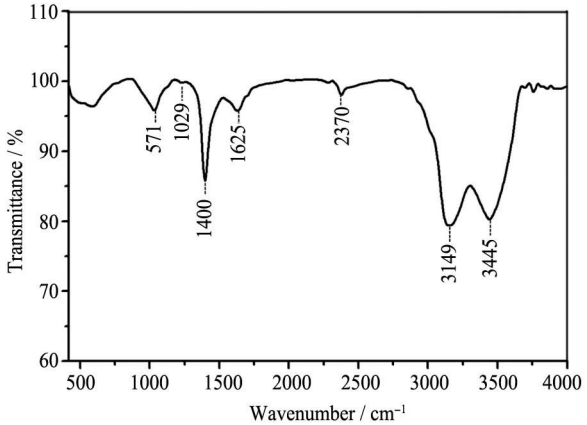

Fig. 2 FTIR pattern of $La_3Ba_3Cu_6O_{14}$