COBALT DOPING OF BARIUM TITANATE CERAMIC

VARAN SINGH

Defence Science Laboratory, Delhi.

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Pure barium titanate ceramic cannot be used as underwater transducer where high electric fields of the order of 1 K. V./cm. are applied across the two faces of the ceramic. High field dielectric losses are reduced by the addition of small percentage of cobalt to barium titanate ceramic. Dielectric constant of cobalt doped barium titanate ceramic as a function of temperature shows a marked change over plain barium titanate ceramic.

Pure barium titanate ceramic cannot be used as a transducer material for underwater work because of such factors[1] as (*a*) second transition point which lies at 10°C (*b*) loss of remanent polarization and (*c*) high field dielectric losses. By the addition of 5 per cent calcium or lead in the form of calcium or lead titanate as impurity to the ceramic, the remanent polarization can permanently be retained and second transition point shifted below 0°C. Barium calcium titanate composition exhibited high field dielectric losses[2] of the order of 0·1 at 1 K.V. r.m.s./cm. It was reported in a U.K. provisional patent[3] that the addition of small percentage of cobalt to barium-lead titanate composition produced a large reduction in high field losses. Berlin Court[4] reported that the addition of cobalt improved piezo-electric properties but with the evidence of increased aging rates. A composition of barium titanate ceramic containing 5 per cent calcium or lead titanate and 0·75 per cent cobalt was recommended by Schofield and Brown [2,5] to be used as underwater transducer material.

This paper describes the preparation of barium titanate ceramic with cobalt doping (0·75 per cent) and compares its characteristics with pure barium titanate ceramic and barium titanate ceramic containing 5 per cent *Ca* or *Pb* and a small percentage of cobalt.

MATERIALS AND METHOD

Normally $Ba\ TiO_3$ is prepared by heating *Bao* and TiO_2 . In this process, however, a unimolecular ratio of *Ba* and *Ti* is not achieved. In studying the effect of doping it was considered necessary to prepare $BaTiO_3$ in pure form *i.e.* with unimolecular ratio of *Ba* and *Ti*. Pure $BaTiO_3$ was prepared chemically by the method of Clabangh *et al.*[6]

Preparation of barium titanate powder containing exactly equal molar ratio of barium and titanium

As a first step Barium Titanyl oxalatetetrahydrate $Ba\ TiO\ (C_2O_4)_2\ 4H_2O$ was obtained by adding slowly aqueous solution of Titanium tetrachloride ($TiCl_4$) and barium chloride to a hot solution of oxalic acid containing about 10 per cent more of the acid. $TiCl_4$ and $BaCl_2$ was made nearly in equimolar proportion with barium in slight excess. The slight excess of Barium and somewhat greater excess of oxalic acid were intended to minimise competing reactions that might result in the formation of insoluble partially hydrolysed compounds of titanium. Procedure in one batch is given below:

(1) 41 gm. of $BaCl_2$ were dissolved in 400 c.c. of distilled water and to it were added 200 c.c. of $TiCl_4$ (15%). 46 gm. of oxalic acid were dissolved in 250 c.c. of distilled water in one litre beaker. $TiCl_4 + BaCl_2$ mixture was added to this oxalic acid slowly drop by drop. The oxalic acid was kept in waterbath at 80°C. A mechanical stirrer was employed. The white cyrstalline precipitate was washed with cold water several times and dried. This was kept in a furnace at

950°C for about 12 hours. The double oxalate decomposed and gave the necessary barium titanate powder. It was chemically analysed as 99·8%. X-ray photo-graph taken on a Debye Scherrer camera showed a tetragonal structure with $a_0=3 \cdot 99$ and $C_0=4 \cdot 04$. These values compare favourably with the standard values $a_0=3 \cdot 994$ and $C_0=4 \cdot 038$.

(2) 60 gm. of $BaTiO_3$ powder was mixed thoroughly with 1·903 gm Cobalt acetate. A little ammonium hydroxide, tannic acid (1%) and citric acid (1%) were added to the mixture. The mixture was thoroughly mixed in a ball mill for about one hour. The wet filter cake was dried at 110°C. The powder was tempered with 3c.c. of a 10 per cent solution of polyvinyl alcohol per 50 gm. of the powder. Dampened mixture sufficient for a disc (1″ dia., 0·18″ thick) was charged into a mould and pressed at 8000 p.s.i. These discs were kept on Zirconia powder in a silica dish in a furnace. The temperature was raised within one hour to 1000° C and then increased by 100°C per hour upto 1400°C. After maintaining this temperature for about an hour, the furnace was switched off. The fired discs were polished and given a very thin coat of conductive silver and fired to 700°C.

Polarization—With the specimen discs immersed in transformer oil bath an electric field of the order of 24 K.V./cm. was applied across the electrodes of the discs to polarize them at room temperature.

EXPERIMENTAL PROCEDURE

R.F. bridge type 916, which is a Null instrument for use in measuring impedances at frequencies varying from 50 k.c./s. to 5 m.c./s., was used to determine impedance. The low frequency limit is mainly determined by sensitivity considerations. Electrical energy at different frequencies was fed to the ceramic mounted in a suitably designed brass holder, from well shielded type 1330-A Bridge Oscillator (Fig 1). Impedance was directly read from R.F. bridge after finding out Null point by bringing to minimum the deflection of the needle of Unit Null Detector (Type 1212), whose sensitivity is of the order of 1—10 μ v. R.F. bridge, Oscillator and Null Detector should, in general, be grounded at a single point through as low reactance as possible.

Fig. 2 gives reactance of the ceramic as a function of frequency polarized at room temperature with high d.c. field (24 K.V./cm.) applied across its electrodes.

