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METHOD OF CONTROLLING THE RESISTIVITY
OF P-TYPE CRYSTALS

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2 Sheets-Sheet 1

RESISTIVITY OF $\text{NH}_4\text{H}_2\text{PO}_4$ CRYSTAL
VS. IMPURITY OF SALT IN GROWING SOLUTION

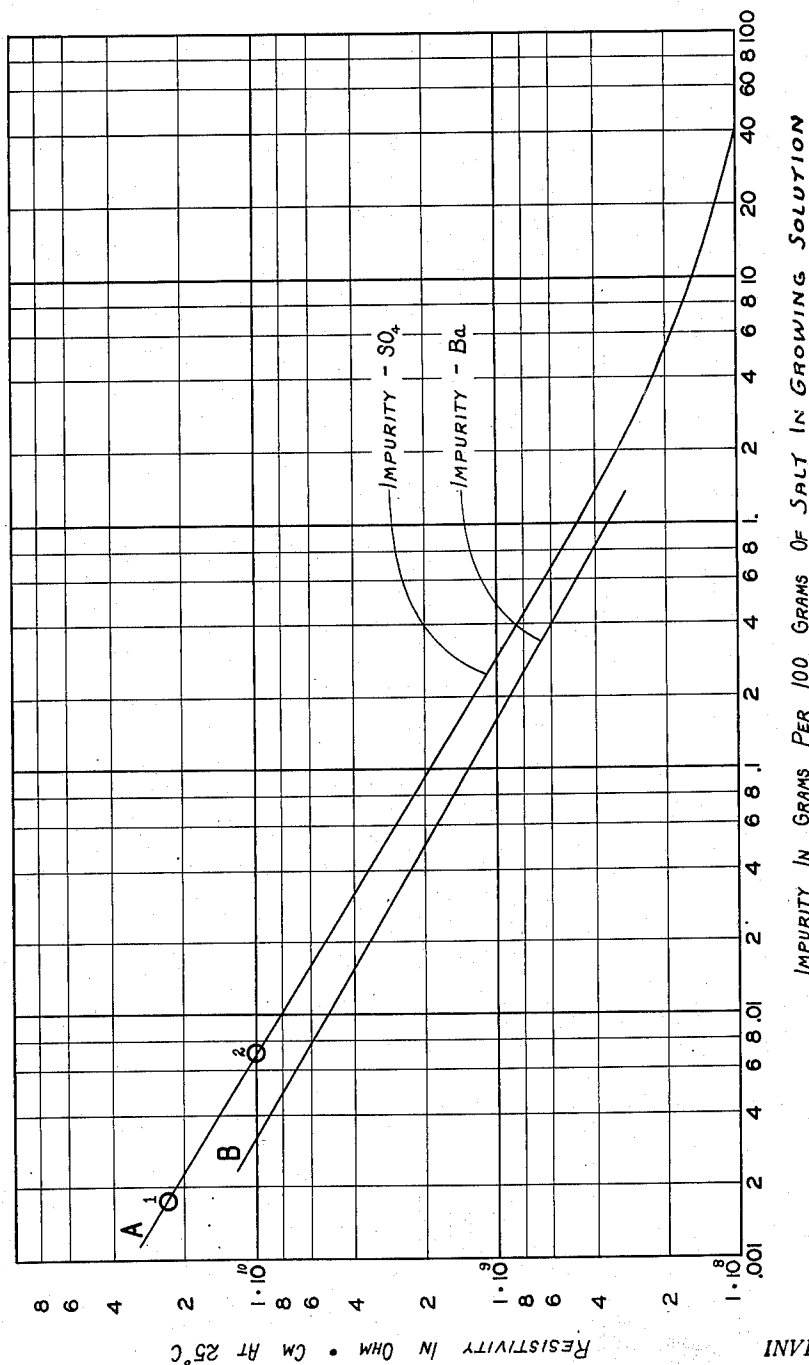


FIG. 1

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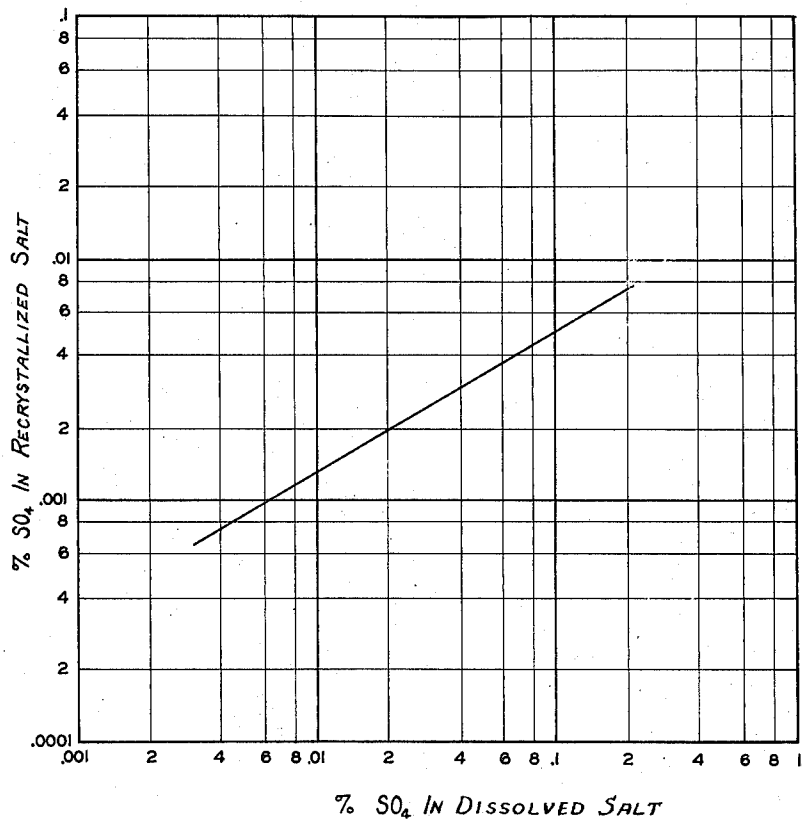


FIG. 2

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METHOD OF CONTROLLING THE RESISTIVITY OF P-TYPE CRYSTALS

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15 Claims. (Cl. 171—327)

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This invention relates to the growing of crystals of the P-type, by which is meant crystals of primary ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and all other crystalline materials isomorphous with it.

In the practical applications of crystals for piezo-electric and some other purposes the volume resistivity of the crystalline body is an important consideration. For many uses a high resistivity is desirable, while for certain specific uses, especially in the case of P-type crystals, it is desirable to be able to provide crystals having different specific resistivities.

In the use of synthetic piezoelectric crystals the maintenance of an adequately high resistance of the crystal elements has been something of a problem. In the case of Rochelle salt crystals it had been demonstrated that the comparatively high leakage frequently exhibited by these crystals was practically entirely due to a surface leakage caused by condensation of atmospheric moisture on the crystal; and if such a crystal of Rochelle salt is brought into a dry atmosphere or suitably protected from moisture its resistance reaches values which are well beyond technical requirements if unduly high temperatures are avoided. In the case of the P-type crystals recently introduced for piezoelectric purposes, in particular the primary ammonium