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Original Scientific Paper

Some Dielectric and Piezoelectric Properties of Lead Zirconate Titanate Ceramic in a Mixture with Formaldehyde Resin

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$Pb(Zr, Ti)O_3$ with modifiers was prepared and hot pressed with different amounts of formaldehyde resin. Such pellets were polarized in an electric field. The relative dielectric constant and the piezoelectric strain constant were then measured and the results related to the existing theories. The temperature dependence of the dielectric constant was also determined.

INTRODUCTION

The term piezoelectric texture is applied to a system composed of preferentially oriented electric dipoles causing an overall piezoelectric effect. The most frequent example of such texture is a polarized piezoelectric ceramic. In order to prepare a ceramic element, the sintering method is usually used. In 1955 some Russian authors published the results of their investigation of other types of piezoelectric textures[1]. I. S. Zheludev, one of the coauthors, investigated the properties of polycrystalline barium titanate suspended in a suitable organic binder. Zheludev showed that piezoelectric elements could be prepared in a simple way without sintering. He also found an expression for the dependence of piezoelectric properties on the concentration of ceramics.

The present paper is mainly concerned with a similar investigation of the system lead zirconate titanate in a mixture with formaldehyde resin. It is the purpose of this paper to investigate the possibility of the application of Zheludev's relation to other systems. The method of compacting with a suitable binder might be of importance for the investigation of piezoelectric properties of materials which cannot be sintered, or when it is impossible to prepare large single crystals.

EXPERIMENTAL

Samples

In order to prepare the ceramic material lead zirconate titanate, a mixture of corresponding quantities of metal oxides was used: 0.95 PbO; 0.53 ZrO_2 and 0.47 TiO_2. For modification of the ceramic material, $SrCO_3$ and Nb_2O_5 were added in quantities of 0.05 and 0.01, respectively[2]. This mixture with an addition of water (5%) was pressed under 300 atmospheres, dried and gradually heated in an alumina crucible to 850° C within 6 hours and then at 850° C and at 910° C for one and a half hour each. After that the samples were allowed to cool gradually to room temperature for 6 hours. The samples were then ground and the whole process was repeated. Pure formaldehyde resin containing some hexamethylentetramine was used as raw material for the binder. In order to prevent excessive fluidity on heating, the resin was subjected to 10% condensation and then ground.

To prepare samples of compacted ceramic material, the ceramic powder and the resin powder were mixed and hot pressed under 200 atmospheres at 170° C for 4 minutes. Pellets of 2.2 cm in diameter were obtained. A number of samples was prepared for which the ceramic - to - binder weight ratio in the original mixture was varied from 0 to 21.7. It was not possible to prepare samples with a smaller quantity of resin due to the poor mechanical strenght of the pellets. The pellets were ground to a thickness of 0.18 cm and the electrodes applied by dispersion of colloidal silver onto the faces of each pellet.

Polarization was performed in an electric field of 50 kV/cm at room temperature in a transformer oil bath for 6 hours.

Electric Measurements

For dielectric constant measurements a closed air cell equipped with an elastic sample holder was used. The interior of the cell was kept dry by means of Molecular Sieve 5A. Capacitance measurements were performed at room temperature at 1 kHz using an UM-3 bridge. Measurements of the temperature dependence of the dielectric constant were made by placing the cell in a constant temperature bath containing paraffin oil. The heating rate was about 0.5° C per minute.

The piezoelectric strain constants d_{33} were determined at room temperature by measuring the direct piezo effect under static conditions applying a force of 1 kp. The electric potential was measured by Lindemann's electrometer (0.01 V sensitivity). The sample cell was dried using P_2O_5.

Determination of Sample Composition

The sample composition is given by the relations

$$\Theta_1 = \frac{m_1 \cdot \varrho_g}{\varrho_1 \cdot 100} \tag{1}$$

$$\Theta_2 = \frac{m_2 \cdot \varrho_g}{\varrho_{2p} \cdot 100} \tag{2}$$

$$\Theta_3 = 1 - (\Theta_1 + \Theta_2), \tag{3}$$

where Θ_1, Θ_2 and Θ_3 are volume fractions of ceramic, binder and air voids respectively, while m_1 and m_2 stand for the weight percent of ceramic and binder in a pellet. The density value ϱ_g is determined from the geometry of the pellet. ϱ_1 is the theoretical density of the ceramic material and ϱ_{2p} is the pycnometric density of the binder. For m_1 and m_2 the initial values of weight before pressing cannot be used, since the weight of the binder changes during the thermal treatment. Also, a certain mechanical loss of resin occurs while pressing. Therefore the actual weight composition of all pellets had to be determined after the electrical measurements had been completed. The electrodes were removed and the binder and ceramic material content determined by TGA using an RG Electrobalance. The theoretical density was calculated from X-ray data (unit cell content and dimensions) on lead zirconate titanate of the composition $Pb(Ti_{0.47}Zr_{0.53})O_3$[3] and was found to be 8.195 g cm^{-3}. Possible changes in density due to the addition of small amounts of strontium and niobium oxide were neglected. The density of pure resin was determined by means of a Beckman Air Comparison Pycnometer Model 930. The resin samples for density measurements were prepared following the same procedure as described previously for the preparation of ceramic-resin specimens.

