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NEW TWO- AND THREE-PHASE FERROELECTRIC-FERROMAGNETIC MATERIALS

(SOME PROBLEMS AND RESULTS)

By K. Leibler,* V. A. Isupov,** H. Bielska-Lewandowska*

Institute of Physics, Polish Academy of Sciences, Warsaw*

Institute of Semiconductors, USSR Academy of Sciences, Leningrad**

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A study was made of the properties of a number of two- and three-phase ceramic materials of the ferromagnetic-ferroelectric type which display high values of ε, μ and tan δ simultaneously. These parameters were investigated in the frequency range 50 KHz $\div$ 30 MHz and in the 3-cm band, and in the 77°–693°K interval of temperatures. The materials were classified into 3 categories according to properties. The first category, covering ceramics of compositions I–V, displays a very distinct max $\varepsilon = f(T)$ and inflexion tan $\delta = f(T)$ at temperatures 463$\div$473°K. The second, consisting of compositions VI and VII, possesses a somewhat lower value of ε but a high value of μ and low losses tan δ. The third, compositions VIII and IX, has large values of ε for low frequencies, and has low losses. It has been found that materials of interest as far as engineering applications are concerned can be obtained by appropriately choosing the mixture and the technology employed to prepare it.

1. Introduction

Obtaining materials which would possess ferroelectric and ferromagnetic properties at one and the same time (*i. e.* ferro-electro-magnetics) has been a problem of considerable interest to many researchers for a number of years now. The work in this field has hitherto been concentrated on obtaining crystals, *i. e.* homogeneous materials with high dielectric and magnetic permittivities. Such substances (solid solutions of $PbFe_{2/3}W_{1/3}O_3 — PbMg_{1/3}W_{1/3}O_3$) were first produced by Smolenski *et al.* [1], [2]. Other crystals of this type have been discussed by Tomashpolski *et al.* in [3].

Investigation of the electric properties of two-phase mixtures as a function of the properties of the components by Leibler [4], Konopka [5] suggested that materials of this type

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* Address: Instytut Fizyki PAN, Warszawa, Zielna 37, Poland.

** Address: Institute of Semiconductors, USSR Academy of Sciences, Leningrad, Naberezhnaya Kutuzova 10, USSR.

could be obtained as sinters of ferroelectric and ferromagnetic powders [6]. Such materials ($BaTiO_3$+nickel ferrite) were obtained by Bielska-Lewandowska and discussed in [7]. It was demonstrated in the latter paper that mixtures of two phases can be produced so as to have a high magnetic permittivity μ and dielectric permittivity ε. The dependence of these parameters on the percentage composition of the mixture was studied and the experimental results were in agreement with theoretical calculations.

From the point of view of theoretical considerations and possible technical applications, it is important the examine various mixtures of this type and to learn how the components used affect their properties. The present paper discusses some materials obtained with the desired electric properties and the values of their parameters as a function of frequency and temperature. The choice of components and percentage composition was based on theoretical considerations with an eye to ensuring the least possible interaction between the ferroelectric and ferromagnetic phases in the course of the technological process.

2. *Experimental problems and preparation of specimens*

A number of problems must be solved in order to obtain a ceramic consisting of a mixture of a segnetoelectric and ferromagnetic. The first is that of producing a mixture of the desired composition. Obviously, diffusion occurs at the sintering temperature of the ceramic and the original (initial) composition may be altered considerably. At the same time, the properties of the components — both the ferroelectric and the ferromagnetic — may also change. Another difficulty is encountered in getting materials with low dielectric losses. Thus, there is the problem of so modifying the segnetoelectric and ferromagnetic phases as to improve the dielectric and magnetic properties of the resultant ceramic. Measurements of the physical properties of such ceramics also entail a number of specific difficulties (*e. g.* simultaneous measurements of ε and μ in the microwave region) which call for separate solution since measuring methods hitherto known do not meet the requirements. In the work described in this paper an attempt was made to produce systems with as good parameters as possible and their electric and magnetic properties were investigated.

As is known, in order to reduce the reaction between the grains of the individual components it is desirable to choose starting materials which differ little in chemical composition; *e.g.* if $CoFe_2O_4$ is taken as the ferromagnetic component, it is desirable that CoO and Fe_2O_3 enter the segnetoelectric component in a similar percentage ratio.

