CHAPTER III

Preparation of Ferrites and Experimental Techniques

Preparation of Ferrites and Experimental Techniques

3.1 Introduction

Ferrites were first prepared by nature. The naturally occuring mineral magnetite, ferrous, ferrite aroused scientific curiosity among the Greeks countries before the Christian era.

Magnetite can be altered by substituting and combining other constituents with it to produce improved ferromagnetic spinels. Hilpert took out patents on magnetic core materials in 1909[1]. Forestier[2], in 1928 prepared ferrites by basic precipitation technique using Chloride solutions and giving subsequent heat treatment.

Since it has been reported[3] that the properties of ferrites are sensitive to the structural aspects like grain size and the physico-chemical history, efforts were made to prepare ferrites by various methods[3,4,5]. The chemical methods are advantageous as far as the control of grain size is concerned. But they have their own disadvantages regarding picking up of impurities and non-crystallinity. Again wheqther we start from the mixture prepared by chemical method or by ceramic method, we must resort to heat treatment for sintering.

The ceramic method makes it possible to prepare complex chemical composition with desired microstructures the much more economically. Ceramics have sufficient mechanical strength to allow it to be formed in desired shape and can be machined according to appdication. Ceramics provide a way of avoiding undesired effects such as eddy current losses which can be suppressed by internal and amination along grain boundaries[6].

In this chapter a brief review of the methods of preparation, ceramic processes and development of - milro-structure relating to time and temperature are discussed. In the second part a brief explanation of the experimental techniques used in the present case is given.

SECTION 'A'

3.2 Preparation of Ferrites

In the ferrite preparation, the starting materials are allowed to undergo solid state reaction and therefore, it is unually called eeramic method. There are four steps in the preparation of ferrite materials by this technique.

1) Preparation of materials to form an intimate mixture with the metal ions in the ratio which they will have in the final product.

2) Heating this mixture to form ferrite,

3) Powdering the prepared material and pressing or forming into the required shape,

4) Sintering to form the final product.

3.3 Preparation of ferrite composition

The general methods for preparation of ferrite compositions are given as follows :

(a) Oxide method,

(b) Decomposition method,

(c) Hydroxide precipitation,

(d) Oxalate precipitation.

3.3.a Oxide method

Generally ferrites are prepared by this method. High purity oxide materials in the required proportions are mixed together. This mixture is wet milled for a long period in a rubber lined pot using steel balls. After milling, the mixture is dried, then the powder is passed through the mesh screen. The mixture is calcined at elevated temperatures and powdered and dried. Then it is pressed into suitable shapes and finally sintered.

3.3.b Decomposition method

Instead of using oxides as starting materials, one may start with chemical compounds such as carbonates, nitrates and oxalates. They are mixed in required proportion and preheated usually in air to produce oxides by thermal decomposition. The oxide prepared 'in situ' can more radily undergo solid state reaction[7]. Other details of this method are similar to oxide method.

3.3. c Hydroxide precipitation

In this method the lengthy milling process in dry mixing is avoided. Attempts have been made to precipitate simultaneously the required hydroxides from a solution so that the precipitate contains the required metals in correct proportion, already intimately mixed. Knowledge of the solublity products of the substance is essential in order to determine pH value for complete precipitation. Economos[8] established this method for the preparation of ferrites. Hydroxide precipitation method is also applied for preparation of YIG[9]. Chemical process much be understood quantitatively in order to ensure the simultateous precipitation of the hydroxides. If the simultaneity is not achieved the value of method is lost. One or both the precipitates may form in a state which may make filtration difficult. Sodium ions may be absorbed on the precipitate getting occuluded as impurities. Co-precipitation method is similar to this method.

Sato[10] and hislowarker[11] prepared ultrafine spinel ferrites by this method and studied their properties.

3.3.d Oxalate precipitation

Precipitation of metallic oxalates is preferable for some a reasons. Precipitation can be carried out by using ammonium oxalate which does not leave any residue after heating. Most of metal oxalates are very similar in crystal structure. Therefore, precipitation tends to mixed crystals which contain the metallic cations in correct proportions in which they were present in solution. Thus the mixing in correct ratio can be achieved in molecular scale[8]. If the precipitation occurs at widely different rates, mixed crystals do not form uniformly. Careful calcination at temperature of the precipitation yield ferrite with particle size less than 1 mi/ron.

