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New method for measuring magnetoelectric effect in pulsed magnetic fields

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A new measurement method for magnetoelectric effect in pulsed magnetic fields has been developed. The pulsed field system generates in a bore of 25 mm fields up to 10.0 T with a typical pulse duration of 20 ms. Besides the magnetization, the system allows the measurement of the magnetoelectric effect in both transversal and longitudinal modes. The magnetoelectric effect on well known cobalt ferrite/ barium titanate composites and single-phase materials was measured as a function of the temperature. A maximum magnetoelectric coefficient of 1.5 mV/(cm·Oe) was obtained for a composite with a composition of 50 mass % ferrite sintered at 1200 °C. A model to explain the results obtained by this measurement method is discussed.

Разработан новый метод измерения магнитоэлектрического эффекта в импульсных магнитных полях. Система импульсного поля генерирует в 25-мм отверстии поля до 10,0 Т с типичной длительностью импульса 10 мс. Помимо намагничивания, система позволяет измерять магнитоэлектрический эффект как в поперечном, так и в продольном направлениях. Измерен магнитоэлектрический эффект для хорошо известных композитов феррит кобальта/титаната бария и для однофазных материалов в зависимости от температуры. Максимальный магнитоэлектрический коэффициент 1.5 mV/(cm·Oe) получен для композита, содержащего 50% мас. феррита, спеченного при 1200 °С. Предложена модель для объяснения результатов, полученных описанным методом.

Magnetoelectric materials is one of the research areas in multifunctional materials which has centered the attention of scientist around the world due to its potential applications, such as, transducers, actuators, sensors, and new and improved data-storage media [1–3]. The primary magnetoelectric materials, as a kind of multiferroic materials, become magnetized when placed in an electric field and polarized when placed in a magnetic field. The induced polarization **P** is related to the field **H** by $\mathbf{P} = \alpha\mathbf{H}$, where α is the second rank ME-susceptibility tensor in SI units (s/m). The magnetoelectric voltage coefficient $\alpha_E = dE/dH$ which is related to α by $\alpha = \varepsilon_0\varepsilon_r\alpha_E$ (where ε_r is the relative permittivity of the material), as a result of a product property [2], can be considered as the product of the piezomagnetic deformation dr/dH and the piezoelectric charge generation dQ/dr. This idea leads not only to the search for single phase materials, but also for two-phase composites which can be a coupling either of magnetostrictive / piezoelectric, piezomagnetic / piezoelectric, or pyromagnetic / pyroelectric phases [4]. Since the magnetoelectric effect in two-phase composites is more than a hundred times that of the single phase materials, more intensive research on this kind of compounds has been conducted [2, 5, 6].

To measure the magnetoelectric (ME) effect, the most established method consists in determining the voltage V_E between the

