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Study of Structural and Electrical Transport Properties of $YBaCuFeO_5$ Multiferroic

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Abstract : Double perovskite oxide $YBaCuFeO_{5+\delta}$ samples, were sintered by a solid state reaction technique. Crystal structure was analysed in the space group P_{4mm} by x-ray diffraction and further confirmed by Rietveld refinement using full-prof-suit program. The fully ordered structure was obtained in which the Fe^{3+} and Cu^{2+} ion have occupied distinct crystallographic sites. Microstructural investigation has been carried out with scanning electron microscope (SEM) which revealed randomly oriented, non-uniform grains and a certain amount of intergranular porosity in the sample. The electrical behaviour of the samples has been studied over a wide range of temperature and frequency using CIS technique. RC model circuits are connected in series in order to analyse the electrical and dielectric behaviour of prepared $YBaCuFeO_{5+\delta}$. the data obtained is described by RC circuit representing the grain boundary resistance (R_{gb}) and capacitance (C_{gb}) in the temperature regime 25^{o} C- 175^{o} C and frequency range 1Hz- 1 Mhz. A Debye character was observed in the impedance behaviour in its frequency dependence. It was observed that the resistance of the material suddenly drops with rise in temperature. Relaxation mechanism of charge carriers was confirmed by modulus study. A single relaxation was observed in the prescribed temperature and frequency range and was identified due to extrinsic sample-electrode interface conduction effect.

Keywords : Multiferroic, Magnetism-driven ferroelectricity, Double perovskite

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1. Introduction

Recently, considerable attention has been concentrated on multiferroic materials due to their multi-functionality. These materials propose chances for potential applications in highly sensitive sensors as well as multistate memory devices. Lot of reforms has been carried out to improve both magnetic and electric properties for its wide applicability. Multiferroic materials are characterised by their magnetic as well as electrical polarization ordering and the

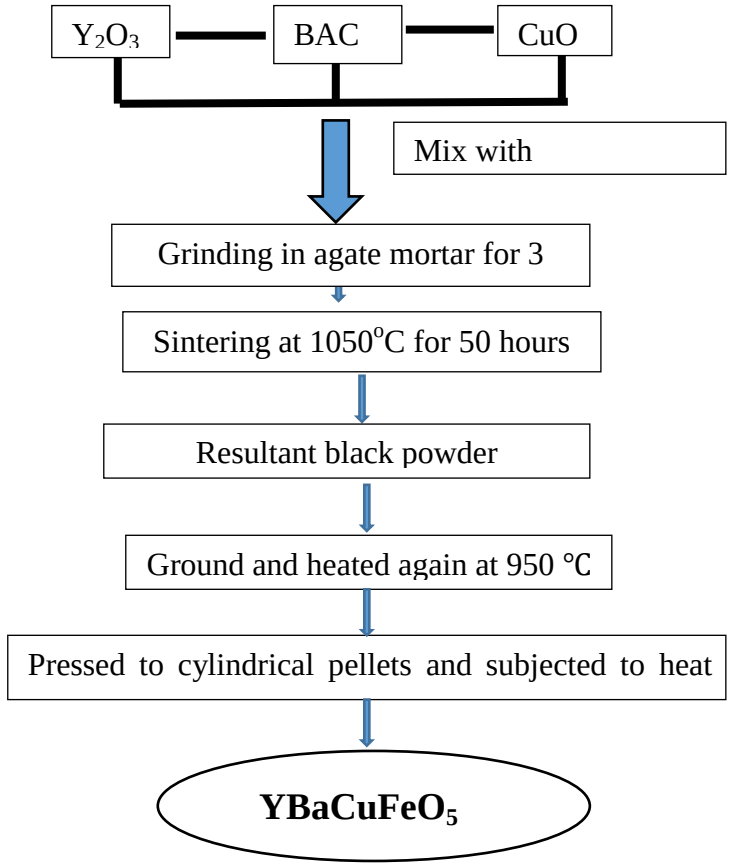
coupling between these two order parameters. The study of magnetic properties of the compounds showing multiferroic behaviour, having a crystal structure similar to that of the high T_c superconductor is of great interest. This class of compounds includes the oxygen-deficient layered perovskite $YBaCuFeO_{5+\delta}$, first synthesized by Rakho et al. and is expected to be a worth contender for novel superconductor [1]. As the structure, is related to those of some well-known high Tc superconductors (HTSC) such as the $YBa_2Cu_3O_7$), there exists some important features in common (copper-oxygen planes, ordered oxygen vacancies, oxygen hyper stoichiometry, etc.). Although it is not superconducting [2], most of the literatures have reported that $YBaCuFeO_5$ displays magnetism-driven ferroelectricity at unexpectedly high temperatures ($T < TN_2 \sim 230$ K) [1] and in a temperature range more than 10 times larger than CuO [3]. $YBaCuFeO_5$ has a tetragonal structure with lattice parameters a= 0.3867 nm and c =0.7656 nm. According to Ruiz-Aragon, the space group of this compound is P_{4mm}, refined by neutron powder diffraction data [4]. The compound $YBaCuFeO_5$, is one of a double perovskite superstructures with a highly ordered vacancy distribution. The structure can be described as formed of [CuFeO] double layers of comer-sharing CuOs and FeO pyramids, perpendicular to c [1].

