Barium Titanate Ceramics and their Applications

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1. INTRODUCTION

The years have passed since barium titanate was discovered. The discovery posed new problems to physics of matter and the studies on them made great contributions to the world of ferroelectricity. In fact, the discovery of barium titanate led to a series of discoveries of many new ferroelectric substances, on which interesting studies, both experimental and theoretical, have been carried on. The discovery of barium titanate is most significant in that it is useful from the technological point of view. Barium titanate as one of the ferroelectric materials corresponding to ferromagnetic materials is opening up new fields of technology with their very promising future. It was used at first as dielectrics, i.e. condenser materials, and has now established its indisputable position as condenser materials for high frequency circuits. Moreover, the excellence of its piezoelectric properties is unsuprassed by any other piezoelectric material. Therefore, it is now beginning to be used for electro-mechanical transducers or electro-acoustic transducers and will surely gain very wide fields of application in future. This report is an outline of the characteristics and applications of barium titanate.

2. PROPERTIES OF BARIUM TITANATE CERAMICS(1)~(8)

(1) Dielectric Property

As the examples of Fig. 1 show, the dielectric constant of pure barium titanate ceramics has a value of 1500～2000 at room temperature and reaches 6000～10000 at Curie point near 120°C. They have ferroelectricity at temperatures below Curie point but lose it beyond the point. Therefore, the dielectric loss suddenly drops at temperatures near Curie point, beyond which the loss is generally small. It is also recognized that the Curie-Weiss law holds good between the dielectric constant beyond Curie point and the temperature.

The dielectric constant and dielectric loss of barium titanate ceramics are greatly affected by the applied field and vary with the frequency to some extent. It is necessary, therefore, to determine the applied field and the frequency as well as the temperature in order to ensure accuracy in describing the dielectric constant or dielectric

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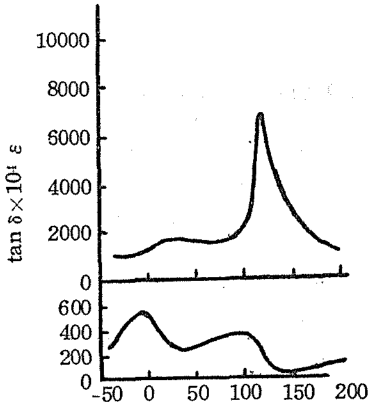


Fig. 1.

loss. Because of the great influence of the applied field, the variations in dielectric constant by biasing field are utilized in dielectric amplifiers. But the influence of frequency is rather small ; it is comparatively large in low frequencies below 10 kc but almost negligible in high frequencies up to about 100 mc.

(2) Electrostrictive and Piezoelectric Phenomena[4][5][7]~[9]

When the electric field is applied to crystals of barium titanate, the domains line up and crystals expand parallel to the field and contracts perpendicularly to the field. Therefore, in ceramics which are polycrystalline substance, the expansion and contraction when domains line up with 100% perfection, should theoretically be 0.67% parallel to the field and 0.33% perpendicular to the field. But in such field intensities as will not cause dielectric breakdown (30~40 kv/cm), the experimental values are smaller by a little more than one order.

Bariun titanate ceramics are aggregate of fine crystals and originally isotropic, but the applied field causes polarization parallel to the field and the piezoelectric phenomena. Once high voltage is applied, polarization remains even after the field is removed, and the ceramics continue to act as piezoelectric material for ever. But when the inverse field is applied, or heated beyond Curie point, the polarization decreases or disappears and the piezoelectric properties are lost. These facts are similar to those of the magnetization of ferromagnetic materials, and the coercive force of pure $BaTiO_3$ ceramics is presumably 5~6 kv/cm. But the time required for magnetization is very short in magnetic materials, while that for barium titanate is comparatively long, the polarization being insufficient if the time is too short. Fig. 2 shows the degrees of polarization according to time with the applied field as parameter. Table shows a comparison between the piezoelectric properties of barium titanate and those of quartz, Rochelle salt, etc. It is amazing that the former, though being aggregate of fine crystals, shows such a large piezoelectric modulus.