In the given case, the segnetoelectric component consisted of a solid solution of the segnetoelectrics ($PbCo_{1/3}Nb_{2/3}O_3$) and ($PbFe_{1/2}Nb_{1/2}O_3$) with a final composition of ($PbCo_{0.143}\,Fe_{0.286}Nb_{0.571}O_3$). A similar method was used to choose components for preparing other specimens of materials studied. The conditions for the heat treatment of the materials were chose so that:

— the starting materials are sintered at as high temperatures as possible

— the mixtures are sintered at the lowest possible temperatures ensuring the desired mechanical properties of the ceramic. A low sintering temperature for the mixture diminishes the possibility of a reaction occurring between the segnetoelectric and ferromagnetic phases.

To lower the sintering temperature of the mixture, a low-melting binding agent (antiseg-

TABLE I

No of ceramic	Ceramic composition (% weight)	Sintering temperature °C (time hr.)	Component sintering temperature and time					
			Component 1, T°C	t (hr)	Component 2, T°C	t (hr)	Component 3, T°C	t (hr)
I	$65\% PbCo_{0.143}Fe_{0.286}Nb_{0.571}O_3+35\% CoFe_2O_4$	1160(1)	1150	(1)	1300	(1)	—	—
II	$35\% BaTiO_3+35\% Ni_{0.3}Zn_{0.7}Fe_2O_4+30\% Pb_4SiO_6$	950(1)	1360	(1)	1300	(1)	550	(2)
III	$35\% BaTiO_3+35\% CoFe_2O_4+30\% PbCd_{0.5}W_{0.5}O_3$	950(1)	1360	(1)	1300	(1)	650	(1)
IV	$32\% PbTiO_{0.47}\ Zr_{0.53}O_3+36\% CoFe_2O_4+32\% Pb_4SiO_6$	950(1)	1280	(1)	1300	(1)	550	(2)
V	$60\% PbNi_{0.117}Fe_{0.234}Nb_{0.468}Ti_{0.181}O_3+40\% NiFe_2O_4$	1150(1.5)	1150	(1)	1300	(1)	—	—
VI	$75\% PbNi_{0.143}Fe_{0.286}Nb_{0.571}O_3+25\% Ni_{0.3}Zn_{0.7}Fe_2O_4$	1160(1)	1150	(1)	1300	(1)	—	—
VII	$50\% PbNi_{0.143}Fe_{0.286}Nb_{0.571}O_3+50\% Ni_{0.3}Zn_{0.7}Fe_2O_4$	1160(1)	1150	(1)	1300	(1)	—	—
VIII	$40\% PbTi_{0.47}Zr_{0.53}O_3+40\% PbFe_{12}O_{19}+20\% Pb_4SiO_6$	970(1)	1280	(1)	1200	(1)	550	(2)
IX	$60\% PbTi_{0.47}Zr_{0.53}O_3+25\% PbFe_{12}O_{19}+15\% Pb_4SiO_6$	970(1)	1280	(1)	1200	(1)	550	(2)

netoelectric Pb_4SiO_6 and $PbCd_{0.5}W_{0.5}O_3$) was introduced into some specimens. Naturally, in this case the ceramic consisted of three phases.

The compositions of the ceramics investigated and the heat treatment data are listed in Table I.

3. Measuring methods

The parameters ε, μ, and tan δ were studied over the frequency range from 50 KHz to 30 MHz and in the 3-cm band in the 77–693°K range of temperatures.

Measurements of ε' and tan δ were made by the resonance method with a Marconi TF 1245 Q-meter in the 50 KHz-30 MHz range at room temperature and in the 80 KHz-8 MHz range in the 20–420°C temperature range. The accuracy of the measurements was 2% and 5%, respectively.

The magnetic permittivity μ was measured similarly with a Q-meter. The specimens were cylinders about 4 mm in diameter and about 20 mm in length. The method used was that of varying the inductance of a short coil without the specimen and with the specimen (core) inserted [8]. The accuracy of the measurements of μ' was 2% but when $\mu' > 100$ the accuracy fell off considerably, down to about 5%. Measurements were made for frequencies of 80, 800 and 8000 KHz at room temperature.

For measurements of the dielectric and magnetic permittivity in the 3-cm band (frequency 9.3 GHz), the specimens were prepared as disks 25 mm in diameter and 1.5–2 mm thick. Inasmuch as the materials measured had a large dielectric constant (of the order of 100–1000), an original measuring method was used [9]. This method consists in utilizing the properties of a circular waveguide in which a TM_{11} mode is propagated with a frequency close to the cut-off frequency of the waveguide. Under such conditions the ratio of the characteristic impedance of the waveguide filled with the dielectric being measured to that of the empty waveguide is of the order of up to five and a satisfactory measuring accuracy can be achieved.

