Vol. A39 (1971) *ACTA PHYSICA POLONICA* Fasc. 6

ELECTRIC AND MAGNETIC MEASUREMENTS OF CERTAIN TWO-PHASE FERROELECTRIC-FERROMAGNETIC MIXTURES[1]

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(Received November 16, 1970)

Measurements of electric and magnetic properties of two-phase ferroelectric ($BaTiO_3$) and ferromagnetic (nickel-zinc-ferrite Fe_2O_5, NiO, ZnO) mixtures were carried out within $10^4 \div \div 10^7$ Hz frequency range and $-150°C \div +300°C$ temperature range.

The investigated materials were found to behave regularly with changing admixture content and to follow, with reasonable accuracy, theoretical predictions.

1. *Introduction*

Electrical properties of two-phase systems, *i.e.* macroscopic mixtures of two materials, were investigated by many authors. So far, the investigations concerned only dielectric mixtures (artificial dielectrics). It was shown that the observed behaviour of such systems depends on the properties of component materials, in particular on the volume concentration of admixture and on the size of admixture particles.

The results obtained earlier by Leibler [1], [2], [3] and Konopka [4], [5] for dielectric-metal, ferroelectric-metal and dielectric-dielectric mixtures indicate clearly that by a proper selection of components and proper technological processing one can realise materials exhibiting specified parameters.

In this work we investigate the properties of macroscopic ferroelectric-ferromagnetic mixtures. Electric (permittivity) and magnetic (permeability) properties were measured against frequency and temperature for various compositions of the mixtures. The influence of other parameters (volume concentration, grain size, sintering procedure) on these properties was also investigated.

2. *Preparation of samples*

Component materials used for the investigation were: barium titanate $BaTiO_3$ (ferroelectric) and nickel-zinc ferrite 49.3% Fe_2O_3; 17.5% NiO; 33.2% ZnO (ferromagnetic). The weight content of the ferrite admixture in the samples was varied from 0 to 100%.

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[1] This work is based on papers read at International Colloquium on Ferromagnetism, Poznań 1964 and at International Conference on Physics of Ferroelectricity, Poznań 1965.

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Samples were made by sintering of the powdered components. The main difficulty in the preparation of samples was the problem of obtaining reproducible results. It was found that both the preparation of powders and the firing process (pressure *vs.* temperature) are not without effect in this respect. The finally adopted procedure was as follows:

a. Sintered samples of pure $BaTiO_3$ were powdered and the required grain size was obtained

b. Pre-baked nickel-zinc ferrite samples were ground and grains of required size were separated,

c. Component powders were mixed in required, accurately determined proportions and pressed under experimentally determined pressure. The value of the pressure was found to be critical for the reproducibility of results.

d. Samples were subjected to the final sintering process under carefully determined conditions (temperature against time) of heating, actual sintering and cooling.

The sintered samples were subsequently machined and, if required, silver electrodes were attached to them. The shape and size of the machined samples were determined by the requirements of the measuring apparatus.

3. *Measurements*

a. Measurements of dielectric properties

Dielectric properties of the samples were measured in the frequency range 50 kHz÷÷30 MHz at temperatures from −130°C to +300°C. Additional measurements were carried out at 10 GHz (*X*-band).

Within the 50 kHz÷30 MHz frequency range we used the usual *Q*-meter techniques, slightly modified.

It should be noted that the readings of a *Q*-meter are proportional to $\mu\varepsilon$, the product of permeability μ and permittivity ε. Therefore, to evaluate the correct results we had to introduce the value of μ obtained from independent measurements.

The total accuracy was 1% for the real part of the permittivity (ε') and 5% for the imaginary part (ε'').

At 10 GHz we used both perturbational (resonant cavity) and slotted line methods [6]. The accuracy of measurements was estimated at 5% approximately. From these measurements we obtained directly the ε value, since the sample was placed in the maximum of electric field and minimum of magnetic field.

b. Measurements of magnetic properties

Permeability of the investigated compounds was measured at 79.5 kHz. The directly measured quantity was the change of inductance of a measuring coil caused by the introduction of the sample.