3.4.a Presentering

The purpose of the presintering is to decompose higher oxides and carbonates which reduces the evolution of gas in the final sintering process. Secondly, it assists in homogenising of the material and also to reduce the variations in the composition of raw material. Lastly it is necessary to control the shrinkage of the material which occurs during final sintering. During the presintering the raw materials

partly react to form final product and the amount of reaction depends on the reactivity of the components and on the presin-
-tering temperature[11].

3.4.b Sintering

The final microstructure develops during sintering process. We assume that the cations are present in correct proportions, the object then remains to achieve a suitable microstructure together with correct oxygen content and the distribution of cations. These are affected by time and temperature of sintering[12], the partial pressure of oxygen or any other sintering atmosphere and the cooling rate. By qualitative considerations good results can be obtained and improvement can be achieved.

3.4.c. Sintering Atmosphere

It has been observed that sintering atmosphere plays an important role in sintering process. It could be remembered that Fe_2O_3 content can depend on the degree of oxidation or reduction of ferrite. It can result of varying the MO/Fe_2O_3 ratio of ferrite. Deficiency of Fe_2O_3 appears to lead to the highest eventual density for Ni-Zn ferrite but introduces second phase inclusions. It is fortunate that with second phase inclusions, it is possible to achieve 100% density at or very near to stoichiometric composition[13]. The reduction

of ferric to ferrous ion occures at high temperature or at oxygen pressure[14]. The explanation for the effect of deficit Fe_2O_3 was given by Reignen[14]. In an anion deficient ferrite the principle process whereby pores shrink consists of the diffusion of anion vacancies to the grain bouhdries. In cation deficient ferrites on the other hand, pores can be pulled along the grain boundries coalesing with other pores when they meet or come very close to them by involving oxygen transport via the gas phase and the cation vancancies through the material surrounding the pore. The cation diffusion is facilitated by cation vacqncies.
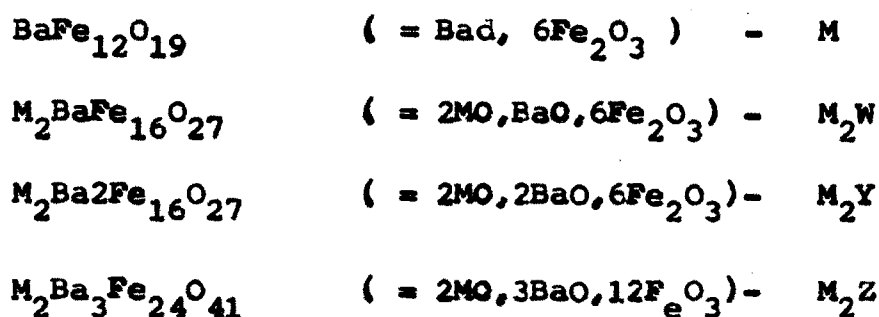
3.4.d Hot Pressing

Although only associated with sintering the use of isostatic pressing rather than unidirectional pressing in a conventional die is of great experimental value. The powder is enclosed in a flexible container of rubber or plastic which may be evacuated and is compacted by immersing the container in an oil bath to which pressure is applied. The effect is to give much more uniform and higher density than conventional methods. It also encourages continuous grain growth and favours to obtain low porosity and small grain size. Hot pressing and sintering under pressure has been used increasingly in the preparation of ferrites. It seems apparent that pressure should lead to high degree of compaction and enhance contact between grains during sintering. At $1000^{o}C$ ferrites have

sufficient plasticity to flow a considerable extent at high pressures. It is favourable to produce high density compacts in which the original grain size is maintained. The composi- -tions containing volatile elements like Zn, Li benefit particularly when sealed containers are used, the net composition must be maintained, althrough the velatility may be associated with phase segregation. Theoretically, hot pressing has been much less unambiguously investigated with regard to densification mechanism. It is generally accepted that both plastic flow and Naburrao-Herring creep mechanism play a role[15].
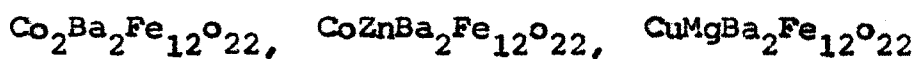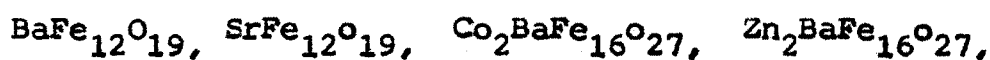
3.5 Preparation of Ferrite Samples :

3.5.1 Preparation

In the present case the ferrite samples were prepared by the ceramic method starting with the constituent oxides. The ferrites having following general formulge have been prepared.