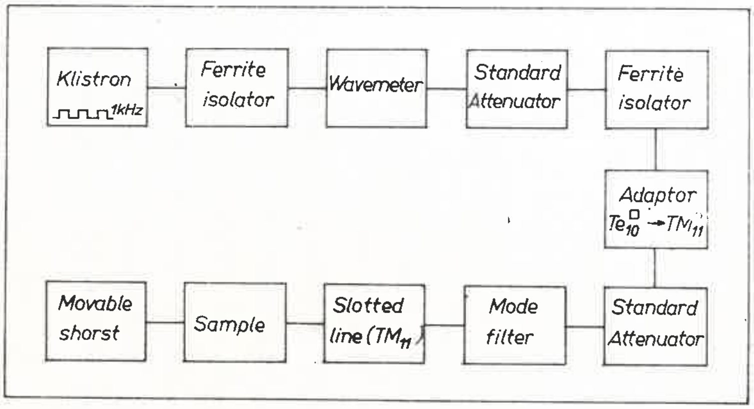

Fig. 1. Experimental arrangement for measuring ε and μ in the microwave region

The experimental arrangement for the measurements is shown in Fig. 1. The complex dielectric and magnetic permittivities were determined by measuring the propagation constant and the characteristic impedance of the waveguide completely filled with the material under investigation:

$$z_0 = \frac{\sqrt{\varepsilon\mu - (\lambda_0/\lambda_c)^2}}{\varepsilon\sqrt{1 - (\lambda_0/\lambda_c)^2}}$$

$$\gamma = j2\frac{\pi}{\lambda_0}\sqrt{\varepsilon\mu - (\lambda_0/\lambda_c)^2}$$

where: z_0 — the characteristic impendance of the waveguide when filled with the relative permittivities ε and μ, reduced to the impedance of the empty waveguide) γ — the complex propagation constant, λ_0 — the free-space wavelength, λ_c — the cutoff wavelength of the waveguide.

The impedance and propagation constant were measured by the "short circuit-open circuit" method [9], for which the propagation constant and characteristic impedance are related to the quantities measured directly by the relationship:

$$Z_0 = \sqrt{Z_z Z_r}$$

$$\tanh \gamma d = \sqrt{\frac{Z_z}{Z_r}}$$

where: Z_z — the reduced impedance, when the specimen is replaced by a short circuit, Z_r — the reduced impedance, when the specimen is replaced by an open circuit, d — the thickness of the specimen being measured.

Apart from the usual errors in impedance measurements (the inaccuracy of the attenuator and of the measuring line, the instability of the oscillator frequency, *etc.*), the inaccuracies in the measurement of ε and μ are due principally to the error caused by the propagation of undesirable modes in the waveguide and the error due to the fact that the waveguide is incompletely filled by the specimen (gaps at the specimen-waveguide interface). Mode filters were used in order to reduce the influence of undesirable modes, whereas the error due to the waveguide being incompletely filled was diminished considerably by the special preparation of the specimens (keeping dimensional tolerances and wrapping in thin silver foil). Measurements were made for three frequencies which differed only slightly, and the results were averaged. The measurement accuracy was estimated to be about 5%.

4. *The results of measurements*

The ceramic materials studied could be classified into several categories according to dielectric properties. Figure 2 gives the plots of ε', and tan δ against frequency for ceramics with compositions I–IV. A characteristic feature of all ceramics in this group is that the values of ε' and tan δ decrease slightly with an increase in frequency. The influence of the third, low-melting dielectric component, which causes the value of tan δ to fall off considerably (especially for the lower frequencies) can be seen clearly in Fig. 2. The dielectric losses of ceramic I, which does not contain this component, rise sharply with the temperature, but ε' grows at the same time. Tan δ is also seen to increase with the temperature in materials of different compositions, but at a much slower rate.

The plots of ε' and tan δ *versus*. temperature are given in Fig. 3 for ceramics with composition II. It is seen that ε' attains a maximum at 195 °C (characteristic of the ferroelectric state),

