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A new method for studying piezoelectric materials

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Résumé. — L'élaboration de matériaux piézoélectriques nécessite généralement l'application d'un champ électrique intense à un matériau isolant, afin d'y créer une polarisation permanente. Pendant cette opération, divers effets peuvent se produire et influencer considérablement les performances du transducteur obtenu. Jusqu'à présent les conditions de polarisation n'étaient déterminées que par l'expérience et le savoir-faire. La mise au point d'une technique expérimentale nouvelle qui apporte des informations directes sur la distribution de charges ou de polarisation à l'intérieur du matériau pourrait radicalement changer cette situation. Cette technique utilise l'effet de la propagation d'une onde de pression (méthode PWP) dans le matériau à tester.

Nous analyserons les divers processus qui peuvent se produire lorsqu'un champ électrique est appliqué à des matériaux isolants tels que des céramiques ou des polymères. Nous exposerons ensuite le principe de la méthode PWP et montrerons qu'elle peut conduire à des informations cruciales. Un dispositif expérimental sera décrit et des résultats préliminaires obtenus sur des matériaux pour transducteurs tels que des monocristaux de quartz, des films de polymères et des céramiques seront présentés et discutés.

Abstract. — In the preparation of piezoelectric materials, it is generally necessary to apply to an insulating material a high poling electric field. During this operation various processes can take place which can strongly influence the performances of the obtained transducer. Until now experience and know how have been the leading factors for the determination of the poling parameters. This may change due to a new experimental technique which can bring informations on what is happening in the bulk of the material. This technique uses the effect of a pressure wave propagation (PWP) in the sample.

In the present paper we will analyze the various processes which can occur while applying an electric field to insulating materials such as ceramics or polymers. We will then describe the basic principles of the PWP method and show how it can lead to crucial informations. A typical experimental set up will be presented and preliminary data obtained on such transducer materials as quartz, polymer or ceramics will be described and discussed.

1. Introduction.

In the preparation of piezoelectric materials it is generally necessary to apply to an essentially insulating material a high poling electric field. During this operation three basic processes can take place. The dipoles tend to rotate and to orient themselves, ions migrate under the internal electric field and space charge can be injected at the interfaces.

The relative importance of these processes depends on many parameters such as poling temperature, or applied electric field. The field can be created either with adjacent electrodes or with charges deposited on the material itself in a corona discharge or by electron or ion bombardment. The strength and duration of the applied field are also of great importance.

In order to get the highest possible piezoelectric

coefficients it is necessary to use poling fields as large as possible. However one must remain at values low enough to prevent electrical breakdown which would be destructive. Until now, experience and know how have been the leading factors for the determination of the poling parameters. This may change in the coming years due to a new experimental technique which can bring informations on what is happening in the bulk of the material. This technique uses the effect of a pressure wave propagation (PWP) in the sample.

In the present paper we will first analyse the various processes which can occur while applying an electric field to insulating materials such as ceramics or polymers. We will then describe the basic principles of the PWP method and will show how it can lead to crucial informations. A typical experimental set up

will be presented and preliminary data obtained on such transducer materials as quartz, ceramics or polymers will be described and discussed.

2. Effect of an electric field on an insulating material.

2.1 CREATION OF THE ELECTRIC FIELD. — In order to polarize an insulating material and to give it piezoelectric properties, it is necessary to apply a high electric field. This can be done in various ways. Electrodes can be placed on opposite surfaces of the material and a voltage difference can be applied across these electrodes. In a different technique, charges can be deposited on the material itself and the poling field is the field created by these charges. These two situations are illustrated in figures 1a and 1b for a particularly simple geometry.

Fig. 1. — Polarization of an insulating material, a) by application of a high voltage between electrodes in contact with the sample, b) by deposition of charges on a non metallized surface of the material, the other being grounded.

Figure 1a shows a plate of material to be polarized, of thickness d and relative permittivity ϵ_r , placed between two electrodes a and b. A voltage difference V is applied across a and b and creates in the sample a field $E = V/d$.

In figure 1b a similar plate has one side covered by a grounded electrode a. The other side is charged by any known technique, such as corona effect or ion or electron bombardment, with a surface density σ . These charges create in the material, as long as they stay on or near the surface, an electric field $E = \sigma/\epsilon$.

2.2 EFFECT OF THE ELECTRIC FIELD. — The applied electric field can have three basic effects which are shown respectively in figures 2, 3 and 4.

