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PIEZOELECTRIC ORGANOMETALLIC CRYSTALS: GROWTH AND PROPERTIES OF TETRAPHENYLSILICON, -GERMANIUM, -TIN AND -LEAD

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SUMMARY

Techniques are described for growing large, optical-quality single crystals of tetraphenylsilicon, -germanium, -tin and -lead. Several optical, electro-optical and electrical properties have been measured in order to evaluate these materials for possible application in quantum electronic devices.

INTRODUCTION

This paper reports the successful growth of large piezoelectric organometallic crystals and properties pertinent to their possible application in quantum electronic devices. The compounds studied were the tetraphenyl derivatives of the Group IV elements, namely, silicon, germanium, tin and lead. The other member of this family, tetraphenylmethane, was also studied and will be described in a separate publication. Although these compounds belong to the same tetragonal scalenohedral $\bar{4}2\,m$ symmetry class as several important ionic piezoelectric materials, such as potassium dihydrogen phosphate and its isomorphs, and beryllium sulfate, they are expected to exhibit unique properties characteristic of metallic-covalent bonding and the structural variation possible with these ring systems.

PRELIMINARY STUDIES

Important crystallographic and physical property data reported in the literature are summarized in Tables 1–3. The compounds were found to be stable in air at 100° for long periods of time and to be insoluble in water, alcohol, dilute acids and alkalis. The fact, however, that they are soluble in a wide variety of organic solvents, and can be melted and volatilized, makes crystal growth by a wide variety of techniques possible. Growth from the melt in a Bridgman apparatus[1] and by vapor phase transport, using a Piper–Polich type experimental arrangement[2], was initially applied to these compounds since it offered an alternative to the time-consuming solution growth process. Experience with these methods showed that, while large crystals

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TABLE 1

CRYSTALLOGRAPHIC DATA AND STRUCTURAL PARAMETERS[23-28]

Compound	*Cell parameters (Å)*		*Z*	*Space group*	*Molecular Symmetry in crystal*	*Packing coefficient k*	*Ring orientations*	
	a	*c*					φ	θ
$Si(C_6H_5)_4$	11.30	7.05	2	$P\bar{4}2_1c=D^4_{2d}$	$(S_4)\ \bar{4}$	0.71	8.0	37
$Ge(C_6H_5)_4$	11.60	6.85	2	$P\bar{4}2_1c=D^4_{2d}$	$(S_4)\ \bar{4}$	0.71	8.0 (estd.)	39 (estd.)
$Sn(C_6H_5)_4$	11.85	6.65	2	$P\bar{4}2_1c=D^4_{2d}$	$(S_4)\ \bar{4}$	0.70	8.0	42
$Pb(C_6H_5)_4$	12.05	6.55	2	$P\bar{4}2_1c=D^4_{2d}$	$(S_4)\ \bar{4}$	0.69	5.5	50

TABLE 2

PHYSICAL PROPERTY DATA

Compound	*Mol. wt.*[a]	*Density*[a] *(g/cm³)*	*M.p.*[a] *(°C)*	*B.p.*[a] *(°C)*	*Latent heat of sublimation at 25°*[b] *(kcal/mol)*	*Latent heat of decompostion at 25°*[b] *(kcal/mol)*	*Sublimation pressure at 25°*[b] *(mmHg)*	*Molal heat capacity at 25°*[c] *(cal/degree)*
$Si(C_6H_5)_4$	336.51	1.190	238	430	12.18	24.36	1.8×10^{-4}	94.6
$Ge(C_6H_5)_4$	381.02	1.360	235	>400	13 (estd.)	26 (estd.)	1×10^{-6} (estd.)	98.3 (estd.)
$Sn(C_6H_5)_4$	427.12	1.490	229	>420	14.21	28.42	6.39×10^{-9}	101.9
$Pb(C_6H_5)_4$	515.62	1.750	225	240	19.80	39.60	6.70×10^{-10}	105.6 (estd.)

[a] Refs. 29–37. [b] Refs. 38–40. [c] Refs. 41–43.

TABLE 3

CALCULATED LATTICE ENERGIES[44]

Compound	*a*	*c*	φ	*U (kcal·mol⁻¹)*
$Si(C_6H_5)_4$	11.326	6.889	7.5	−34.30
$Sn(C_6H_5)_4$	11.808	6.486	7.0	−36.04
$Pb(C_6H_5)_4$	12.033	6.380	5.5	−35.88

could be grown, they always appeared light grey in color, indicating that some thermal decomposition had indeed occurred during the preparation. The instability of tetravalent compounds of the Group IV elements has been reported to arise from a decrease in strength of the covalent bonds formed by the metal atom as the atomic number increases in this series[3-10]. Eventually, the largest, most perfect crystals in terms of clarity and dislocation density, were obtained by a slow cooling technique[11].

