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RESEARCH ARTICLE

STUDIES ON THERMAL BEHAVIOUR OF NANO CRYSTALLINE CERAMIC LAZRYBACA2CU3O11

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ABSTRACT

Nano crystalline ceramic $LaZrYBaCa_2Cu_3O_{11}$ is prepared by the solid state reaction method. The process is mechanically done by high energy ball milling. The mixed powder is synthesised and calcined in a specially designed high temperature furnace. The pure material prepared is then calcined in ambient air and optimum temperature so that the desired homogeneity and phase formation is acquired. Using TGA, DTA and DSC thermal behaviour of the sample at a high temperature is studied. EDX analysis is done to find out the elemental composition.

INTRODUCTION

$LaZrYBaCa_2Cu_3O_{11}$ has perovskite structure. The most familiar ceramic superconducting materials have perovskite structure (Willander *et al*., 2012). The perovskite structure is adopted by many oxides. The representative cubic structure of perovskite compounds undergo some distortion. The most common variants are orthorhombic and tetragonal phases (Anitha S. Nair *et al*., 2014). The perovskite systems are considered as a potential candidate in ceramic industry. Ceramic materials are inorganic non metallic solid comprising metal, non metal or metalloid atoms primarily held in ionic and covalent bonds. They withstand chemical erosion that occurs in an acidic or caustic environment.

Ceramic materials are brittle, hard, Strong in compression, weak in shearing and tension. Conventional solid state reaction method is a common and effective way to fabricate modern ceramics (Leow Chun Yan *et al*., 2011). Ceramics materials generally can withstand very high temperature such as 1000˚C to 1600˚C (1800˚F to 3000˚F). Conventional solid state reaction method is applied here to fabricate modern ceramics (Leow Chun Yan *et al*., 2011). The Lanthanum Zirconium Yttrium Barium Calcium Copper Oxide ($LaZrYBaCa_2Cu_3O_{11}$) is a type of perovskite ceramic superconductor with high dielectric constant. Before final heating at 950˚C, the material $LaZrYBaCa_2Cu_3O_{11}$ is treated at different temperatures, 30˚C, 500˚C and 800˚C (Anusha Mony *et al*., 2014). It is having a complex structure.

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Detailed understanding of this class of materials will help electronic industry in planning, design and processing of these materials. High dielectric constant (High-K) ceramic composites have become potential candidate materials for integration into high frequency electronics. Here $LaZrYBaCa_2Cu_3O_{11}$ nano crystalline ceramic high-TC superconductor material is fabricated by the solid state thermo chemical reaction technique and it was characterized to show good quality, homogeneity and the desired stochiometry of the sample prepared (Anusha Mony *et al*., 2014). The results were analyzed by X-Ray Diffraction (XRD), SEM, and EDX. The thermal behaviour of lanthanum zirconium yittrium barium calcium copper oxide ($LaZrYBaCa_2Cu_3O_{11}$) calcined at 950^0C is presented here. TGA, DTA and DSC is used to analyze thermal behaviour of nanoparticles (Wendlandt *et al*., 1986; Yao *et al*., 1995 and Brown *et al*., 1990), at a high temperature. Elemental composition is obtained using EDX.

Nanophase materials are in metastable state of thermal inequilibrium. Large amount of energy is stored in the grain boundaries and in other types of defects. By studying the transition from nanophase-state to thermal equilibrium state one can get information regarding the long-term thermal stability of such systems (Experimental Techniques). The phase transformation in nano materials due to temperature change is much different from that of bulk crystals. The free energy of nano particles are always higher than that of its conventional counterpart (Sankaranarayanan Potty, 2001). Phase transformations in nano structured materials are reported (Qin, Wu and Cheng, 1993).