$BaFe_{12}O_{19}$	(= BaO, $6Fe_2O_3$)	M
$M_2BaFe_{16}O_{27}$	(= 2MO,BaO,$6Fe_2O_3$)	M_2W
$M_2Ba2Fe_{16}O_{27}$	(= 2MO,2BaO,$6Fe_2O_3$)-	M_2Y
$M_2Ba_3Fe_{24}O_{41}$	(= 2MO,3BaO,$12Fe_2O_3$)-	M_2Z

Where M is a divalent metal ion like Mn,Co,Zn,Ni,Mg,Fe.
Several ferrites having these general formulaecan be prepared.
In the present case the ferrites having the following chemical
compositions have been prepared and studied.

$$BaFe_{12}O_{19}, \quad SrFe_{12}O_{19}, \quad Co_2BaFe_{16}O_{27}, \quad Zn_2BaFe_{16}O_{27},$$

$$ZnCoBaFe_{16}O_{27}, \quad CoM_2BaFe_{12}O_{27}, \quad CuZnBaFe_{16}O_{27},$$

$$Co_2Ba_2Fe_{12}O_{22}, \quad CoZnBa_2Fe_{12}O_{22}, \quad CuMgBa_2Fe_{12}O_{22}$$

$$Zn_2Ba_3Fe_{24}O_{41}, \quad CuMgBa_3 24^O41.$$

The AR grade oxides of Ba,Sr,Co,Fe,Zn,Mg,Cu, were
used for preparation. The oxides were weighed in required
mole proportions on a semimicrobalance and mixed throughly
in an Ogate-morter with acetone. This mixture was dried in
an ovan at 100°C. The dry mixture was then transferred into
platinum crucible and heated at 800°C for eight hours, in a
furnace. Then the samples were slowly cooled, taken out and
again thoroughly mixed in a agate-morter with acetone. The
mixture is again heated in an electric furnace at the Deptt.
of Geology, University of Pune at about 1200°C for 12 hours.
The samples were furnace-cooled by switching off the furnace.

were

The sintered samples was taken out from the crucible.

Finally powder was collected in a clean dish.

3.5.b Pellet Formation

Few grams of the sample was taken into agate-morter
and wet mixture was done using P.V.A. as binder. Acetone
was allowed to evaporate till the powder becomes complete
dry. Then the dry powder was poured into the die having
1 cm. diameter and cold pressed in a hydraulic press with
the load about 10-12 tonnes and load was left for 10 to 15
minutes. After removing the load pellet was taken out from
the die.

3.5.c Final sintering

The pellets thus prepared were taken on clean platinum
foil and kept in a electrical furnace and sintered at $1200^{\circ}C$
for about 24 hours. They were furnace cooled. The rate of
cooling of the furnace was nearly $100^{\circ}C$/hour for first
2-3 hours and nearly $50^{\circ}C$/hour for the intermediate stage.
X-ray diffraction was used to ensure the formation of the
ferrites.

SECTION 'B'