phosphate, it was likewise observed that the resistance of crystal elements became very low under conditions of high humidity. However, it was found that a certain residual conductivity remains in the case of the P-type crystals even if they are brought into an extremely dry atmosphere; and it has been established that the conduction in these P-type crystals is a volume conduction rather than a surface effect. It was found, furthermore, that the resistivity in various samples of a given P-type crystal such as ammonium phosphate varied over a wide range if these crystals were grown using solutions from salt of different origins. This latter fact has led to the conclusion that the differences in resistivity in the case of P-type crystals were probably due to the effect of impurities in the salt solutions from which the crystals were grown. As a result it has been the practice, prior to the present invention, in order to secure P-type crystals of high resistivity to grow the crystals from salt solutions prepared with salt of high purity. However, even the use of materials commercially classed as "chemically pure" has not made possible the production of P-type crystals having resistivity as high as is required for some uses of such crystals; and, furthermore, it has not heretofore been feasible in the production of

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P-type crystals to have reliable control of their resistivity so as to secure crystals having different resistivities when desired. Furthermore, the use of the "chemically pure" materials to attain higher resistivity increases the cost of producing the crystals substantially and thereby restricts their field of usefulness.

It is an object of the present invention to provide a method of growing P-type crystals by means of which such crystals having very high resistivity can be produced by the use of technical grade raw materials of moderate cost and with correspondingly low production cost for the piezoelectric crystals produced.

