# MAGNETIC TEMPERATURE TRANSDUCERS MADE FROM COPPER BASED SOFT FERRITE

C. MICLEA, C. TANASOIU, C. F. MICLEA, I. SPANULESCU*, C. PLAVITU*, M. CIOANGHER, C. T. MICLEA*, T. TANASOIU*
NATIONAL INSTITUTE FOR MATERIALS PHYSICS, Bucharest-Magurele, ROMANIA
*HYPERION UNIVERSITY, Faculty of Physics, Str. Calarasi 169, Bucharest, ROMANIA

## 1. INTRODUCTION

Ferrites represent an important class of functional magnetic materials, largely used in electronic industry and many other fields of interest, like high frequency devices, solid state physics, mobile communications or information technology. By virtue of their magnetic and semiconducting properties the copper ferrite and its solid solutions with other ferrites can be employed as magnetic temperature sensors. CuZnTi ferrites proved very sensitive to thermal treatments having different cation distribution upon annealing and cooling speed from high temperatures. Curie temperature strongly depends on composition and magnetic properties, (magnetization and the initial permeability), drastically depend on cation redistribution which can be tailored by the cooling speed. Since magnetic properties of such ferrites are very sensitive to temperature they can be exploited for designing magneto-thermal transducers that can be used in devices for temperature control or measurement.

## 2. OBJECTIVES

- To find new magnetic materials with highly sensitive magnetic properties against temperature. Such materials were found to be soft ferrites in the Cu-Zn-Ti-Fe system;
- To use such dopants able to finely change the Curie temperature of materials. Dopants that fulfiled this requirement were Zn and Ti which modified the Curie temperature of materials with approximately 10÷12 $^{o}$C for each atomic percent of Zn and/or Ti.
- To elaborate a technology capable to provide the highest rate of change of permeability with temperature around Curie point. Such a technology proved to consist in a well controlled cooling speed from the sintering temperature.

## 3. EXPERIMENTAL

The ferrite compositions had the formula: $Cu_{1-x-y}Zn_xTi_yFe_2O_4$ with $x$ and $y$ ranging within $0.5 \leq x \leq 0.7$ and $0.00 \leq y \leq 0.05$ respectively. The materials were prepared by a slightly modified mixed oxide route followed by a prolonged milling. The oxides were mixed together from 3 hours in a Retsch 400 PM planetary ball mill in hardened steel vessels using steel balls. The mixtures were dried at 150 $^{o}$C, then crushed and sieved and next calcined at 1100 $^{o}$C for 4 hours. The milled powders were pressed into toroidal samples of 20 mm outer diameter, 14 mm inner diameter and about 2 mm thickness and discs of 15 mm diameter and 3 mm thick and were sintered in air, at temperatures between 1000 and 1250 $^{o}$C for 4 hours. From the sintering temperature they were either slow or rapid cooled down to room temperature or quenched in water. Different cooling speeds were achieved from an average of about 10-100 $^{o}$C/min for slowly cooled samples, (with the furnace), to 500-5000$^{o}$C/min for rapid cooled ones, (in air), and to more than 10.000-40.000 $^{o}$C/min for quenched ones.

## 4. RESULTS

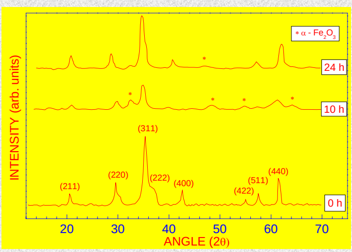


*Fig. 1. X-ray diffraction patterns of CuZnTi ferrite*

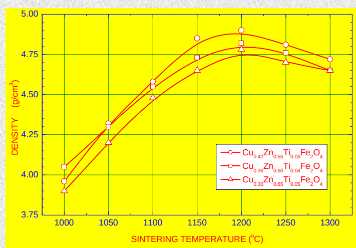


*Fig. 3. The density behavior with sintering temperature for three compositions of CuZnTi ferrite*

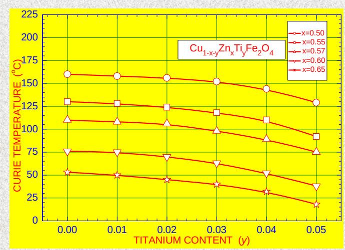


*Fig. 4. Effect of composition on $T_C$ of some CuZnTi ferrites*

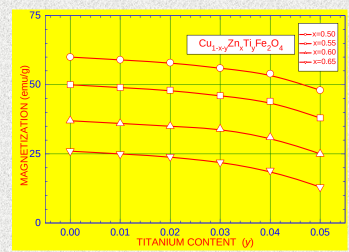


*Fig. 5. Effect of composition on magnetization of some CuZnTi ferrites*

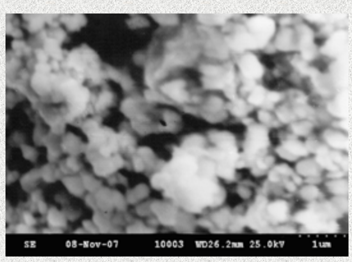


*Fig. 2. SEM image of the morphostructure of the milled powder of the CuZnTi ferrite*

