*Journal of the European Ceramic Society* **19** (1999) 373–379

PII: S0955-2219(98)00176-9
0955-2219/99/$—see front matter

# Time Temperature Stability of Magnetic Properties of Ceramic Magnetic Temperature Transducers

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(Received 6 March 1998; revised version received 25 June 1998; accepted 6 July 1998)

***Abstract***

*Three ceramic magnetic compositions within the CuZnTi ferrite system, having the Curie temperatures centered around 60, 80 and 100°C, respectively, were investigated in order to determine the time-temperature stability of their main magnetic properties. Permeability and the slope of permeability around their Curie points were determined on ring shaped samples, before and after being subjected to long term (over 6000 h) ageing at their Curie temperature and for a shorter time of about 50 h at higher temperatures up to 700°C. Rates of changes of 33, 66 and 100 ppm $h^{-1}$ of the maximum slopes of permeability were found for the samples aged at 60, 80 and 100°C, respectively. The samples aged at temperatures higher than 200°C show a rather sudden decrease of maximum slope of permeability, but no shift of the Curie temperature and the working point, corresponding to the temperature where the slope has the maximum value. This is the most interesting result as concerns the use of such magnetic temperature sensors for the construction of highly sensitive temperature controllers, for example ultrathermostats. The results are discussed in terms of the migration processes of the cations, especially $Cu^{2+}$, from metastable positions on which they were frozen during the rapid cooling of the sample from the sintering temperature, to the more stable ones, namely the octahedral sites into the spinel lattice.*


*Keywords*: magnetic properties, ferrites, aging, sensors, transducers.

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## 1 Introduction

There exists at present a large number of temperature sensors used both for temperature measurements and for temperature control. Among them, thermocouples, negative temperature coefficient thermistors (NTC) and positive temperature coefficient thermistors (PTC), metal or carbon resistors, semiconducting diodes or transistors are only a few of the most known ones, and they were successfully used as temperature sensitive elements in the construction of sophisticated devices for temperature measurement and control.

The choice of one or another of such temperature-sensing element depends upon the scope of measurement and on the temperature interval within the device is used. For example the platinum resistor sensors are extremely stable within a large temperature interval, but their precision is highly dependent on the electronics associated. Thermistors, on the other hand, show a higher fractional resistance variation per degree centigrade, i.e. a higher sensibility, about 10 times greater, but they cannot be used at temperatures higher than a couple of hundred degrees.

During the last few decades a new type of temperature sensor, used for construction of high sensitive devices for temperature control, such as thermostats, was reported.[1–5] It is made of a magnetic oxidic ceramic core in the MnCu,[1] NiZn,[2] MnZn,[3] CuZnTi ferrite system[4,5] and is based on the sudden change of the initial permeability near the Curie temperature. The sensitivity and performance of the devices using such magnetic temperature transducers (MTT) are direct functions of this sudden change, given by the slope of the magnetic permeability versus temperature, near the Curie point, i.e. the slope of the $\mu$(T) curve. The higher the slope the more sensitive the device. Values of the slope as higher as 50%°C, were reported, for MTT made from CuZnTi ferrites,[6] the highest value reported so far for such ferrite ceramic cores.

The advantage of using MTT sensors over the conventional ones consists in their very high fractional change of magnetic properties per °C, which, consequently, implies a more simple electronics in the construction of the temperature controller device.

As it was already mentioned before, a magnetic temperature sensor consists of a magnetic oxidic ceramic core having a given Curie temperature and the highest possible fractional change of permeability per °C near the Curie point.

In order to attain ferrite materials with the highest possible slopes of $\mu(T)$ curves, a special preparation technology must be used. The main point of this technology proved to be the cooling process of the sample from the sintering temperature.[6,7] This process simply consists in a rapid cooling in air of the samples from the sintering temperature up to room temperature, with a cooling speed, approximated to, somewhere, around $10^4$°C min$^{-1}$.[7]

Compared to the two other possible ways of cooling, i.e. natural cooling with the furnace, when each atom in the lattice occupies a stable position, and quenching in water, where the high temperature distribution of the ions is frozen, the rapid cooling process may be considered an intermediate one in which the ions occupy some metastable position in the lattice, so that, in time, under the influence of temperature, they will tend to redistribute to more stable position. Therefore the migration of the ions to some other positions in the lattice is expected to bring about some changes in the properties of the magnetic sensors.

