Internship on $Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$ (Ferrite) Sample Preparation, Planetary Ball Milling and Calcination

Internship Report Submitted To

The Department of Mathematics and Natural Sciences, BRAC University in partial fulfilment of the requirements of the award of the degree of Bachelor of Science in Applied Physics and Electronics

By

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DECLARATION

I hereby declare that the internship report titled "$Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$ (Ferrite) Sample Preparation, Planetary Ball Milling and Calcination" is submitted to the Department of Mathematics and Natural Sciences of BRAC University in partial fulfilment of the requirements for the degree of Bachelor of Science in Applied Physics and Electronics. This report is the work of my own and has not been submitted elsewhere. Every work that has been used as reference for this work has been cited properly.

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Acknowledgement

It was not only me whose time and effort was invested behind this piece of work. So I would like to acknowledge the people who had my back throughout.

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I would also like to thank Mr. Bablu Chandra Das, PhD student at BUET, who was gracious enough to let me observe his research work and patiently walked me through the entire process, answering all my queries.

Abstract

The purpose of the internship was to provide with a firsthand experience on how to measure and prepare a precise amount of the ferrite composite, $Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$ which was then further planetary ball milled for fourteen hours to achieve homogeneous distribution at 230 rpm, hand milled for a further four hours in two separate sessions using an agate pestle and mortar and finally calcined at 950°C afterward using a Nabertherm p330 to drive off water, carbon dioxide, other volatile constituents and to oxidize the whole composite. In order to prepare the sample, first the stoichiometric ratio was found and then the exact amount of each required compound was measured separately using an AX120 electronic balance as it provides a high precision of 10 µg and has a full range TARE to allow unladen weight measurement. Planetary ball mill was used for grinding to ensure quick contamination free grinding down of the prepared sample to nano range. Nabertherm P330 was used for calcination as it can be functioned to allow and ensure easy setting of temperature values, time specifications and gradient specifications. These were crucial as the calcination process required the buildup of temperature over a span of two hours in intervals of 10°C up to 950°C, held at that for five hours and then cooled back in instalments of 5°C. The final product was again ball milled to get rid of clusters and turned into powder thereby completing the preparation of the ferrite sample.

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Introduction

The sole purpose of the internship is to provide us with practical experience. It teaches us how to implement all that we have learned so far in real life because what is the point of all these knowledge if we do not understand how to use it once we have stepped out of our academic atmosphere. It is crucial for us to amalgamate our theoretical knowledge with our empirical one because if not so then there will not be any advancement for us in this ever so expanding world of science. Short-lived experience it might be but working in Bangladesh University of Engineering and Technology's solid state physics laboratory provided me with just that.

Laboratory Facilities Available in the Department of Physics in Bangladesh University of Engineering and Technology

- Ferroelectric measurements
- UV visible spectrometer
- High power Xenon Lamp for Photocatalytic experiment
- Gas Chromatograph
- High temperature inert gas atmosphere furnace
- Close Cycle Cryocooler
- Torque Magnetometer
- Vibrating Sample Magnetometer
- Plasma polymerization
- Thin Film Deposition
- High Temperature Furnace
- Hydraulic pressing machine
- Optical Polarizing Microscope

- Crystal Growth
- Spray Pyrolysis Deposition Unit
- Modelling and Simulation facilities
- Scanning Electron Microscope (SEM) & X-ray Diffractometer

Solid state physics laboratory's research areas

This part of the institution has their activity mostly set on different fields of Material Science like:

- Multiferroics
- Nanocrystalline Ferrites
- Nanocrystalline Alloys and
- Colossal Magnetoresistance.

Examples of specific research projects

- Preparation and characterization of nanostructured spinel type ferrites
- Preparation and characterization of perovskite type material
- Preparation and characterization of nanocrystalline alloys
- Manganites for colossal magneto resistance/ giant magneto resistance study
- Ferroelectric and dielectric (high k) material
- Mutliferroic materials

Sample Preparation of $Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$

$Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$ is a spinel ferrite. Spinel ferrites have the general molecular formula$(A^{2+})\ [B_2^{3+}]O_4^{2-}$. A ferrite is a ceramic-like material with magnetic properties that are useful in many types of electronic devices. Ferrites are hard, brittle, iron-containing, and generally gray or black. They are polycrystalline, i.e., made up of a large number of small crystals. They are composed of iron oxide and one or more other metals in chemical combination. Ferrites exhibit a form of magnetism called ferrimagnetism, which is distinguished from the ferromagnetism of materials like iron, cobalt, and nickel. In ferrites the magnetic moments of constituent atoms align themselves in two or three different directions. A partial cancellation of the magnetic field results, and the ferrite is left with an overall magnetic field that is less strong than that of a ferromagnetic material.