The real part of the permeability μ' was measured with an accuracy of 1% for $\mu' < 100$ and 5% for $\mu' > 100$. The imaginary part μ'' could be only very roughly estimated.

4. *Experimental results*

The experimental data are shown in Figs 1÷5. Each experimental point is the result of repeated measurements carried out on several different samples.

As it should be expected, the investigated mixtures exhibit in general a regular behaviour and their magnetic as well as electric properties change gradually with the admixture (*i.e.* ferrite) content.

In Fig. 1 we show ε' as a function of ferrite concentration. The measurements were carried out at 79.5 kHz and at room temperature. Identical conditions were adopted for the measurement of μ; the results are given in Fig. 2.

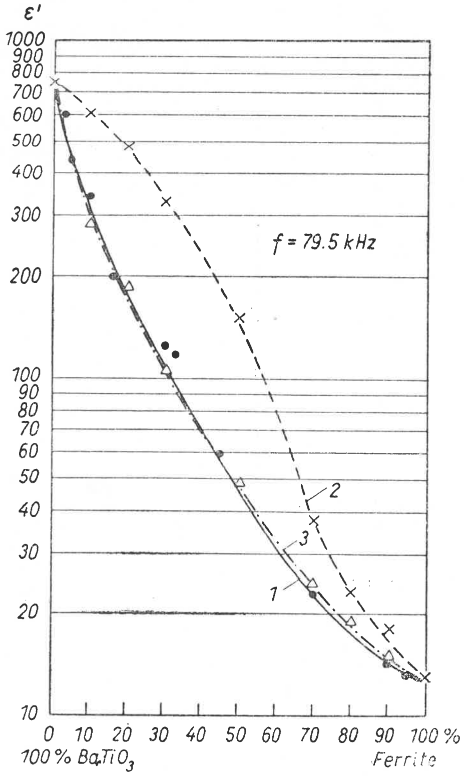

Fig. 1

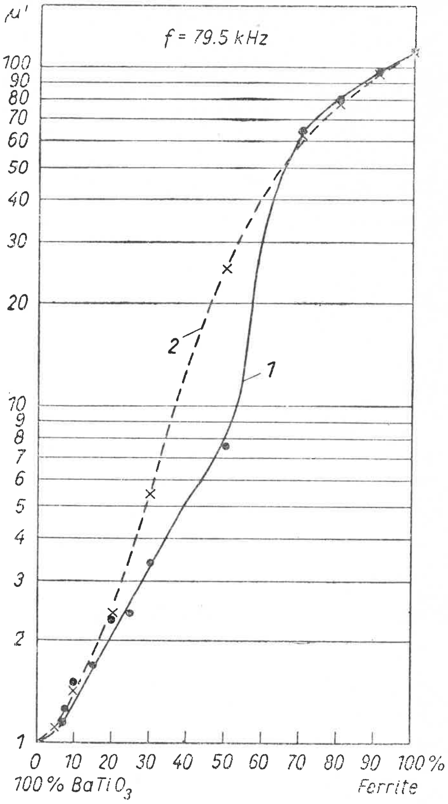

Fig. 2

Fig. 1. Permittivity as a function of ferrite (volume) concentration. *1* — experimental data, *2* — Polder-Van Santen theory, *3* — Polder-Van Santen theory with effective concentration given by formula (3)

Fig. 2. Permeability as a function of ferrite (volume) concentration. *1* — experimental data, *2* — Polder-Van Santen theory

The temperature dependence of $1/\varepsilon'$ for various ferrite concentrations, measured at 100 kHz, is shown in Fig. 3. The existence of Curie temperatures for all compositions, starting from pure $BaTiO_3$, is evident. Tehse temperatures increase slightly with the ferrite concentration — from 125°C for pure $BaTiO_3$ to 135°C for 45% ferrite concentration. At the same time the Curie-Weiss temperatures move towards lower values. Both effects can be probably explained on the basis of the theory of solid state solutions, considering that the permittivity of the ferrite is practically temperature independent.