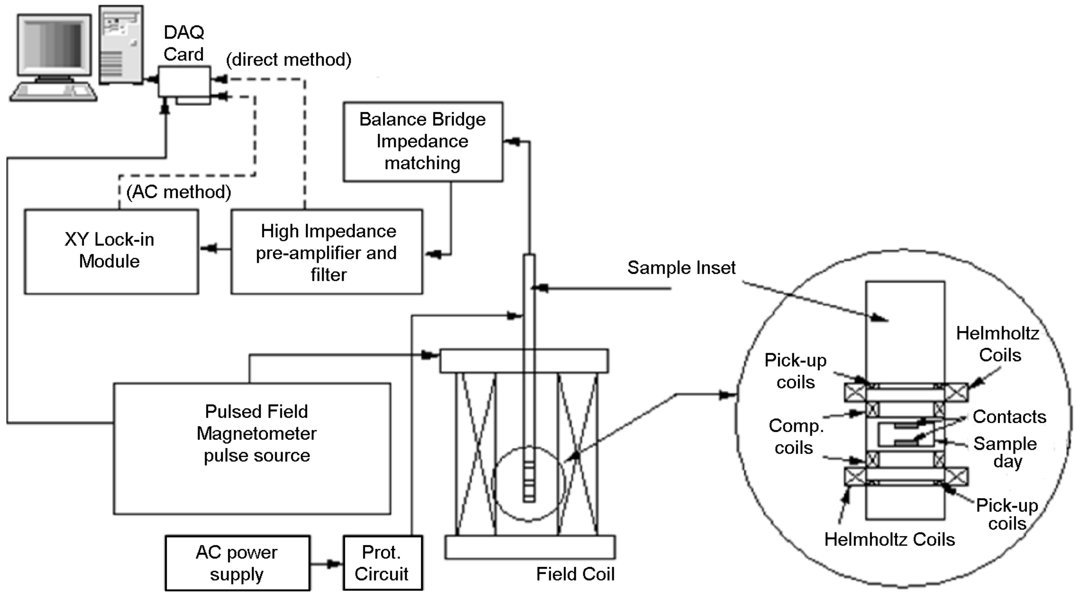

Fig. 1. Block diagram of the pulsed field magnetoelectric setup.

plated surfaces of a sample as a function of an applied low amplitude AC magnetic field H_{AC}, superimposed on a DC bias magnetic field. This voltage is recorded using a high impedance amplifier or a charge amplifier and a lock-in amplifier taking as reference the signal of the AC magnetic field. Here the magnetoelectric voltage coefficient α_E is related to this voltage by $\alpha_E = V_E/(H_{AC}\times t_p)$ [2, 5].

In this work we present a method for measuring the ME voltage coefficient using pulsed magnetic fields. This new method results not only suitable for measuring the ME coefficient, but also could be useful to study the relaxation and hysteresis behavior of the ME materials as a function of the applied field.

The system for measuring magnetoelectric properties is built on top of a tailored pulsed field magnetometer developed at CIMAV, with a field coil of 25 mm bore and typical pulse duration of 25 ms. The block diagram of the whole system is shown in Fig. 1.

The main part of the measurement system is a specially designed sample holder, which contains the fixed electric contacts for measuring the voltage across the sample, two special coils (compensation coils) to compensate the induced signal on the contacts wiring during the field pulse, and a pick up coil for sensing the field amplitude. Special care was taken in the design of contacts in order to warranty the reproducibility of the measurements and to avoid an excessive pressure, which could pre-stress the samples. The holder is built as a part of a measuring inset which also contains a pair of Helmholtz coils for applying a high frequency, low amplitude AC magnetic field on top of the main pulse, a small furnace and a temperature sensing device for measuring the ME voltage coefficient as a function of the temperature.

Two insets with two different sample holders were made, one for measuring the transversal ME effect, and the other for the longitudinal ME effect. Additionally, a balance bridge with an impedance matching circuit was built in order to improve the zero signal and to match the sample impedance with the input impedance of the measuring electronics. The AC Helmholtz coils are driven by a AC current power supply with an input protection circuit to avoid damage in the supply due to the large induced voltage on the coils resulting from the main field pulse.

The output voltage from the sample is amplified and filtered with a high impedance pre-amplifier, and can be measured either i) directly with a DAQ Card (NI PCI-6110E) or ii) as the output of a fast analog lock-in XY module in the case of an AC field measurement. Here, the reference signal from the AC current supply is used as reference signal for the lock-in module. In both cases, after setting all devices, the measurement is triggered and controlled by the PC computer of the pulsed field magnetometer. To warranty the reproducibility of the measurements a zero signal is always taken and then subtracted to the signal from the sample.

With this system, the ME voltage coefficient can be measured by two different methods, i.e: i) during the application of a magnetic field pulse the voltage appearing on the sample is directly recorded, and ii) as a function of a high frequency ($f = 1$–10 kHz) AC field superimposed to the main field pulse, as in the case of the well established method based on AC and DC bias field [2, 5]. In the first case (*direct method*), the measured voltage is proportional to the current in the circuit which is the first derivative of the charge (dQ/dt) generated by the induced polarization due to the deformation caused by the magnetic field pulse. Considering that the impedance of the sample is much bigger than the impedance of the matching circuit, the charge can be obtained from Eq. 1:

$$Q = \frac{1}{Z_{in}}\int V_{out}dt, \qquad (1)$$

where Z_{in} is the input impedance of the electronic circuitry, and V_{out} is the voltage measured on the sample. Considering the sample as a plane parallel capacitor with an area A, the electric field will be:

$$E = \frac{1}{Z_{in}\varepsilon_0\varepsilon_r A}\int V_{out}dt, \qquad (2)$$

where ε_r is the relative permittivity of the material, and A is the area of the plated surface of the sample. Then the magnetoelectric voltage coefficient can be obtained from Eq. 2 and the magnetic field $H(t)$, taking the time as a parameter, according to the relation:

$$\alpha_E = \frac{d}{dH}\left[\frac{1}{Z_{in}\varepsilon_0\varepsilon_r A}\int V_{out}dt\right]. \qquad (3)$$