EXPERIMENTAL EQUIPMENT AND MATERIALS

For this process many solvents were tried but the compounds were soluble in the order chloroform > benzene > dioxane[12]. Fig. 1 (a–d) shows the temperature

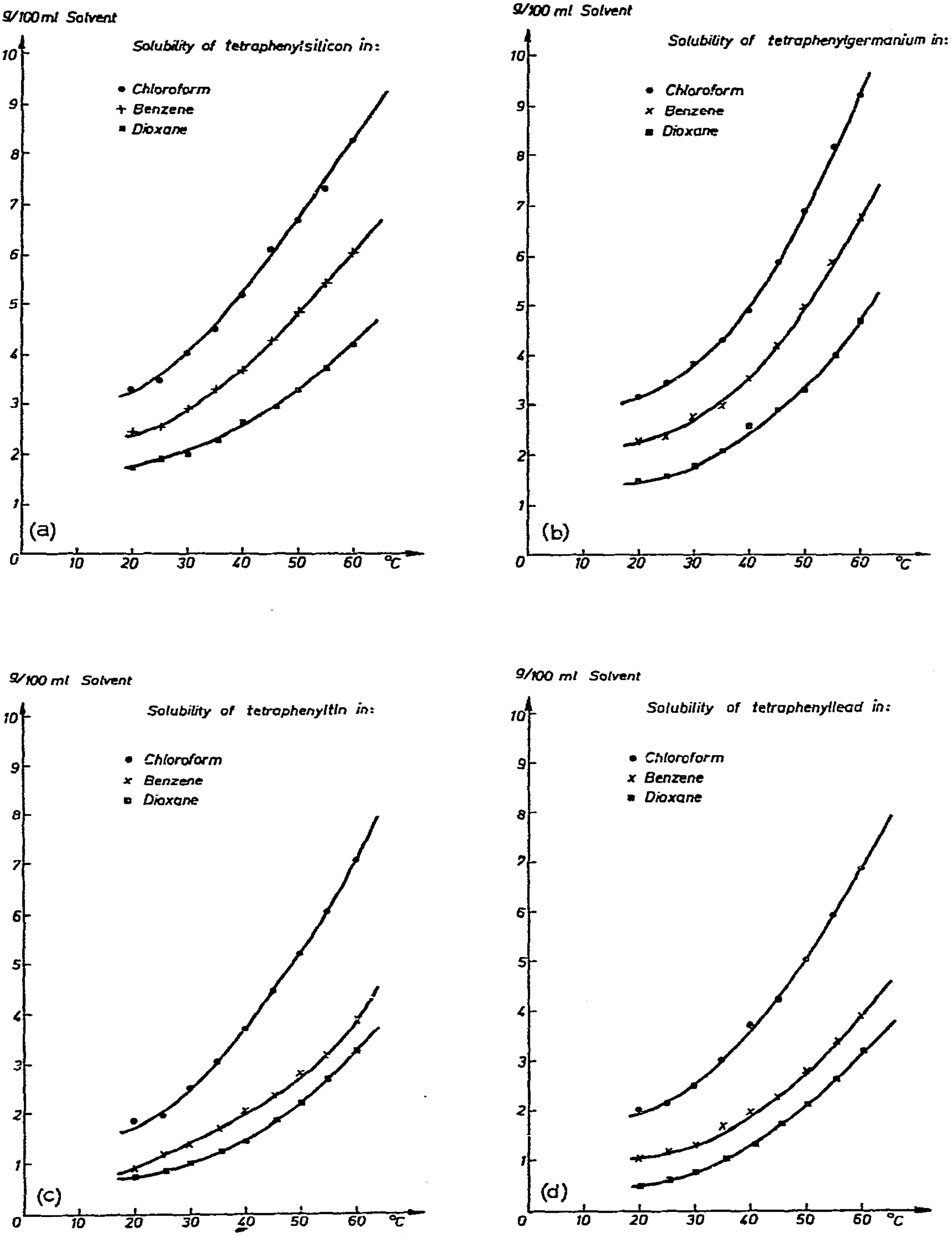

Fig. 1. Temperature dependence of the solubility (in chloroform, benzene and dioxane) of (a) tetraphenylsilicon, (b) tetraphenylgermanium, (c) tetraphenyltin, and (d) tetraphenyllead.