A further object of the invention is to provide a process for the growth of P-type crystals by means of which the resistivity of the crystals grown can be controlled at will, with resultant production of crystals having different specific resistivities, as desired.

The present invention is based upon the discovery that low resistivity of P-type crystals is not due to the presence in the growing solutions of impurities or contaminants generally, but rather to the presence of certain specific impurities which by the similarity in value of their ionic radii are able to substitute in the crystal lattice for the positive or negative ions normally present but have valencies different from the replaced ions and thus introduce a valency unbalance and a heretofore unrecognized type of electric conductivity. By way of example, in the case of primary ammonium phosphate, the specific effective impurities have been found to be barium and sulfate ions. The ionic radius of the barium ion (Ba^{++}) is 1.43 Å, which is the same as the radius of the ammonium ion (NH_4^+); on the other hand the size of the sulfate ion (SO_4^{--}) closely approaches the size of the phosphate ion (PO_4^{--}) and the internal arrangement of these two ions is known to be similar.

The causal impurities having been discovered I have found it possible to produce P-type crystals having relatively high resistivity or different predetermined resistivities by the comparatively simple expedient of controlling, by elimination, or addition, or counteraction as hereinafter explained, the specific ion contaminants affecting the respective P-type crystals.

To facilitate disclosure and explanation of the invention reference is had to the accompanying drawings, in which,

Fig. 1 is a chart presenting two graphs each of which shows the resistivities of primary ammonium phosphate crystals grown from solutions

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containing different amounts of a specific impurity, the graph for each impurity showing resistivities, in ohm-centimeter, for different weights, in grams, of the impurity in each 100 grams of the primary ammonium phosphate salt in the growing solution, both the resistivity and the impurity being plotted on logarithmic scales.

Fig. 2 is a chart presenting a graph which shows the varying sulfate contamination of primary ammonium phosphate crystals resulting from varying sulfate contamination of the primary ammonium phosphate salt in the solution from which the crystals are grown, the sulfate impurities in both the salt and the crystal being plotted on logarithmic scales.

It has been established that the effect of the sulfate ion (SO_4^{--}) contamination of a primary ammonium phosphate solution can be represented by a linear relationship between the logarithm of sulfate concentration in the solution and the logarithm of the crystal resistivity, at least up to sulfate concentrations of 1% relative to the phosphate. This is shown by graph A in Fig. 1 of the accompanying drawing. In this graph point 1 represents the average composition and resistivity obtained in a large number of crystal growings carried out according to the present invention; point 2 represents the average of crystal growings made with a solution of "chemically pure" salt. The lower end of the graph is based upon crystals grown with a series of solutions prepared from primary ammonium phosphate with additions of different amounts of ammonium sulfate.

The effect of barium ion contamination in the growing solution of primary ammonium phosphate on the resistivity of the growing crystal is shown in graph B of Fig. 1. The relationships for sulfate and barium are seen to be quite similar. The quantitative study of the effect of the barium ion has not been carried as far as in the case of the sulfate ion since it has been found economically feasible to avoid the barium contamination substantially completely by choice of economically available raw materials for preparation of the primary ammonium phosphate. The contamination of the phosphate with the sulfate ion cannot be so readily avoided but, on the other hand, it has been found possible, at a permissible cost, sufficiently to eliminate the sulfate, or (alternatively) to counteract its harmful effect by addition to the phosphate solution of an agent, preferably the silicate ion (SiO_4^{--}), which restores the chemical valency balance disturbed by the presence of the sulfate in the crystal. The silicate ion may be added as silica in hydrated form or one of its compounds. For instance, it was found that the resistivity, measured in the direction of the optic or Z axis and at 25° C., of ammonium phosphate crystals grown from a solution containing .0016% sulfate per ammonium phosphate present could be raised from an average value of 25,000 megohms-cm. to about 37,000 megohms-cm. by the addition of .055% silica in the form of sodium silicate. However, there are indications that an excess of silica may reduce the resistivity.

As might be expected, the amount of the contamination by barium and/or sulfate ions which enters the structure of the P-type crystal is much less in amount than the contamination of the solution in which the crystal is grown. The approximate relationship between the sulfate contamination of the growing solution and of the crystal formed, in the case of primary ammoni-

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um phosphate crystals, is shown by the graph of Fig. 2 of the accompanying drawings. As will appear from a study of the graphs of Fig. 1 and Fig. 2, very small contaminations of the crystal may markedly affect its resistivity.