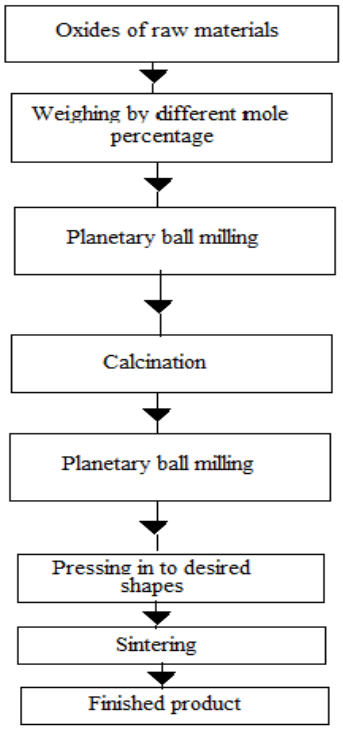

Figure 1: Flowchart of the stages in preparation of spinel ferrite

Stoichiometric ratio calculation

Stoichiometric ratio calculation is crucial in order to find out how much amount of reactant is required to acquire a particular amount of product in chemical reaction. It is founded on the law of conservation of mass where the total mass of the reactants equals the total mass of the products. Though the required weight of the ferrite for making expected number of pellets and toroid was 124g it was rounded off to 135g on purpose to compensate for any loss during the process. Calculation for 135 g sample preparation of ferrite part is given below:

Composition	Molecular Weight (g/mol)	Need of (g/mol)
$Ni_{0.48}Cu_{0.12}Zn_{0.40}Gd_{0.04}Fe_{1.96}O_4$	$58.6934 \times 0.48 + 63.546 \times 0.12 + 65.38 \times 0.40 + 157.25 \times 0.04 + 55.845 \times 1.96 + 15.999 \times 4 = 241.698152$	
NiO	$58.6934 \times 15.999 = 74.6828$	$\frac{0.48 \times 74.6828 \times 135}{241.698152} = 20.025364$
CuO	$63.546 \times 15.999 = 79.5454$	$\frac{0.12 \times 79.5454 \times 135}{241.698152} = 5.33159012$
ZnO	$65.38 \times 15.999 = 81.3894$	$\frac{0.40 \times 81.3894 \times 135}{241.698152} = 18.183952$

Gd_2O_3	157.25×2 $+ 15.999 \times 3$ $= 362.4982$	$\frac{0.04 \times 362.4982 \times 135}{241.698152}$ $= 4.04945231$
Fe_2O_3	55.845×2 $+ 15.999 \times 3$ $= 159.6882$	$\frac{1.96 \times 159.6882 \times 135}{241.698152}$ $= 87.4096417$

Measuring the required amount of raw materials using AX120 electronic balance

For setting the measuring mode on the balance the power key is pressed. When zero is displayed the glass door is opened and aluminum foil is placed inside. It is very important to clean the foil beforehand using acetone to avoid any sort of contamination. To avoid misreading all fans have to be kept turned off as well. When the arrow appears on the scale suggesting the total weight of the foil has been registered the TARE button is pressed to nullify it. Small amount of each compounds were then scooped onto the foil using a clean spatula until the reading matched up to the fourth decimal place of the calculated required amount. After repeating the process for all five compounds they were finally placed in a jar which was cleaned beforehand with acetone ready for planetary ball milling.