The aim of this paper was to investigate the influence of time and temperature on the main properties of such magnetic sensors with special references on the slope of the magnetic permeability near the Curie point.

## 2 Experimental

### 2.1 Materials

In a previous paper[7] there were investigated materials in the CuZnTi ferrite system within a compositional range that gave samples with Curie temperatures from about 160°C to room temperature. These particular compositions were chosen only from practical reasons, since there were needs for temperature control devices with given temperatures within this temperature interval. [4] For the present study we chose only three compositions, namely:

$$C60 \div Cu_{0\cdot40}Zn_{0\cdot60}Ti_{0\cdot03}Fe_{1\cdot97}O_4,$$
$$C80 \div Cu_{0\cdot43}Zn_{0\cdot57}Ti_{0\cdot04}Fe_{1\cdot96}O_4,$$
$$C100 \div Cu_{0\cdot43}Zn_{0\cdot57}Ti_{0\cdot02}Fe_{1\cdot98}O_4,$$

having the Curie temperatures centered around 60, 80 and 100°C, respectively.

The materials were prepared by the usual ceramic technique using as starting raw materials reagent grade oxides and carbonates. The mixed stoichiometric raw materials were calcined at 1200°C for 4 h and the calcined powders were milled in steel vessels in a planetary mill for 4 h. The milled powders were mixed with a 1·5% polyvinyl alcohol solution and granulated by means of a 35-mesh sieve. Ring shaped samples with $d_{outer} = 22$ mm, $d_{inner} = 16$ mm and 1·5 mm thickness were pressed in a steel die at pressures of about 5 t cm$^{-2}$, and sintered in air at 1100°C for 2 h. Then the samples were rapidly cooled in air directly from the sintering temperature, with an approximated cooling speed of $10^4$°C min$^{-1}$.

### 2.2 Measurements

#### *2.2.1 Permeability and Curie temperature*

Since the shape of the MTT sensor for practical application is the ring, all the experiments were carried out on ring-shaped samples of 20 mm outer diameter, 14 mm inner diameter and 1 mm thick. The main characteristics investigated here were the time behavior of permeability and the slope of permeability around the Curie temperature because their modification during the life time or under the influence of temperature, could possible alter the sensibility or, even worse, could change the working temperature.

From practical point of view it is not of interest the permeability itself, but the mutual coupling between two coils, primary and secondary, on the ring, i.e. the response in the secondary coil, when the primary one is excited at a certain signal.

Therefore, we recorded this mutual coupling signal in the secondary coil as a function of temperature.

The two coils were identical and made of 100 windings from copper enameled wire of 0·08-mm diameter. The primary coil was excited with a 3 V signal at a frequency of 32 kHz (found to give the best signal in the secondary one). The experimental set up is shown in Fig. 1.

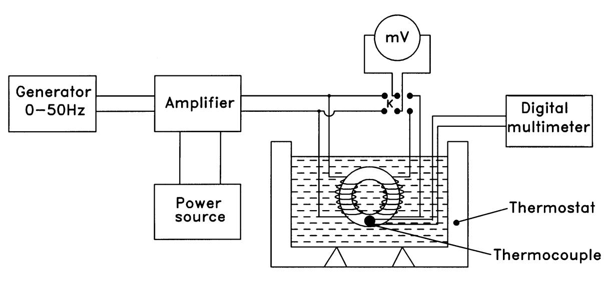


**Fig. 1.** Experimental setup for the measurement of the permeability of ring shaped ceramic magnetic cores.

An example of such a curve is shown in Fig. 2. The slope of $\mu(T)$ curve, determined as a derivative of this function, is also shown in the figure. The temperature corresponding to the maximum of this derivative, i.e. the maximum value of the slope, is considered as the working temperature $T_f$ of the devices using MTT ring. The Curie temperature $T_c$, was considered as the temperature corresponding to the intersection point of the straight line of the decreasing $\mu(T)$ curve, with the temperature axis.

The ring samples were immersed in a small oven, in a bath of silicon oil, heated up to a temperature, about 20°C higher than the Curie point of the sample, and then the measurement of the signal was recorded during the natural cooling process of the bath, so as to be sure that there is no thermal hysteresis. The bath temperature was recorded by means of a thermocouple placed on the ring surface.