Experimental

Preparation of the Sample

The sample with the chemical formula $LaZrYBaCa_2Cu_3O_{11}$ was prepared from the pure form of raw materials. The raw materials were first weighed according to the stoichiometric formula for the preparation of the ceramics. The powders of the required ceramics then mixed mechanically by hand mixing, then ball milled for a long time followed by attrition milling. Then the material was calcined at different temperatures, 500^0C and 800^0C. After the furnace is off, on cooling oxygen was allowed to flow into the furnace at intervals (Oxygen Annealing) (Anitha S. Nair *et al*., 2014). Then the material was calcined at a temperature 950˚C. 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 (Sankaranarayanan Potty, 2001). For thermal studies TGA, DTA and DSC data were analyzed. From EDX, the composition details of the prepared ceramics were confirmed. Then X-ray diffraction spectrum of these materials were taken and analyzed (Anusha Mony *et al*., 2014).

TGA –Analysis

Thermo gravimetric analysis involves heating a sample in an inert or oxidizing atmosphere and measuring the weight. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability (Materials, 2000). 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. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is especially useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibres, coatings and paints.

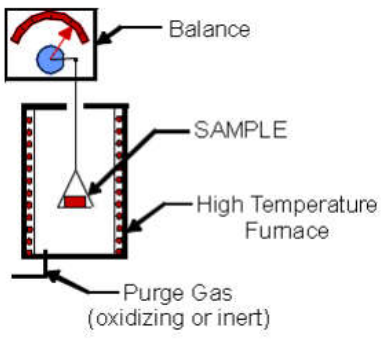

Fig. 1. Schematic principle of TGA measurement

TGA measurements provide valuable information that can be used to select materials for certain end-use applications, predict product performance and improve product quality. The technique is particularly useful for the measurements (Fleming polymer testing and consultancy). Using TG curve we could associate the mass changes to the stoichiometry involved (Experts mind.com). 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 (16). The thermal gravimetric analysis (TGA) and the differential scanning calorimetry (DSC) are methods to investigate the thermal characteristics of substances.

The schematic principle of the TGA measurement is shown in Figure 1. Thermo gravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique, DSC. 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. 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. The measurements are used primarily to determine the thermal and oxidative stabilities of materials as well as their compositional properties.

DSC Analysis

DSC measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes [17]. DSC curve was plotted using Mettler Toledo DSC 822e which is shown in Figure 4. The applications of DSC are numerous, either for routine quality control measurements or in research, where high sensitivity and flexibility are important aspects. Heat effects associated with chemical reactions and phase transitions as a function of temperature is monitored by Differential scanning calorimeters (DSC). Schematic principle is shown in Figure 5. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes. The heat flow difference between sample and reference can be either positive or negative. The reference is an inert material such as alumina. The temperature of both the sample and reference are increased at a constant rate.

EDX Analysis

The EDX analysis system is valuable in determining the composition of unknown materials such as inclusions in metal product, corrosion byproducts, coatings, reverse engineering, etc. The composition details (EDX) of the prepared nano crystalline ceramic powder$LaZrYBaCa_2Cu_3O_{11}$ at 950^oC (Anusha Mony *et al*., 2014) is plotted in Figure 6 using ISIS Link Oxford Instrument UK. 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.

