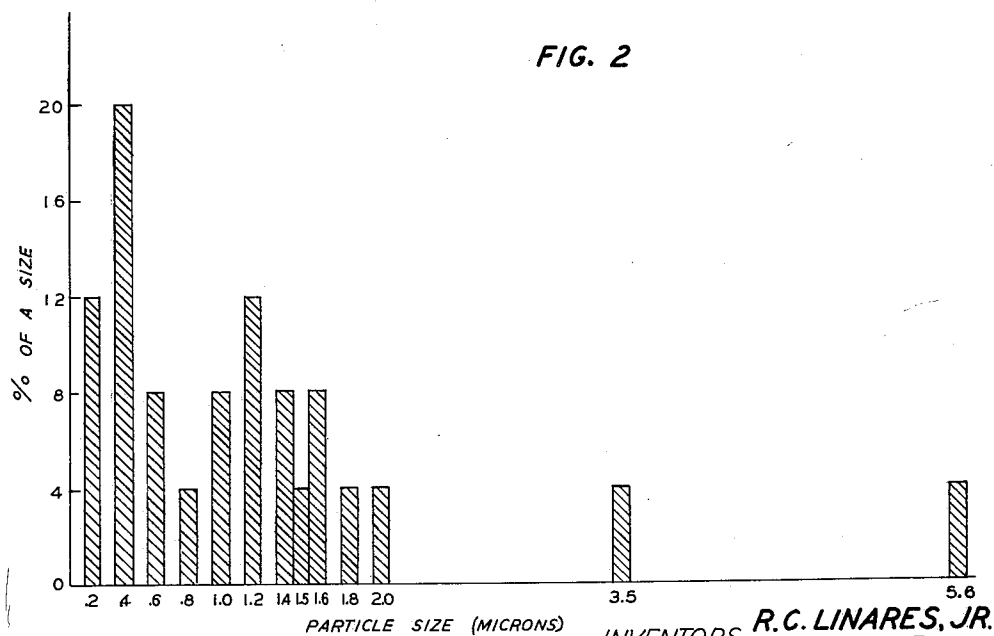
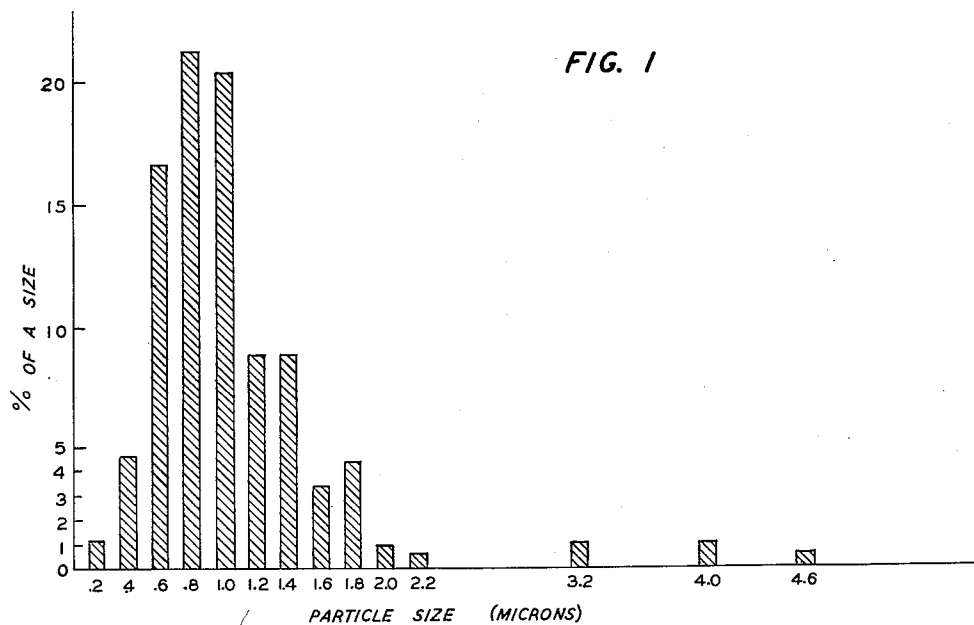


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BARIUM TITANATE SINGLE CRYSTALS

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BARIUM TITANATE SINGLE CRYSTALS

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This invention relates to an improved method for producing single crystal barium titanate having a crystal habit consisting of two approximately triangular-shaped thin plates joined along a common side.