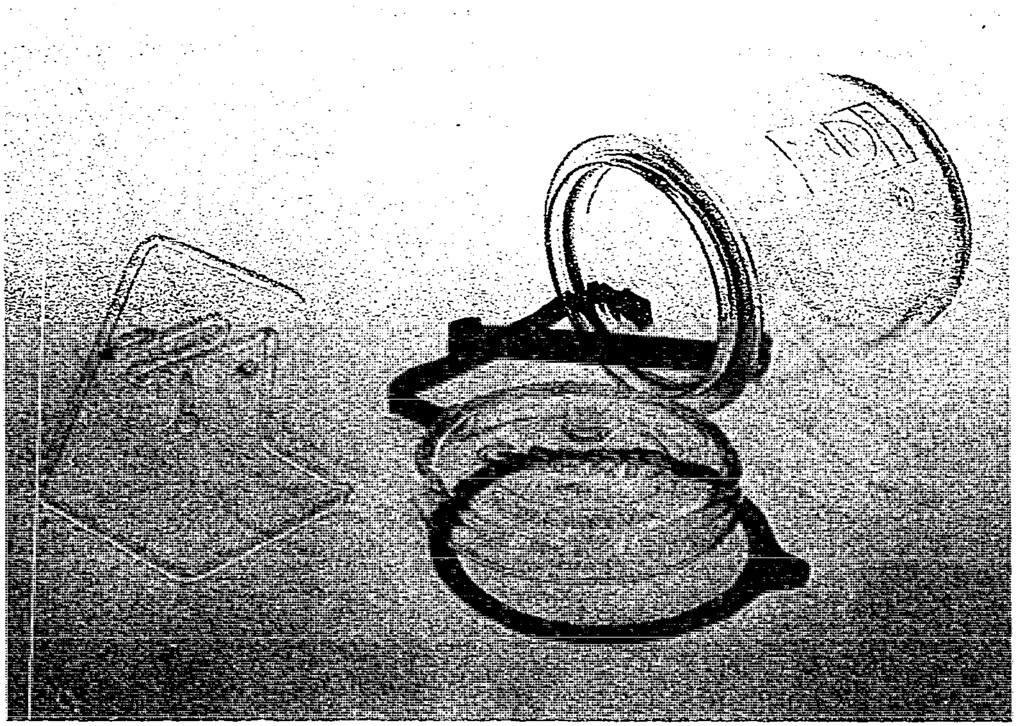

Fig. 2. Right: crystallization jar, clamp and cover assembly. Left: glass tweezer-crystal holder-stirrer assembly.

dependence of the solubility of the compounds in each of these solvents. Starting materials for these experiments and for the crystal synthesis described below were obtained from commercial suppliers. Before use, the tetraphenyl compounds were purified by two repeated crystallizations from hot chloroform. Reagent grade solvents were used in all cases without further purification.

The water baths that were used contained 30 l of water which was continuously circulated by a pump. Close control of the water temperature to ±0.005°, together with a slow and continuous change in temperature to maintain a uniform degree of supersaturation, was achieved with commercially available equipment. This equipment employed a platinum resistance thermometer as the sensing element, in conjunction with a proportioning temperature controller, and utilized a motor-driven Wheatstone bridge circuit. Crystallization generally occurred spontaneously in the absence of seeds within individual 750 ml glass jars. Figure 2 shows one of these jars which could be sealed by the silicon ring and clamp assembly. Each bath accommodated six of these jars in a specially designed rack. When seeds were used they either floated free or were held in the solution by the specially designed glass tweezer-holder-stirrer assembly also shown in Fig. 2.

CRYSTAL GROWTH TECHNIQUE

In a typical program, 500 ml of solution were prepared at 50° from solvent and the compound to be crystallized. The solution was filtered hot to remove insoluble material. On transfer to the growth jar the temperature was raised to 55° ensuring the absence of nuclei which would induce spontaneous growth. When the largest crystals were desired, a seed crystal, mounted or unmounted, was added at this stage. The jars were then quickly capped, sealed and transferred to the water baths maintained at 55°. After equilibration, the temperature of the baths was lowered to room temperature at the rate of 0.2° per day. Under these conditions the rate of growth of homogeneous crystals in the *c* direction is estimated to be 0.5 mm per day.