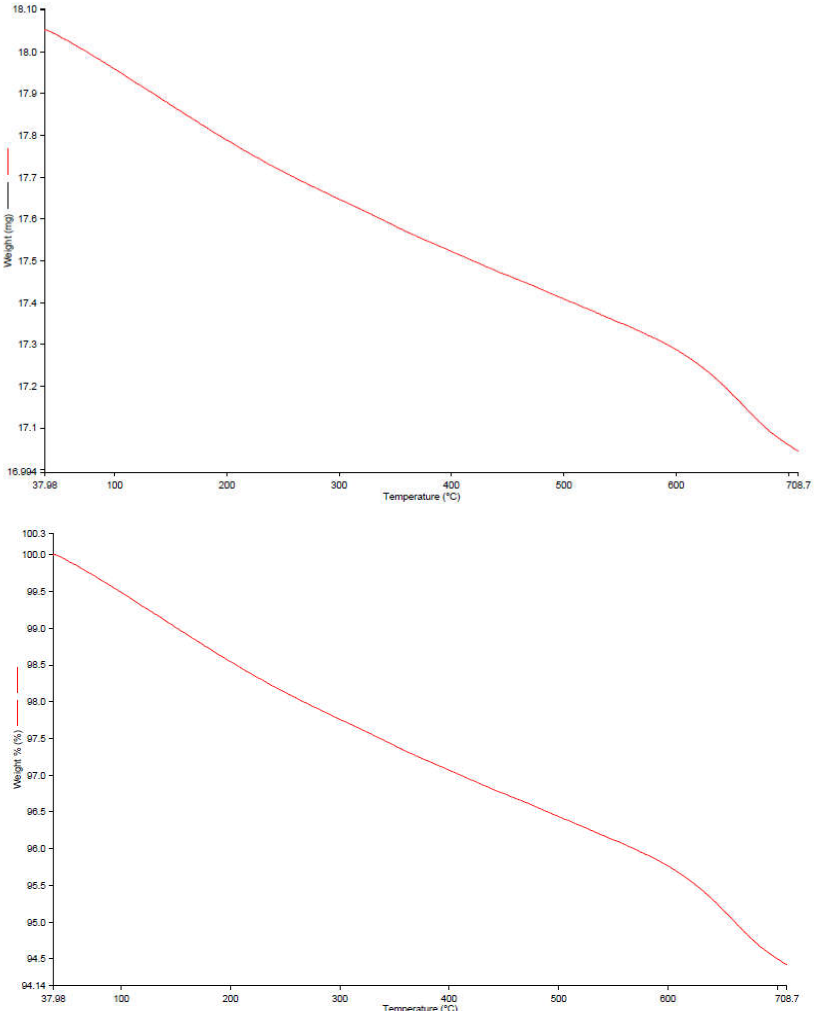

Fig.2 (a) & (b) TGA curve $LaZrYBaCa_2Cu_3O_{11}$ (in weight and in percentage vs. Temp.)

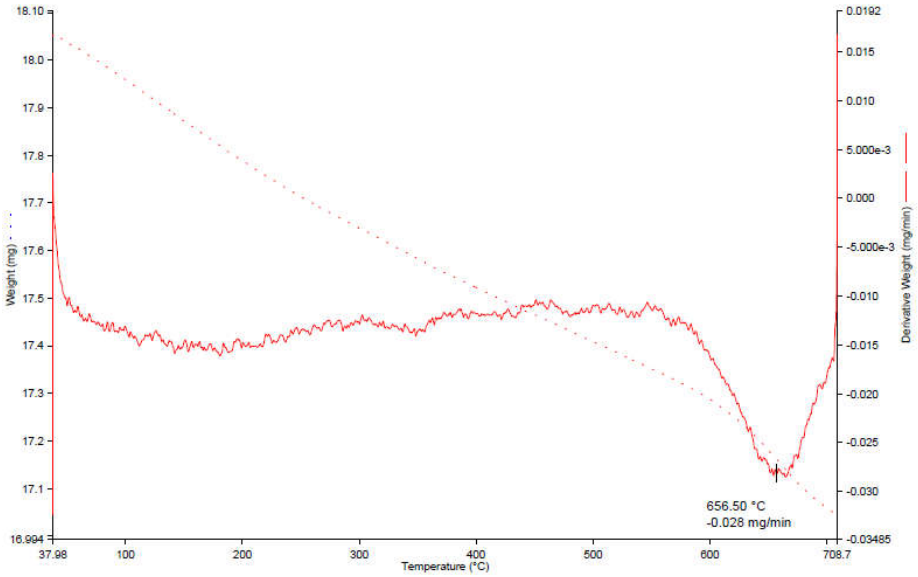

Fig. 3. TG/DTA /DTG curve of the sample $LaZrYBaCa_2Cu_3O_{11}$

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. 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 [17]. Table 1 indicates the composition of the material in the prepared sample.