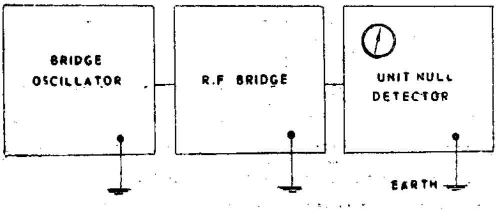

Fig. 1—Block diagram of bridge oscillator, R.F. bridge and Unit Null Detector to measure impedance.

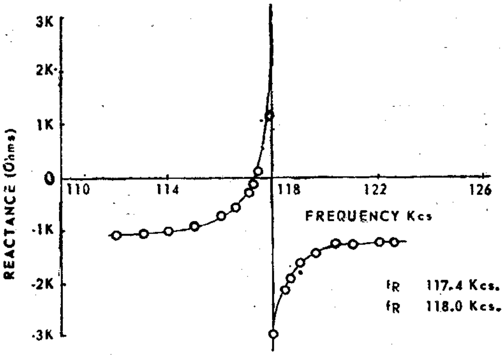

Fig. 2—Reactance of Co-doped bariumtitanate ceramic as a function of frequency.

The electromechanical coupling coefficient (k) which is defined as the square root of the ratio of mechanical energy stored to electrical energy supplied, is obtained by the formula

$$k^2 = \frac{\pi^2}{4}\cdot\frac{\Delta f}{f_R}\left[1 + \left(\frac{4-\pi^2}{4}\right)\cdot\frac{\Delta f}{f_R} + \left(\frac{\pi^2-4}{4}\right)\left(\frac{\pi}{4}\right)^2 \times \left(\frac{\Delta f}{f_R}\right)^2 + \cdots\right]$$

Values of f_R (resonant frequency), f_A (Anti-resonant frequency) and $(f_A - f_R) = \triangle f$ are known from Fig. 2.

The value of k came out to be 11·2 per cent for ceramic (dia. 2·52 cm., thickness 4·5 mm.). In order to obtain high value of k, it is proposed to use improved manufacturing techniques and hot polarization which is done by allowing the ceramic to cool down through curie point with a high d.c. field (10K.v./cm.) applied across its electrodes with the specimen immersed in silicone or transformer oil bath. Hot polarization technique is more satisfactory than room temperaure polarization. Shamro[7] has adopted a slightly different method by polarizing ceramics at temperatures 5 to 10°C below curie point. This is also known as hot polarization but differs from hot polarization as described previously. In this case, electric field is removed at polarization temperature after which the specimen is maintaned at a given temperature for one hour. In hot polarization where the ceramic is allowed to cool to room temperature when exposed to high d.c. field, a considerable part of piezo-electric modulus is lost. In polarization method as described by Shamro where the field is removed at high temperature piezoelectric modulus is stable. Hence the ceramic is more suitable to be used as electromechanical transducer.

The maximum power which oscillator could deliver into a load of 50 ohms, was 500 milliwatt. This was insufficient for working of the ceramic as a transducer, *i.e.* conversion of electrical energy into accoustical energy.

The dielectric constant (Fig. 3) has been plotted as a function of temperature after finding out its value from static capacity which was determined from precision capacitance bridge type 320 at 800 cps. Dielectric constant K is given by the formula :

$$K = \frac{t \times c}{\cdot 088 \quad \pi r^2}$$

where t=thickness in cm.

c=capacity in $\mu\mu f$

r=radius in cm.

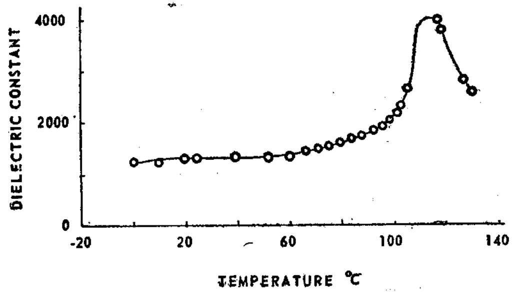

Fig. 3—Dielectric constant of Co-doped bariumtitanate ceromic as a function of temperature.

At a phase transition the characteristics of a material usually change abruptly. In $BaTiO_3$ ceramic at each of three phase transition temperatures the dielectric constant exhibits a maximum. A comparison. between two curves (*a*) Cobalt-- doped and (*b*) plain barium titanate ceramic shows that the value of dielectric constant is considerably reduced at the curie point by the addition of Cobalt but change is negligible at room temperature Addition of cobalt brings down the curie point which in case of pure ceramic is 120°C. Curie peak is considerably broadened. A comparison of cobalt-doped $BaTiO_3$ and pure $BaTiO_3$ ceramic with $Ba\text{-}CaTiO_3$ containing cobalt shows that the addition of Ca or Pb brings down second transition point from 10°C to a temperature below 0°C.

DISCUSSION

The low value of electromechanical coupling coefficient and dielectric constant are due to aging[8] effects since the samples have been put to test after two years of polarization. Dielectric constant and electro-mechanical coupling coefficient decrease by about 15% during the period of a year and stabilise later on. It has earlier been reported that the addition of small quantities of cobalt to barium titanate produces improvement in piezoelectric qualities and reduction in dielectric loss tangent in high a.c. field; other characteristics are little affected by the addition of cobalt to the basic composition. 0·75 per cent by weight of cobalt has been shown to be an optimum composition to attain desired effects.

The mechanism whereby the addition of cobalt to barium titanate composition decreases high field dielectric loss is not fully understood. Further evidence that the addition of cobalt has some basic effect on the structure of ceramic lies in the variation of dielectric constant with temperature. The curie temperature is decreased but the curie peak is considerably broadened. It appears that the addition of cobalt has caused phase transition from tetragonal to cubic to be less clearly defined and takes place over a wider temperature range.

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