In figure 2a, one can see the orientation of the dipoles of the material. If we assume an homogeneous situation, the space charge distribution $\rho(z)$ through the plate is shown in figure 2b. It is essentially zero in the bulk of the material and is limited to surface charges on both sides of the plate. As expected this orientation process creates an induced field which tends to reduce the field in the material but to increase it at the interfaces.

Fig. 2. — a) Orientation of the dipoles of the material by the applied electric field. b) Resulting space charge distribution.

In figure 3a, one can see the second effect which can occur. Under the effect of the applied field, ions present in the material can migrate with a mobility which depends on the nature of the ion, the temperature at which the polarization is made and of course the material itself. This motion of ions produces a space charge buildup such as the one shown in figure 3b, which depends in addition to the already mentioned parameters on the duration of application of the electric field and on the nature of the interface electrode-insulating material.

Fig. 3. — a) Migration of ions produced by the applied electric field. b) Resulting space charge distribution.

An important effect of these charge migration and buildup is to create a non uniform internal electric field, in principle smaller than the applied electric field and also to increase the interface fields.

In figure 4a, one can see the third basic effect, that

is to say charge injection at the interfaces. Indeed if the interface fields or if the nature of these interfaces are such that charges can flow through them, a space charge of same polarity as that of the adjacent electrode is injected in the material. This space charge, depending on its mobility and on the trapping properties of the insulating material, can travel through the plate. In figure 4b, an example of space charge distribution is shown.

Fig. 4. — a) Injection of charges at the interfaces. b) Resulting space charge distribution.

The effect of this process is to create also a non uniform internal field, eventually larger in some regions than the applied field, but to reduce the interface fields.

In practice all these effects can occur simultaneously with different relative strengths. It is clear that they can have very unfavorable effects on the fabrication of the piezoelectric material. This is particularly clear with the third considered effect which by increasing locally the applied field can lead to destructive electrical breakdowns. But even without going to such extreme situations the simple fact that the polarizing field may not be uniform inside a sample due to space charges will lead to non uniform piezoelectric properties. Such a situation will never be at optimum since the piezoelectric coefficients measured on a sample result from the integration over the thickness of the material of all the local contributions. Ideally these local values should all be maximum.

For all these reasons it would have been of great interest to measure directly the space charge, polarization or piezoelectric activity distributions within the materials. This is now possible using a method which was proposed in 1976 [1-2] in which a pressure wave which propagates in the sample is used as a probe sensitive to these parameters.

We will now briefly describe the principle of this method and see how it can be experimentally set up.

3. The pressure wave propagation method.

3.1 PRINCIPLE. — Let us consider as shown in figure 5a a plate of an homogeneous dielectric material with zero conductivity containing space charges

Fig. 5. — Principle of the pressure wave propagation method : a short rise time compressional wave propagates in the sample at the velocity of sound v .

and permanent dipoles and having piezoelectric properties.

We assume that all the involved variables are uniform in planes perpendicular to the z axis. The charge distribution is described by a function $\rho_e(z)$. The permanent polarization can be represented by an equivalent charge distribution $\rho_p(z) = -dP/dz$. The piezoelectric activity can be represented for instance by the component $e_{zz}(z)$ of the piezoelectric stress tensor.

We now assume that at the time scales involved, the induced polarizations have an instantaneous response to electric field variations and are described by an infinite frequency relative permittivity ϵ_r . The slow variations such as those occurring during dipole reorientation and space charge migration are neglected.

At time $t = 0$, a compression is applied uniformly on the area S through electrode a, as shown in figure 5b.

The wave front z_f of the pressure p travels through the sample at the sound velocity v . Under this mechanical perturbation the atomic structure is compressed.

Three effects result :

- the charges which follow the atomic lattice are displaced,
- the relative permittivity ϵ_r varies because of the variation of the local concentration of dipoles and charges,
- charges are generated by piezoelectric effect in the compressed region.

These three effects produce a variation of the image charges on electrodes a and b which depends on the space charge distribution, on the variation of piezoelectric activity in the sample, and on the time dependence of the pressure wave.

Depending on the boundary electrical conditions applied to the electrodes, for instance open-circuit or short-circuit conditions, the variation of the induced charges produces a voltage difference across the electrodes or a current.

The evolution in time of this voltage or of this current contains an information on the space charge distribution and piezoelectric activity, the wave front of the pressure wave acting as a virtual probe travelling at the velocity of sound through the sample.