Barium titanate is a well-known ferroelectric material which is particularly well suited for use in memory devices by virtue of its rectangular hysteresis loop characteristic. (See Electrical Engineering, volume 71, pages 916-922, November 1952; I.R.E. Transactions on Component Parts, volume CP-3, pages 3-11, March 1956.) The ferroelectric elements used in such devices are fabricated from single crystals of barium titanate.

Single crystals of barium titanate grow in one of two different crystal habits, the crystals growing either as thin plates or as chunky rectangular crystals. The thin plate single crystals, which are preferred for use in devices, are generally triangular in shape and grow in pairs, the two crystals being joined along a common edge. Because of the similarity of these pairs of single crystals to the wings of a butterfly, such crystals have come to be known as "butterfly twins."

Heretofore, one of the most advantageous methods of producing single crystals of barium titanate in the butterfly twin habit was in accordance with a method developed by J. P. Remeika, and described in a note to the editor in volume 76 of the Journal of the American Chemical Society, page 940, 1954. The first step in this procedure consists of introducing barium titanate powder into a crucible and covering it with a flux, such as potassium fluoride, which is a solvent for the barium titanate. The crucible is then heated to a temperature in the range of from approximately 1100° C. to 1200° C. and maintained at this temperature for a time in the range of approximately 8 to 16 hours.

The amounts of barium titanate and flux which are added to the crucible are chosen to assure the presence of undissolved barium titanate at the end of the high temperature soaking period. The entire body of flux becomes liquefied a short time after the inception of the soaking step. The solution of the barium titanate, which is situated at the bottom of the crucible, proceeds at a very slow rate and is largely diffusion-controlled because of the necessity of removing barium titanate away from the barium titanate-flux interface. Because of the exceedingly slow rate of solution of barium titanate, an essentially equilibrium condition prevails at the barium titanate-flux interface in that a large proportion of the total amount of barium titanate which dissolves is recrystallized on nuclei present at the interface. This equilibrium phenomenon, which is generally associated with crystal growing, increases the size of the larger particles at the expense of the smaller particles. The reason for such mass interchange is that the smaller particles have a higher thermodynamic energy level than the larger particles by virtue of their high ratio of surface area to volume and, accordingly, tend to dissolve more readily. Thus, at the end of the high temperature soaking period, the barium titanate which remains undissolved predominates in large particles.

The next step in the Remeika technique involves slowly cooling the crucible at a rate, for example, in the range of 10° C. to 25° C. per hour until a temperature in the range of from approximately 800° C. to 1000° C. is

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attained. During this cooling step, the barium titanate crystals grow in size due to the decrease in solubility of barium titanate in the flux which results from the temperature decrease. After this cooling period, the flux, which is still in the liquid state, is generally decanted and the crystals which remain in the crucible are then further cooled slowly to room temperature.

An inherent disadvantage of the Remeika process was the fact that the yield of single crystals in the preferred butterfly twin habit varied over a wide range. The factors influencing the ratio of butterfly twin crystals to rectangular crystals were not known and in many instances careful attention to process parameters and conditions was rewarded by the complete absence of crystals of the butterfly twin habit. A great deal of work has been done in the past to discover the identity of these factors, but all efforts heretofore have proven unsuccessful.

In accordance with the present invention, the Remeika process is modified in such manner as to facilitate the control of yield of butterfly twin single crystals of barium titanate. It has been discovered that the particle size distribution of the barium titanate powder which is used to prepare the melt from which the crystals are grown has a substantial effect on the yield of butterfly twin crystals. The essential features of the inventive method are based on the discovery that the yield of butterfly twin crystals is increased by the use of barium titanate powder predominating in particles smaller than approximately 6 microns, and, further, that the yield of butterfly twin crystals is adversely affected by the presence of particles larger than approximately 6 microns.

The invention will be more readily understood when taken in conjunction with the following drawings in which:

FIG. 1 is a bar graph depicting particle size distribution of barium titanate powder samples employed to produce butterfly twin single crystals in accordance with the present invention; and

FIG. 2 is a bar graph depicting particle size distribution of barium titanate powder samples employed to produce butterfly twin single crystals in accordance with the present invention.