The above derivative should be done numerically using the data obtained from the sample and from the field pick-up coils. Here a fast, highly accurate and sensitive electronics is desirable, in order to obtain a smooth experimental data to minimize the numerical noise generated in the mathematical procedure. In this simple model, another problem could arise from the fact that in some samples during poling, there is a possibility of charges gets accumulated at the grain boundaries, which will move towards the electrodes during the measurement [7].

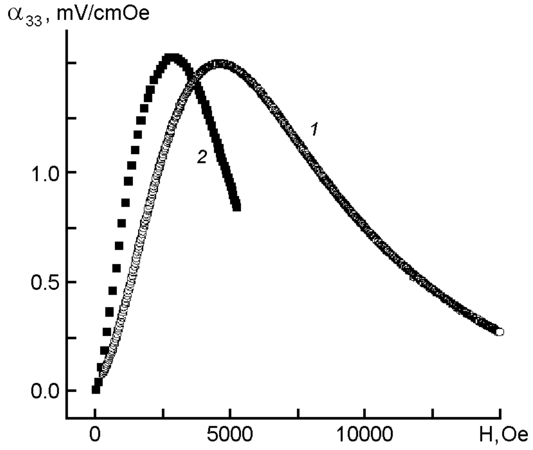

Fig. 2. ME voltage coefficient for the sample CoTi50 measured by direct method, curve *1*. For comparison the curve obtained by DC method, curve *2* (DC values were measured in a static system at TU Wien University with f_{HAC} = 1.2 kHz, H_{AC} = 4.7 Oe) is also included.

In the case of AC measurements (*AC pulsed method*), an AC voltage appears in the sample which is proportional to the charge change $\Delta Q = Q_0\sin(\omega t + \varphi)$. Using a lock-in amplifier, the ME voltage coefficient can be obtained in the same way as in the well established method based on AC and DC bias magnetic fields (*DC method*):

$$\alpha_E = V_{out}/(H_{AC} \times t_p). \qquad (4)$$

Where V_{out} is the output voltage from the lock-in amplifier, H_{AC} is the amplitude of the AC magnetic field, and t_p is the thickness of the sample [2, 4, 5].

The system was tested with well known composites of cobalt ferrite and barium titanate. Composites, consisting of a mixture of magnetostrictive and piezoelectric phases, were obtained starting from coprecipitated cobalt ferrite ($CoFe_2O_4$) and sol-gel barium titanate ($BaTiO_3$). Samples were sintered at 1200°C for 12 hours. Silver paint was coated on the sintered pellets to provide electrical contacts. Finally, the samples were poled in an electric field of 6 kV/cm at 110°C for 30 minutes.

Piezoelectric d_{33} constant was measured with an APC model 8000 piezo d_{33} tester. The relative permittivity was calculated from the data obtained with an HP 4192A impedance analyzer.

The magnetoelectric voltage coefficient as a function of the magnetic field for the sample CoTi50 (weight fraction of 0.5 of cobalt ferrite / 0.5 barium titanate) meas-

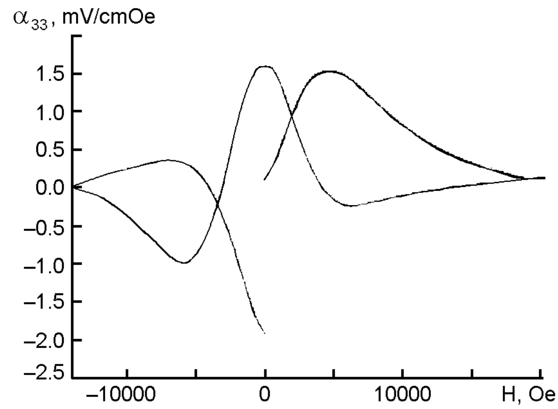

Fig. 3. ME voltage coefficient for the sample CoTi50 as a function of the magnetic field pulse.