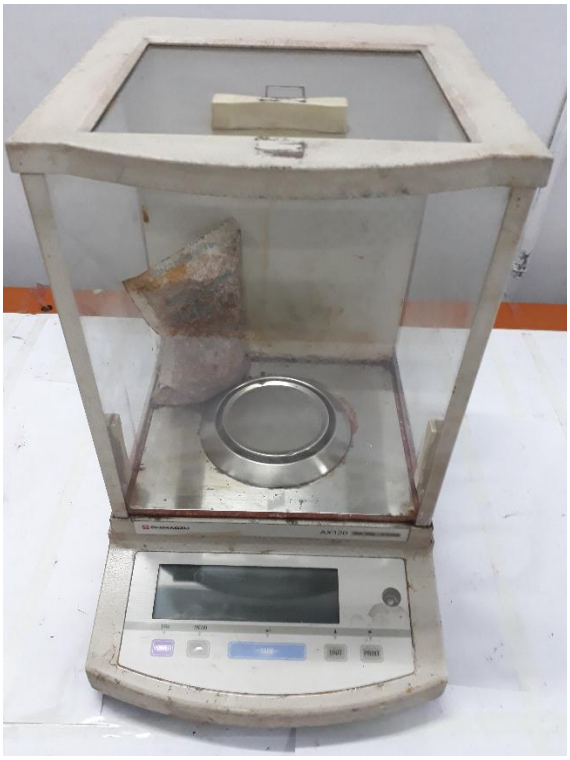

Figure 2: AX120 Electronic Balance

Figure 3: Control Fields and Display of AX120 Electronic Balance

Figure 4: Ferrite Sample

Advantages of AX120 electronic balance

- Extremely high precision balance, around ten micro gram
- Draftshield for preventing the influence of convection and other factors
- Can check weighing, parts counting and percent weighing
- Over-weighing protection
- Full range tare

Planetary Ball Milling

Planetary Ball Mills are used wherever the highest degree of fineness is required. In addition to well-proven mixing and size reduction processes, these mills also meet all technical requirements for colloidal grinding and provide the energy input necessary for mechanical alloying. The extremely high centrifugal forces of a planetary ball mill result in very high pulverization energy and therefore short grinding times. The type of balls used for milling was made of zirconium oxide because it provides a virtually contamination-free ball milling.

As five different raw materials had to be mixed together for preparing the ferrite composite it had to be ensured that they were all uniformly mixed because if not so the desired chemical composition could have gotten compromised. The fact that the sample was ball milled at 230 rpm for fourteen hours ensured just that. Still to demolish any speck of doubt, the sample was further hand milled for further four hours in two separate sessions using an agate pestle and mortar.

Function principle of MSK-SFM-1 bench-top planetary ball mill

The grinding jars are arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel is opposite to that of the grinding jars in the ratio 1:-2.

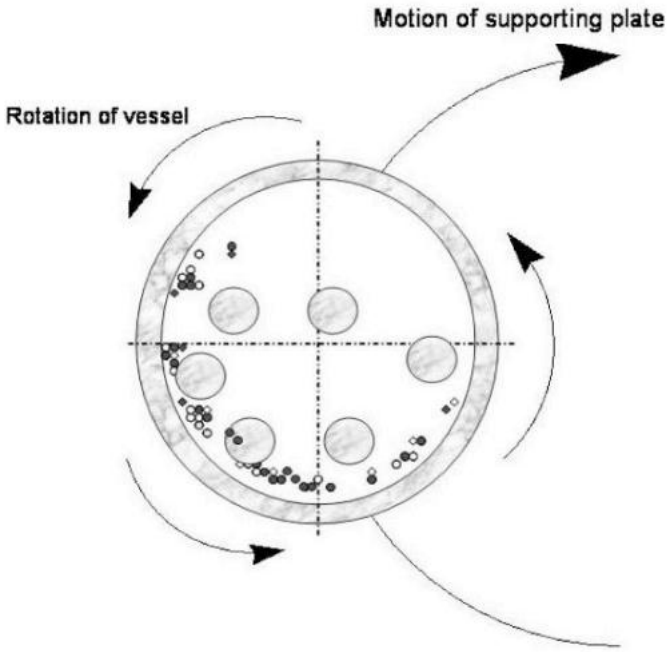

Figure 5: Sun wheel's and grinding jars' direction of movement in a Planetary Ball Mill

The grinding balls in the grinding jars are subjected to superimposed rotational movements, i.e., the so-called Coriolis forces. The difference in speeds between the balls and grinding jars produces an interaction between frictional and impact forces, which releases high dynamic energies. The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill.

In planetary mills the different heights of the centers of gravity of differently-sized grinding jars can be compensated in order to avoid disturbing oscillations of the machine.

Any remaining vibrations are compensated by feet with some free movement. This technology is based on the d'Alembert principle and allows very small circular movements of the machine housing that result in an automatic mass compensation. The laboratory bench is only subjected to minimal frictional forces generated in the feet.

This ensures a quiet and safe operation with maximum compensation of vibrations even with the largest pulverization forces inside the grinding jars and therefore can be left on the bench unsupervised.