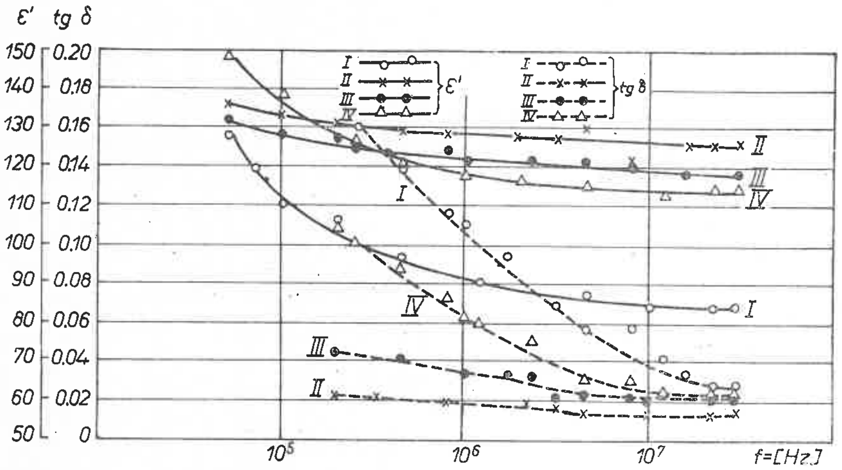

Fig. 2. Dielectric permittivity ε' and tan δ as a function of frequency for ceramics of compositions I–IV

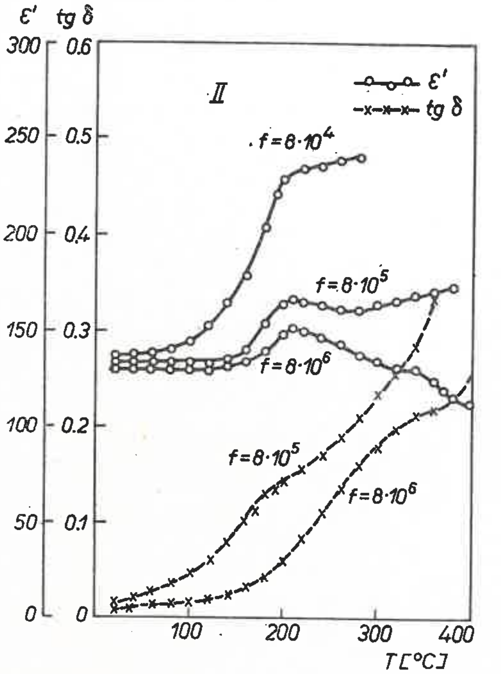

Fig. 3. Dielectric permittivity ε' and tan δ as a function of temperature for ceramic of composition II for three values of measuring frequency f (Hz)

whereas the curve tan δ (T) has distinct inflexions. The curve $\varepsilon'(T)$ for $f = 8$ MHz has an additional inflexion at a temperature of about 360°C. The value of the Curie temperature (max ε') of the material, at about 195°C, is much higher than for pure $BaTiO_3$ (120°C) and this, coupled with the existence of the aforementioned point of inflexion, testifies to the interaction between grains of $BaTiO_3$ and Pb_4SiO_6 during sintering; this leads to the formation of solid solutions of $(Ba, Pb)TiO_3$ of uneven concentrations of Ba and Pb. (The Curie temperature of solid solutions of $(Ba, Pb)TiO_3$ is known to increase as the content of lead titanate increases.) Thus, it should be supposed that the segneto-electric grains in

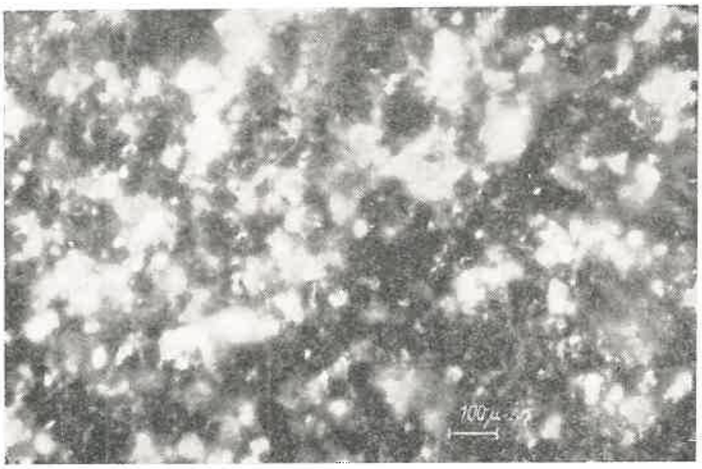

Fig. 4. Microphotograph of etched surface of ceramic II

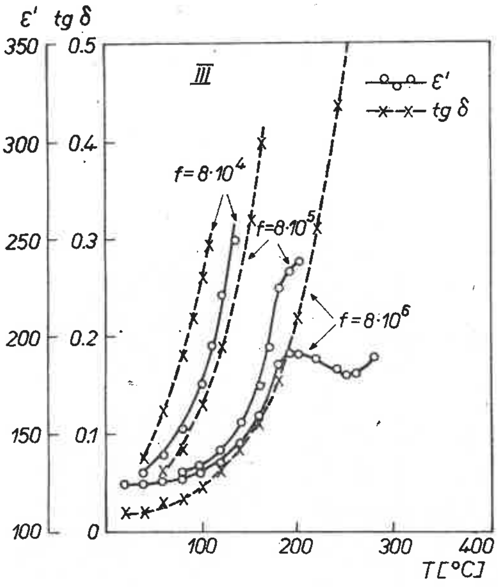

Fig. 5. Dielectric permittivity ε' and tan δ as a function of temperature for ceramic III for three values of measuring frequency f (Hz)

