Thermal properties of Superconducting Nano Crystalline L\(_{0.1}\)ZY\(_{0.9}\)BCCO

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Abstract: The crystalline ceramic Lanthanum Zirconium Yttrium Barium Calcium Copper Oxide (L\(_{0.1}\)ZY\(_{0.9}\)BCCO) was prepared by the solid state thermo chemical reaction method. In order to show the viability of the proposed method, this super-conducting ceramic powder was prepared in a special furnace. It was then calcined in ambient air and optimum temperature so that the desired homogeneity and phase formation was acquired. The thermal properties of the sample were studied using TGA, DTA and DSC at higher temperatures. EDS spectrum shows the elemental composition of the sample.

Keywords: L\(_{0.1}\)ZY\(_{0.9}\)BCCO, nonstoichiometry, DTA, EDX

I. INTRODUCTION

The most familiar ceramic superconducting materials have perovskite structure[1-4]. Most of the perovskites are an extremely important class of ceramic nano materials. These compounds have a chemical formula ABO\(_3\) where A is either a monovalent or divalent cation or B is either a pentavalent or tetravalent metal [5]. The non stoichiometric sample of Lanthanum Zirconium Yttrium Barium Calcium Copper Oxide (L\(_{0.1}\)ZY\(_{0.9}\)BCCO) is a type of perovskite ceramic superconductor with high dielectric constant. Ceramics generally can withstand very high temperatures such as temperatures that range from 1000°C to 1600°C (1800°F to 3000°F). Conventional solid state reaction method is a common and effective way to fabricate modern ceramics [6]. The authors fabricated L\(_{0.1}\)ZY\(_{0.9}\)BCCO nano crystalline ceramic type II high-TC superconductor material by the solid state thermo chemical reaction technique in a special furnace and it was characterized to show good quality, homogeneity and the desired stoichiometry of the sample prepared [7]. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. Solid state thermo chemical reaction method is a common and effective way to fabricate modern ceramics [8-10]. Before final heating at 950°C, the material L\(_{0.1}\)ZY\(_{0.9}\)BCCO was treated at different temperatures, 30°C, 500°C and 800°C [11]. In the present work the authors describes the thermal behavior of nano crystalline superconductor material Lanthanum Zirconium Yttrium barium Calcium Copper oxide (L\(_{0.1}\)ZY\(_{0.9}\)BCCO) calcined at 950°C [11]. TGA, DTA and DSC is used to analyze thermal behaviour of nanoparticles [12-15] at high temperatures. Elemental composition is obtained using EDX.

II. EXPERIMENTAL.

2.1. Preparation of the Sample

The pure form of the raw materials were taken in order to prepare the sample. The non stoichiometric sample prepared have the chemical formula L\(_{0.1}\)ZY\(_{0.9}\)BCCO. In order to prepare the ceramic sample L\(_{0.1}\)ZY\(_{0.9}\)BCCO the raw materials were weighed first. The powder materials were mixed well mechanically ie by hand mixing, then ball milled for a long period followed by attrition milling. Then the material was calcined at different temperatures, 30°C, 500°C, 800°C and 950°C. After the furnace was off, each time on cooling oxygen was allowed to flow into the furnace at intervals (Oxygen Annealing) [16]. During the calcination the solid phase reaction took place between the constituents. The best electrical and mechanical properties are obtained by proper
calcination at the right temperatures. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [17]. For thermal studies TGA, DTA and DSC data were analyzed. From EDX, the composition details of the prepared ceramics were determined. X-ray diffraction spectrum of these materials were taken and analyzed [18] at different treating temperatures 300°C, 500°C, 800°C and 950°C. In order to obtain a good quality superconductor additional grinding and firing under flowing oxygen is necessary [19] which was applied with special care. In the process of being heated under oxygen flow, the oxygen content of each crystal unit is increased. A final furnace temperature of 950 °C was maintained after the intermediate firings. Material becomes harder at much higher temperature above this. Temperatures above 1130 °C may destroy the crystal structure. From EDX the composition details of the prepared ceramics were determined [11] with standard universal analyze.