3.6 Experimental Technique for

Condultivity Measurement -

The circuit diagram for measurement of conductivity is shown in Fig. 3.1. The pellet was polished and pasted with silver paste. The pellet was mounted in a special sample holder the block diagram of which also appears in the same figure. The sample holder consists of two brass rods in which the sample was sandwitched. Three screws are provided to fighten the sample for firm contults. Two ceramic discs are put in between the screws and brass plates which give good insulation. Contacts were taken from the brass plate with the help of small screw as shown in figure and are very near to the sample. Platinum wires electrically insulated were brought from the holder. Resistivity measurements were carried out by measuring current on P.M. 2503 electronic meater at constant voltage of 3 Volts for various temperatures from $25^{\circ}C$ (R.T.) to $700^{\circ}C$. A calibrated[16] cromet Alumel thermocouple having fine tip was used to measure the temperature of the sample and was kept near the sample. The measurements were carried out while heating and sufficient time was allowed for the sample to attain equilibrium temperature.
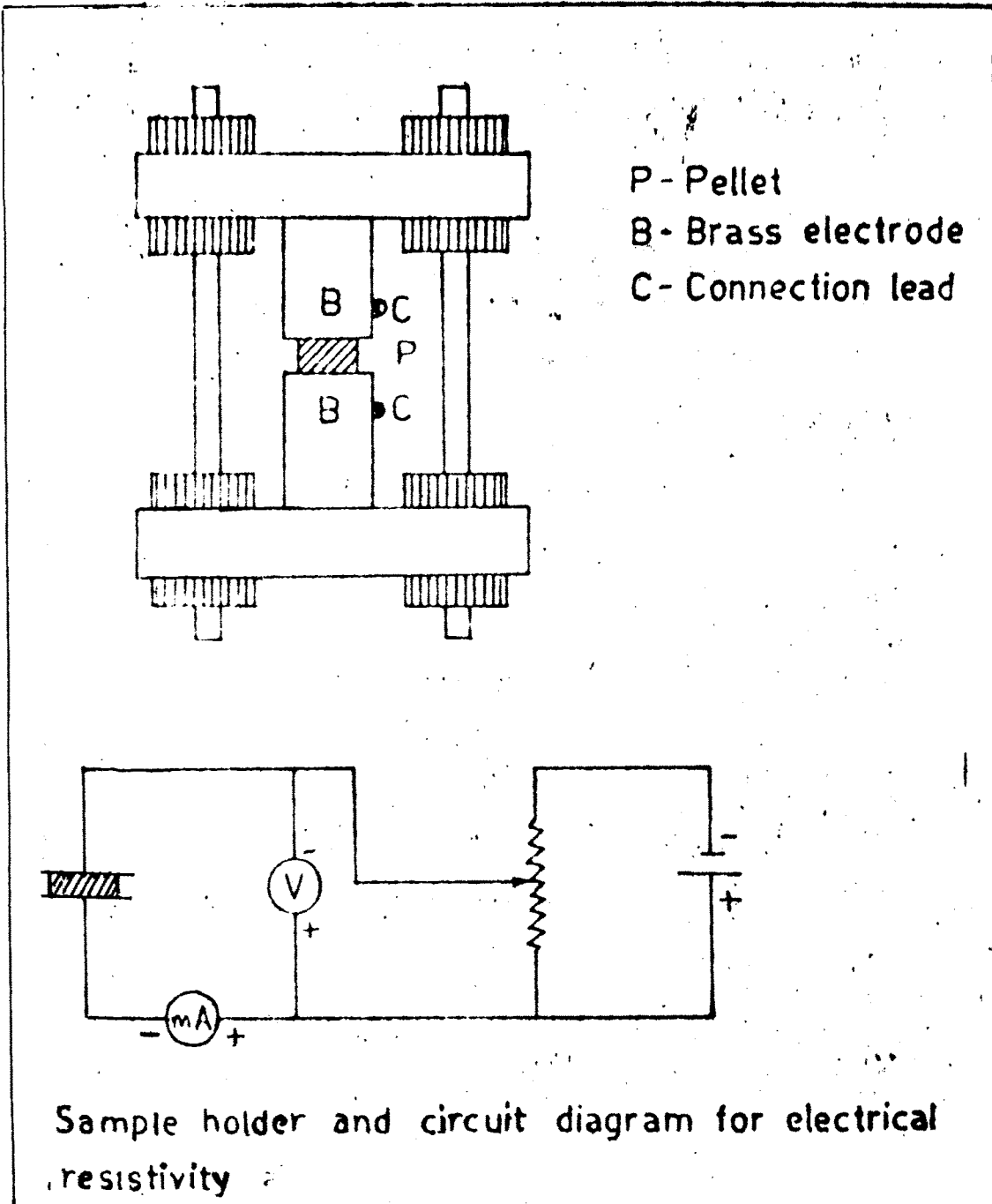
P - Pellet
B - Brass electrode
C - Connection lead

Sample holder and circuit diagram for electrical resistivity

Fig. 3.1

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