With reference now to FIG. 1, there is depicted the particle size distribution of a sample of barium titanate powder which was used to produce butterfly twin single crystals in accordance with the present invention. Barium titanate powder in commercial form contains particles which range in size as high as 10 microns. Such powder was the type customarily used to produce butterfly twin single crystals in accordance with the prior art Remeika process described above. The sample, whose particle distribution is depicted in FIG. 1, was prepared by treating commercially available barium titanate powder in a flotation apparatus to remove certain particle size fractions including particles larger than approximately 5 microns. The results of such treatment on the yield of butterfly twin crystals prepared from the sample in accordance with the Remeika method, are shown in Table I below.

Table I

	Yield of butterfly twin crystals
Example 1—Commercial BaTiO ₃ powder	76
Example 2—BaTiO ₃ powder of FIG. 1	278

The data of Table I were obtained in the following manner:

Thirty grams of barium titanate powder, C.P. grade, were placed in the bottom of a 100 cc. Pt crucible. 67.5 grams of potassium fluoride were then added to the

crucible, and the crucible was heated to a temperature of 1125° C.

The crucible was maintained at 1125° C. for a period of approximately 11 hours. The crucible and contents were then cooled at a rate of approximately 25 degrees per hour until a temperature of approximately 1000° C. was attained.

The flux, which was still molten, was decanted and the crucible and contents then allowed to cool to room temperature at a rate of approximately 1000 degrees per hour.

The solidified flux was removed by washing with water and the butterfly twin single crystals were then removed from the crucible. As indicated in Table I, 76 butterfly twin crystals were produced.

The sample whose particle distribution is depicted in FIG. 1, was produced by treating a portion of the commercial barium titanate powder employed in the above-described process, in a water elutriator similar to that described by Wilder and Fitzsimmons in the Ceramic Bulletin, volume 34, No. 4, (1955). As shown in FIG. 1, substantially all of the particles larger than approximately 5 microns were removed by this flotation treatment. The treated barium titanate powder was then processed exactly as above to produce butterfly twin single crystals. As indicated in Table I, 278 butterfly twin crystals were produced, representing an increase of almost 400 percent over the yield obtained by the use of the commercial barium titanate powder.

FIG. 2 depicts a particle size distribution of a sample of barium titanate powder from which the larger particles have been removed by flotation methods. The commercial barium titanate powder from which the sample of FIG. 2 was prepared, was different from that involved in FIG. 1 as can be inferred from the difference in particle size distribution of the two treated samples. Table II illustrates the superiority of the barium titanate powder sample whose characteristics are depicted in FIG. 2 over the commercial powder from which it was produced with respect to the yield of butterfly twin crystals produced.

Table II

	Yield of butterfly twin crystals
Example 3—Commercial BaTiO ₃ powder	100
Example 4—BaTiO ₃ powder of FIG. 2	205

Additional substantiation for the proposition that butterfly twin yield is dependent upon particle size distribution is provided by the following examples which involve the production of butterfly twin crystals by the Remeika method using barium titanate powder samples containing substantially no particles in the size ranges depicted in FIGS. 1 and 2. Table III depicts the yields obtained from such powder samples.

Table III

Particle Size Distribution of Sample	Yield of Butterfly Twin Crystals
Example 5—10 ³ microns to 10 ⁴ microns	0
Example 6—149 microns to 297 microns	2
Example 7—74 microns to 149 microns	2
Example 8—57 microns to 74 microns	4
Example 9—44 microns to 57 microns	10
Example 10—37 microns to 44 microns	46

The samples listed in Table III were prepared by grinding crystals of barium titanate to form particles of relatively large diameter. The particles were then sieved using standard mesh sieves to produce the samples. The upper and lower size limits of the samples as noted in Table III represent the openings in the two sieves used to produce the particular fraction. It is noted that the yield in all cases was substantially lower than that ob-

tained from the commercial barium titanate powder as shown in Table I and II.

The yield of butterfly twin crystals produced in accordance with the Remeika method may be controlled by judicious choice of the particle size distribution of the barium titanate powder used to produce the melt. As may be inferred from the data in Tables I and II, additions of particles larger than approximately 6 microns results in a decrease in the yield of butterfly twin crystals. In certain instances, it may be desirable to so limit the yield, as for example, where a small number of perfect large-sized crystals are desired.