The present invention can be practiced by proceeding in a variety of ways, as will be apparent to those skilled in the art. Suitable procedures to provide, for example, primary ammonium phosphate crystals of either very high resistivity or various lower resistivities will now be described.

To attain the high resistivity, a preferred procedure is to select, for the preparation of the primary ammonium phosphate salt to be used for the growing solution, raw materials relatively free from contamination with barium and sulfates. Technical grade phosphoric acid and ammonia meeting this requirement are commercially available. Thus a commercial 75% phosphoric acid (U. S. Agricultural Chemical Company) which has been found satisfactory contains less than .01% SO_4 and less than .0005% Ba. Technical grade aqua ammonia free from barium and sulfate contamination also is commercially available (Harshaw Chemical Company). It is made by passing synthetic anhydrous ammonia into distilled water prepared and handled in a manner which avoids contamination with barium and sulfates.

Using the specified raw materials the following procedure is suitable:

Add 1131 lbs. of the phosphoric acid to 102 gallons of distilled water in a stainless steel tank. To the acid solution add slowly 518 lbs. of 26% aqua ammonia with constant stirring and keeping the temperature below 60° C.

The resulting solution of primary ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) has a volume of approximately 252 gallons and contains 1000 lbs. of the phosphate. The specific gravity of the solution should be approximately 1.213 at 60° C. The concentration of the phosphate at this specific gravity corresponds to 475 grams of salt per liter of solution, or 637 grams per liter of water. As some evaporation occurs during the reaction of the acid and ammonia some additional water has to be added. The specific gravity of the solution varies .0004 per 1° C. of temperature change.

It has been found that the phosphate solution has a tendency to cake which varies with its pH and to avoid resultant clogging of valved passages it is desirable to adjust the pH of the solution to $4.36 \pm .15$ by adding acid or ammonia as may be required.

In normal practice the primary ammonium phosphate solution would be crystallized so that the phosphate can be held in crystalline form for use as required in the growing of piezoelectric crystals. The crystallization of the solution can advantageously be carried out by evaporating the solution in a glass lined tank equipped with a glass coated anchor stirrer. The evaporation is continued until the specific gravity is 1.273 at 100° C. The concentrated solution is then cooled to 25-26° C. with continuous stirring and is crystallized.

The resulting crystal slurry is next run into a stainless steel centrifuge and the crystals washed with distilled water. The yield of the first crystallization is approximately 600 lbs. of $\text{NH}_4\text{H}_2\text{PO}_4$. The mother liquor and wash water remaining from the crystallization are now evaporated to the same specific gravity as before, namely, 1.273, and again crystallized with the

production of an additional 240 lbs. of $\text{NH}_4\text{H}_2\text{PO}_4$ salt, the total yield realized being 84%.

By this procedure I have succeeded in regularly producing primary ammonium sulfate salt containing between .0009 and .0011% SO_4 . This salt is suitable for the preparation of solutions for the growing of crystals having a resistivity in excess of 20,000 megohms-cm. measured at 25° C. If crystals of specified lower resistivities are desired ammonium sulfate can be added to the crystal growing solution in quantities shown by graph A of Fig. 1.

For the purpose of further explaining and illustrating the present invention it may be assumed that the phosphate salt prepared in the manner above described may be used in growing piezoelectric crystals by methods such as are disclosed in U. S. patent to Kjellgren, Reissue 19,697. In this latter method seed crystals or pieces of crystalline material are planted in the growing solution and the container is rocked to cause the solution to flow back and forth in relation to the seeds while the temperature of the solution is progressively lowered at a suitable rate to effect the desired crystallization. P-type piezoelectric crystals have heretofore been produced by this method. As is known to those skilled in the art it is the practice in growing the crystals to utilize a particular salt solution to grow a series of crystal crops, the concentration of the growing solution being restored after the gathering of each crop, by addition of a suitable amount of the salt employed. In the practice of the present invention this procedure should be modified in the following manner.