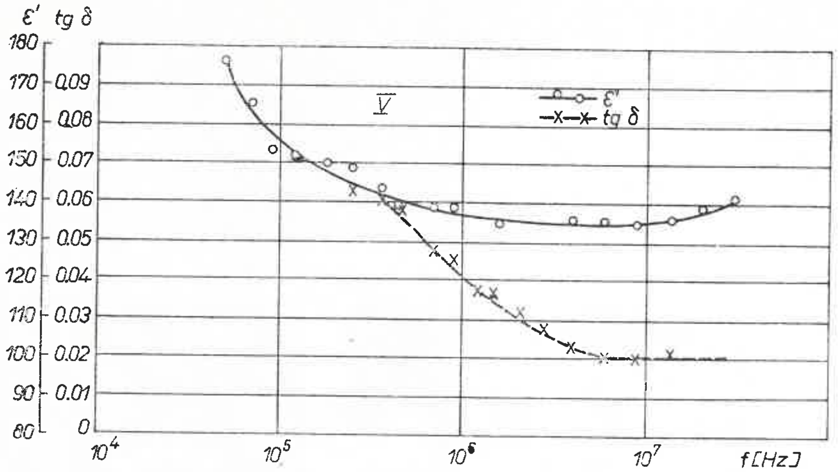

Fig. 6*a*. Dielectric permittivity ε' and tan δ as a function of frequency for ceramic of composition V

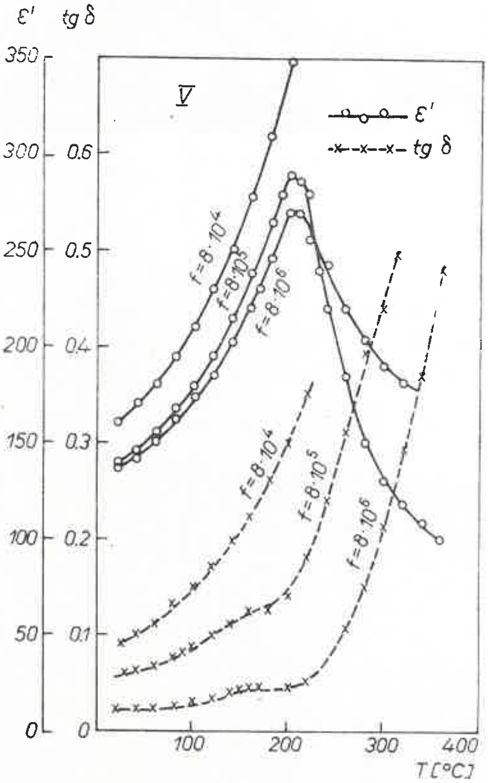

Fig. 6*b*. Dielectric permittivity ε' and tan δ as a function of temperature for ceramic V for three values of measuring frequency *f* (Hz)

ceramic II remain but change their composition somewhat. This also emerges from the microphotograph of the ceramic (Fig. 4).

Figure 5 presents the temperature dependence of ε' and tan δ for ceramic III. Another low-melting component, also containing lead, was used in this case. As a result, the maximum ε' occurs at a high temperature, which is indicative of the formation of a solid solution $(Ba, Pb)TiO_3$. Because of the introduction of the third component, the tan δ obtained is smaller than in ceramic I, but is distinctly larger than in ceramic II. The higher values of tan δ for ceramics I and III are due probably to the presence of cobalt ferrite. This is confirmed by the fact that in the case of ceramic IV, which also contains $CoFe_2O_4$, the value of tan δ increases markedly and rapidly with a rise in temperature.

In Fig. 6(*a*, *b*) ε' and tan δ are plotted as functions of the frequency and temperture for ceramic V. Ceramic V does not contain any low-melting material and it does have a large tan δ at low frequencies. However, in the region of frequencies above 6 MHz the value of tan δ is not very large. This ceramic differs from the previous ones in that it has a sharp maximum ε' at 200° and, hence, clearly retains ferroelectric properties.

