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焦電應用之硫酸三甘氨酸單晶片之配製
Crystal Preparation of TGS for Pyroelectric Purpose

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Abstract — Single crystals of TGS are prepared by acqeous solution-cooling method. Powder of TGS is obtained by stoichiometric mixing of sulfuric acid and glycine solution. A systematic analysis of the crystal geometry let us be able to find out the polar axis of the grown TGS crystal easily and to cleave the crystal along its b face accordingly. The resulting crystal plates are being used for pyroelectric thermal detector.

I. Introduction

Triglycine sulfate (abb. as TGS), its modified forms as well as its isomorphous are known to possess the highest pyroelectricity, [1], [2] and in many cases are the most suitable materials for making pyroelectric detectors operated at the room temperature. It is also known that TGS has been used as piezoelectric material. Therefore, the preparation of the single crystal thin plates of TGS becomes important as it is the first step towards these applications.

Crystal of TGS is monoclinic of class 2/m above its Curie temperature (~49°C), while below this temperature, it becomes non-centrosymmetric monoclinic of class 2 [3]. Its characteristic parameters are shown in Fig. 1.

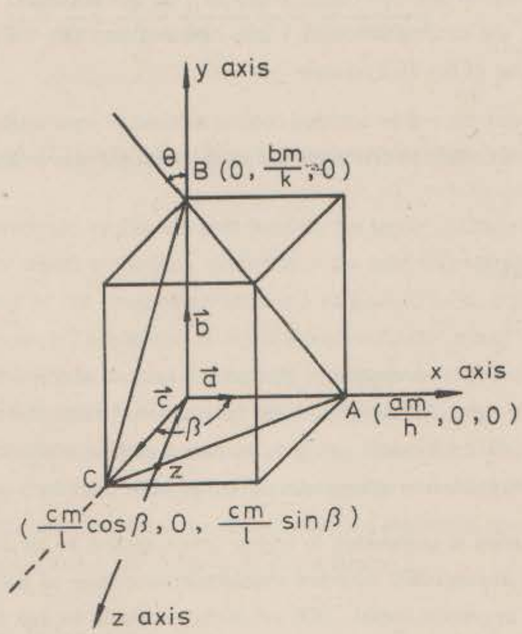

Fig. 1. Crystal structure of monoclinic TGS. Lattice parameters: a=9.147Å, b=12.643Å, c=5.735Å, $\alpha=\gamma=90^{\circ}$C, $\beta=110^{\circ}23'$, spontaneous polarization along b axis only.

There is only one polarization direction which is along the b axis of the crystal. So, unlike perovskite ferroelectrics which possess three polarization directions, it is important when the TGS crystals are used for pyroelectric device with face structure [4] to prepare crystal plates with the b axis perpendicular to the plate surfaces which are also the b faces. However, crystal habit often makes the b face absent or very small in grown crystal [3], instead, the most predominant plane is often the c face, (001). Yet the grown crystals often appear to have many unidentified surfaces of higher indices as examplified in Fig. 2.

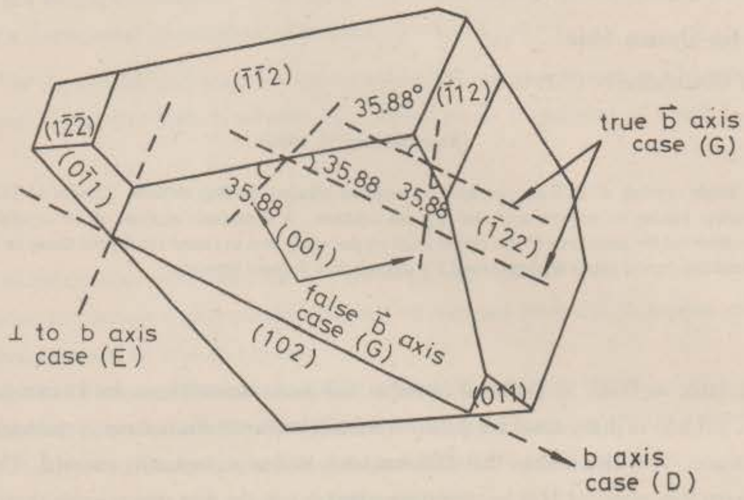

Fig. 2. Determination of b⃗ axis from the complexion of a real TGS crystal.