At the end of the program, great care was exercised in removing the crystals as they were sensitive to thermal shock. Experience shows that crystals with highly anisotropic thermal expansions are likely to crack in the slightest thermal gradient. The most satisfactory method, which also preserves the quality of the crystal faces, was to slowly remove the crystals from the organic solvent into water at the same temperature. This was best accomplished by a displacement technique, utilizing the density difference between the water from the bath and the solution. The water-filled jars were then removed from the bath and placed in a heating oven. Next, the satisfactory removal of any organic solvent for the crystals was accomplished by slowly heating the jars from room temperature to 80° and maintaining this temperature for 12 h. After slow cooling to room temperature the crystals were mechanically and individually removed from the jars, dried with a soft tissue paper and stored until used.

PROPERTIES

Fig. 3 shows several examples of the crystals that were grown for the several

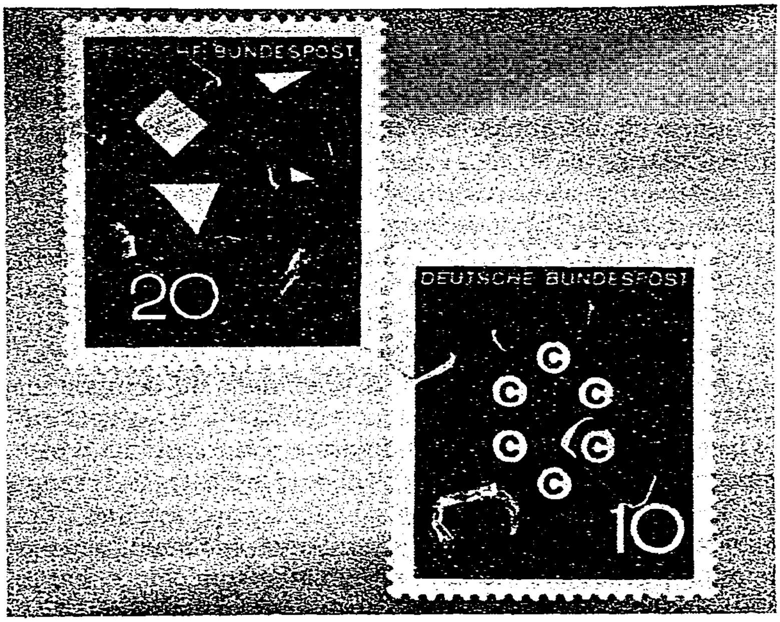

Fig. 3. Examples of the crystals grown of the various tetraphenyl metal compounds.

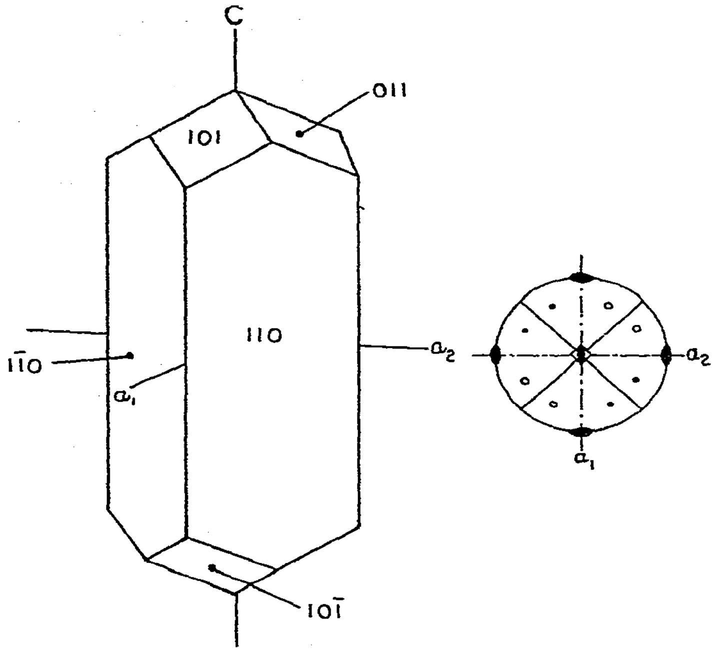

Fig. 4. Schematic drawing of an idealized crystal showing the relationship between external morphology, the crystallographic axis, and the symmetry elements for this crystal class.

compounds. Crystals of this size were normally used as seeds from which crystals as large as 3 cm have been grown to date. Fig. 4 depicts an idealized crystal and the relationship between external morphology, the orientation of the crystallographic axis and the symmetry elements of this crystal class.