Table II lists the values of μ', ε', and tan δ for ceramics I–V, measured for several frequencies at a temperature of 20°C.

TABLE II

No of ceramic	$f = 8\times10^4$ Hz		$f = 8\times10^5$ Hz			$f = 8\times10^6$ Hz		
	μ'	ε'	μ'	ε'	tan δ	μ'	ε'	tan δ
I	1.25	117	1.29	91	0.119	1.28	86	0.048
II	3.76	134	3.97	128	0.018	3.9	127	0.012
III	1.85	131	1.9	122	0.034	1.89	120	0.022
IV	1.24	137	1.26	118	0.072	1.22	115	0.028
V	3.63	162	3.68	138	0.046	3.62	135	0.020

It is evident from the Table that the magnetic permittivity μ' is distinctly greater than 1, the highest value occurring for ceramic II which has the high μ' nickel-zinc ferrite as the ferromagnetic component.

Ceramic V, which contains nickel ferrite, has a somewhat smaller μ' but a larger ε'. Ceramic V was also studied at a frequency of 9.25–9.3 GHz at room temperature. The results obtained were:

$$\varepsilon' = 120,\ \varepsilon'' = 7.5,\ \tan\delta = 0.06,$$

$$\mu' = 1.45,\ \mu'' = 0.11.$$

It is clearly seen that with an increase in the frequency to 9.3 GHz the value of ε' decreases slightly, tan δ increases, and μ' falls off sharply.

Ceramic V was also used to investigate the influence of heat treatment T (sintering) on the magnetic and segnetoelectric properties of the material. When the maximum sintering temperature was raised by 30°C, the values obtained in the 3-cm band were: $\varepsilon' = 400$,

$\varepsilon'' = 70$, $\tan\delta = 0.17$, $\mu' = 1.05$, $\mu'' = 0.18$. On the other hand, when the maximum sintering temperature was raised by 20°C while the sintering time was extended by an hour, the results in the 3-cm band were: $\varepsilon' = 450$, $\varepsilon'' = 50$, $\tan\delta = 0.11$, $\mu' = 1$, $\mu'' = 0.15$. As can be seen, when the normal sintering temperature is exceeded, ε' increases considerably but μ' decreases greatly. This is due to the influence of the reactions between the grains of the ferrite and segnetoelectric in thermal processes. A microphotograph of ceramic V is shown in Fig. 7*a*.