Figure 1 shows the X-ray diffractograms for composition with x=0.6 and y=0.04 after calcining (0 h) and after milling for 10 and 24 h respectively. The patterns could be indexed as spinel single phase. The morphostructural aspect of the milled powders is illustrated, as an example, in figure 2 after 24 hours of milling. One can see the nanometric scale of the particles, though some agglomerates were still present. The density as a function of composition can be seen, in figure 3. Changes of magnetic properties are brought about by both dopant nature and amounts as well as the cooling speed. Thus, it was estimated that the Curie temperature changes with about 8 to 10 $^{o}$C for each percentage of Zn and Ti respectively, while the magnetization changes with only 2.5-3 uem/g for the same percentages respectively (figures 4 and 5). Grain size is the main factor that strongly influences the permeability. Larger grains lead to higher permeabilities and its behavior with temperature showed rather sharp maxima just before $T_C$ and a sudden decrease to zero. The sharpness S is a measure of the thermo-magnetic sensitivity. The greater S, the highest thermo-magnetic sensitivity of the device. Intermediate cooling speeds of the order of a couple of thousands degrees per minute produced the highest S, (figure 6). Up to about 100 $^{o}$C/min the slopes are very low and then increases up to about 60 %/$^{o}$C along a rather larger interval of cooling speeds between 900 and 3000 $^{o}$C/min and then suddenly decreased for higher cooling speeds.

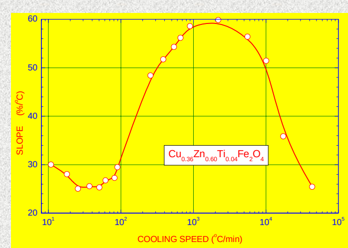


*Fig. 6. The dependence of the slope of μ(T) curves on the cooling speed for one composition of CuZnTi ferrite*

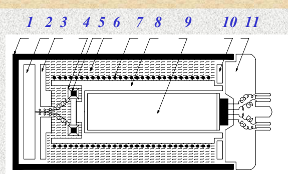


*Fig. 7a: 1- outer metallic case; 2 – electronics; 3 – protective disc; 4 – coil; 5 – magnetothermal sensor; 6 – thermal isolating blanket; 7 – heating resistance; 8 – hollow thermostat body; 9 – thermostat chamber; 10 – protective disc; 11 – external connector.*

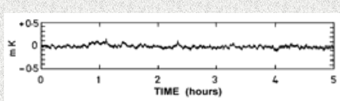


*Fig. 8 The short term stability of the thermostat*

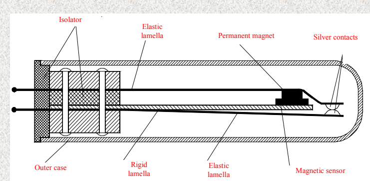


*Fig. 9b*
*The main elements of the thermomagnetic relay*

## 5. APPLICATIONS

*Fig. 7b Cross section in the thermostat*

*Fig. 9a. Cross section in the thermomagnetic relay*

Two applications were made that used thermomagnetic sensors: a **minithermostat** for which the magnetic sensor is a ring shaped sample and a **relay** for which the sensors is a disc shaped samples in connection with a tiny permanent magnet. They are shown in. figs. 7 and 9 respectively.

### THE THERMOSTAT

The operating principle is rather simple. An electrical signal provided by a multivibrator is fed into the primary winding of MTS. As a consequence a proportional output voltage Vs, will be generated into the secondary coil, by mutual coupling, as long as the MTS remains magnetic, at temperatures under Curie point. This voltage is fed into a difference amplifier together with a reference voltage Vr and their difference ΔV=Vs-Vr is fed into a multivibrator, which changes the fill factor of the square wave output and controls the power applied to the heating resistance, so that it takes a constant value around ΔV=0, corresponding to the thermostating temperature. Long and short-term performance of the thermostat, determined by means of a miniature NTC thermistor, showed a stability of ± 0.5 mK for longer periods and about ±0,1 mK for shorter periods.

### THE RELAY

The whole construction of the relay is encapsulated in a protecting glass tube. The working principle is simple: at any temperature lower than the Curie point of MTS, the magnet and MTS, are stuck together, so that the electrical contact between (5) and (6) is on and between (6) and (7) is off. At temperatures equal or above the Curie point they are released and the contacts (5) and (6) switch off and (6) and (7) are on. Such a relay works quite well and is able to command the thermostating of small or large chambers around a fixed temperature, given by the Curie temperature of MTS. Such a relay with Curie point of 80 $^{o}$C was tested in a thermostated chamber of about 1 cubic meter, inside which the temperature was kept constant to within ±2 K.

## 6. SUMMARY

A number of CuZnTi ferrite compositions corresponding to the formula $Cu_{1-x-y}Zn_xTi_yFe_2O_4$ with $0.5 \leq x \leq 0.7$ and $0.00 \leq y \leq 0.05$ were prepared and their structural, magnetic and thermo-magnetic properties were investigated. Their magnetic properties depend on structure but mostly on the thermal treatment applied after sintering, specifically the cooling speed. Low and very high cooling speeds produced materials with low slopes of μ(T) curves while intermediate cooling speeds of 900-3000 $^{o}$C/min produced samples with slopes of about 60 %/$^{o}$C. Such materials are very suited for magnetothermal sensors and they were used to construct a high sensivity minithermostat and thermomagnetic relays.