Figure 6: MSK-SFM-1 Bench-Top Planetary Ball Mill Machine

Figure 7: MSK-SFM-1 Bench-Top Planetary Ball Mill with cover opened

Figure 8: Control Panel of MSK-SFM-1 Bench-Top Planetary Ball Mill

Advantages of using planetary ball mill

- Powerful and quick grinding down to nano range
- Reproducible results due to energy and speed control
- Suitable for long-term trials
- Two different grinding modes (dry and wet)
- Optional pressure and temperature measuring system
- Wide range of materials for contamination free grinding
- Safety Slider for safe operation
- Perfect stability on lab bench
- Innovative counter weight and imbalance sensor for unsupervised operation
- Comfortable parameter setting
- Automatic grinding chamber ventilation
- Programmable starting time
- Power failure backup ensures storage of remaining grinding time
- Jars with O-type sealing for safe operation, etc.

Calcination of the Sample Using Nabertherm P330

Calcination is the process of subjecting a substance to the action of heat, but without fusion, for the purpose of causing some change in its physical or chemical constitution. The objectives of calcination are usually:

- To drive off water
- To drive off carbon dioxide or other volatile constituent
- To oxidize a part or the whole of the substance.

For calcination it is very important to keep the temperature used below the melting or fusing point. Calcination is an important step because ball milling the composite cannot cause completion of the chemical fusion in between the different compounds. Calcinating the sample ensures total sealing of the composite and wards off all sorts of impurities.

To start the process of calcination, crucibles were first cleaned with detergent followed by distilled water. It was then further cleaned with acetone, left to dry for a while, filled with the composite and placed in the furnace to be calcined at 950℃ for five hours. The crucibles in question were made of alumina. This is because alumina is the hardest of the oxides, has great heat conductibility, large thermal expansion coefficient, low impact resistance and is chemically stable which means it will not react with the composite. The temperature was gradually raised in increments of 10℃ for 2 hours until 950℃ was reached. It was then held steady at 950℃ and calcined for 5 hours.

After 5 hours the temperature was brought down gradually in increments of 5℃ over a span of 4 hours. This is important to ensure that the composite forms a crystalline structure. The final

product was again ball milled to get rid of clusters and turned into powder thereby completing the preparation of the ferrite sample.

Figure 9: Ferrite sample after calcination.

Nabertherm P330 operation

First the power is switched to "I" position. The controller first displays the controller type and version number and then the temperature display. If the temperature is displayed, the controller is ready to operate.

Figure 10: Nabertherm P330

P 330

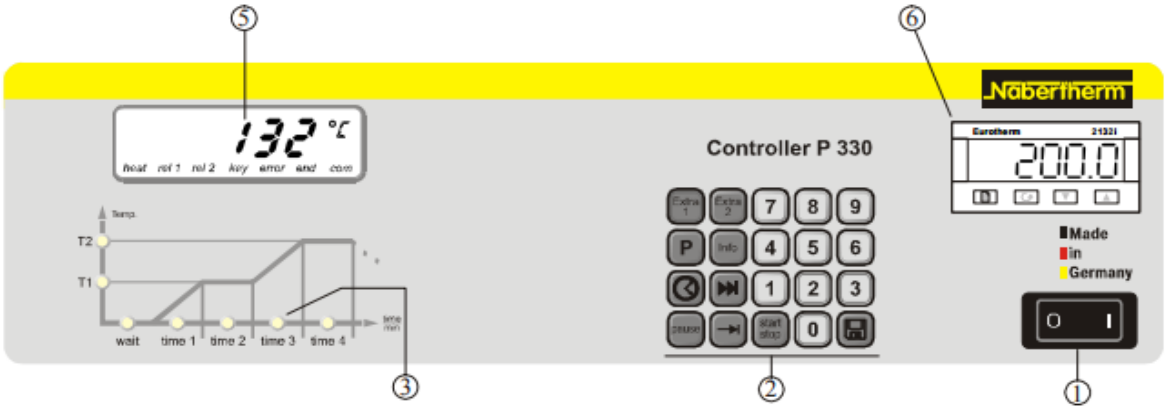

Fig. 2: P 330 control panel

1 = Power switch
2 = Keyboard block
3 = Program LED
4 = - - -
5 = Display
6 = Over-temperature limit controller (optional)