The existence of Curie temperatures for the investigated materials is also well demonstrated in Fig. 4, where we present the results of microwave permittivity measurements. Dashed curves represent dielectric losses; it can be seen that the losses increase with the ferrite content. The same behaviour was observed at lower frequencies: the losses tend to increase with ferrite concentration and with temperature.

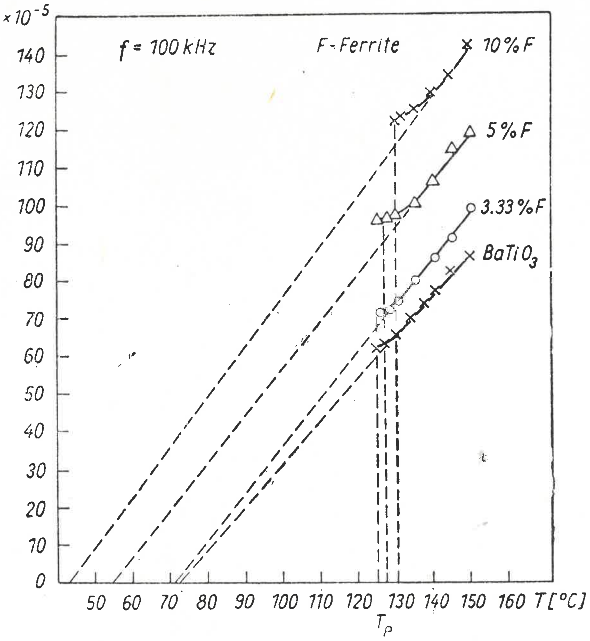

Fig. 3. Temperature dependence of permittivity at 100 Hz

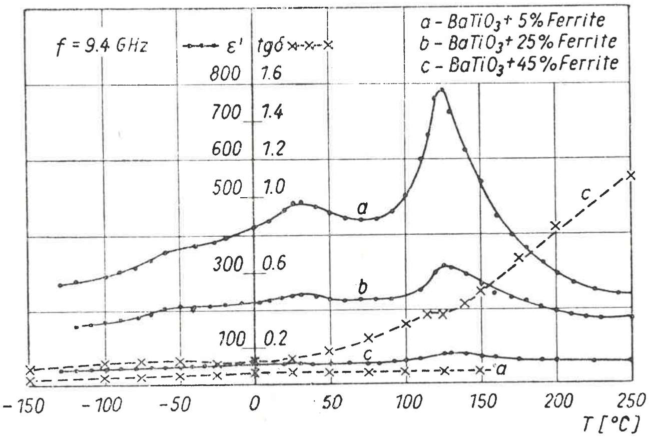

Fig. 4. Temperature dependence of ε' (continuous curves) and tg δ (dashed curves) at 9.4 GHz.

In Fig. 5. is shown the permittivity of various mixtures (at room temperature) as a function of frequency. Observe the good correlation of r.f. and microwave (*cf.* Fig. 4.) values. This indicates that in the whole investigated frequency range there is no anomalous dispersion of the permittivity. On the other hand, the measured permeability of pure ferrite samples at X band is $\mu' = 1.4$, while samples with lower ferrite concentration have respectively lower permeabilities, which is in good agreement with the results of other authors [7].