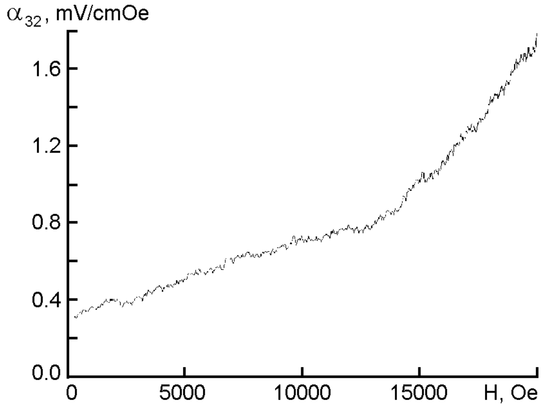

Fig. 4. ME voltage coefficient measured at 150 K in transversal mode by direct method for a single phase sample of $Bi_5Ti_3FeO_{15}$.

ured at room temperature using the longitudinal holder by the *direct method* up to the maximum positive field is shown in Fig. 2. For comparison the ME voltage coefficient measured by the *DC method* for the same sample is also included. Table summarizes the values of the maximum ME voltage coefficients obtained by the different methods.

The values for the maximum ME coefficients are found very similar, and also the shape of the curves in Fig. 2 are very close. The higher values in the case of the direct method can be related to the impedance matching. These values are in good agreement with those reported for ball-milled, and sintered $BaTiO_3/CoFe_2O_4$ composites [2, 8].

The ME coefficient, measured by the direct method using the longitudinal holder for the sample CoTi50 for the whole field pulse is shown in Fig. 3. The curve shows a complex hysteresis behavior. At low fields, α_E shows a good linearity with the field, reaching a maximum around 5 kOe, and then decreasing for higher fields. At high fields the magnetostriction gets saturated, producing almost no charge change and nearly constant electric field in the $BaTiO_3$, thereby causing a decrease in α_E [9]. The behavior shown by the curve when the field is returning to zero could be related to hysteresis and relaxation effects on both magnetic and piezoelectric components of the sample and is presently a subject of an intensive research by the authors.

Fig. 4 shows the transversal ME voltage coefficient as a function of the magnetic field for a single phase sample of $Bi_5Ti_3FeO_{15}$ measured at 150 K by the direct method. As can be noted the behavior of this single phase materials is quite different from the composites. Up to fields of 20000 Oe there is no saturation, neither a decrease in α_E suggesting a different origin of the magnetic order.

A new kind of system to measure the magnetoelectric voltage coefficient using pulsed magnetic fields has been setup. Besides the ME voltage coefficient, the system could be used to study the hysteresis and relaxation behavior of the magnetoelectric materials. Direct and AC based measurements, in transversal and longitudinal modes can be made from low up to room temperature. The system was tested with core shell particulate composites of $BaTiO_3/CoFe_2O_4$ and single phase materials. Values measured by the different methods were very close, with a maximum for the direct measurement of 1.50 mV/cm·Oe for a composition of 50 % of $BaTiO_3$.

Table. Maximum ME voltage coefficient obtained by different methods

Sample	ε_r	d_{33} (pC/N)	α_E (mV/(cm·Oe))		
			long.direct	AC pulsed	DC*
CoTi50	1165	18	1.51	1.47	1.52

* DC values were measured in a static system at TU Wien University with f_{HAC} = 1.2 kHz, H_{AC} = 4.7 Oe.

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Новий метод вимірювання магнітоелектричного ефекту в імпульсних магнітних полях

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Розроблено новий метод вимірювання магнітоелектричного ефекту в імпульсних магнітних полях. Система імпульсного поля генерує у 25-мм отворі поля до 10,0 Т з типовою тривалістю імпульсу 10 мс. Окрім намагнічування, система дозволяє вимірювати магнітоелектричний эффект як у поперечному, так і у поздовженьому напрямках. Виміряно магнітоелектричний ефект для добре відомих композитів ферит кобальту/титанат барію та для однофазних матеріалів в залежності від температури. Максимальний магнітоелектричний коефіцієнт 1,5 мВ/(см·Е) одержано для композиту, що містить 50 мас % фериту, спеченого при 1200 С. Запропоновано модель для пояснення результатів, одержаних згаданим методом.