Table

Crystal Type	Mode	d	g	ε	κ
Rochelle Salt	Lateral	165	0.093	200	0.54
Quartz	{Parallel / Lateral	2.3	0.058	4.5	0.10
A.D.P.	Lateral	24	0.177	15.3	0.28
$BaTiO_3$ Ceramic	Parallel	190	0.0125	1700	0.46
	Lateral	78	0.0052	1700	0.19

d : Piezoelectric modulus (10^{-12} meter/volt)
g : Voltage output coefficient (volt-meter/newton)
ε : Dielectric constant
κ : Electro-mechanical coupling coefficient

(3) Electrostrictive Vibration

In barium titanate ceramics, when the electric field is applied or once polarized under large field, can be produced electrostrictive vibration as in the case of quartz. As to the modes of vibration, there are longitudinal length mode, radial mode, longitudinal thickness mode and shear mode, though the last mentioned is rather difficult to realize because in this mode the direction of ramanent polarization and that of the fileld should not be parallel. The characteristics of electro-mechanical coupling coefficient versus D.C. biasing field in these modes of vibration are shown in Fig. 3.[4] The coupling coefficient is largest in longitudinal thickness mode.

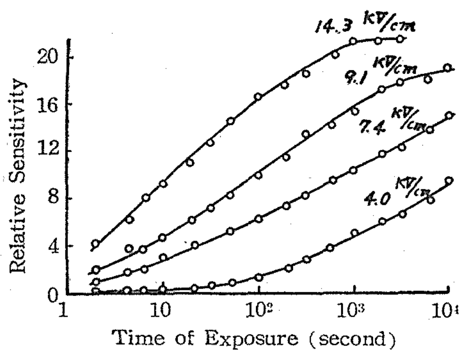


Fig. 2.

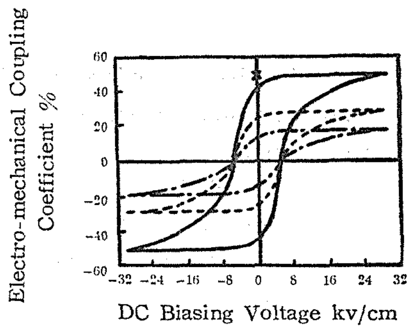


Fig. 3.

—— : Longitudinal thickness mode
...... : Radial mode
-·-·- : Longitudinal length mode
× : Shear mode

Young's modulus E, Poisson's ratio σ and density ρ in barium titanate ceramics have the following values though they may be slightly different depending on how the materials are prepared :

$$E = 0.97\sim1.12\times10^{12} \text{ dynes/cm}^2 \text{ (at 20°C)}$$
$$\sigma \cong 0.27$$
$$\rho \cong 5.5$$

Therefore, the frequency constant is 210~225 kc-cm for longitudinal length mode, 140~150 kc-cm for radial mode and 235~255 kc-cm for longitudinal thickness mode.

In obtaining high intensity acoustic power by the use of electrostrictive vibration of barium titanate ceramics, the biggest problem is the question of power limit. This limit generally depends on the elastic limit of the ceramics. Let us take up the case of radiating sound waves into liquids. The acoustic power P can be expressed as follows ;

$$P = \frac{1}{2}\,\frac{\rho_1 V_1}{\rho_0^2 V_0^2}\,(\Delta p)^2$$

where ρ_1 and V_1 are the density and sound velocity, of the liquid and ρ_0 and V_0 are that of barium titanate ceramics; $\triangle p$ is the maximum stress in the interior of the vibrator and must be smaller than the mechanical strength of the vibrator. In the case of water,

$$\rho_1 = 1, \quad V_1 = 1.5\times10^3 \text{ m/s}$$

Therefore,

$$P = 1.22\,(\Delta p)^2\times10^{-8}$$

If, for instance, the allowable maximum stress of the vibrator is 100 kg/cm^2,

$$P \leqq 1.22\times10^8 = 12.2 \text{ watt/cm}^2$$

When statically measured, the mechanical strength of barium titanate ceramics is much larger than this, but not so large a value can be expected when the irregular distribution of stress in vibrating state is taken into consideration. The above value seems to be a safe limit.