The manner in which particle size distribution affects butterfly twin yield is not presently understood. However, data thus far obtained, suggest a mechanism of the following nature. Each of the particles in the barium titanate powder can be considered to be a single crystal, those particles having a butterfly twin structure being the nuclei which grow during the process to form the resultant butterfly twin crystals. It may be inferred from the data of Table III that the smaller particles are predominantly butterfly twin nuclei, whereas the larger particles possess the non-preferred crystal habit. That is to say, the absence in the examples of Table III of a substantial amount of small particles in the powder used to form the melt is considered responsible for the low yields of butterfly twin crystals.

The data shown in Tables I and II may be interpreted as being indicative of the fact that the presence in the melt of particles larger than approximately 6 microns has an adverse effect on the yield of butterfly twin crystals. A hypothetical explanation of this effect involves certain assumptions regarding particle growth activity during the soaking period. If, as suggested above, butterfly twin crystals are produced primarily from the smaller particles, it is essential that such particles be present at the beginning and also at the end of the soaking period. The phenomenon usually associated with equilibrium solution of the type encountered in the soaking step of the Remeika process involves growth of the larger particles at the expense of the smaller ones. Therefore, if there are particles larger than 6 microns initially present in the melt, these particles will grow at the expense of the smaller particles. Thus, the number of smaller particles in the melt is continually reduced during the soaking step and the ultimate yield of butterfly twin crystals, in turn, is reduced.

Additional experimentation has shown that the high yields of butterfly twin crystals obtained from the samples of FIGS. 1 and 2 are not restricted to distributions of this type. Thus, using a water elutriator of the type described above, a fraction was removed from commercial barium titanate powder which had a smaller average particle size than the samples shown in FIGS. 1 and 2. The yields from such small average particle size samples were comparable to yields of the samples of FIGS. 1 and 2.

The high yields obtained in accordance with the present invention are not restricted to processes utilizing a flux of potassium fluoride. Excellent yields of butterfly twin crystals have been obtained using both lead fluoride and barium fluoride as flux materials.

It is to be understood that the examples described above are intended to be illustrative of the present invention. Variations may be made therein within the skill of the art without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of producing butterfly twin single crystals of barium titanate comprising the steps of adding barium titanate particles of size up to 6 microns to a flux material which, in the liquid state, is a solvent therefor, heating the mixture of barium titanate and flux to an elevated temperature to form a melt, maintaining the said mixture at the said elevated temperature for a period of

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time during which a portion of the barium titanate dissolves, the ratio of barium titanate to flux in the said mixture being greater than the solubility limit of barium titanate in the flux material at the said elevated temperature, and cooling the melt to promote the crystal growth. 5

2. The process of claim 1 in which the barium titanate added to the flux consists essentially of particles in the size range of from .2 to 4.6 microns.

3. The process of claim 1 in which the barium titanate added to the flux consists essentially of particles in the size range of from .2 to 5.6 microns. 10

4. The method of claim 1 in which the said elevated temperature is in the range of from 1100° C. to 1200° C., the said period of time is in the range of from 8 to 16 hours, and the melt is cooled at a rate in the range of from 10° C. to 25° C. per hour to a temperature in the range of from 800° C. to 1000° C. 15

5. The process of producing butterfly twin single crystals of barium titanate comprising the steps of treating barium titanate powder to remove substantially all particles larger than 6 microns, adding said treated barium titanate powder to a flux which, in the liquid state, is a solvent therefor, heating the mixture of barium titanate and flux to an elevated temperature to form a melt, maintaining the said mixture at the said elevated temperature 20 25

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for a period of time during which a portion of the barium titanate dissolves, the ratio of barium titanate to flux in the said mixture being greater than the solubility limit of barium titanate in the flux material at the said elevated temperature, and cooling the melt to promote the crystal growth.

6. In the process of producing butterfly twin crystals of barium titanate comprising the steps of adding barium titanate powder to a flux material which, in the liquid state, is a solvent therefor, heating the mixture of barium titanate and flux to an elevated temperature to form a melt, maintaining the said mixture at the said elevated temperature for a period of time during which a portion of the barium titanate dissolves, the ratio of barium titanate to flux in said mixture being greater than the solubility limit of barium titanate in the flux material at the said elevated temperature, and cooling the melt to promote the crystal growth, the improvement which comprises treating the said powder to remove substantially all particles larger than 6 microns prior to its addition to the flux material.

References Cited in the file of this patent

Remeika: J. Am. Chem. Soc. (1954), vol. 76, pages 940, 941.