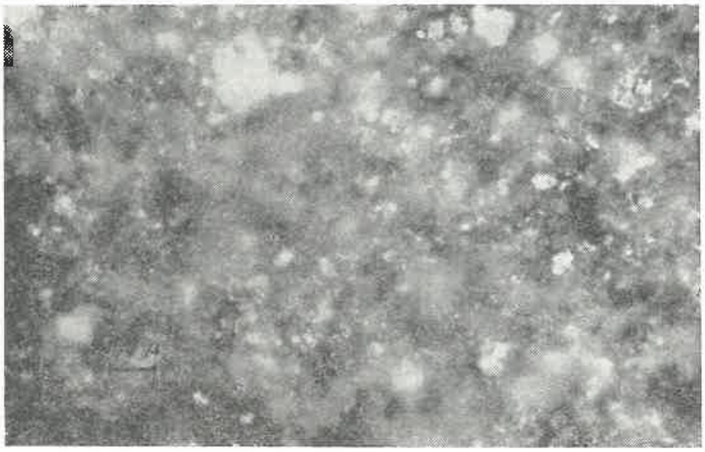

Fig. 7*a*. Microphotograph of etched surface of ceramic V

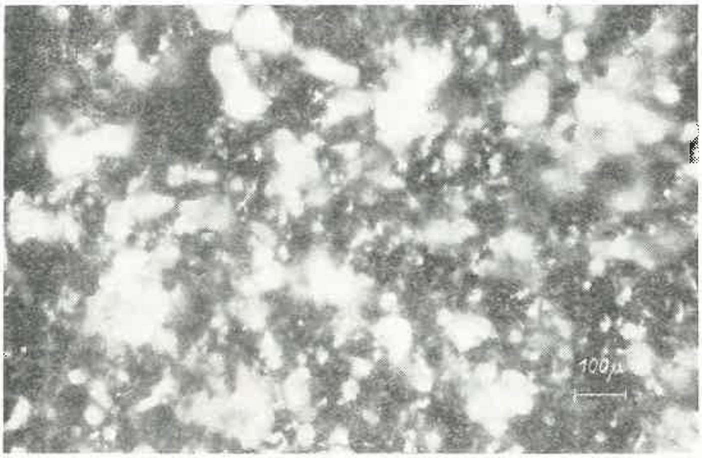

Fig. 7*b*. Microphotograph of etched surface of ceramic VI

A different character is displayed by the magnetic and dielectric properties of ceramics VI and VII which constitute a solid solution of $PbNi_{0.143}Fe_{0.286}Nb_{0.571}O_3$ and the ferrite $Ni_{0.3}Zn_{0.7}Fe_2O_4$. These materials have slightly smaller values of ε', but very low losses of $\tan\delta$ (0.005–0.008 at 20°C at frequencies higher than 7 MHz). In this frequency band, $\tan\delta$ remains almost constant up to a temperature of +60°C, and ε' keeps increasing up to a temperature of 100–110°C. At the same time, the values of the magnetic permittivity are large.

Table III presents the dielectric and magnetic properties of ceramics VI and VII, as measured at 20°C. For comparison, the Table also contains the values of μ' and ε' of the most commonly used segnetoelectric materials and ferrites in electronics.

TABLE III

Ceramic composition	Frequency kHz	μ'	ε'	$\mu'\varepsilon'$	μ'/ε'	$\sqrt{\mu'/\varepsilon'}$
VI	80	69.8	58	4050	1.20	1.10
	800	69.5	51	3540	1.36	1.16
	8000	70	50	3500	1.40	1.18
VII	80	79.5	43	3420	1.85	1.36
	800	80.7	40	3230	2.02	1.42
	8000	81	39	3160	2.07	1.44
segneto-ceramic		I	2000–5000	2000–5000	0.0002–0.0005	0.014–0.022
ferro-ceramic		of the order of 3000	10–15	30.000–45.000	200–300	14–17

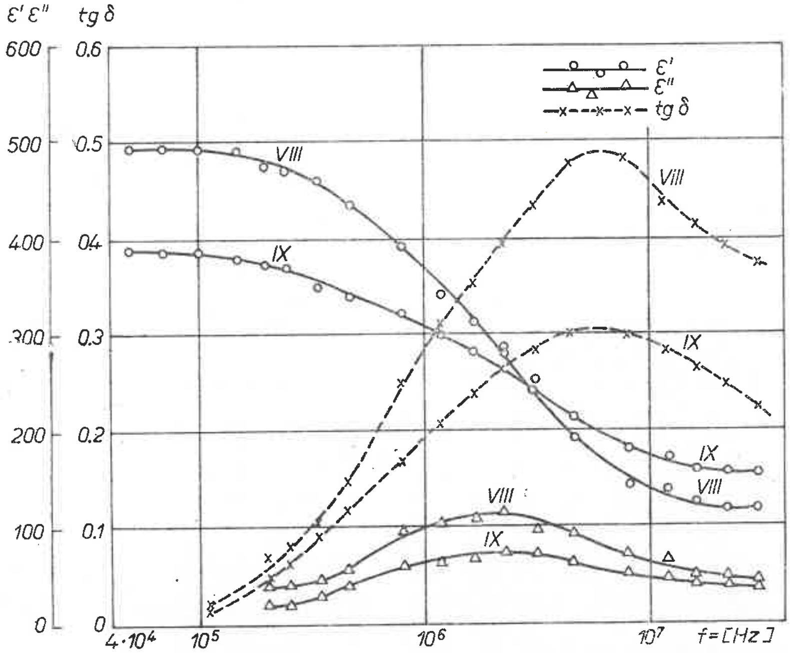

Fig. 8. Plots of ε', ε'', and tan δ *versus* frequency for ceramics of compositions VIII, IX

A perusal of Table III shows that the product $\varepsilon'\mu'$ is of the same order as for segnetoceramis, but the quantities μ'/ε' and $\sqrt{\mu'/\varepsilon'}$ differ substantially from those for segnetoceramics and ferrites.

In Fig. 8 the plots of ε', ε'', and tan δ *versus* the frequency are given for materials VIII and IX. Their dielectric properties differ distinctly from those of the other materials. The values of ε' for low frequencies is high (400 and 500) and the losses low (tan $\delta = 0.005$–0.002). With an increase in frequency, however, tan δ is seen to rise greatly (the maximum tan δ occurs in the 5–6 MHz band), whereas ε' decreases to 120–160, of the order observed in materials I–V. Increasing the amount of segnetoelectric in the mixture (IX) thus causes a rise in ε' at higher frequencies. The reverse is true at low frequencies, contrary to expectations.