2.2. TGA –Analysis

By the effect of heat there are reactions and physical changes occurred in materials. That can be analysed by TGA.TGA gives a quantitative measurement of mass change in materials associated with thermal degradation and transition. Using TGA we can record the change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature. The variation is due to specific temperature ranges and heating rates. By these characteristics we can identify the molecular structure of the sample. Thermo gravimetric Analysis is used to measure the percent weight loss of the sample. The sample must be heated at a uniform rate in an appropriate environment. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability [20]. Using TG curve we could associate the mass changes involved [21]. Thermogravimetric (TG) analysis provides determination of endotherms, exotherms, weight loss on heating, cooling and more. Of materials include polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives and biological samples. Because most events that occur in a TGA are kinetic in nature, any experimental parameter that can affect the reaction rate. The reaction is characterized by two temperatures, Ti and Tf , which are called the procedural decomposition temperature and the final temperature [22].TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. Fig (1) shows a TGA apparatus and the schematic representation of a modern TGA-DTA. Thermogravimetric Analysis (TG) determines the weight changes of a sample, whereas Differential Thermal Analysis (DTA) measures changes in temperature between a sample and a reference, as a function of temperature or time. TG and DTA curves of the sample were recorded using Perkin Elmer, Diamond TG/DTA with Flexible axial and radial view instrument, with high concentration capabilities. TGA is plotted in figure 2 (a) & (b). DTA/DTG is plotted in figure 3.

![Fig(1) Thermogravimetric analysis apparatus and a modern TGA - DTA](image-url)
Fig. 2 (a) & (b) TGA curve of $L_{0.1}ZY_{0.9}BCCO$ (Temperature vs. weight and weight in percentage)
2.3. DSC Analysis
Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to measure changes in heat flows associated with material transitions. DSC measurements provide both qualitative and quantitative data on endothermic (heat absorbing) and exothermic (heat evolving) processes. DSC is commonly used to determine the glass transition temperature and crystalline melting point of polymeric materials [23]. Differential scanning calorimetry (DSC) measures Specific Heat Capacity, Heat of Transition, and the Temperature of Phase Changes and Melting Points, measures the rate of heat flow, and compares differences between the heat flow rate of the test sample and known reference materials. The difference determines variations in material composition, crystallinity and oxidation. The applications of DSC are numerous, either for routine quality control measurements or in research, where high sensitivity and flexibility are important aspects. DSC curve of the sample was plotted using Mettler Toledo DSC 822e which is shown in figure 4. Figure 5 gives a schematic outlay of the apparatus.
Due to the effect of a controlled temperature program Differential Scanning Calorimetry (DSC) measures the change of the difference in the heat flow rate to the material (sample) and to a reference material \[24\]. The result of DSC is a curve of heat flux versus time or temperature and is therefore used also for determination of the enthalpy, specific heat (cp ) etc.\[25\]. Heat flow rate signal (DSC signal) is internally calculated from the temperature difference between the sample material and the reference material.

2.4. EDX Analysis

EDX is an analytical technique used for the chemical characterization and elemental analysis of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum\[26\]. Energy Dispersive X-ray Spectroscopy is based on the detection of characteristic x-rays emitted of an element as a result of the de-excitation of core electron holes created by a high energy electron beam. An electron from a higher binding energy electron level falls into the core hole and an x-ray with the energy of the difference of the electron level binding energies is emitted. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic
structure of the emitting element, EDS allows the elemental composition of the specimen to be measured [22]. Due to the quantization of electron energy levels, the emitted characteristic x-ray energies for elements will generally be different from element to element with only a few spectral peaks overlapping. If the identification of one peak is ambiguous, other peaks or limited knowledge of the sample history will often allow a reasonable elemental identification of the peak [27]. Using ISIS Link Oxford Instrument UK the composition details (EDX) of the prepared nanocrystalline ceramic powder $L_{0.1}Z_{Y_{0.9}}BCCO$ at 950°C [11] is plotted in figure 6. Table 1 indicates the contents of the material.