RESULTS

The composition of samples used in this work is shown in Fig. 1. The volume fraction of ceramic Θ_1 and voids Θ_3 in samples after pressing are plotted against the values of ceramic — binder weight ratio before pressing. It is clearly seen that an increase in ceramic content in the mixture before pressing is not followed by a corresponding increase in ceramic content of the pressed pellets. At higher ceramic contents an increase in porosity of the

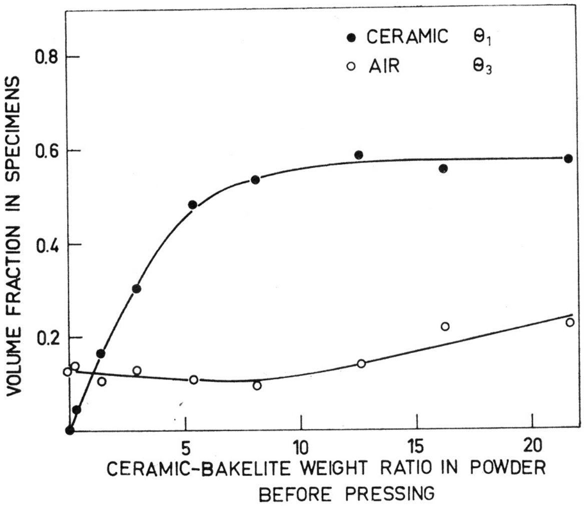

Fig. 1. Composition of ceramic-bakelite binder samples before and after pressing.

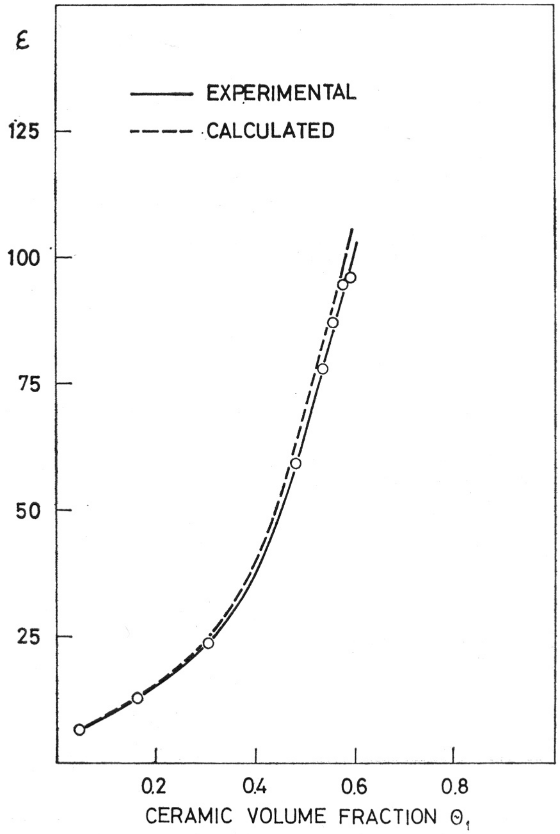

Fig. 2. Dielectric constant of samples with different concentrations of ceramic material. Comparison of experimetal and calculated values.

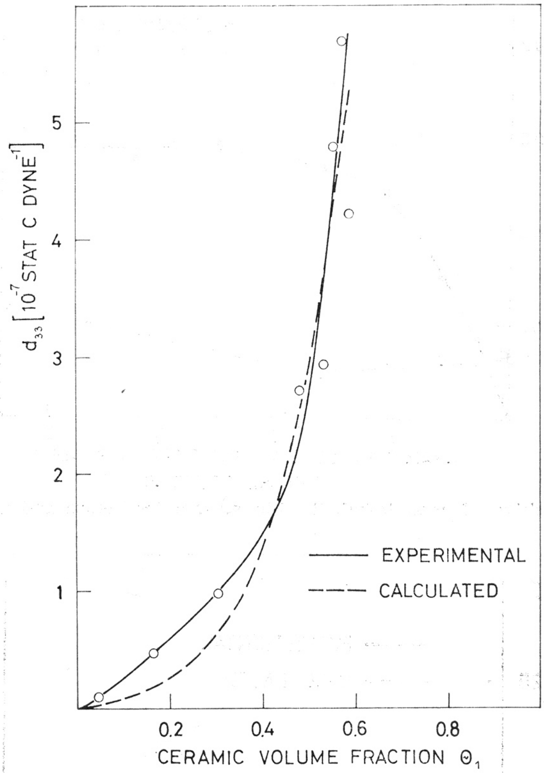

Fig. 3. Comparison of experimental and calculated values of the piezoelectric strain coustant d_{33} for samples with different ceramic content.