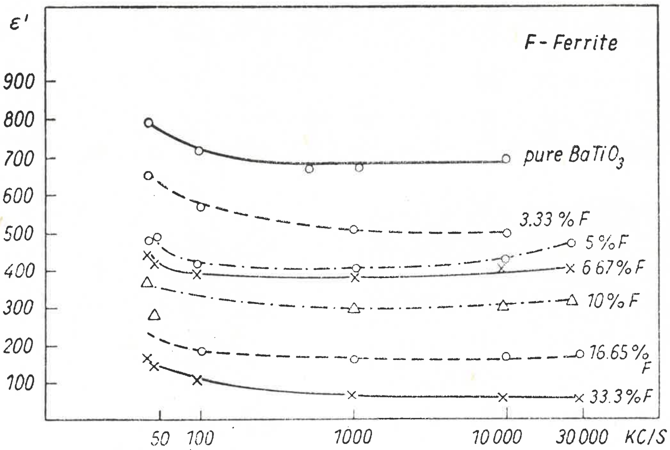

Fig. 5. Frequency dependence of permittivity

5. *Comparison with theory*

As yet there exists no generally valid theory of dielectric and magnetic properties of two-phase mixtures. All known theories give accurate results only for low concentrations of the admixture and/or for small differences in the constitutive parameters of component materials [8], [5]. Grain shape and size is also an important factor, and solutions are available only for certain shapes which can be derived from the general ellipsoid [5].

Having these limitations in mind, we chose for comparison purposes the relatively simple Polder-Van Santen theory [8], which was proved reliable in other experimental works [5], [9], [10]. Constitutive parameters $x = \mu\varepsilon$ of N-phase mixture are given in this theory by the general formula

$$x = x_b \left[1 - \frac{1}{3} \sum_{k=1}^{N} \sum_{i=1}^{3} \frac{p_k(x_k - x_b)}{x^+ + (x_k - x^+) A_{ki}} \right]^{-1} \tag{1}$$

where x_b — constitutive parameter of the basic component,
x_k — constitutive parameter of the k-th component,
x^+ — additional parameter which satisfies the inequality

$$x_b \leqslant x^+ \leqslant x$$

A_{ki} — depolarization factor for grains the of k-th component along x_i coordinate axis,
p_k — volume concentration of the k-th component.

In our case $N = 1$, and further simplification of formula (1) can be obtained by assuming $x^+ = x$ and $A_i = 1/3$. The latter assumption means that the admixture grains are taken to be spheres; this is rather supported by the microscopic analysis of the samples (Fig. 6.). Then (1) is reduced to

$$\frac{x_b}{x} = 1 - \frac{p(x_1 - x_b)}{x + 1/3(x_1 - x)}. \tag{2}$$

The results of calculations based on this formula are shown as dashed curves in Figs 1 and 2. In both cases the ferrite is consistently taken as the admixture. This is not strictly correct, as for $p > 0.5$ barium titanate should appear in the role of admixture, but it was found that our assumption yields a better fit of the theoretical and experimental curves.