These make the determination of the monoclinic b axis of TGS not apparent. Since it is known the b face is the pronounced cleavage plane, the determination of b axis can also facilitate the cleavage of b faces without the necessity of knowing c and a axas of the TGS crystals.

In this report, we have used the regular solution-cooling method to grow single crystals of TGS. Geometric analysis of the crystal of TGS let us be able to determine the polar b axis and thus to cleave the grown TGS crystals accordingly.

II. Crystal Growth of TGS

The Powder

Powder of TGS is obtained by the reaction of glycine and sulfuric acid in 3 to 1 molar ratio. However, since the reaction is very exothermic, direct mixing of both the reactants will cause the burnings and the decompositions of the glacine and the TGS product. A better way is to prepare a sulfuric acid solution in 80 w/0 concentration to let most of the heat of mixing evolve before mixing into glycine acqeous solution.

The obtained mixed solution is evaporated to higher concentration to let TGS powder precipitate due to over saturation. Because of the impossibility of exact stoichiometric mixing of the two reactants, complete-dried evaporation should be avoided to prevent impure TGS products. It would be bad when the sulfuric acid is over rich in the mixing, as it might cause leakage in the future pyroelectric devices. To have higher purity, the formed TGS powder can be redissolved in D.I. water and dried one more time.

The Seed

Seeds with enough size (~ $0.6x0.6x0.4\ cm^3$) for the crystal gowth can be selected among the precipitates from a fast cooled saturated TGS solution. They may also be selected from an evaporated TGS solution.

The Growth of Crystals

Solution growth [5], [6], [7] of TGS single crystal by cooling of a saturated solution (Fig. 3 shows the solubility curves) is performed with a temperature bath unit. A cylindrical glass container with the saturated solution is put into the water bath of the constant temperature unit and covered with a plastic plate to prevent the evaporation. A hole is drilled at the center of the plate to let the seed-holding rod to pass through. The rod is held and rotated by a dc motor with a rotating speed of about 300 rpm.

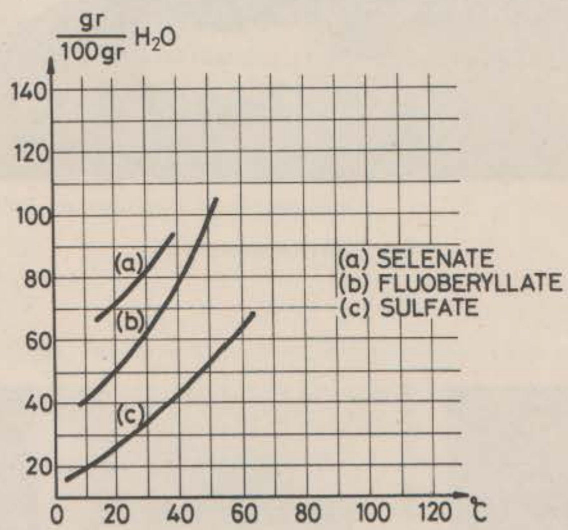

Fig. 3. Acqeous solubilities of TGS families (from R. Nitsche, Helv. Phys. Acta 31, p-306, 1958).