3.2 RELATIONS BETWEEN MEASURABLE VARIABLES AND CHARGE OR PIEZOELECTRIC DISTRIBUTIONS. — Using the basic laws of electrostatics and taking into account the boundary conditions and hypotheses already considered, it is possible to establish various relations between the measurable electrical variables and the space charge or piezoelectric activity distributions through the sample [2-6].

Let us first consider the case of a sample containing only space charges and a permanent polarization P , resulting in a total charge density

$$\rho(z) = \rho_e(z) - \frac{dP(z)}{dz}. \quad (1)$$

— In open-circuit conditions, the voltage difference $V(t)$ which appears on electrode b when electrode a is grounded, during the propagation of the pressure wave in the sample, can be expressed as

$$V(t) = \chi G(\varepsilon_r) \int_0^{z_f} E(z, 0) p(z, t) dz. \quad (2)$$

In this expression z_f is the abscissa of the wave front ($z_f = vt$), $p(z, t)$ is the pressure profile, $E(z, 0)$ is the initial spatial distribution of the electric field and χ is the compressibility of the material. $G(\varepsilon_r)$ is a function of the relative permittivity ε_r containing the dependence of ε_r with pressure.

— In short-circuit conditions, the current $I(t)$ flowing in the external circuit is related to the electric field distribution by

$$I(t) = \chi C_0 G(\varepsilon_r) \int_0^{z_f} E(z, 0) \frac{\partial}{\partial t} p(z, t) dz, \quad (3)$$

where C_0 is the capacitance of the non-compressed sample $C_0 = \varepsilon_0 \varepsilon_r S/d$, and S is the sample area.

These relations show that if $p(z, t)$ is known, the electric field distribution can be obtained from the measurement of $V(t)$ or $I(t)$, by resolving the integral equations (2) or (3).

The total charge distribution $\rho(z)$ is further obtained through Poisson's equation, by derivation :

$$\frac{dE(z, 0)}{dz} = \frac{\rho(z)}{\varepsilon_0 \varepsilon_r}.$$

For particular pressure profiles, equations (2) and (3) can be simplified, as follows :

— If the pressure wave profile is a step-like function of amplitude Δp , the open-circuit voltage is the image of the spatial distribution of the potential $V(z_f, 0)$

$$V(t) = - \chi \Delta p G(\varepsilon_r) V(z_f, 0) \quad (4)$$

whereas the short-circuit current is directly related to the electric field

$$I(t) = \chi \Delta p v C_0 G(\varepsilon_r) E(z_f, 0). \quad (5)$$

— If the pressure wave can be described by a short duration pulse, of amplitude Δp and duration τ , $V(t)$ and $I(t)$ give directly the spatial distributions of the electric field and charge density :

$$V(t) = \chi \Delta p G(\varepsilon_r) v \tau E(z_f, 0) \quad (6)$$

$$I(t) = \chi \Delta p v^2 \tau C_0 G(\varepsilon_r) \rho(z_f, 0). \quad (7)$$

Note that equations (6) and (7) are only valid after the complete penetration of the pulse in the sample. During this penetration, the behaviour of $V(t)$ and $I(t)$ is represented by equations (4) and (5). Moreover, if the imperfect elastic properties of the material produce a modification of the pressure wave profile during its propagation through the sample, relations (2) and (3) will preferably be used as this effect can be taken into account by a proper description of $p(z, t)$ [7].

The above results, which were obtained for a non piezoelectric material, can be adapted to the case of a material exhibiting piezoelectric properties. When a layer of the sample, extending from z to $z + dz$ is compressed in the z direction, an additional polarization dP is induced, arising from two effects.

If the unstrained material is non polarized, the elementary dipoles can be modified by the deformation of the elementary crystalline cell, creating a non zero polarization along the z axis. If a preexisting polarization P is present in the unstrained sample, originating from an orientation of the elementary dipoles, the increased concentration of these dipoles gives another contribution. Both of these effects are taken into account in the piezoelectric stress coefficient $e_{zz}(z)$, which is related to dP by

$$dP(z) = e_{zz}(z) s_z$$

where s_z is the z component of the strain.

Consequently, superficial charges equivalent to dP are induced in the planes limiting the compressed region, producing a variation $\Delta Q(z)$ of the image charges on the electrodes, proportional to the local piezoelectric coefficient $e_{zz}(z_f)$.

