

CRYSTAL CHEMICAL RELATIONS IN INORGANIC PIEZOELECTRIC MATERIALS

S. ZERFOSS, L. R. JOHNSON,
Naval Research Laboratory, Washington, D. C.

ABSTRACT

An attempt is made to establish a relation between the structure and the piezoelectric activity of a number of inorganic salts. The possession of activity by a salt appears to depend in many cases on the presence of an asymmetric radical and is further influenced by the nature of the cationic environment of this radical.

Increased interest in specialized electronic gear has resulted in a renewed search for new synthetic piezoelectric materials. The wartime production of large single crystals of $\text{NH}_4\text{H}_2\text{PO}_4$ is a notable example.

Piezoelectric activity depends on the absence of a center of symmetry in the crystal structure of a compound. Thus, when it is definitely known that a compound crystallizes in one of 20 of the possible 32 crystal classes, piezoelectric response can be assumed without testing.¹ The magnitude of the effect, however, cannot be so simply predicted.

Crystal symmetry data, moreover, are thoroughly reliable for relatively few materials. A large proportion of the older data which assigned the crystal to a class on the basis of morphological observations is not correct; even with modern *x*-ray data, determination of the crystal class is often very difficult. Where the final determination depends on the presence or absence of a center of symmetry, the decision can often be made only on the basis of a test for piezoelectricity. A thorough search of the literature resulted in a rather long list of materials that had been tested, and also revealed many discrepancies and many results which, on the basis of later reliable symmetry data, were obviously incorrect. Accordingly, the Crystal Section of the Naval Research Laboratory has undertaken a comprehensive laboratory survey of piezoelectric materials and has completed the testing of all the likely water-soluble inorganic compounds which were obtainable in the necessary form. From a list of 400 potentially active compounds, 155 compounds were measured, and the remainder eliminated for lack of practical value and because of difficulty of preparation. Sixty-six active salts were reported in this study.² Thirty-

¹ Wooster, W. A., "Crystal Physics," Cambridge Press (1938) pp. 217. Wooster makes the following statement of this point: "Where a piezoelectric effect cannot be detected, even though the external development shows a center of symmetry to be absent, the piezoelectric observation does not affect the assignment of the crystal to its symmetry class."

² Egli, P., A survey of inorganic piezoelectric materials: *Am. Mineral.*, **33**, 623-634 (1948).

one of the compounds tested were inactive despite the fact that the literature either reported them as belonging in active crystal classes or disagreed as to the symmetry class.

The purpose of this paper is not to present the revised data but to summarize some of the general relations observed which add additional information on the structural relationships between various types of ions in inorganic chemicals.

The device³ used to detect piezoelectricity is a modification of the circuit originally used by Giebe and Scheibe in which activity is excited in the crystal sample by the electric field from a high-frequency oscillator. The frequency of the oscillator is varied rapidly and as various resonances are excited in the crystal, the modulation between the frequency of the crystal vibration and the changing oscillator frequency causes clicks that are audible in earphones. The Naval Research Laboratory design of this device has proved highly reliable and free of spurious responses so that clicks over a range of frequencies constitute a positive indication of piezoelectric activity. A negative response is less certain since several conditions must be satisfied before activity may be detected. For instance, high conductivity or poor elastic properties may interfere with detection of piezoelectricity, though they usually result in a sizzling noise which is readily identified. In inorganic materials conductivity is rarely a factor except in oxides and sulfides, and no case was found in which poor elastic properties were a problem. The crystal specimen must also, of course, be of such a size that it will have a resonance within the range of the oscillator, which has a top frequency of 10 Mc. In general, well formed crystals as small as +100-mesh could be tested reliably. As there is relatively little variation in conductivity and elastic properties among inorganic materials, the strength of the click provides an approximate quantitative measure of the effective strength of the piezoelectric response.

STRUCTURAL RELATIONS

The correlation of piezoelectric activity with structure does not appear to be a simple matter. Given a favorable symmetry structure for piezoelectric response, the magnitude of the effect depends in a complex way on the difference in strength of the anion and cation. The strongly active compounds usually contain cations of the alkali metals, hydrogen or ammonium.