Heating of the bath water is performed by a power unit fixed on the top of the bath tank. The power unit is controlled by a thermometer-requlator which is partially dipped into the bath water to detect the instantaneous temperature of the water. The accuracy of the temperature setting is at least down to 0.05°C in this apparatus. Continuous change of the thermometer setting is made by fixing an aluminum pully, which has many radii, on the setting knob of the thermometer head so that the knob can be turned by a synchronous motor (1/24 rph) through a connecting belt. With the largest radius of the pully, the rotation speed is so slow that the water can be cooled as low as 0.02°C per day. The whole set of the apparatus is shown in Fig. 4. Saturated TGS solution of about one liter is cooled at a rate of 0.05°C per day from 35°C down with increasing rate of cooling when the crystal grows larger. With careful control at the begining, one almost can be sure to obtain a successful growth each time. Fig. 5 shows one of the grown crystal in a three-day period has a volume of about 10 cm^3.

III. The Determination of the Polar Axis

In Fig. 1 we have chosen the reference coordinate in such a way that the crystal b axis is coincident with the y axis and the a axis with the X axis, hence the monoclinic c axis makes an angle of 20°23' with the z axis. This reference coordinate is slightly different from that used by Konstantanova [8].

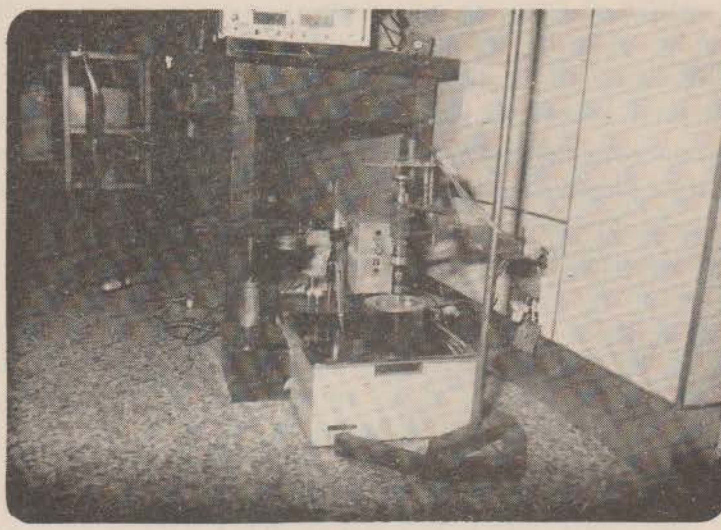

Fig. 4. Crystal growth set-up.

Fig. 5. Grown TGS crystal.

A plane of Miller indices $hk\ell$ will intercept at the three crystal axas at $\frac{am}{h}$, $\frac{bm}{k}$, and $\frac{cm}{\ell}$ respectively, where m is the least multiplier to make $\frac{1}{h}$, $\frac{1}{k}$, $\frac{1}{\ell}$ integers. The vector AB which is the line of intersection of $(hk\ell)$ and (001) planes is written as

$$\overrightarrow{AB} = -\frac{am}{h}\,\hat{i} + \frac{bm}{k}\,\hat{j}$$

therefore the angle, θ, between $\overrightarrow{AB}$ and the polar b axis is given by

$$\theta = \cos^{-1}[\frac{\overrightarrow{AB} \cdot \hat{j}}{|\overrightarrow{AB}| \cdot |\hat{j}|}]$$

$$= \cos^{-1}[\pm\{1+(\frac{ka}{hb})^2\}^{-1/2}]$$

$$= \cos^{-1}[\pm\{1+0.5234(k^2/h^2)\}^{-1/2}] \quad (1)$$

The + and - signs, which depend on the parity of k and their θ form the complimentary angle of each other, are used because it is difficult to define the to or from of a vector direction in a real crystal. Therefore identifying a crystal plane will let us obtain two possible choices of the b axis from equ. (1). In such case, another plane identification will give us the information to lift out the false one. However, when the θ is calculated to be 90°, this second plane identification is not necessary. Therefore, at most two plane identifications are required to determine the b axis. Plane identification is made by measuring the angle, δ , **between** the predominant c face and the unknown plane and comparing this measure to the calculated values according to the geometry of the monoclinic TGS crystal. As shown in Fig. 1, the plane (hkℓ) is represented by the equation