*2.2.2 Long term stability*

The experiments for long term stability were simply made as follows. Four nearly identical samples were chosen from each composition and were subjected to the first measurement after sintering, say at time zero. Two samples of each composition were left at room temperature and the two others were put separately in three little ovens with fixed temperatures of 60, 80 and 100°C, with a maximum variation of ±2°C, and left there for about 1 year. From time to time both, the samples kept at room temperature and the ones kept in the ovens, were taken out and measured, each one, around their corresponding Curie temperatures, i.e. 60, 80 and 100°C and then left again at room temperature or put into their corresponding oven. Thus the long term stability (over 6000 h) curves versus time were recorded, for both types of samples, i.e. kept at room temperature and at their corresponding working temperatures.

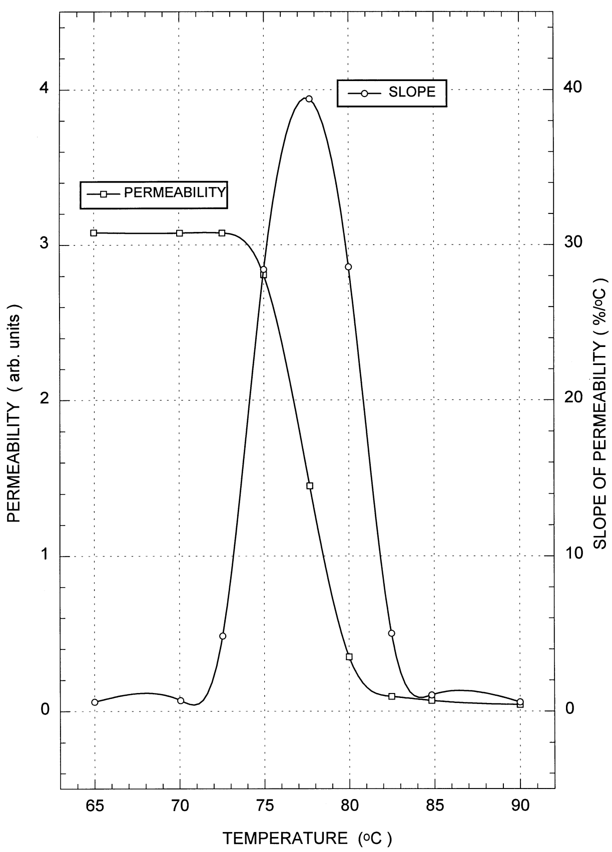


**Fig. 2.** Typical curves for permeability and slope of permeability versus temperature for ring shaped ceramic magnetic cores around Curie temperature, for composition C80.

*2.2.3 Temperature stability*

The temperature stability measurements were carried out on three sets of four ring samples from each of the three compositions.

The permeability around their Curie temperature was measured, at first, for each of the three groups. Next, two samples from each composition, were put into small ovens at different temperatures and let to age there for 50 h at 100, 200, 300, 400, 500, 600 and 700°C, respectively. Then they were taken out from the ovens and their permeabilities versus temperature, around their corresponding Curie points were recorded again.

The 50 h for ageing was considered as time enough for the cations to reach their equilibrium positions at that given temperature. Of course, a question arises whether a longer or a shorter ageing time would bring about a different cation distribution but this can be the subject for further investigations.

## 3 Results and Discussions

Figure 3 illustrates the behavior of the permeability versus temperature for typical samples of the three compositions: C60, C80 and C100. One can see that the permeability drastically drops with temperature from the maximum value to zero, within a narrow temperature interval, which means that the slope of $\mu(T)$ curves reaches high values. In our case the maximum slope were centered somewhere around 40% °C$^{-1}$, for C60 and C80 samples and a little lower (about 37% °C$^{-1}$) for C100 samples.

For the stability tests, samples, as identical as possible, were chosen from each composition.