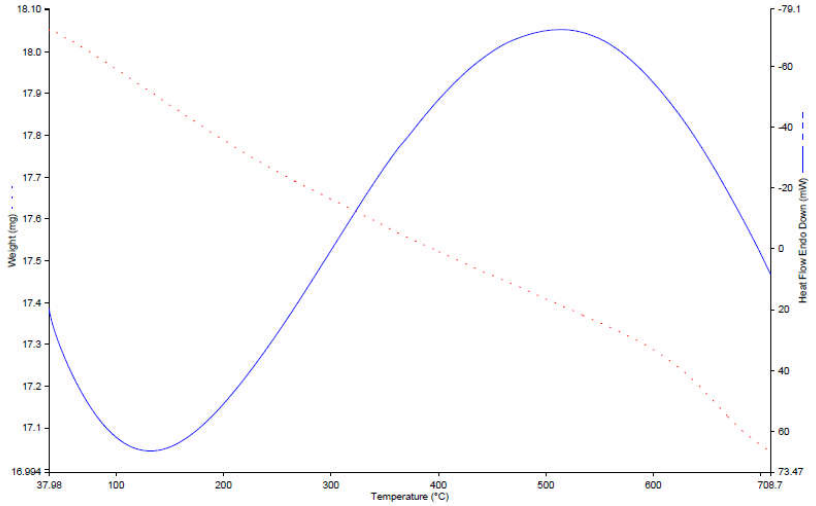

Fig. 4. DSC curve of LaZrYBaCa2Cu3O11

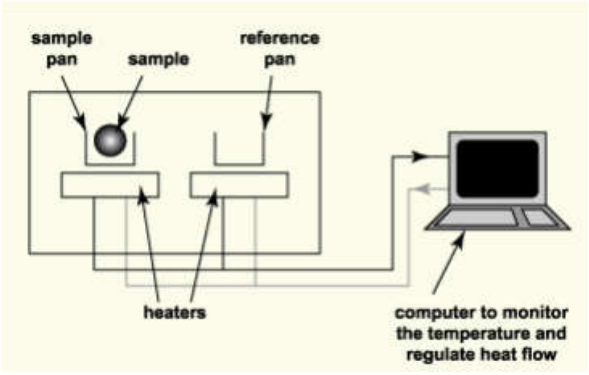

Fig. 5. Schematic Principle of DSC Measurement

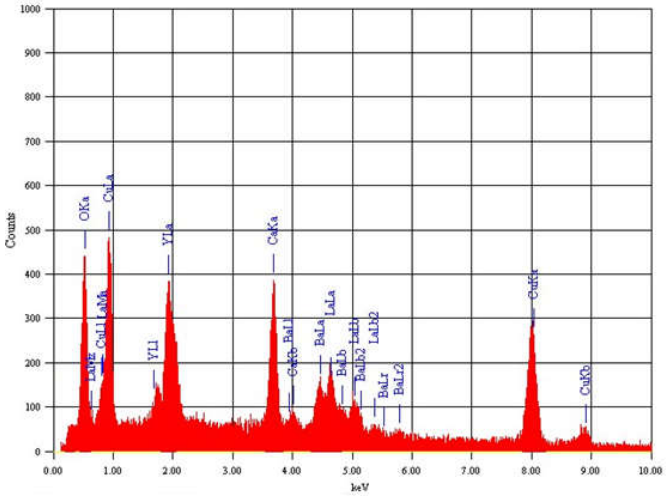

Fig. 6. EDAX spectrum of $LaZrYBaCa_2Cu_3O_{11}$

RESULTS AND DISCUSSION

The intensities of the peaks decreases on increase of temperature from the XRD profile of the sample $LaZrYBaCa_2Cu_3O_{11}$ (Anusha Mony *et al*., 2014). The intensity anomaly is due to the rigorous thermal agitations of the lattice planes resulting in the formation of new phase at the high temperature. As the temperature of the material is heated from room temperature to high temperatures, the amplitude of the thermal vibrations increases.