$$\frac{X}{am/h} + \frac{Y}{bm/k} + \frac{Z}{z_o} = 1 \quad (2)$$

in terms of the reference coordinate. Here z_o is the intercept of the plane (hkℓ) with the Z axis. It can be found by substituting the coordinate of point C, i. e., (cm cos β / ℓ , 0, cm/ ℓ sin β), into eq. (1), and obtains the result

$$z_o = \frac{acm \sin \beta}{a\ell + ch \cos\beta} \quad (3)$$

Since the angle between two planes is also the angle between their normals, hence for TGS crystal

$$\delta = \cos^{-1}[\frac{\overrightarrow{N}_{(hk\ell)} \cdot \overrightarrow{N}_{001}}{|\overrightarrow{N}_{(hk\ell)}| \cdot |\overrightarrow{N}_{001}|}]$$

$$= \cos^{-1}[\{(\frac{hz_o}{am})^2 + (\frac{kz_o}{bm})^2 + 1\}^{-1/2}]$$

$$= \cos^{-1}[\ (\frac{hc \sin\beta}{a\ell + ch \cos\beta})^2 + (\frac{k\ ac \sin\beta}{b(a\ell + ch \cos\beta)})^2 + 1\}^{-1/2}]$$

$$= \cos^{-1}[\{(\frac{5.376h}{9.147\ell + 1.998h})^2 + (\frac{3.889k}{9.147\ell + 1.998h})^2 + 1\}^{-1/2}] \quad (4)$$

where

$$\overrightarrow{N}_{(hk\ell)} = \frac{\hat{i}}{am/h} + \frac{\hat{j}}{bm/k} + \frac{\hat{k}}{z_o}$$

and

$$\overrightarrow{N}_{(001)} = \hat{k}$$

are the normals of (hkℓ) and (001) planes respectively. Table I is the calculated values of δ and θ for various (hkℓ) planes according to equations (1) and (4).

Table I

h	k	ℓ	δ degree	θ degree	180−θ degree
0	0	±1	0.00	–	–
0	±1	0	90.00	90	90
±1	0	0	69.61	0	180
±1	1	0	73.24	35.88	144.12
1	0	1	25.75	0	180
-1	0	1	36.94	0	180
0	±1	1	23.03	90	90
1	1	1	30.77	35.88	144.12
-1	1	1	42.87	35.88	144.12
1	-1	1	30.77	144.12	35.88
1	1	-1	42.87	35.88	144.12
2	0	1	39.29	0	180
2	0	-1	64.40	0	180
2	1	0	70.74	19.89	160.11
2	-1	0	70.74	160.11	19.89
±1	2	0	78.07	55.35	124.65
1	0	2	14.84	0	180
-1	0	2	18.26	0	180
0	±1	2	12.00	90	90
0	2	±1	40.38	90	90
1	1	2	18.11	35.88	144.12
1	-1	2	18.11	144.12	35.88
-1	1	2	22.15	35.88	144.12
-1	-1	2	22.15	144.12	35.88
1	2	1	40.31	55.35	124.65
1	-2	1	40.31	124.65	55.35
1	2	-1	52.91	55.35	124.65
-1	2	1	52.91	55.35	124.65
2	1	1	41.02	19.89	160.11
2	-1	1	41.02	160.11	19.89
2	1	-1	65.75	19.89	160.11
2	-1	-1	65.75	160.11	19.89
2	2	1	45.28	35.88	144.12
2	-2	1	45.28	144.12	35.88
2	2	-1	68.79	35.88	144.12
2	-2	-1	68.79	144.12	35.88
1	2	2	24.98	55.35	124.65
1	-2	2	24.98	124.65	55.35
1	2	-2	30.12	55.35	124.65
1	-2	-2	30.12	124.65	55.35
2	1	2	27.16	19.89	160.11
2	-1	2	27.16	160.11	19.89
2	1	-2	38.65	19.89	160.11
2	-1	-2	38.65	160.11	19.89

In summary, the following rules are the guidances to the determination of the polar b axis in a monoclinic TGS crystal.