Figure 11: Control Fields and Display of Nabertherm P330

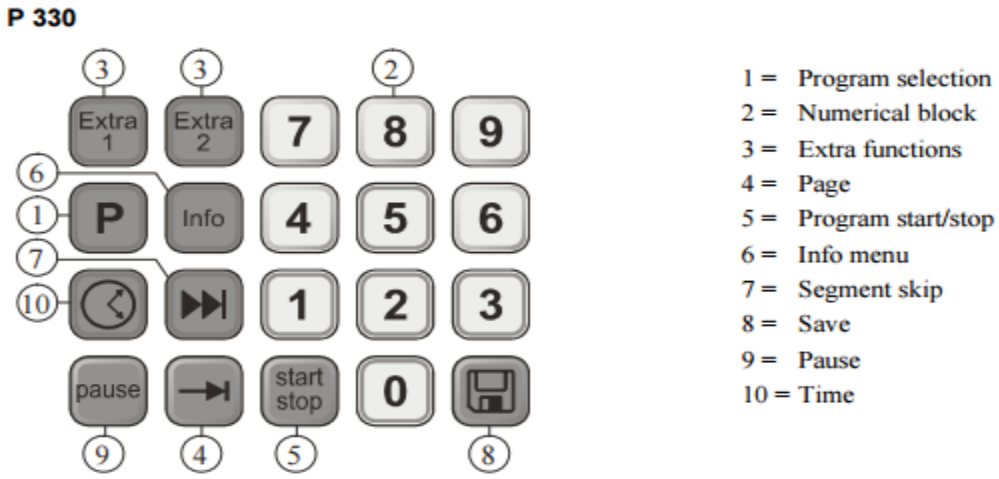

Figure 12: P 330 keyboard block

Setting or changing program/waiting time

For the automatic operation of the furnace, before starting the controller a temperature characteristic must be configured which describes the desired temperature behavior. This is known as the heating program.

Each heating program has two heating ramps, one holding time, and one cooling ramp.

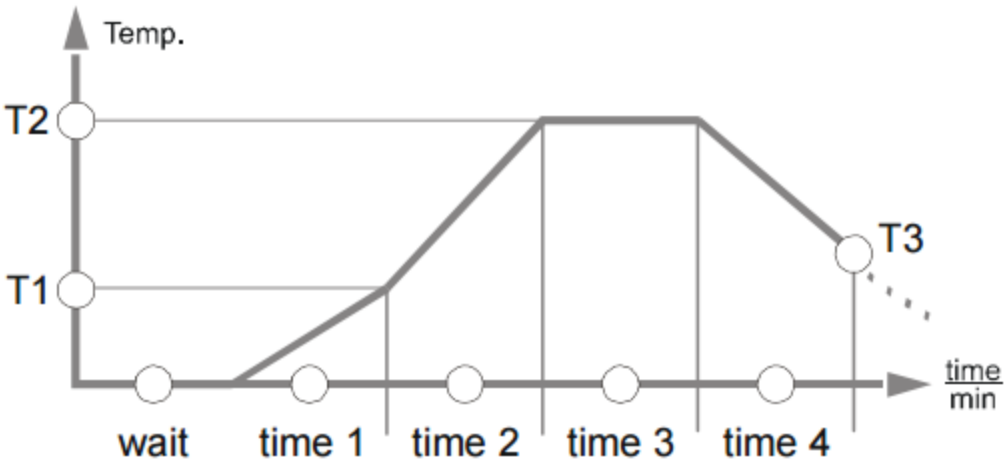

Figure 13: Program Graphic

- In the ramps, a segment temperature "T" and a segment time, "time 1" and "time 2" define a linear temperature increase (slow heating).
- In the holding time, "time 3" determines how long the temperature value configured in "T 2" should be held.
- In the cooling time, the natural cooling can be slowed using the rate set in "T 3" and "time 4".

The page key is used to:

- set temperature values with °C/°F
- set time specifications with hr:min
- set gradient specifications with °C/hr:min or °F/hr:min

To turn it off main switch is switched at position "O".