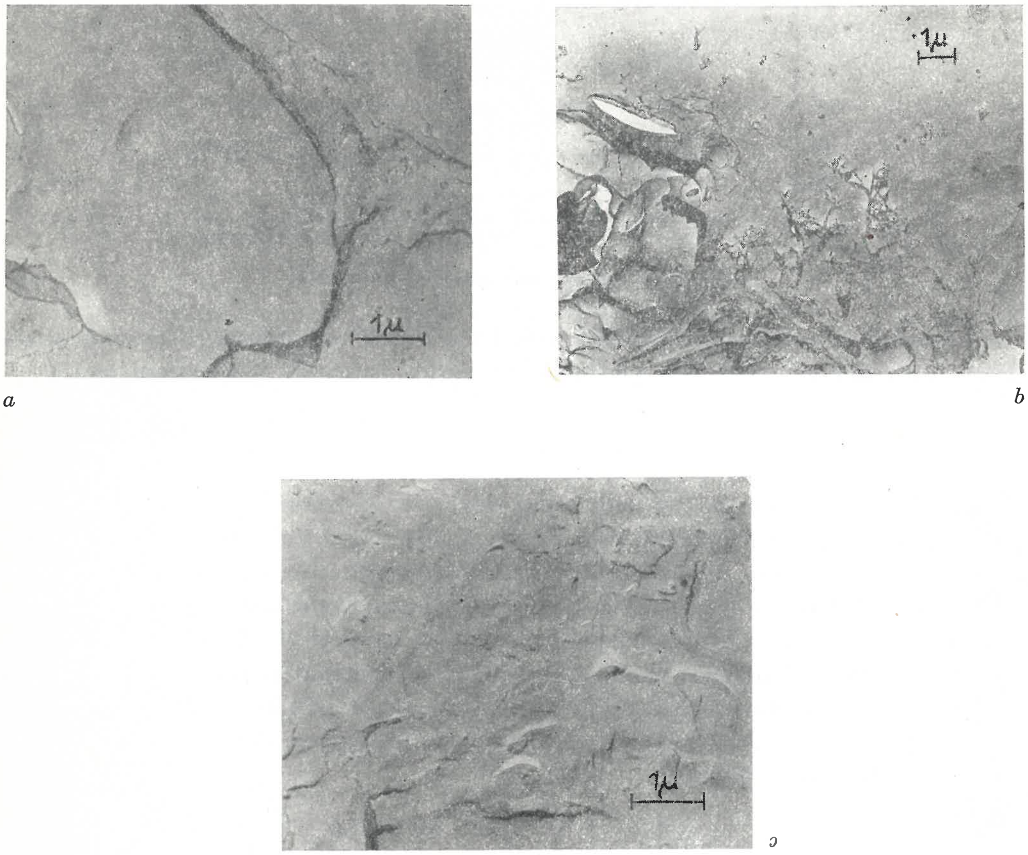

Fig. 6. Microscopic view of the samples. Shadow lines are the boundaries of barium titanate grains. Circular pits and dark clusters (*b*) are ferrite grains. *a* — 5% ferrite concentration, *b* — 15% ferrite concentration, *c* — 50% ferrite concentration

The agreement between theory and experiment is reasonably good in the case of μ for $p \leqslant 0.2$ and $p \geqslant 0.7$ (Fig. 2). It is much worse in the case of ε (Fig. 1), for which the intermediate region, where the Polder-Van Santen theory is not valid, is much broader. However, if we introduce the effective concentration p' given by

$$p' = p + k(1-p) \tag{3}$$

where k is a constant, the agreement becomes nearly perfect for $k = 0.35$ (dash-dot curve in Fig. 1).

This result apparently indicates that the ferrite admixture induces some structural changes in surrounding barium titanate grains and destroys their ferroelectricity. Thus, the effective density of high ε material descreases, and the effective density of low ε material increases, as indicated by (3). Further evidence supporting this conclusion is that no such effective concentration can be introduced for μ (although in this case the theoretical estimate is also too high). Then, under the microscope, samples with 50% ferrite concentration show a nearly amorphous structure with no clearly defined boundaries between ferrite and barium titanate grains (Fig. 6*c*).

6. *Conclusions*

Our results indicate that in ferroelectric-ferromagnetic mixtures there is, as in other two-phase mixtures, a gradual transition of electric as well as magnetic properties from purely ferroelectric to purely ferromagnetic.

Permeabilities and permittivities of various compositions depend regularly on admixture concentration. Functional dependence must, in principle, be determined experimentally for a given method of preparation of samples, but to some extent it can be predicted theoretically. Obviously, such materials, whose μ and ε can be regulated in wide limits, can find several possible applications in electronics and microwave techniques.

The author wishes to thank Professor K. Leibler for her quidance and encouragement in this work, and is deeply indebted to Dr S. J. Lewandowski for his valuable advice and assistance in editing the text, especially the theoretical section.

The assistance of Dr I. Puchalska and Mrs. K. Brańska, M. Sci., who have taken the electron microscope pohtographs, is also gratefully acknowledged.

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