It can easily be shown that if the sample contains no space charge and no permanent polarization, the propagation of a pressure step at the sound velocity v creates a short-circuit current $I(t)$ proportional to $e_{zz}(z_f)$

$$I(t) = -s\chi \Delta p \frac{v}{d_0} e_{zz}(z_f) \quad (8)$$

whereas a pressure pulse induces a current proportional to the gradient of $e_{zz}(z_f)$

$$I(t) = -s\chi \Delta p \frac{v^2 \tau}{d_0} \frac{\partial e_{zz}}{\partial z}(z_f). \quad (9)$$

On figure 6, we present the expected current appearing during the transit of a pressure pulse through a sample in which e_{zz} is uniform. During the penetration of the pulse ($0 < t < \tau$), the amplitude of the signal is related to the value of $e_{zz}(z)$ by equation (8). Consequently the comparison of this amplitude to that obtained for a sample such as crystalline quartz, of known piezoelectric coefficients, permits to determine the value of e_{zz} . For times ranging from τ to the total transit time T , the current vanishes, according to equation (9). Then the pulse is reflected, due to the acoustic mismatch at $z = d_0$. If the rear surface of the sample is acoustically free, the amplitude of the reflected pulse should be twice that of the incident one.

Fig. 6. — Theoretical short-circuit current produced by the propagation of a pressure pulse in a material containing no space charge, no permanent polarization, with uniform piezoelectric coefficient e_{zz} . T is the transit time through the sample.

It is interesting to note that, in a practical case, the comparison of the amplitudes and widths of the reflected and incident pulses gives an information on attenuation and dispersion of the elastic waves in the material, for the frequencies corresponding to the main Fourier components of the pulse.

3.3 EXPERIMENTS.

3.3.1 Orders of magnitude. — It has just been shown how a pressure wave propagation could be used to scan the charge or piezoelectric profile inside an

insulating material. This scan can lead to the determination of this profile if the wave form is known. The sensitivity and the resolution of the method are directly associated with the rise time of the pressure wave.

In most materials the sound velocity can be found in the range 1 000-6 000 m/s. In polymeric materials it is typically of the order of 1 000 to 2 000 m/s and in ceramics it is typically of the order of 3 000 to 6 000 m/s. The transit time of the pressure wave depends moreover on the thickness of the sample. For instance a polymer foil 100 microns thick will give a transit time of the order of 50 ns whereas a 5 mm thick ceramic sample will give a transit time of the order of 1 500 ns. In order to obtain a good spatial resolution the rise time of the pressure wave should be a fraction of these values.

3.3.2 Generation of the pressure wave. — Various techniques can be used to generate a short rise time pressure wave. Presently, they have involved shock wave tubes [1, 8], the discharge of condensers in fluids [9], the use of piezoelectric transducers [6, 10] and the use of short rise time laser pulses [3, 4, 7, 10-13].

In the following, we will mainly be concerned with the laser technique which has been used to obtain many of the data which will be presented.

3.3.3 Laser. — The generation of high amplitude pressure waves by the impact of a laser pulse on an absorbing target originates from a rapid heating of the surface of this target. The mechanisms involved in this generation depend on the energy of the pulse, on the absorbing properties of the target and on the mechanical conditions imposed to the absorbing surface, and will be discussed in the following.

The absorbing surface must be made of a material having a high absorption coefficient at the wavelength emitted by the laser, a low thermal conductivity and a low heat of vaporization. It can be for instance a metal or carbon. Aluminium is one of the most commonly used metals. Zinc and nickel are also well suited for operation with a Nd-YAG laser emitting 1.06 μm radiation.

The choice of a laser suitable for studying charge, polarization, or piezoelectric activity distributions in insulating material is governed by two conditions. First, the homogeneity of the laser beam must be as good as possible to give a good uniformity of the pressure pulse over the whole irradiated area. For this reason, solid-state lasers are preferable to gas lasers. Second, the duration of the laser pulse must be less than a few nanoseconds, in order to permit a resolution of a few microns. The development of easily available, short-duration (typically 30 ps to a few ns) Nd-YAG pulsed lasers makes them convenient for the experiments described in this paper. The best spatial homogeneity can be obtained if the last stage of amplification is made of a Nd-glass rod.

The experimental data which will be presented in the next section have been obtained with a Nd-YAG laser from Quantel, emitting 5 mJ to 350 mJ in 3 ns, at 1.06 μm , with a beam diameter of 8 mm.

The time dependence of the pressure pulse, which can be characterized by its rise time τ_r , and its full width at half magnitude (FWHM), may differ significantly from that of the laser, and is influenced by the thickness of the target and the coupling between the target and the sample. Moreover the duration of the pulse depends strongly on the energy of the laser pulse and on the environment of the absorbing surface.