The crystals are first order tetragonal prisms {110} elongated in the *c*-direction and terminated by the pyramidal faces {101}. The prismatic faces were identified as {110} by X-ray diffraction using the known lattice constants. The pyramidal faces were identified as {101} by measuring the angles between normals to the faces; angle between [101] and [011]: calculated, 40.5°, measured, 39.3°; angle between [110] and [101]: calculated 69.8°, measured 68.7°. Crystals grown from chloroform and benzene normally grew fastest in the [001] or *c*-direction, whereas, crystals grown from dioxane were generally more tabular in habit resulting from a decreased growth rate in this direction. In all solution-grown crystals, the dislocation density, as judged by etch figures and verified by X-ray topography, was $< 10^2 \cdot \text{cm}^{-2}$. This was 10^3–10^5 per cm^2 fewer dislocations than was found in vapor or melt-grown material[13].

The fact that large, non-hygroscopic crystals of this family of compounds could be grown with few defects suggested their use as analyzers for X-ray spectrochemical analysis. Table 4 lists, for each crystal, the diffracting plane spacings which have relative diffracted intensities over 25% of that from LiF and indicates their range of usefulness.

The crystals are uniaxially positive with the *c*-crystallographic direction containing the optic axis. The refractive indices did not vary greatly from compound to compound and were generally in the 1.58 ± 0.05 range. The optical transmission of a 2 mm thick tetraphenyltin crystal is depicted in Fig. 5 and shows that materials in this

TABLE 4

CALCULATED CRYSTALLOGRAPHIC AND SPECTROSCOPIC DATA

Compound	*Useful reflection plane*	*2d spacing (Å)*	*Lowest atomic number detectable*	
			K series	*L series*
$Si(C_6H_5)_4$	[110]	16.0	Na(11)	Ni(28)
$Ge(C_6H_5)_4$	[110]	16.4	Na(11)	Co(27)
$Sn(C_6H_5)_4$	[110]	16.8	Na(11)	Co(27)
$Pb(C_6H_5)_4$	[110]	17.0	Na(11)	Co(27)

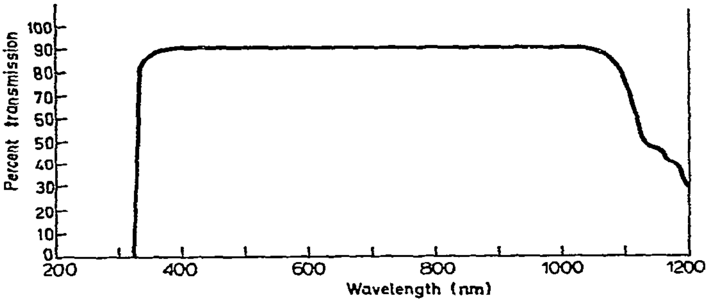

Fig. 5. Optical transmission of a 2 mm thick crystal of tetraphenyltin.

family are essentially transparent from 325 to 1200 nm. The UV and IR spectra for these compounds have been previously determined by other workers[14-18]. Measurements show that the fundamental or intrinsic absorption edge lies in the 3–4 eV range. The crystals are Class B second harmonic generators with coefficients similar to KDP[19]. Measurements of linear electro-optic effects show the r_{63} coefficients to be in the range $17 \pm 1 \times 10^{-12}$ m·V^{-1} with half-wave retardation voltages of 5 kV[20].

At room temperature, the crystals are temperature-insensitive insulators having a relative dielectric constant of 10 and an electrical resistivity over 10^{10} ohm·cm. Tests for the presence of a significant electro-luminescent effect were negative because of complex electrode problems associated with contacting this type of material. Carrier mobilities and concentrations have been measured to the limit of our Hall effect equipment and are less than 10 cm^2·V^{-1}·sec^{-1} and less than 10^{12}·cm^{-3}, respectively. The electrical–mechanical coupling coefficient parallel to the *c* axis is 5–10% for these crystals. The crystals exhibit moderately strong piezoelectric resonances. DTA analysis shows the structure to be stable from liquid nitrogen to the melting points of the compounds and, therefore, the compounds are not ferroelectric within this temperature range.

In agreement with the structure, cleavage of the crystals is easy parallel to {001} faces and poor perpendicular to the [001] direction. The crystals are soft and easily compressible with hardness values similar to that of tin[21].

CONCLUSIONS

Statistically the number of possible combinations of metalloids and inorganic compounds that will yield potentially useful piezoelectric materials is very limited[22]. On the other hand, organic or organometallic compounds, particularly those with ring systems, offer a wide range of structural variation. In addition, these classes of compounds can be prepared with extreme purity and with little stoichiometric variation; thus minimizing gross changes in the dielectric and optical properties. It seems probable, in view of the interesting properties exhibited by the tetraphenyl compounds of the Group IV elements, that they will become increasingly more valuable as piezoelectric materials now that large crystals of optical quality have been grown.

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