Wooster¹ has listed some of the general crystal-chemical relationships found to exist in piezoelectric inorganic salts. These relationships involved a consideration of the constituent anion and cation groups in the

³ Stokes, R. G., An improved apparatus for detecting piezoelectricity: *Am. Mineral.*, **32**, 670-679 (1947).

lattice. In general, it is true that asymmetry in either a complex anion or cation may influence the whole lattice in favor of piezoelectricity, but it is also often necessary to consider the interaction of the two groups as they affect the over-all symmetry of the crystal. These interacting structural relationships can be formulated as follows:

1. *Simple Ionic Salts.* Simple ionic salts (without complex ions) are not piezoelectric, while simple homopolar salts are often active. For example, no anhydrous halides of the alkali or alkaline earth metals have been shown to be piezoelectric. This is no longer true as the character of the bond becomes more homopolar so that many compounds of the AX type are piezoelectric, for example, CuCl and ZnS.

2. *Salts Containing Radicals that Lack a Center of Symmetry.* These salts are often piezoelectric. Thus, there are several chlorates, bromates, iodates, and dihydrogen phosphates that show activity. In most of these salts the structure can be pictured as containing a discrete anionic group or radical.

The sulfate, perchlorate, and phosphate radicals are tetrahedral in shape and as such lack a center of symmetry. Yet many anhydrous sulfates, perchlorates and phosphates are inactive, indicating that this asymmetry in the radical is not always reflected in the lattice. For example, K_2SO_4 is not piezoelectric.⁴ However, if we substitute one Li^+ for one of the K^+ ions in K_2SO_4 we obtain an active crystal, $LiKSO_4$. The change in ion environment of the SO_4^{--} as a result of this substitution has emphasized the asymmetry of the SO_4 radical through polarization and rendered the crystal piezoelectric.

An attempt will be made to show that, given a radical lacking a center of symmetry and the proper ion environment, the crystal will be found to be piezoelectric. For activity in the lattice the lack of a center of symmetry in the radical is not a sufficient specification.

Salts Containing Radicals of Octahedral, Planar or Tetrahedral Form. These are usually not piezoelectric. Typical octahedral ions whose simple salts are not piezoelectric include SiF_6^{--} , $SnCl_6^{--}$, and $PtCl_6^{--}$. The same applies to planar complexes such as $PtCl_4^{--}$. This generalization is not however, intended to apply to compounds with two complex radicals. For example, $Be \cdot 4H_2O$ forms a tetrahedral complex in $BeSO_4 \cdot 4H_2O$ ⁵ which shows moderate piezoelectric activity.

The essentially planar NO_3^{--} and CO_3^{--} also usually result in inactive compounds, but are more easily distorted as in the case of Rb and

⁴ It has been suggested that the inactivity of these tetrahedrally shaped- XO_4 salts might be explained on the basis that adjacent tetrahedra would be so placed as to possess, together, a center of symmetry. Examination of typical XO_4 structures does not show any such arrangements of the units in these salts.

⁵ Wells, A. F., *Structural Inorganic Chemistry*, Oxford University Press (1945), pp. 369.

Cs salts. Several complex nitrates such as $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$ and $\text{KLa}(\text{NO}_3)_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ are active and do not lend themselves to this generalization, again because of the presence of H_2O and the multiple cations. None of the simple carbonates are active although several mixed carbonates such as LiNaCO_3 do exhibit piezoelectricity.

The following tabulation shows (by a +) which of the chlorates, bromates, and iodates combined with univalent cations are active:

	Li	Na	K	Rb	Cs	Ag	H
ClO_3		+				+	(high form)
BrO_3		+	+	+	+		
IO_3	+		+	+?	+?	+	+

The chlorate and bromate structures are similar,⁶ the X atom of the XO_3 group being located at the apex of a low pyramid with the unshared pair of electrons occupying the 4th tetrahedral position. Here the radical XO_3 exists as a discrete building unit since the coordination of X for O is according to the chemical formula. The building unit, like all tetrahedral-shaped ions, is without a center of symmetry.

Of the chlorates only three active crystals are known: sodium, silver (high form) and strontium. No simple reason can be given for the inactivity of the other members except to say that of these anions, the polarizability of the ClO_3^- would be the least.