Figure 4 shows the results of the long-term stability at room temperature and at the working temperature $T_f$, for the three compositions. One can see that the properties of the samples from each composition, kept at room temperature, remain practically unmodified over the whole time interval investigated, and the slopes do not change (curve 1 from Fig. 4). As for the samples aged at

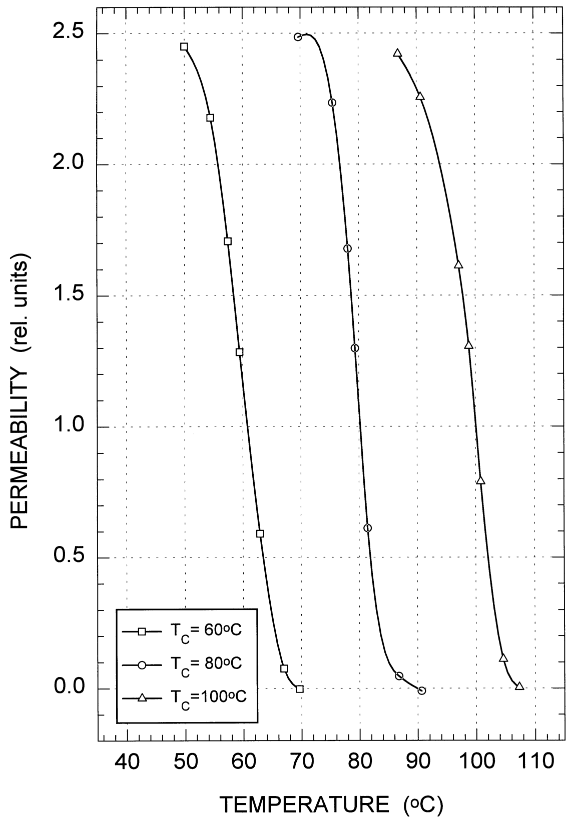


**Fig. 3.** The permeability versus temperature curves for the three compositions C60, C80 and C100 with the Curie temperature centered around 60, 80 and 100°C, respectively.

their working temperatures some modifications begin to appear after 500 h (for C100), 1000 h (for C80) and 1500 h (for C60) ageing time, respectively. The changing rates were estimated to be about 33, 66 and 100 ppm $h^{-1}$ for C60, C80 and C100 samples, respectively. Such a decrease of the slopes in time and temperature may be considered insignificant, but it exists and shows that temperature is a factor that initiates the migration process of the ions within the lattice and this process is a direct function of the temperature.

But at the same time it is noteworthy here that the insignificant modifications of the slopes versus time observed have no significance from the practical point of view of temperature controllers. Indeed, if one assumes that the rate of change of slope in time would be the same, a simple estimation shows that such a temperature controller should modify its slope with about 33, 66 or 100 parts after a continuous life time of over 100 years! So it may be considered that, if very stable temperature controllers are required, such magnetic temperature transducers seem extremely useful.

Some important changes appeared in the process of ageing. Thus for example in Fig. 5, the results of permeability changes after 50 h of ageing at different temperatures are shown for C80 samples, only. The 20°C curve represents the initial measurement of permeability versus temperature for fresh samples. The next ones show the modifications that appeared after 50 h ageing time at 100, 200, 400, 600 and 700°C. One can see that ageing temperatures up to 200°C practically do not affect the $\mu(T)$ curves. For higher temperatures the modifications become visible. Thus the maximum value of the permeability decreases but, interesting enough, the Curie temperatures remained unaffected. The permeability decreased