As a method suitable for obtaining a very strong sound field, it can be considered to prepare, for instance, a disc vibrator having spherical surfaces or a hollow cylindrical vibrator and make the polarization axis concentrate in the center of sphere or the axis of cylinder. The easiness with which this method can be put to practcal use is a useful feature of barium titanate ceramics, which no other piezoelectric materials can surpass and which promises wide applications in future.

As has already been mentioned, the coercive force of barium titanate ceramics is usually 5~6 kv/cm. Therefore, polarized ceramics can be used in weak field without trouble, but when they are continuously driven at high voltage, there arises a fear of depolarization. Especially when they are continually used and the temperature rises to a considerable point as in the case of generation of high intensity supersonic, they had better be used in a state where D. C. bias is applied. On the other hand, studies are being conducted on materials of large coercive force. For instance, the solid solution mixed with several per cent $PbTiO_3$[9] does not depolarize so much even in the inverse field of 25 kv/cm, as is shown in Fig. 4 ; the coupling coefficient is also large. Therefore, it is suitable as an electro-mechanical transducer. This requires, however, the process of cooling in electric field, which makes the first process of polarization a little more complicated.

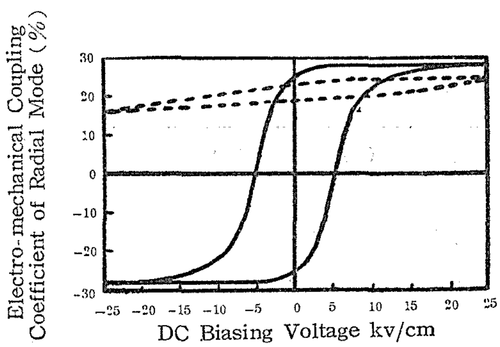


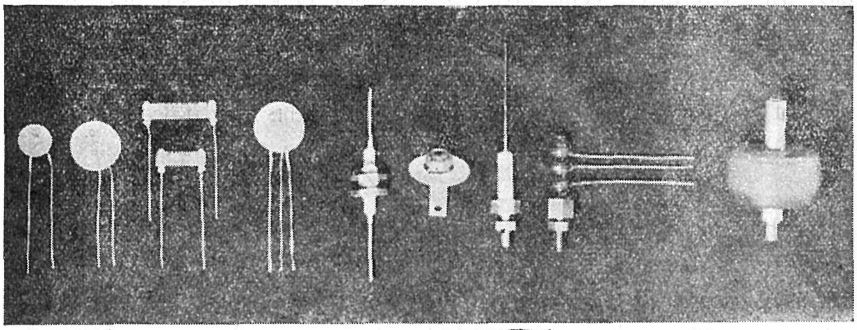
Fig. 4.
——— : $BaTiO_3$ ceramic
...... : (Pb 4% Ba 96%) TiO_3

3. APPLICATION AS CONDENSER MATERIALS

The uses of barium titanate ceramics as condenser materials are considerably limited by the fact that their dielectric constant, though quite large, is much affected by temperature and electric field and that the dielectric loss is pretty large. But their reliability as condenser materials is high enough in their mechanical strength, puncture voltage, insulation resistance, resistance against heat and humidity, etc., so that they are used in the fields where their shortcomings in capacity tolerance or dielectric loss become much less important. For instance, as condencers for coupling, bipass, and filter. Moreover, they are indispensable as components of high frequency circuits as they are small in size and the inductance of elctrode can be made very small.

As condenser materials, nearly pure $BaTiO_3$ ceramics (whose Curie point is around 120°) are generally good for practical purposes because their temperature characteristics are flat around room temperature. But their dielectric loss is comparatively large and the value of dielectric constant actually used is low (1500~2000), so that solid solutions are also used in which Curie point is shifted to the neighborhood of room temperature by adding some other substances.

As to the structure of $BaTiO_3$ ceramic condensers, there are (a) disc type, (b) cylinder type, (c) composition type, (d) feed-through type, (e) grounded type, etc. The examples are shown in Fig. 5. The capacity of those actually manufactured is up to about 0.1 μF. (f) is an example of a condenser suitable for the filter circuit of the high tension source of television. The capacity is 500 pF, and the working voltage is 10~20 kv.