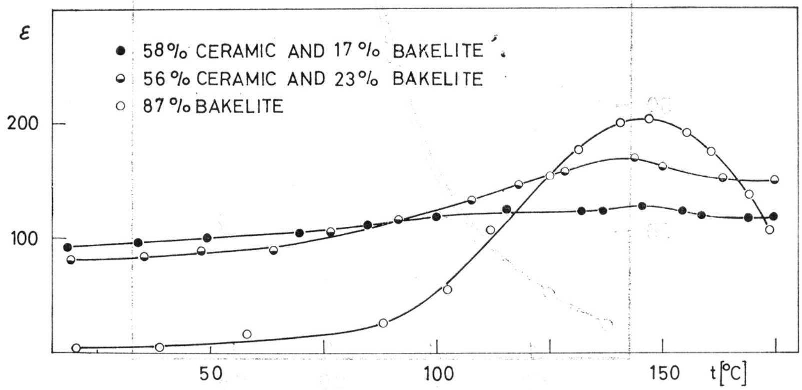

Fig. 4. Temperature variations of the dielectric constant. The composition of samples is given in volume percent. The balance are air voids.

samples is observed. Using the described method of preparation it was not possible to obtain samples with higher ceramic content than about 59% by volume.

The total error in Θ_1 for samples containing the highest ceramic concentration is less than ± 1% and increases up to ± 8.5% for samples of the lowest ceramic content. The error in Θ_3 amounts to ± 3.6% and increases to about ± 11%. In the calculation of the maximum error, errors of all variables in expressions (1), (2) and (3) were taken into account.

The results of dielectric constant measurements are shown in Fig. 2. The error of measurement for samples having higher ceramic content is about ± 3%, whereas for lower ceramic concentration it amounts to ± 19%.

The results of measurements of the piezoelectric strain constants d_{33} are shown in Fig. 3. The total error in d_{33} varies from ± 13% to 18%.

Each experimental point in Figs. 1, 2 and 3 represents the mean value for several samples.

Fig. 4 shows the temperature variations of the dielectric constant from room temperature up to about 175° C for samples having the lowest and the highest content of resin respectively. Above 175° C a slight carbonization process of the binder begins to occur.

DISCUSSION

Solid two-component systems are divided into two groups with respect to the distribution of the two components in question. The first group comprehends the so called matrix systems containing the basic medium matrix in which the particles of the other component are included. The included particles are isolated from each other by the matrix component. The systems of the second group are ordinary mixtures. In that case none of the components has a matrix character.

The dielectric constant ε of an ideal matrix system is expressed by the Maxwell relation:

$$\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\,\varepsilon_m} = \Theta_i\,\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i - 2\,\varepsilon_m}, \qquad (4)$$

where ε_m and ε_1 are the dielectric constants of the matrix and the included component respectively. Θ_i stands for the volume fraction of the included component. For ordinary mixtures, however, a Lichtenecker logarithmic expression is more suitable

$$\log \varepsilon = \Theta_1 \log \varepsilon_1 + \Theta_2 \log \varepsilon_2, \qquad (5)$$

where ε_1, ε_2 and ε are the dielectric constants of the components involved and of the mixture respectively, and Θ_1 and Θ_2 correspond to the volume fractions of the components.

In the investigation of the dielectric behaviour of $BaTiO_3$ + A, where A stands for a binder of low dielectric constant, Zheludev[1] has found that these systems follow the logarithmic expression (5) almost completely. He has also shown that this relation can be successfully applied to the three component system if air appears as one of the components. The logarithmic expression, however, fails badly if in the preparation of samples higher pressures

(5500 atmospheres or more) are applied. This causes layering within the pellets. Also, in general, this expression is not valid if the technology of sample preparation causes the formation of a matrix structure in a two component system.