Table 1. Shows the composition of the elements in the sample $LaZrYBaCa_2Cu_3O_{11}$

Element	(keV)	Mass%
La M	0.833	16.95
LaLα	4.650	
ZrLα	2.042	2.13
YLα	1.922	20.49
BaLα	4.465	9.5
BaLβ	4.75	
BaLγ	5.50	
CaKα	3.690	10.9
CuKα	8.040	32.59
CuKβ	8.95	
CuLα	0.930	
Okα	0.525	7.44
Total		100

The intensity of the diffracted beam decreases as the atomic vibration amplitude increases because it has the effect of smearing out lattice planes. The intensity of a diffracted beam decreases as the temperature is raised (Qin, Wu and Cheng, 1993). XRD spectrum of the sample at different temperatures gave a clear idea about the maximum intensity peak shifting corresponds to the different treating temperatures. And also get the maximum intensity peak difference (Anusha Mony *et al*., 2014). The large particle size of sample at 950^{o}C (highest temperature here) is confirmed by studying the XRD spectrum at different temperatures. Heat treatment causes the particles to anneal and form larger grains, which of course indicates that the particles become larger. This also agrees with the higher crystallinity, as having larger grains means more long-range order, and hence more crystallinity (Sankaranarayanan Potty, 2001 and Vinila *et al*., 2014).

By the thermal studies we can evaluate the Chemical and Physical Properties of Ceramic Materials. From the TGA/DTA curves it is observed to be having mainly four stages. The sample $LaZrYBaCa_2Cu_3O_{11}$ shows a linear decrease in weight up to 250^{0}C, which initially has a weight of 18.5mg attains17.7mg on heating to a temperature of 250°C. The weight percentage gradually reduces and the loss percentage is 2.0. Then the weight reduces to17.3mg up to 625^{0}C. Then there is a sudden decrease in weight. This may be due to distortion in lattice.

Then the total weight loss percentage is 4.5. From the curve it is observed that above these temperatures the sample is a good ceramic material that much loss is not expected. These can be observed from the TG curve given above (Fig.2). Moisture content is not observed. Loss on ignition is in total 10% up to 1000^0c. These observations are confirmed by the study of DTA curves. From the study it is observed that phase transition is taking at a very high temperature. Phase transitions are affected by the free energy inside the interface regions of the nano materials. Changes in lattice imperfections also arise due to the miniature size of the particles. Hence nano materials have a different or modified behaviour than that of the bulk materials. Thus the thermal stability of the sample can be confirmed from the TGA, DTA & DSC analysis. From the DSC curve (Fig.4) of the sample it is evident that the process is endothermic. Polymorphism in crystalline structure also can be observed.

EDX spectrum of $LaZrYBaCa_2Cu_3O_{11}$ is shown in Fig (6), which gave the information on the elemental composition of the material. The elemental compositions agree with the stoichiometric relations 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 $LaZrYBaCa_2Cu_3O_{11}$. Table.1 shows the percentage composition of the elements in the prepared $LaZrYBaCa_2Cu_3O_{11}$ sample.

Conclusion

The crystalline ceramics $LaZrYBaCa_2Cu_3O_{11}$ were prepared successfully and characterized by XRD, SEM, and particle size measurement. The formation of the perovskite phase structure is confirmed by the XRD data (Anitha S. Nair *et al*., 2014 and Anusha Mony, 2014). In this work TGA, DTA and DSC analysis was carried out and 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 study of the EDX analysis the presence and percentage of the elements existing in the sample were noted and it agrees with the stoichiometric relations of the prepared compound.

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