Impedance spectroscopy is an important and powerful technique in studying the electrical properties such as contribution of bulk (grain), grain boundary and electrode polarization of the materials by different equivalent circuits. In this work, our main objective is to study Impedance spectroscopy of $YBaCuFeO_5$.

2. Experimental Details

2.1. Synthesis

This material was synthesized by solid-state technique. Stoichiometric amounts of the materials Y_2O_3, $BaCO_3$, CuO and Fe_2CO_3 were mixed and thoroughly ground in an agate mortar for about four hours. The resulting powder was sintered at 1050 ℃ in air for 50 hours. The resulting black powder was then ground and heated again at 950 ℃ for 50 hours. This process was repeated for three times. After thorough grinding, the well homogenized samples were pressed to cylindrical pellets of 13 mm diameter and 2-4 mm thickness and subjected to heat treatment in furnace at 1050 ℃ for 24 hours.



Flow chart for synthesis of $YBaCuFeO_5$ using solid state method.

2.2. Experimental techniques:

The resultant powder was characterized by qualitative X-ray powder diffraction measurements to check the phase purity of the sample with the help of Rigaku X-ray Diffractometer (using Cu-K_α radiation, λ=1.54 Å) at room temperature. X-ray diffraction peaks may be indexed in the space group P_{4mm}. No trace of impurity was detected by X-ray diffraction. Revised Rietveld analysis of the X-ray data also shows that the compound crystallizes with space group P_{4mm}. The XRD data for Rietveld refinements were collected over the range of $2\theta = 20° – 80°$ with a step size of 0.02°. The FULLPROF program was used for Rietveld

structural refinement [4] and the refinement was carried out in the space group P_{4mm}. The cell parameters from the refinement are verified to be a=b= 2.9002 Å and c= 14.4344 Å [1]. Impedance measurement has been performed using H20KI LCR meter (IM3570) in the temperature range from 25-175 ^{o}C. Microscopical investigation has been carried out with Jeol JSM 6480LV scanning electron microscope (SEM) for surface analysis and elemental composition with EDAX attached to SEM.

2.3. Impedance and modulus of spectroscopy study

Complex impedance spectroscopy is a powerful and versatile technique to analyse the microstructure-property relationship, and it also allows distinguishing between intrinsic bulk and extrinsic contributions grain boundary, surface layer, and electrode contact problem. This technique enables us to separate the real and imaginary component of the electrical parameters so as to get the material properties. This technique is based on analysing the ac response of the system to sinusoidal perturbation and subsequent calculation of impedance as a function of frequency of perturbation. The frequency dependence of electrical properties of a material is represented in terms of complex impedance and Z^* electrical modulus (M^*) , complex dielectric constant (ε^*) and tangent loss ($tan\delta$) [5]. The following are the complex impedance related parameters:

Complex impedance

$$Z^* = Z' - jZ'' = R_s - {}^{j}/_{\omega C_s} \quad (1)$$

Complex modulus $M^* = 1/\varepsilon^* = M' + jM'' = j\omega C_0 Z$ (2)

Loss tangent $tan\delta = \varepsilon''/\varepsilon = M''/M' = -Z'/Z''$ (3)

Where Z', M', ε' are the real components of impedance, modulus and permittivity and Z'', M'', ε'' are the imaginary parts of impedance, modulus and permittivity, $j = \sqrt{-1}$ is the Impedance and modulus of spectroscopy study is the imaginary factor and $\omega = 2\pi f$ is the angular frequency.