During the concentration of the growing solution to effect crystallization in accordance with the method of the Kjellgren patent the contamination of the solution with barium and/or sulfate becomes more concentrated, and in order to prevent continuance of this concentration throughout the growing of a series of crops of the piezoelectric crystals with resultant variation in the resistivities of the crystals of different crops, a portion of the mother liquor remaining after the gathering of each crop is removed from the growing tray or tank. Thus, for example, if the P-type salt prepared in the manner which has been described should contain .0009 to .0011% SO_4 , it would be suitable, following the gathering of a crop of the piezoelectric crystals, to discard one-third of the mother liquor remaining and then adjust the remaining mother liquor for the growing of another crop by adding to it a suitable amount of the P-type salt. The amounts of the mother liquor discarded in the manner described may be accumulated and eventually be re-crystallized along with the solutions obtained by the above described reaction of technical phosphoric acid and ammonia.

Following the above described specific procedure it is possible to produce primary ammonium phosphate crystals having volume resistivities up to about 30,000 megohms-cm., measured at 25° C. The high resistivity is attained by the use of technical grade raw materials costing much less than "chemically pure" materials and the process makes possible practical applications of the P-type crystals which, without the process, would not be possible.

When, for specific applications, various resistivities are required, they can be provided as desired by adding to the growing solution prepared as above described suitable amounts of one or the other of the contaminants in accordance

with the graphs of Figs. 1 and 2 of the drawing. Primary ammonium phosphate crystals of any desired resistivity between about 30,000 megohms-cm. and 100 megohms-cm. can be obtained in this way. Alternatively, a crystal having moderate resistivity can be grown directly from a solution prepared by mixing technical grade phosphoric acid and ammonia, eliminating the process of crystallizing primary ammonium phosphate salt above described, with resultant reduction in over-all production cost.

The present invention is applicable advantageously to P-type salts other than primary ammonium phosphate because experience has indicated that all of the P-type salts are subject to large variations in resistivity due to specific impurities. In the case of primary potassium phosphate, crystals grown from a "chemically pure" salt supplied on identical specifications at different times varied from 5,000 megohms-cm. to 50,000 megohms-cm. measured at 25° C. The application of the process to the production of primary ammonium phosphate crystals having been described in detail, its application to other salts of the P-type will be sufficiently indicated by a further discussion of the mechanism which is involved in the ionic substitutions which have already been referred to.

It is believed that the variable conductivity introduced in P-type crystals by certain ionic impurities contained in the crystal-growing solution is explained by the following considerations, involving the size, structure and valency of the ions composing, respectively, the crystal substance and the impurities. The size of ions is commonly expressed by the ionic radius in case of positive ions, and in terms of the interatomic distances between the central atom and any one of the four oxygen atoms in case of negative ions such as occur in the P-type salts. The trivalent negative PO_4^{---} or AsO_4^{---} ions of the P-type crystal can be partly replaced by the bivalent negative sulfate ion or other bivalent negative ion of the type AO_4^{--} (where "A" stands for any hexavalent positive element) provided that such ions have the same tetrahedral arrangement and similar interatomic distances A—O as the PO_4^{---} and AsO_4^{---} ions. Likewise the monovalent ions of the P-type salt, that is NH_4^+ , K^+ , or Rb^+ may be replaced by a bivalent ion of similar ionic radius. The most suitable ion for replacing ammonium or rubidium is the bivalent barium ion whereas the bivalent lead ion and perhaps the bivalent strontium ion can substitute for K^+ .

The substitution either of a bivalent negative ion for a trivalent negative ion, or the substitution of a bivalent positive ion for a monovalent positive ion introduces one excess positive charge into the crystal lattice. As electrostatic balance always prevails in a crystal (otherwise it would be highly electrically charged) it follows that there must be one positive charge lacking for each of the substitutions discussed. It is believed that this occurs through the absence of one positive hydrogen ion (proton) occurring for each one of the substitutions, and accordingly that a P-type crystal grown from a solution containing the discussed impurities, and having included some of these impurities, will be characterized by the absence of a certain proportion of the protons normally occupying regular locations in the crystal lattice. If now an electric potential be applied to such a crystal it can be expected that protons will travel from points of higher to points of lower potential by successively changing their lo-

cations for empty locations in the lattice produced by the discussed proton defect. This type of conduction which may be termed "proton deficiency conduction," it is believed, has not been disclosed before, although it is to some extent analogous to the electron deficiency conduction introduced by theoretical physicists to explain the conductivity of certain semi-conductors.