(a) (b) (c) (d) (e) (f)

Fig. 5.

4. APPLICATION OF FERROELECTRICITY

(1) Dielectric Amplifier[(10)~(14)]

As ferromagnetism is utilized in magnetic amplifiers, ferroelectricity can be used for amplifiers on the same principle, and such amplifiers are now attracting attention. The D-E curve of $BaTiO_3$ ceramics has saturation characteristics as are shown in Fig. 6, so the reversible permittivity, i.e. the dielectric constant measured by A.C. of small amplitude shows the characteristics as in Fig. 7. Therefore, the current of the circuit i is controlled by the variation of biasing field E_0 as is evident from Fig. 8. In this case, the value corresponding to g_m of vacuum tube can be shown as $\omega E_m(dC/dE_0)_{E0}$ and becomes a very large value when the frequency of source is high. With well-chosen materials and circuits, the power gain reaches 10^6 per one stage.

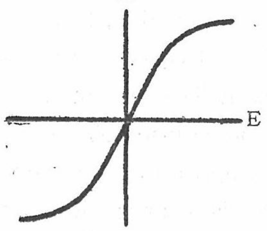
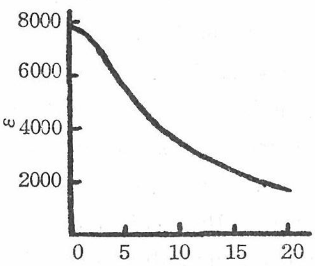


Fig. 6.



DC Biasing Voltage KV/cm

Fig. 7.

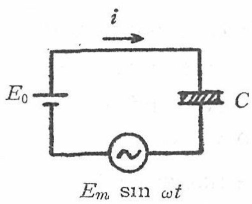


Fig. 8.

As to materials, those with a steep inclination of ε-E curve of Fig. 7 are desirable, and the inclination becomes steepest around Curie point. This explains the use of solid solutions whose Curie point is shifted near room temperature as has already been mentioned. But the temperature variation around Curie point is so large that some materials which are specially made flat in temperature characteristics or the combination of more than two condensers with different Curie points are used in order to improve temperature characteristics. In special circuits, however, it is desirable to increase stability by the use of thermostat.

Amplifiers of this kind, as in magnetic amplifiers, do not require filament heating and are stronger, smaller in size, and higher in reliability and efficiency than vacuum tubes ; amplification of high gain is possible from D. C. to radio frequency ; and the cost is cheaper. These are the merits which promise wide uses. On the other hand, the necessity of A.C. source, poor stability against temperature, and hysteresis phenomena limit the uses. But these amplifiers are considered to display their merits in amplifying relay circuits, servomechanism and other on-off circuits.

(2) Other Uses

Recently attempts have been made in Bell Laboratory to use barium titanate in digital computers and other memory devices. The dielectric characteristics required for elements of memory circuit are that they should have a rectangular hysteresis loop and their coercive force should be small. As ordinary $BaTiO_3$ ceramics do not have these characteristics, single crystals are used. A good crystal saturates at about 200 volt/mm and draws a rectangular hysteresis loop. Condensers with such crystals as dielectrics, when given a pulse of a certain direction, are polarized and almost all the polarization remains. This means that they have a very small capacity for a pulse of the same direction, but a very large one for a pulse of inverse direction and turn into another stable state which makes possible the memory action. With crystal plates about 0.1 mm thick, they saturate at a pulse of about 20 volt peak, which makes them highly practical.

5. APPLICATION AS PIEZOELECTRIC MATERIALS

(1) Application in Supersonic Devices(16)(17)

The supersonic vibrators which have been used so far are magnetostriction vibrators of Nickel, Alferro, etc. or electrostriction vibrators of quartz. But barium titanate ceramics have striking features superior to any of the above and their future is very promising. The possible uses can be divided into three : (i) underwater supersonic devices such as depth sounder, sonar, and fish finder, (ii) supersonic devices such as flaw detector and thickness detector and (iii) powerful supersonic devices for causing physical or chemical action by energy of supersonic.