3. Results and discussion

3.1. Structural analysis

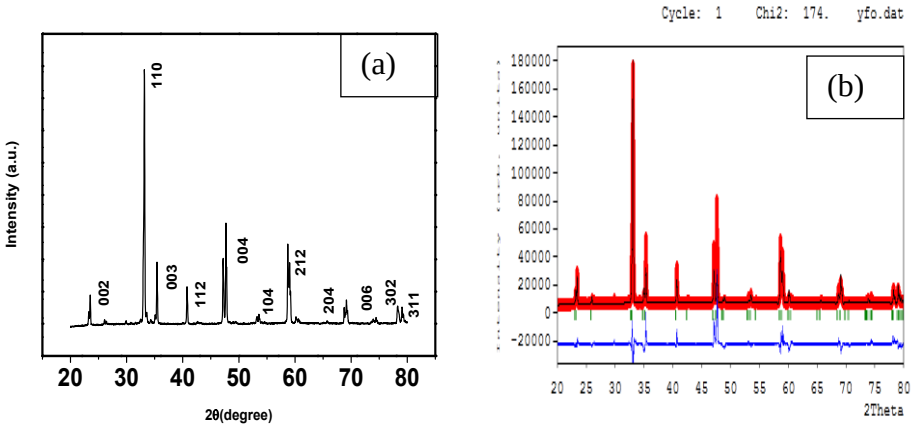


Fig. 1. (a) XRD patterns of $YBaCuFeO_5$ **(b)** Rietveld analysis of XRD data**.**

The XRD patterns of the sintered pellets of $YBaCuFeO_5$ are compared in Fig. 1. All the peaks are indexed using standard computer software JCPDS. The special position and intensity of the peaks indicate the material has double perovskite like tetragonal superstructure. The reflection peaks matched those of unalloyed $YBaCuFeO_5$ and are indexed as a pure phase of $YBaCuFeO_5$ (JCPDS Card No. 81-0029). As studied from literatures, Rietveld analysis of the X-ray data verifies that the compound crystallizes with space group P_{4mm} with lattice parameter a= 3.865 A and c=7.642 A. The sample is crystalline in structure.

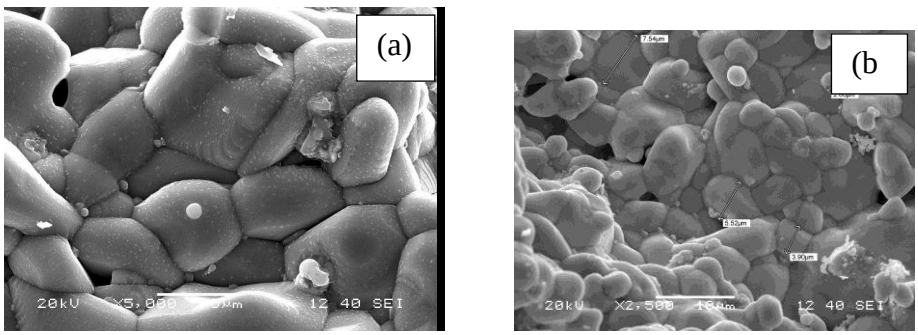


Fig 2. SEM image showing the grains of different sizes of YBaCuFeO5.

The scanning electron micrograph of $YBaCuFeO_5$ pellets is shown in Figs. 2(a, b). The SEM image reveals the microstructure consisting of small well interlinked, randomly oriented, non- uniform grains (in shape and size) with arbitrary distribution and non-uniform size of the grains. Fig 2(b) depicts the micrograph of the pellet surfaces of well-structured grains of $YBaCuFeO_5$ with an average grain size of ~2-5 μm with small porosity.

3.2. Impedance studies

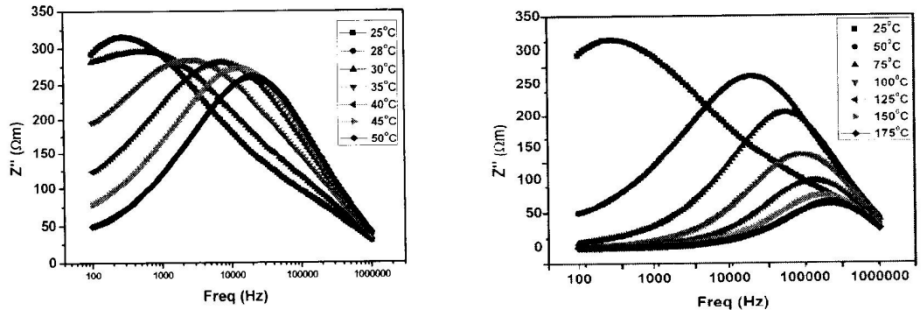


Fig.3. Frequency dependence of imaginary part of impedance (Z'') at different temperatures.