In the simplest configuration, the laser beam impinges on a bare surface in air. In this case, the width of the pulse is related to the properties of the ionized plasma created near the absorbing surface by evaporation of a small amount of material.

Depending on the nature of the target, the power density can be optimized between 10^6 to 10^8 W/cm².

In figure 7 a block diagram of the experimental set up used for these measurements is presented. The photodiode which appears on this figure is used for synchronization purposes.

Fig. 7. — Experimental set-up used for the laser-induced pressure wave propagation method.

4. Examples of experimental results.

4.1 CRYSTALLINE QUARTZ. — Crystalline quartz is an ideal material to test a method since the space charge is negligible as compared to the piezoelectric effect. Moreover the uniformity of the piezoelectric activity may be excellent.

In figure 8 we show the signal observed in short-circuit conditions on an X cut, 1.5 mm thick, quartz crystal.

The energy of the pulse was of the order of 3 mJ and the resulting power density was 1 MW/cm².

One can observe the penetration of the pressure pulse during the first 50 ns then a pure propagation for 220 ns until the pressure pulse reaches the opposite surface. It can be noticed that no space charge is

Fig. 8. — Short-circuit current during the propagation of a pressure pulse in a 1.5 mm thick quartz crystal.

present and that the piezoelectric activity is very uniform throughout the crystal.

Moreover it is clear that there is very little attenuation or dispersion of the pressure pulse during its propagation.

4.2 POLYMERS. — Many experiments have been carried out on polymeric samples. Depending on the way the material has been polarized, various structures can be observed [14-15]. A very clean method is that used by Bauer [16] in which the polarization takes place using a slowly increasing alternating voltage.

The transducers obtained in such a manner have a good spatial homogeneity as can be seen in figure 9 which was obtained with a 110 microns thick polyvinylidene fluoride foil. Figure 9a shows the signal obtained in short-circuit conditions for a propagation of the pressure pulse in one direction. Figure 9b shows the corresponding signal for the reverse direction of propagation.

Fig. 9. — Same as in figure 8, for a 110 μm thick polyvinylidene fluoride film. a) For a propagation in one direction, b) For the reverse direction of propagation.

It can be observed that the uniformity of the piezoelectricity is very good over the whole thickness of the sample.

It can also be observed that the attenuation and dispersion of the Fourier components of the pressure pulse are low enough to be neglected. The piezoelectric coefficient determined from such a curve is of the order of 70 mC/m^2 .

4.3 CERAMICS. — Various types of ceramics have been tested. In figures 10 to 12, we present some of the corresponding data.

Figure 10 shows the measurement made on a 1 mm thick plate [17]. It can be observed that the uniformity is not good. The signal is not zero during the propagation of the pressure pulse.

Figure 11 shows a typical measurement made on a X31, 2.5 mm thick ceramic transducer [18]. During

Fig. 10. — Same as in figure 8, for a 1 mm thick ceramic transducer.

Fig. 11. — Same as in figure 8, for a X31-2.5 mm thick ceramic transducer.

the first 50 ns the pressure pulse penetrates the sample then propagates for about 510 ns until it reaches the opposite surface. It can be observed that the uniformity is excellent.

The piezoelectric coefficient can be evaluated to be of the order of 2.5 C/m^2 .

Figure 12 shows a typical measurement made on a X51-05, 2.5 mm thick ceramic transducer [18]. Very similar results than those obtained in figure 11 can be observed. The uniformity is also excellent.

Fig. 12. — Same as in figure 8, for a X51-0.5-2.5 mm thick ceramic transducer.

5. Conclusion.

In the present paper we have described the principle of a new method for the analysis of piezoelectric materials.

Some examples of application have been given for crystalline quartz, polymers and ceramics. The model can be adapted [7] in the case of thick transducers to take into account the attenuation or dispersion of the high frequency Fourier components of the pressure wave during its propagation.

The method can also be used to scan laterally the transducer in order to measure its homogeneity. To do this, it is sufficient to focus the laser pulse on a localized area of the target [19].

This new method can lead to a large variety of informations ranging from the presence of space charges to the homogeneity of the piezoelectric activity.

These informations which could not be obtained until very recently can help to define the basic materials to be used in the manufacturing processes. They can also be of great interest in the definition of the various steps involved in the fabrication of piezoelectric transducers and on the poling conditions.

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