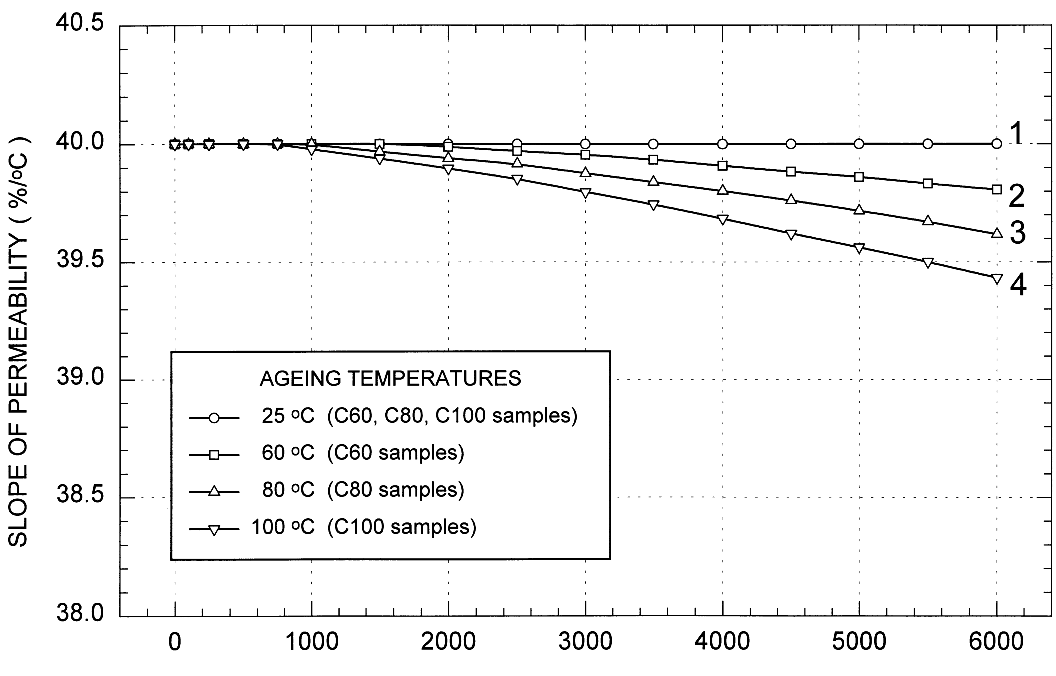


**Fig. 4.** Typical long term behavior of the slopes of permeability for samples of the three composition, aged at 25, 60, 80 and 100°C respectively.

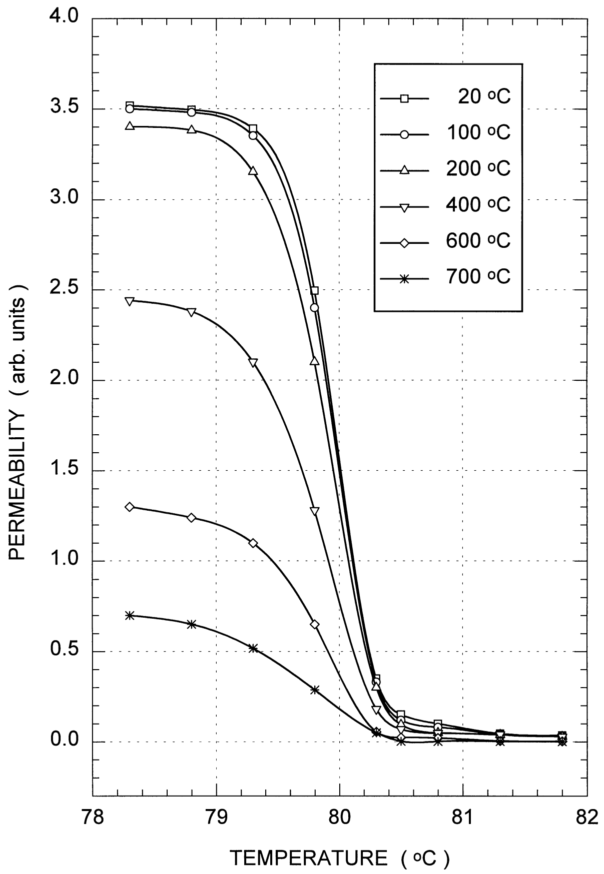


**Fig. 5.** Typical behavior of the permeability versus temperature around Curie point for C80 samples after ageing for 50 h at 100, 200, 400, 600 and 700°C, respectively.