Figure 3 illustrates the frequency dependence of the imaginary part of impedance (Z") at different temperatures. At room temperature (RT ~ 25^o C), a relaxation peak appears at the low frequency (10^2) end of the spectrum. The frequency corresponding to the maximum of the peak is known as relaxation frequency which is the maximum frequency at a particular temperature that the charge carriers can follow during polarisation mechanism. Above this frequency, the charge carriers remain inert and cannot contribute to any polarisation mechanism. As temperature elevates, this relaxation peak shifts towards the higher frequency side but the nature of peak shifting varies differently after ~ 50^o C. It is observed that the rate of shifting of relaxation frequency from room temperature (10^2) up to 50^o C (10^4) is of 10^2 orders however above 50^o C up to 175^o C (10^5), the frequency shifting is of order 10^1. The peak height decreases very slowly up to 50^o C and above this point, significant reduce in peak height is observed. Throughout the entire measured temperature only one relaxation peak is visible in the frequency domain of 100 Hz-1 MHz. It is expected that different thermal activated conduction mechanism are responsible for this type of varying behaviour of relaxation peak. To further examine and distinguish the microstructure like

intrinsic (grain) and extrinsic (interfaces like grain boundary, sample-electrode, defects, etc.) Cole –Cole of impedance (Z' vs. Z") is plotted.

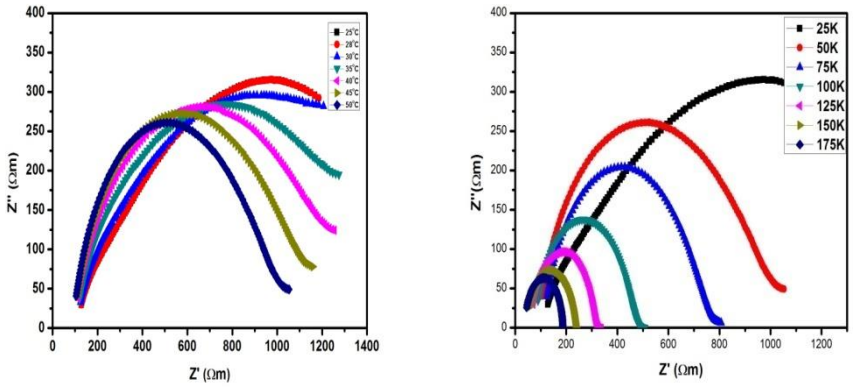


Fig. 4. Complex plane plots (Z" vs Z') at different temperatures.

The electrical behaviour of the samples have been studied over a wide range of temperature and frequency using CIS technique. The complex plane plots (Z" vs Z') at different temperatures have been presented in figure 4. Appearance of semicircle in the diagram represents a relaxation process, whose radius measures the resistance of the sample and centre lies on the abscissa (Z' - axis) if the conduction is of Debye type. For a non-Debye type conduction process, a depressed semicircle appears in the diagram. [6] For the appearance of three distinct semicircles in the diagram, the one appears at high frequency end is assigned to grain effect, the semicircle at intermediate frequency zone corresponds to grain boundary effect and that of at lower frequency end is ascribed to sample surface conduction effect. [7] Only one Cole-Cole semicircle appears in the diagram of the studied compound. The radius of the semicircle decreases very slowly below 50^{o} C and above this point, it reduces comparatively much higher rate. This indicates the resistance of the material suddenly drops above 50^{o} C. Though a single relaxation process appears in the experimented temperature range it is tough to assign it due to intrinsic conduction effect as the resistance of the material is sufficiently low to prevent arrival of extrinsic interfacial conduction effect. In order to properly distinguish the intrinsic and extrinsic effect on conduction mechanism we illustrate the frequency dependent imaginary part of Modulus (M") in Fig. (5) to verify the relaxation behaviour.

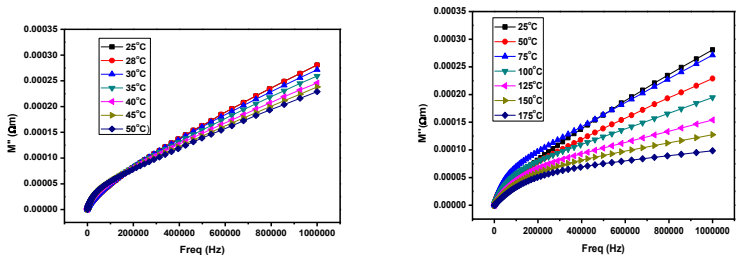


Fig. 5. Variation of M'' ~ frequency at different temperature for $YBaCuFeO_5$

Electric modulus varies inversely to the capacitance of the material and hence has the ability to suppress the highest capacitive region of sample-electrode surface conduction effect and highlight the least capacitive grain conduction effect [7]. In figure 5 it is observed that no relaxation peak corresponding to that in the Z" is appeared in the M" plot or we can say that the relaxation peak is suppressed in the latter. This indicates the relaxation mechanism of charge carriers is due to the conduction process in sample-electrode surface effect.

4. Conclusion

$YBaCuFeO_5$ was prepared by solid state reaction route and its relaxation behaviour was studied by complex impedance spectroscopy technique. A single relaxation was observed in the prescribed temperature and frequency range. Extrinsic sample-electrode interface conduction effect has been identified.

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