(i) Underwater supersonic transducers. For underwater supersonic vibrators, the Langevin type structure of historic fame is efficient in barium titanate ceramics also. The excellence of barium titanate ceramic vibrators of this type was proved in Japan in 1951 and has already been put to practical use. Fig. 9. shows the structure of a typical one in which steel plates are adhered to both sides of one ceramic plate. At present they are used mainly as transducers of fish finders, but their uses are widening for depth sounders or sonars. Large-sized, rectangular and other kinds of vibrators are being trially manufactured and studied. In cylindrical kinds, it is easy to make the diameter up to 100 mm. As for frequency, those of 20 kc to several hundred kc are manufactured.

Fig. 9.

Vibrators of this kind have to be made water-proof so that they may be used in the water. Possible methods include metal-casing and rubber-wrapping, of which the latter is better both in theory and in practice. As the internal loss of vibrators of this kind is much smaller than that of magnetostrictive vibrators and the electro-acoustic efficiency reaches as high as over 80%, they are useful for economizing electric power, for making devices smaller and simpler and other purposes.

Though the above description concerns the Langevin type vibrators only, those of other structures are of course possible. For instance, hollow cylindrical vibrators are actually used and will be used more widely in future as the value of Q in the water can freely be chosen by changing the wall thickness.

(ii) **Supersonic flaw detector.** As is well known, supersonic flaw detectors or thickness detectors are widely used as important non-destructive testing devices, in which at present only quartz is used for transducers. Recent studies on substituting quartz with barium titanate produced very good results which, however, have not yet been widely used. Concerning the flaw detector, here is one example of experimental data at 500 kc～1 mc : In devices where quartz has been, the following improvements are made when the vibrators are replaced with barium titanate. When only transmitter is replaced, the gain is about 20 db ; when only receiver is replaced, 15 db ; and when both are replaced, the sensitivity improves by about 35 db. In thickness detectors also, similar improvements in sensitivity are observed. But these improvements in sensitivity are not due to the difference in efficiency of vibrators but can be considered to be due to the easiness or difficulty of practical use owing to the material constants such as dielectric constant and piezoelectric modulus. That is, $BaTiO_3$ vibrators are much lower in impedance than qnartz vibrators, and work at low voltage, making impedance matching easier.

Flaw detecting is very often required for cylindrical or hllow cylindrical samples, for which it is desirable to give a curved surface to the vibrator. Barium titanate is ideal in this respect ; the vibrator can easily be given any curved surface. Therefore, wide uses are expected in future.

(iii) Generation of powerful supersonics. Physical and chemical actions of supersonics have long been studied and many interesting sesults have been obtained, but they are not so much used industrially as yet. This may be ascribed to the lack of powerful supersonic generator, both stable and economical. In the past, magnetostriction vibrators and quartz vibrators have been used for low and high frequencies respectively, but the former are not suitable for high frequency because of their large internal loss, and in the latter, it is difficult to obtain a vibrator of large size because quartz is a natural product. Barium titanate ceramics seem to have removed these shortcomings and enhanced the possibility of industrial uses of supersonics. But they are as yet in an experimental stage with few examples of actual uses. The practical merits of barium titanate include, as has already been mentioned, large dielectric constant and piezoelectric modulus, low impedance and action at low voltage, which make it easy to insulate vibrator holders or feeders and reduce the loss. That the vibrator can be given any curved surface in a very important feature in this case also. Vibrators of various shapes are manufactured and used in order to increase intensity of acoustic pressure. In a vibrator which has spherical surfaces, it is possible to make the intensity of acoustic pressure in the center about 1000 times as that near the vibrating surface. In large and powerful vibrators, the heat generated in the interior is apt to cause irregularity of stress distribution. It is advisable, therefore, to divide the vibrating plate in order to ensure cooling and at the same time to avoid large stress.

Supersonic soldering and supersonic cutting are now being industrialized, in which magnetostriction vibrators are used at present. For this purpose, however, electrostrictive vibration of barium titanate can be considered more efficient.