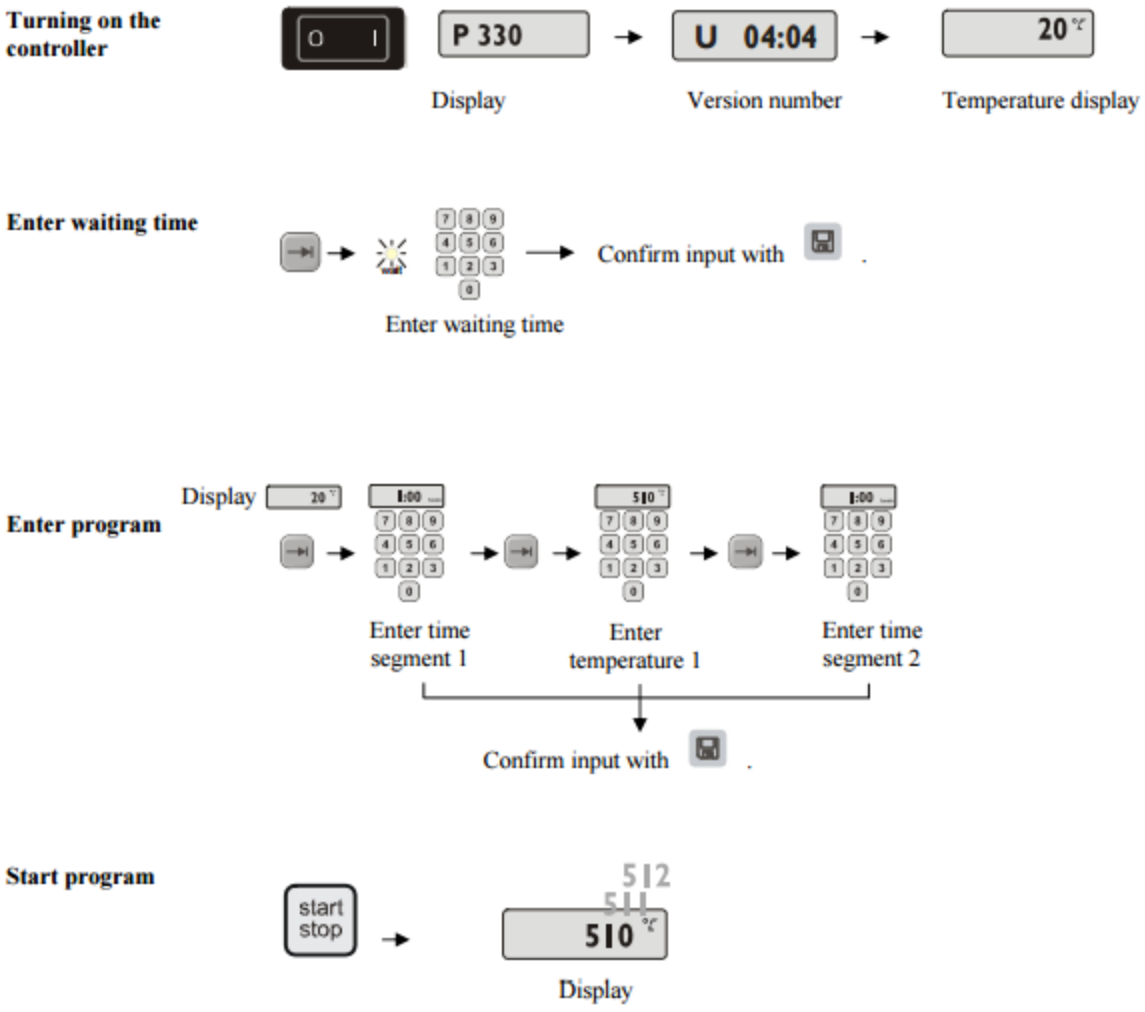

Figure 14: Operating Instructions Summary

Hazard Summary and Safety Precautions

The processes mentioned earlier each have their own list of both acute and diminutive hazards which must be kept in mind to steer clear of accidents. The list includes:

- Exposure to zinc oxide, copper oxide and ferric oxide can cause metal fume fever when breathed in.
- Gadolinium oxide can cause serious eye irritation.
- Nickel oxide is a carcinogen and may cause skin allergy. It can also affect once inhaled.
- Gas released during calcination may be harmful as well.
- There is a risk of getting burned if the crucibles after calcination are not handled using tongs.

To carry out all the procedures risk and error free the following steps must be followed:

- Use of safety goggles.
- Use of nose mask.
- Use of gloves.
- Use of tongs.
- Turning off the fans while measuring the weight.
- Keeping the compounds in sealed jar to avoid contact with humidity as this might change their weight. So while measuring we will always get less amount of the original compounds and the overall composition will be faulty.

- Ritualistically cleaning the jars, spatula, foil and every other thing that is supposed to come in contact with the compounds to avoid contamination.
- Avoid carrying out the process in dusty rooms to avoid contamination.

Finally once the sample has been prepared X-Ray diffraction can be used to determine the desired crystal structure has been achieved.

Conclusion

The internship at Bangladesh University of Engineering and Technology's solid state laboratory has made me learn new skills and added to my knowledge base while making me gain confidence in my abilities. Due to this experience I now know how to apply some of the ideas learned in my academic career as it provides a bridge between academic and the professional world. It has made me gain some insight on how the world beyond the book pages actually functions or what kind of tactical approach one must adopt to perpetrate research.

List of Figures

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