A) Identify a predominant c face from the real crystal to be ckecked.

B) Measure the angle between the predominant c face and an adjoining face.

C) Check table I to identify the plane indices hkℓ, which would give the same δ value as that of the measurement.

D) If the index k found out for the plane is zero, then the edge of this plane with the predominant c face, namely the line $\overline{AB}$, is itself the b axis to be determined.

E) If the index h found out is zero, then the edge line AB is normal to the b axis.

F) If it is not the cases of D) or E), then repeat step B) and C) to identify another adjoining face.

G) Two identified planes give four possibilities of the b direction on the predominant c face. Only two of them should be identically parallel and these are the true b direction.

Examples of the analysis are shown in Fig. 2. According to the rule set above, it is best to have the first identified plane with either h or k indices vanished. Otherwise, two plane identifications are required by the rules. Fig. 6 shows the cleaved TGS plates by applying these rules.

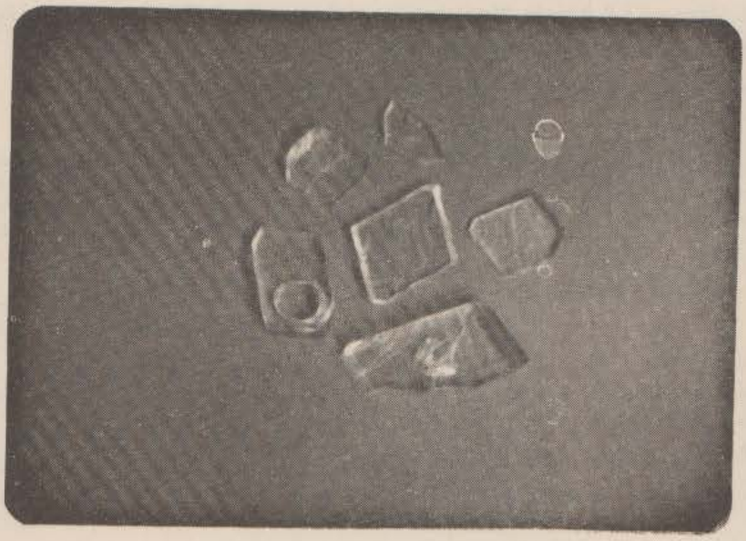

Fig. 6. Cleaved cystal plates.

IV. Conclusions

We have been able to grow the single crystals of pyroelectric TGS easily by the conventional solution-cooling method, starting from the preparation of TGS powder. Cuttings of the crystals along the cleavage b faces are also done successfully according to the systematic method of identification of b axis which is perpendicular to the cleavage b faces. At most two plane identifications are required by the method. Fig. 7 shows the hysteresis of the cleaved TGS plates with author's new type Sawyer-Tower circuit [9, 10]. Value of spontaneous polarization caluclated from the loop is found to be 3.2×10^{-8} c/cm^2 ^{o}K as that has been reported [3].

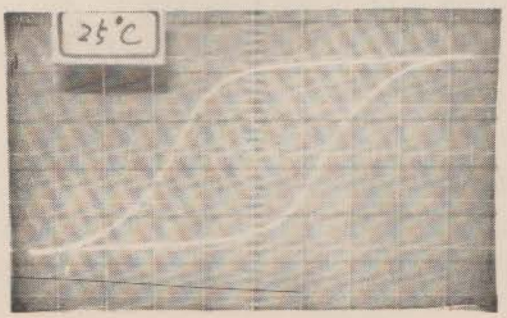

Fig. 7. Ferroelectric hysteresis loop of the grown TGS crystal.

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