(2) Audio Frequency Acoustic Devices[18]~[20]

Barium titanate ceramics are already used as transducers for pick-up, microphone, etc. The usual structure is that thin ceramic plates (thickness 0.2~0.3 mm) are adhered to both sides of a metal foil symmetrically to make a bimorph, and used as bending type. The size of bimorph is 1.5~3.0 mm by 15~25 mm, small enough to gain good frequency characteristics. This, together with good humidity characteristics, is valued very highly in the acoustic world. The sensitivity is considerably lower compared with Rochelle salt, but it is possible to obtain the out-put of about 0.5 volt as a pick-up.

(3) Measuring Devices

As transducers of measuring devices, extensive uses are considered. Pressure gauge, accelerometer[21] and others are in a trial stage. As pressure gauge, there are very wide uses, such as the measuring of water pressure or rail pressure. Usual structures of transducers are compression type and bending type. By compression type is meant that pressure acts perpendicularly on both sides of the ceramic plate ; bending type is either a bimorph structure as is described above or a structure similar to bimorph, in which one of the ceramic plates is replaced by metal. As barium titanate ceramics are isotropic in all directions perpendicular to the polarization axis, the use of discshaped bimorph is especially efficient.

For accelerometers, small vibrators are used whose structure is similar to the Langevin type mentioned above. One metal end of the vibrator is fixed on the object measured, and the other gives pressure proportional to acceleration to the piezoelectric material. In measuring small acceleration, a weight is attached to one end of bimorph and the other end is fixed on the object measured.

An application as standard vibration generator was first tried in Japan. Fig. 10 shows its vibrator. Four ceramic plates, 5 mm thick and 100 mm in diameter, with thin metal plate in their middle and two thick metal plates adhered on both sides--all these are put together as one block. The lowest resonant frequency is about 20 kc, and up to this frequency, amplitude proportional to voltage can be obtained. This vibration bed is used for measuring the resonant frequency and vibration mode of jet-turbine blades, etc. It was designed by the writer in collaboration with The Government Mechanical Laboratory of The Agency of Industrial Science and Technology, and is now used in the laboratory with very good results. With a little modification, it can be made a fatigue testing device.

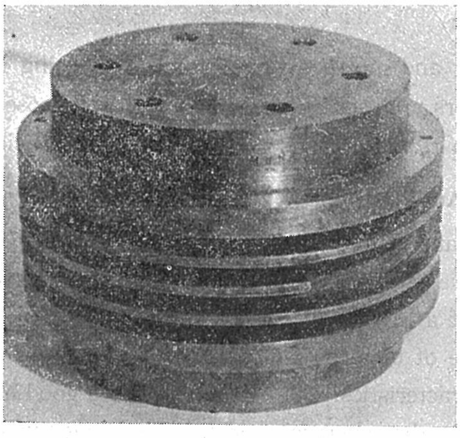


Fig. 10.

(4) Other Uses

Attempts heve been made to use barium titanate ceramics as driver or pick-up by attaching them to other vibrators and good results have been obtained when applied to tuning forks or vibration reeds which were formerly driven magnetically. For instance, the vibrator itself need not be ferromagnetic ; moreover, as the driver can be attached directly to the vibrator, the problem of supporting the vibrator becomes very simple ; the size can get very small, too. The success in these applications is considered due to the fact that barium titanate ceramics are easy to handle and high in reliability.

6. CONCLUSION

The above is an outline of the properties and applications of barium titanate ceramics. The writer is afraid that he has put too much stress on their merits alone. As they are more widely used, some shortcomings may turn up. But at present there are practically no disadvantages, or rather advantages are found one after another. For instance, the writer pressed the powder of barium titanate crystals with organic resin or rubber and obtained various piezoelectric materials, considerably lower in sensitivity but with physical properties different from ceramics. These, too, are considered to have practical uses in future. Though no mention was made in the body of this paper, there are some other ferroelectric substances similar to barium titanate. It is the writer's belief that the time will come when these substances together with their solid solutions play important rôles in technology.

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