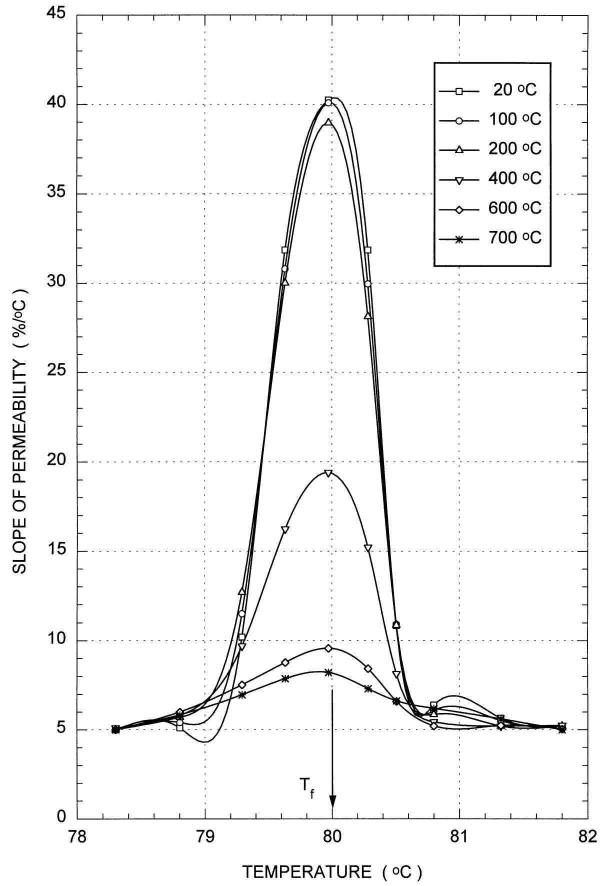


**Fig. 6.** Typical behavior of the slope of permeability versus temperature around Curie point for C80 samples after ageing for 50 h at 100, 200, 400, 600 and 700°C, respectively.

by about a factor of 6 when aged at 700°C, compared to the fresh samples or the ones aged at 100 and 200°C. The most interesting results of the effect of ageing appeared in Fig. 6 where the slope of permeability is shown as a function of ageing temperature.

The maximum value of slope decreases similarly by the same factor of six but the working temperature $T_f$ does not change at all.

This result is extremely important as concerns the use of such transducers for temperature controllers. This means that if, by accident, the MTT was subjected to higher temperatures, the working temperature $T_f$ remains unchanged, only the slopes of $\mu(T)$ curve decrease, lowering insignificantly the sensibility of the device.

Similar curves were recorded for C60 and C100 samples after ageing, but they were not presented here.

Figure 7 shows the decreasing manner of the maximum slope, taken out from Fig. 6, versus ageing temperatures for the same C80 samples.

It may be observed that up to temperatures of 200°C the slopes remain unchanged and only higher ageing temperatures bring about structural changes within the samples. The decreases are rather sudden between 250 and 500°C and become again rather smooth thereafter.

These results have undoubtedly shown that temperatures above a certain value represent a factor of influence on the characteristics stability of such MTT sensors. This influence is connected with the ionic distribution and thermal activated migration of copper ions over the tetrahedral (A) and octahedral (B) positions in the lattice. It is known from early studies[8,9] that pure copper ferrite is cubic at high temperature and tetragonal at lower temperature,transition between the two, being situated within 360–760°C and due to a sufficient concentration of distorting $Cu^{2+}$ ions on B sites in the spinel lattice. With increasing temperature the $Cu^{2+}$ ions from B sites migrate to A sites and even $Fe^{3+}$ migrate in the reverse direction. In the case of mixed copper ferrites the situation became more complex since in such cases, the mixed solutions could be either cubic and tetregonal or always cubic, in function of the amount of foreign dopants.

In our case when both Zn and Ti are used as dopants, unexpected modification of the magnetic characteristics vs. temperature may appear. Ti is on the B sites while Zn may occupy both A and B positions.[10]