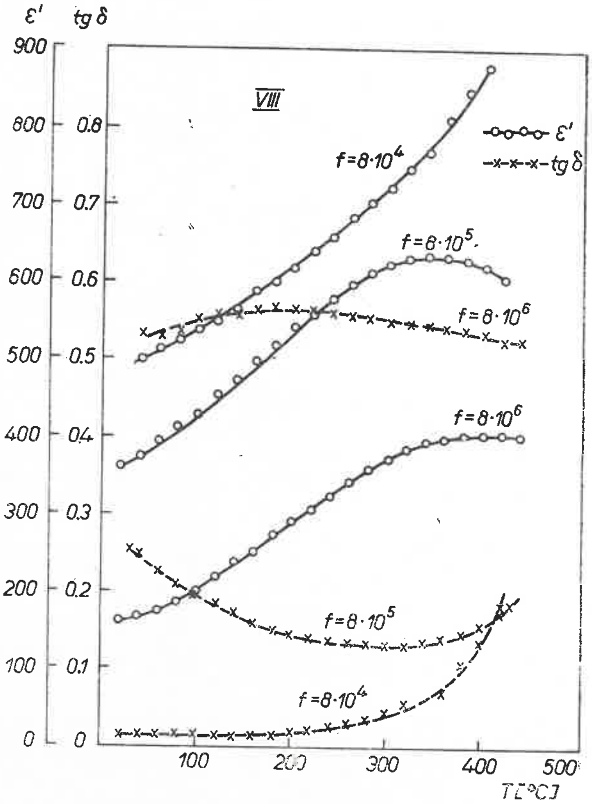

Fig. 9. Temperature dependence of ε' and tan δ of ceramic VIII for three measuring frequencies f (Hz)

The plots of ε' and tan δ for ceramic VIII are presented in Fig. 9 (the plots of ε' and tan δ for IX are similar). These specimens are characterized by a rather high content of itron.

Table IV lists some parameters of materials VIII and IX.

TABLE IV

Ceramic composition	Frequency (kHz)	μ'	ε'	tan δ	$\mu'\varepsilon'$	μ'/ε'	$\sqrt{\mu'\varepsilon'}$
VIII	80	1.56	495	0.022	722	0.0032	0.056
	800	1.56	370	0.223	577	0.0042	0.065
	8000	1.62	155	0.500	252	0.0104	0.102
IX	80	1.27	385	0.005	490	0.0033	0.057
	800	1.245	320	0.172	398	0.0039	0.062
	8000	1.2	190	0.304	228	0.0063	0.080

The influence of the magnetic field (8000 gauss) on the dielectric permittivity was studied for all specimens of ceramics investigated. No variations exceeding the accuracy of the measuring method were detected for any specimen (1%).

5. Conclusions

As the measurements demonstrate, materials which are simultaneously ferroelectric and ferromagnetic can be obtained by making appropriate mixtures. The choice of compsitions and technologies for preparing the mixture has a pronounced influence on the values of ε' and μ' as well as on the dielectric losses and their temperature and frequency responses.

It would seem that by means of an appropriate choice of components materials which are of interest from the point of view of technical applications will be obtained. A study of the physical properties of systems of this type may yield important data about the interaction of particles in electric and magnetic fields.

REFERENCES

[1] G. A. Smolenski, A. I. Agranovska, S. N. Popov, V. A. Isupov, *Zh. Tekh. Fiz.* (USSR), **28**, 2152 (1958).

[2] G. A. Smolenski, V. A. Isupov, N. N. Krainik, A. I. Agranovska, *Izv. Akad. Nauk* (USSR), *Ser. Fiz.*, **25**, II, 1333 (1961).

[3] I. A. Tomashpolski, I. N. Venevtsev, G. S. Zdanov, *Zh. Eksper. Teor. Fiz.* (*USSR*), **46**, V, 1921 (1964).

[4] K. Leibler, *J. Chim. Phys.*, 000, 677 (1959).

[5] J. Konopka, Ph. D. *Thesis*, Institute of Physics, Polish Academy of Sciences, Warsaw 1964.

[6] H. Bielska-Lewandowska, *Internat. Colloquium on Ferromagnetism*, Poznań 1964.

[7] H. Bielska-Lewandowska, *Acta Phys. Polon.*, **39**, 687 (1971).

[8] A. Hippel, *Diel. Mat. and Appl.*, J. Villay, p. 63, 1954.

[9] M. Kliger, J. Zagrodziński, *Int. Report*, Institute of Physics, Polish Academy of Sciences, Warsaw 1966.