![Fig 6. EDAX spectrum of $L_{0.1}Z_{Y_{0.9}}BCCO$](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>(keV)</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>La M</td>
<td>0.833</td>
<td>2.05</td>
</tr>
<tr>
<td>LaLα</td>
<td>4.650</td>
<td></td>
</tr>
<tr>
<td>ZrLα</td>
<td>2.042</td>
<td>2.75</td>
</tr>
<tr>
<td>YLα</td>
<td>1.922</td>
<td>20.1</td>
</tr>
<tr>
<td>BaLα</td>
<td>4.465</td>
<td>19.45</td>
</tr>
<tr>
<td>BaLβ</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>BaLγ</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td>CaKα</td>
<td>3.690</td>
<td>12.9</td>
</tr>
<tr>
<td>CuKα</td>
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<tr>
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<tr>
<td>CuLα</td>
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<tr>
<td>Okα</td>
<td>0.525</td>
<td>8.01</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSION:

From the XRD profile of the sample it is observed that the intensities of the peaks decreases as the temperature increases [11]. Due to the effect of smearing out of lattice planes the intensity of the diffracted beam decreases as the atomic vibration amplitude increases. The intensity of a diffracted
beam decreases as the temperature is raised [28]. By the study of XRD spectrum the large particle size of sample at 950°C is confirmed. XRD spectrum for the different temperatures gave a clear idea about the maximum intensity peak shifting corresponds to the different treating temperatures[11]. Due to the effect of high temperatures the particles anneal and form larger grains. Hence its crystallinity increases due to long-range order [29,30]. The chemical and physical properties of the crystalline material is analysed from the thermal studies. The TGA and DTA curves give explanation of these. TGA reveals changes of a sample due to weight, whereas DTA and DSC reveal changes not related to the weight mainly due to phase transitions. The sample initially has a weight nearly equal to 6.35mg at room temperature. As temperature increases to a temperature of 550°C the weight gradually decreases linearly to 5.85mg. Due to a lattice distortion there is a sudden change in weight up to a temperature of nearly 675°C. For further increase of temperature the weight gradually decreases. Up to a temperature of 550°C the weight loss percentage is 8. From these observations it is concluded that the sample is a good ceramics. This percentage in weight loss is analyzed from the TG curves (Figure 2). Moisture content is not observed.

From the study of DTA curves it is observed that loss on ignition is in total 10% up to 1000°C. Phase transitions are taking at a very high temperature and it is affected by the free energy inside the interface regions of the nano materials. Changes in lattice imperfections also arise due to the miniaturised size of the particles. Hence nano materials have a different or modified behaviour than that of the bulk materials. The thermal stability of the sample can be confirmed from the TGA, DTA & DSC analysis. The endothermic process and the polymorphism in crystalline structure can be proved by the DSC curves.

Fig.6 gives EDX spectrum of L_{0.1}ZY_{0.9}BCCO which gave the information on the elemental composition of the material. The elemental compositions agree with the compositions of the prepared compound. From the EDX spectrum, the dominant peak positions at 0.833Kev, 4.650Kev (La M, La Lα), 2.042Kev (ZrLα), 1.922 Kev(YLα), 4.465Kev, 4.75Kev, 5.50Kev (BaLα, BaLβ, BaLγ), 3.90Kev (CaKα), 8.040Kev, 8.95Kev, 0.930Kev (CuKα, CuKβ,Cu Lα), 0.525 KeV (O Kα), correspond quite well to the energy pattern of the corresponding materials reported in the EDAX international chart, giving the evidence that La, Zr, Y, Ba, Ca, Cu, O are present dominant in the sample L_{0.1}ZY_{0.9}BCCO. Table 1 shows the percentage of the elements in the prepared L_{0.1}ZY_{0.9}BCCO sample.

IV. CONCLUSION

Nano crystalline ceramics L_{0.1}ZY_{0.9}BCCO was prepared successfully and characterized by XRD, SEM, and EDX. The formation of the perovskite phase structure is confirmed by the XRD data [11]. In this work TGA, DTA and DSC analyses were carried out and the results confirmed that much loss on ignition is not observed which is the characteristic of a good ceramic material. Each of these thermal techniques provides unique information that can be used to optimize the thermal and mechanical properties of the end product. By the analysis of the EDX spectrum the presence and percentage of the elements existing in the sample were noted and it agrees with the compositions of the prepared compound.

ACKNOWLEDGMENTS

The authors are thankful to SAIF, Kochi for providing the instrumental data, UGC for the financial Assistance and to the Principal, CMS College, Kottayam and to the principal D B Pampa college, Parumala, Kerala for providing the facilities.

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