If an increase is made in the size of the central X ion in the XO_3 structure, as in BrO_3^- , an increase in the number of active salts is found. This would seem to indicate that the increased polarizability of the bromate ion by the cation has further emphasized the asymmetry of the radical.

Iodic acid, which consists of hydrogen-bonded, discrete IO_3 groups, is strongly piezoelectric. It is believed that the hydrogen bonding is responsible for the activity, possibly because it further emphasizes the asymmetry of the units from which the lattice is built.

With the exception of sodium iodate, all the alkali iodates are active, as is silver iodate. However, the iodine has a much higher coordination for the oxygen ion than has chlorine or bromine, so that a three-dimensional network results. Therefore, we can no longer speak of discrete anions or radicals. In the series Li-Na-K-Rb-Cs the cation coordination for O^{--} is respectively 6-10-12-12-12. The inactive NaIO_3 , has a deformed perovskite structure, while the active potassium, rubidium, and cesium iodates have a normal one. Even in the absence of discrete building blocks, the possibility of the polarization of the large I ion lends itself to the picture of an anionic asymmetry within the lattice.⁷

⁶ Wells, *Op. Cit.*, pp. 272-273.

⁷ Among the other XO_3 salts we can list one other piezoelectric material, BaTiO_3 . This crystal has a structure similar to KIO_3 .

The Phosphates. Of the univalent and bivalent tertiary phosphates only Ag_3PO_4 is active, despite the fact that all of these phosphates contain a tetrahedrally shaped anion which lacks a center of symmetry. It is of interest to note that in the case of Ag_3PO_4 the P-O distance is increased, although it is normally constant in other orthophosphates. The strong polarization of the PO_4 group by the Ag ions has enhanced the asymmetry of this group to produce the directional properties necessary for piezoelectricity. Ag_3AsO_4 has a similar behavior and structure. This polarization of the silver arsenate and phosphate is also evident in their respective colors, chocolate brown and yellow. In the case of aluminum orthophosphate AlPO_4 which is piezoelectric and isotypic with quartz (SiSiO_4), it is probably not correct to speak of anionic groups, as the isotypic quartz lattice is a three-dimensional network. The O ions are certainly strongly polarized, however, by the trivalent Al and the pentavalent P.

The tabulation below indicates the piezoelectric activity of the H_2PO_4^- salts. In these salts, as far as is known, complete substitutions of D^+ for H^+ and of As^{5+} for P^{5+} are possible:

	H_2PO_4^-	H_2AsO_4^-
Na	+ (H_2O)	+ (H_2O)
K	+	+
Rb	+ (Tetr. form)	
Cs	-*	
NH_4	+	+

+ Indicates activity.

- Indicates inactive salt.

* Not isomorphous.

The following cation substitutions have been reported:^{8,9}

SOLID SOLUTION IN XH_2PO_4

X	Substituting Ions				
	K	Rb	Cs	NH_4	Tl
KH_2PO_4	—	L	L	C	L
KH_2AsO_4	—			C	
$\text{NH}_4\text{H}_2\text{PO}_4$	C	L	L	—	L
$\text{NH}_4\text{H}_2\text{AsO}_4$	C			—	

L Indicates limited solid solution.

C Indicates complete solid solution.

(Incomplete data indicate that the same solid solution relations apply to the arsenate substituted compound.)

⁸ The following selected references are of interest: Bartschi, P. et al., *Helvetica Physica Acta*, **18**, 240 (7/16/47); Matthias, B., and Merz, W., *Idem* **19**, 227 (7/31/46).

⁹ Report No. 1 *NDRC Project 17.3-11* (2/1/43)—unpublished data of Mueller, H. et. al.

In these salts the building unit is a hydrogen-bonded PO_4 group. In fact, the O-H-O distance in KH_2PO_4 is the smallest such distance known.¹⁰

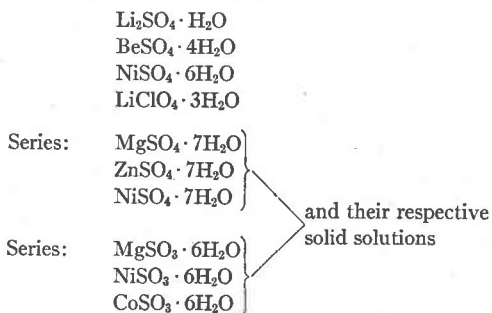
The otherwise inactive PO_4 group is rendered active by the bonding to the cations through hydrogen and the resulting asymmetry of the building unit. The monohydrates $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$, are moderately active and fit into the above picture.