The question arises how general a phenomenon this proton deficiency conductivity is among piezoelectric crystals and crystals in general. The mechanism as outlined above depends on the presence of hydrogen ions in the crystal lattice. According to the known structure of the P-type salts, they contain two hydrogen ions for each negative ion of the crystal; these hydrogen ions are present in the form of the so-called hydrogen bond. It would appear that the presence of a comparatively large number of such hydrogen bonds, in an otherwise fairly simple crystal structure, favors the discussed conduction process. The process cannot, of course, be present at all in crystals not containing hydrogen and probably will also not be noticeable in crystals containing hydrogen only in the form of complete individual water molecules (water of crystallization) or containing hydrogen only in form of non-ionic bonds such as the C—H bond. It appears that among known piezoelectric crystals the P-type group of crystals are the only ones likely to show the proton deficiency conductivity to a considerable extent.

In applying the present process for the production of P-type crystals it has been found that their electric conductivity varies greatly with temperature. In the case of specific salts studied the conductivity increased by between about 5% and 8% per degree centigrade in the vicinity of 25° C. This marked increase of conductivity with temperature can be understood on the basis of the conduction process herein disclosed, as a certain potential barrier has to be overcome by the proton jumping from its location to the next open space.

Recognition that the conduction process introduced in P-type crystals by particular impurities is of the proton deficiency type was followed by the concept and discovery that this conductivity might be suppressed by introducing into the growing solution suitable counteracting impurities, namely, tetravalent negative ions of the type AO_4^{--} (where "A" now stands for any tetravalent positive element) which are of similar structure (tetrahedral arrangement) and size as the PO_4^{--} or AsO_4^{--} ions of the P-type crystal. Such a tetravalent ion is the silicate ion, which can be maintained in the solution of the P-type salt in the small concentrations necessary to counteract the amounts of sulfate and the like occurring in available raw materials for the production of P-type salts. The introduction of one tetravalent ion such as SiO_4^{--} brings about the introduction of one excess proton to restore electrostatic balance; and this proton fills in one "proton hole" caused by the presence of a bivalent impurity such as sulfate ion.

It must be assumed that a certain proton deficiency conductivity is present even in a crystal entirely free of bivalent impurities due to thermal disturbances of the crystal lattice. Introduction of a small amount of silicate ion providing excess protons can counteract this pure-crystal conductivity leading to a resistivity of the crystal higher than would be obtained with the entirely pure P-type crystal material. On the other hand

there is some evidence that high concentrations of silicate in the crystal growing solutions can increase conductivity of a P-type crystal. The amounts of silicate ion to be used for reducing conductivity of primary ammonium phosphate, for example, are in the order of .01%.

From the foregoing discussion it will be seen that the present method of determining or regulating resistivity involves essentially the regulation in the growing solution of impurities which, by virtue of their ionic radii, are capable of substitution in the lattice of the grown crystal with resultant modification of the conductivity of the pure salt crystal. The description of the growth of primary ammonium phosphate crystals has indicated the critical impurities applicable to that salt. A consideration of the known ionic radii of the positive ions and interatomic distances within the negative ions of the P-type salts and their possible contaminants will serve as a guide in the application of the method to other salts of the P-type. These salts comprise the phosphates KH_2PO_4 , $NH_4H_2PO_4$, RbH_2PO_4 , and isomorphous mixed crystals of these and also, within certain limits, of these with TiH_2PO_4 and CsH_2PO_4 ; also the arsenates KH_2AsO_4 , $NH_4H_2AsO_4$, RbH_2AsO_4 and CsH_2AsO_4 , as well as mixed crystals of these arsenates, and of these arsenates with the named phosphates.

For the named salts and possible contaminants we have data as follows:

Ionic radii (according to V. M. Goldschmidt)

	A. U.
35 K^+ -----	1.33
NH_4^+ -----	1.43
Rb^+ -----	1.49
Tl^+ -----	1.49
Cs^+ -----	1.65
40 Sr^{++} -----	1.27
Pb^{++} -----	1.32
Ba^{++} -----	1.43

Interatomic distances in negative ions AO_4 (according to W. H. Zachariasen)

	A. U.
45 P^5-O -----	1.56
As^5-O -----	1.7
S^6-O -----	1.49
50 Se^6-O -----	1.6
Cr^6-O -----	1.7
Mo^6-O -----	1.8
Si^4-O -----	1.63
Ge^4-O -----	1.75

55 It has been established that substitutions of positive ions readily take place if their ionic radii agree within about 5% or less and that substitutions of tetrahedral negative ions may take place if their interatomic distances agree within a somewhat wider limit.