In order to determine the dependence of the dielectric constant on the composition, we analyzed the possibility of fitting our experimental results to Lichtenecker's relation. For the construction of a curve according to that equation a knowledge of the dielectric constant ε_2 of the pure resin binder, and the dielectric constant of the pure ceramic material ε_1 is required. It was possible to calculate the dielectric constant ε_2 by assuming that the pressed resin is actually a matrix system of resin with included air voids. The possible presence of other gaseous components in the closed voids within the pellets was, of course, neglected. A simplified Maxwel relation[1,5] was used for this calculation:

$$\varepsilon_2 \approx \frac{\varepsilon_r}{1 - 3/2\,\Theta_a}, \tag{6}$$

where ε_r and Θ_a are the dielectric constants of the pure resin and the volume fraction of air in the same sample, respectively. The value ε_2 derived was found to be 6.4. The dielectric constant of the pure ceramic ε_1 was calculated by extrapolation for each sample according to:

$$\log \varepsilon_1 = \frac{\log \varepsilon - \Theta_2 \log \varepsilon_2}{\Theta_1}. \tag{7}$$

Here ε, Θ_2 and Θ_1 were substituted by the experimental values obtained for our samples, and ε_1 was calculated for all the samples prepared. The mean value of ε_1, neglecting some extremely high values, was found to be 1140. For our samples we could write eq. (5) as:

$$\log \varepsilon = \Theta_1 \log 1140 + \Theta_2 \log 6.4 \tag{8}$$

The plot of this function is shown in Fig. 2 (dashed line). It is clearly seen that the agreement with the experimental values is quite satisfactory.

For a two component system containing a piezoelectric and a nonpiezoelectric component, Zheludev has shown that for the piezoelectric strain constant the following relation is valid:

$$d_{33} = (d_{33})_1 \cdot \Theta_1 \frac{\varepsilon}{\varepsilon_1}. \tag{9}$$

Here d_{33} and $(d_{33})_1$ are strain constants of the system itself and of the piezoelectric component respectively. ε and ε_1 are the corresponding dielectric constants, while Θ_1 stands for the volume fraction of the piezoelectric component. Although there is no satisfactory theoretical explanation for this relation it can be successfully applied in the analysis of the system containing $BaTiO_3$.

In order to check our results, we plotted the piezoelectric strain constant d_{33} against the ceramic volume fraction Θ_1 according to the relation:

$$d_{33} = 1.04 \cdot 10^{-5} \cdot \Theta_1 \cdot \frac{\varepsilon}{1140} \tag{10}$$

The piezoelectric strain constant of the »pure« ceramic $(d_{33})_1$ was calculated using the same procedure as for the dielectric constant ε_1 in the derivation of eq. 8. Θ_1 and ε were substituted by the experimental values obtained for the samples. It is obvious from Fig. 3. that the experimental and the calculated curves are only in partial agreement. Considerable differences are noted for lower values of Θ_1.

The temperature variations of the dielectric constant were measured in order to find the upper applicability limit for the specimens prepared. The results obtained show that the binder causes a faster increase of the dielectric constant at temperatures up to 70^0 C. The temperature variations of the dielectric constant for a pure binder has a rounded maximum at about 145^0 C. The influence of the binder on the dielectric constant of samples with low binder content (17 volume %) is insignificant.

The described investigation of the dielectric and piezoelectric properties of the prepared samples shows that the samples are typical two-component mixtures and not matrices. Using Lichtenecker's relation it is possible to determine the dielectric constant of pure ceramic by extrapolation. For the piezoelectric properties, however, the extrapolation is not so accurate, and can give only approximate information about the properties of a component.

The described piezoelectric elements are also of practical importance. Samples containing in the average 57% of ceramic by volume have a piezoelectric strain constant $d_{33} = 5.7 \cdot 10^{-7}$ stat C din^{-1}. This is roughly 10 to 20 times lower than the same constant of comercial, sintered ceramics but it is almost 10 times higher than the corresponding strain constant of a quartz single crystal piezoelectric element.

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IZVOD

Neka dielektrična i piezoelektrična svojstva keramike plumbum(II)-cirkonat-titanata u smjesi s formaldehidnom smolom

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Keramika $Pb(Zr, Ti)O_3$ modificirana dodatkom malih količina $SrCO_3$ i Nb_2O_5 priređena je žarenjem smjese oksida na temperaturi od 910^0 C. Umjesto daljnjeg sintrovanja keramika je prešana uz dodatak fenolformaldehidne smole pod tlakom od 200 atmosfera na temperaturi od 170^0 C. Uzorci različitog sastava od 0 do 59 vol. % keramike polarizirani su u polju od 50 kV/cm na sobnoj temperaturi u trajanju od 6 sati.

Relativna dielektrična konstanta, mjerena u smjeru prešanja tableta, zavisi o koncentraciji keramike i smole prema Lichteneckerovoj logaritamskoj formuli. Mjerenje temperaturne zavisnosti dielektrične konstante od sobne temperature do cca 175° C pokazuje neočekivan porast dielektrične konstante iznad 70° C koji je uzrokovan vezivnom smolom.

Rezultati mjerenja piezoelektrične konstante deformacije d_{33} statičkom metodom u zavisnosti od koncentracije keramike u uzorcima tek se djelomično slažu s formulom Želudjeva za dvokomponentne piezoelektrične teksture.

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