However, the inactivity of one of the forms of RbH_2PO_4 and of CsH_2PO_4 is not so readily explained except perhaps on the basis of an extreme distortion of the H_2PO_4 group.

The Anhydrous Sulfates. As mentioned earlier the anhydrous sulfates are usually inactive. The exceptions to this statement are the anhydrous sulfates which contain a large and a small cation. For example, some of the MLiSO_4 salts are active, where M^+ can be the univalent ions Na^+ , K^+ , and NH_4^+ . The mutual presence of a small and a large cation acts on the SO_4 group to produce a one-sided polarization in the structure, as it does in the mixed carbonates. Selenium can be substituted completely, and Cr^{6+} and Mo^{6+} partially, in these sulfates without loss of activity.²

Hydrated Sulfates and Related Compounds. The dithionates of potassium, rubidium, cesium, barium, strontium, and lead are piezoelectric. The dithionate ion consists of two SO_3 groups linked through the sulfur atoms, and has a center of symmetry.¹¹ Thus the dithionate complex offers an exception to the relation of mutual asymmetry in radical and lattice.

The list of active hydrated compounds can be summarized as follows:



The salt $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has a group $\text{Ni}(\text{H}_2\text{O})_6^{++}$ but the coordination arrangements for the six water molecules are not identical and the group, therefore, cannot be considered as similar to the octahedrally shaped $\text{Fe}(\text{CN})_6$ radical.¹² A similar situation probably holds for the hexahydrated sulfites.

¹⁰ Pauling, L., *Nature of the Chemical Bond*, Cornell University Press (1945), pp. 311.

¹¹ Wells, *Op. Cit.*, pp. 305.

¹² Wells, *Op. Cit.*, pp. 368-369.

In the case of the heptahydrate series, there are octahedral groups $M(H_2O)_6$ with the seventh water molecule held between these groups and the anions.

The structure of $BeSO_4 \cdot 4H_2O$ is a packing of SO_4 tetrahedra and $Be(H_2O)_4$ groups.⁵ Here the water molecules have an identical arrangement, but are under strong polarizing influence of the small Be ion. The monohydrate of lithium sulfate is an unusually strong piezoelectric material. In this salt the coordination of the two lithium ions is different; one has an environment of a water molecule and three O ions, while the other is surrounded by four O ions. The lithium perchlorate $LiClO_4 \cdot 3H_2O$ belongs to an isomorphous family of salts which have much the same structure as the sulfate hexahydrates, the lithium being surrounded octahedrally by six water molecules.¹³ Again the presence of a small ion must act to produce those conditions in the lattice that make it piezoelectric.

In the case of the numerous alums $MAI(SO_4)_2 \cdot 12H_2O$ and schönites or picromerites $M_2^I M^{II}(SO_4)_2 \cdot 6H_2O$ the coordination of the various cations by the water molecules is perfectly symmetrical, thus giving no cause for asymmetry in the lattice. None of these salts is active.¹⁴

It should be mentioned that Se^{6+} can replace S^{6+} in any of the above sulfates, either in whole or in part, without loss of piezoelectric activity.²

SUMMARY

This investigation of piezoelectric activity in available inorganic crystals has attempted to find a relationship between crystal structure and the presence of activity.

It will be recalled that all of the active compounds studied belong to crystal classes which lack a center of symmetry. Many of them also contain a complex ion which likewise lacks a center of symmetry. It should be pointed out, however, that not all salts containing such asymmetric radicals are active.

The study has indicated that two conditions are, in general, characteristic of piezoelectric structures: (1) they contain an asymmetric radical, and (2) the ion environment of this radical is such that it further emphasizes the asymmetry.

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¹³ Wells, *Op. Cit.*, pp. 370.

¹⁴ Wells, *Op. Cit.*, pp. 180.