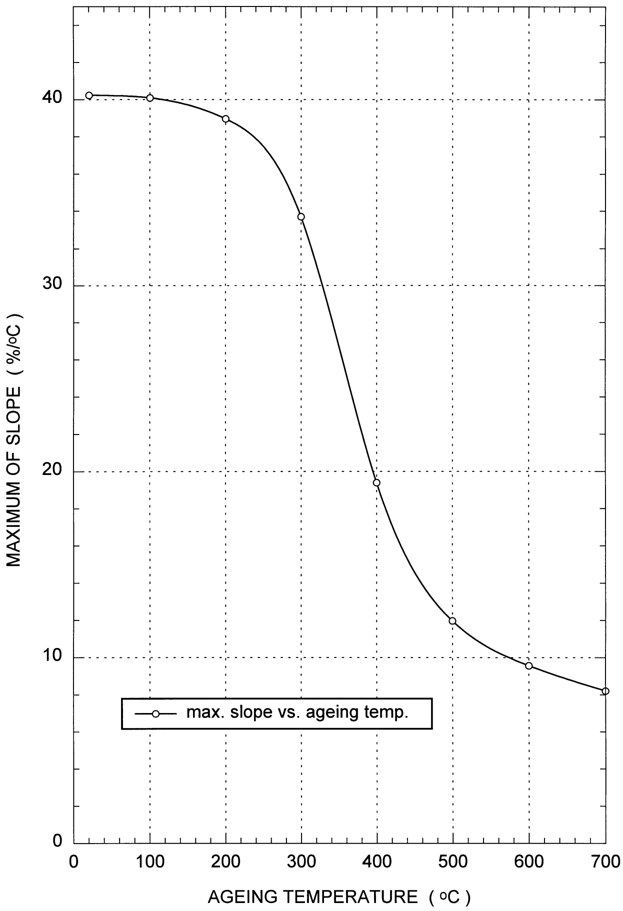


**Fig. 7.** The changing manner of the maximum slopes of permeability for C80 samples after ageing for 50 h at different ageing temperatures between room temperature and 700°C.

The quenched samples preserves the cubic structure down to lower temperatures and only 75% of the $Cu^{2+}$ ions remain located on B sites, while for slowly cooled samples nearly 95% of the bivalent copper ocupy the B sites.[8–11] Our samples were rapidly cooled, i.e. a cooling mode between quenching and slow cooling, and therefore a metastable distribution of the ions over the A and B sites,[6–8] that can easily be thermally activated to a transition toward a stable state, similar to one obtained by slow cooling. Therefore, one can observe from Fig. 7 that ageing temperatures above 200°C drastically modify the slopes of the permeability. Above 500°C the modifications are rather smooth. These facts may suggest that, for our mixed compositions, there exsits a thetragonal to cubic transition and this transition could be situated within 200–500°C temperature range. At temperatures lower then 200°C the cation migration is hardly to take place, but electron transferance seems possible by thermal activation from $Cu^{1+}$ on A site to $Fe^{3+}$ on B site thus beeing possible to generate $Fe^{2+}$ on B site. But at higher temperature both electron transferance and thermally activated cation migration take place, thus giving rise to more stable structures in which more $Cu^{2+}$ ions are located on B site.[12]

In this process the migration can be also influenced by the oxygen deficiency,[13,14] which may act either as an inhibitor of the migration speed or it may create favourable conditions that may shift the transition to lower temperatures.

With increasing ageing temperature, in air, oxygen deficiency decreases so that an increase in transition temperature might be expected. Our results suggest that such a mechanism would be possible and the $Cu^{2+}$ ions migrate easier to the more stable B positions.

Whether such a mechanism is true and in what extent the equilibrium distribution is achieved by the combined effect of oxygen deficiency and migration cannot be answered without further magnetic and X-ray measurements.

Anyhow, the long term stability of the MTT sensor from any composition investigated, proved not to be affected by temperatures up to 200°C so they can be successfully used in constructing temperature control devices such as high sensivity thermostats.

## 4 Summary

Stability of the main properties of ring shaped ceramic samples from three compositions in the CuZnFe ferrite system were investigated as a function of time and temperature.

The three compositions investigated: C60, C80 and C100 were chosen to have their corresponding Curie temperatures centered around 60, 80 and 100°C, respectively, mainly from the practical point of view of constructing temperature controllers (thermostats) with working temperatures at the above values.

The long term (over 6000 h) stability tests made at room temperature, 60, 80 and 100°C showed that their essential properties involved in the temperature control (permeatibility and the slope of permeability around working point) remain practically unaffected by temperatures up to 200°C, but they do drastically change above this value.

Rates of changes of the slope of permeability, by ageing, of about 33, 66 and 100 ppm $h^{-1}$ were found for the samples aged at 60, 80 and 100°C, respectively. But, fortunately, the working temperature of MTT sensor does not change at all even if the ageing was made at temperatures up to 700°C. This is a very important result, which means that such magnetic temperature sensors can be successfully used in the construction of, say, high sensivity thermostats.

The changes observed for the slope of permeability with increasing temperature are due to the migration processes of $Cu^{2+}$ ions from their metastable positions, created by the rapid cooling, to more stable ones, namely, the octahedral sites in the spinel lattice.

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