60 Taking this into account it will appear from the above data that barium will readily enter the ammonium phosphate and the ammonium arsenate crystals, and, less readily, the thallium and rubidium phosphate crystals. Barium will not markedly affect the potassium salt crystals, which, on the other hand, are affected by bivalent lead and possibly by strontium. No bivalent positive ion is available to substitute for cesium; and the conductivity of primary cesium arsenate crystals should therefore be quite independent of the presence of metallic impurities in the crystal growing solution.

75 The table of interatomic distances indicates that sulfate and silicate ions will readily enter

a phosphate crystal. The sulfate is not so well matched to the arsenate crystal; the latter will be more readily affected by the chromate ion.

From the foregoing disclosures those skilled in the art will appreciate that the invention is not limited to the procedures which have been particularly described or indicated but can be carried out in various additional or modified ways within the bounds of the appended claims and their equivalents.

What is claimed is:

1. In the growing of P-type crystals, the step of controlling the resistivity of the crystals grown by regulating the concentration in the crystal-growing solution of contaminant ions having different valencies than the P-type crystal ions and capable of substituting for the P-type crystal ions by reason of similar size and structure.

2. The growing of crystals as claimed in claim 1 in which the crystal grown is a primary phosphate.

3. The growing of crystals as claimed in claim 1 in which the crystal grown is a primary phosphate and the contaminant ions comprise sulfate.

4. The growing of crystals as claimed in claim 1 in which the crystal grown is primary ammonium phosphate.

5. The growing of crystals as claimed in claim 1 in which the crystal grown is primary ammonium phosphate and the contaminant ions comprise sulfate.

6. The growing of crystals as claimed in claim 1 in which the crystal grown is primary ammonium phosphate and the contaminant ions comprise sulfate and barium.

7. The growing of crystals as claimed in claim 1 in which the crystal grown is an ammonium salt.

8. In a method of growing primary ammonium phosphate crystals, the steps of providing a growing solution of the salt to be crystallized that is substantially free of barium ion (Ba^{++}) contamination and regulating the content therein of sulfate ion (SO_4^{--}) contamination to determine correspondingly the volume resistivity of the crystals produced.

9. In a method of growing successive crops of P-type crystals in which the concentration of the growing solution is maintained by addition of salt to the growing solution after the gathering

of a crop of crystals, the steps of initially preparing a growing solution of the P-type material to be crystallized; regulating the concentration in the crystal-growing solution of contaminant ions having different valencies than the P-type crystal ions and capable of substituting for the P-type crystal ions by reason of similar size and structure; planting crystal seeds in the solution; regulating the temperature of the solution to cause crystalline growth on the seeds; gathering the resulting crop of crystals from the solution; and, to effect adjustment of the growing solution preparatory to the growth of another crop of crystals, discarding from the mother liquor left after gathering the first crop of crystals a portion thereof and adding to the remaining mother liquor a sufficient amount of the P-type crystalline material to restore a concentration thereof in the solution suitable for further crystal growth.

10. In the growing of a P-type crystal the step of adding a tetravalent negative ion to the crystal-growing solution for the purpose of reducing the electric conductivity of the crystal grown.

11. In the growing of a P-type crystal from a solution contaminated with bivalent ions capable of substituting for the P-type crystal ions, the step of adding a tetravalent negative ion to the solution for the purpose of reducing the electric conductivity of the crystal grown.

12. In the growing of a P-type crystal from a solution contaminated with ions having different valencies than the P-type crystal ions and capable of substituting for the P-type crystal ions, the step of adding tetravalent negative ions for the purpose of reducing the electric conductivity of the crystal grown.

13. The growing of crystals as claimed in claim 12 in which the crystal grown is a primary phosphate and the tetravalent negative ion added is the silicate ion.

14. The growing of crystals as claimed in claim 12 in which the crystal grown is primary ammonium phosphate and the crystal-growing solution is contaminated with sulfate ions.

15. In the growing of a primary phosphate crystal from a solution contaminated with sulfate ion, the step of adding silica to the solution for the purpose of reducing the electric conductivity of the crystal grown.

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