THE EFFECT OF IMPURITIES ON SOME OF THE PHYSICAL PROPERTIES OF TGS CRYSTAL

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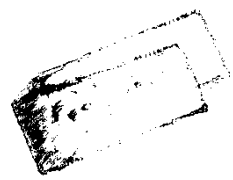

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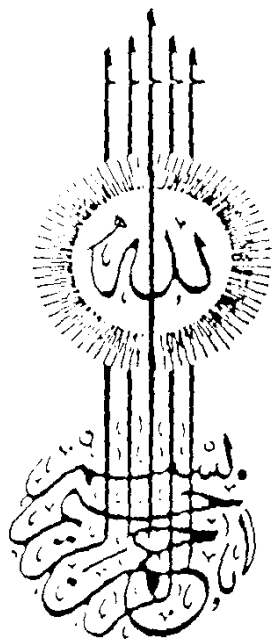

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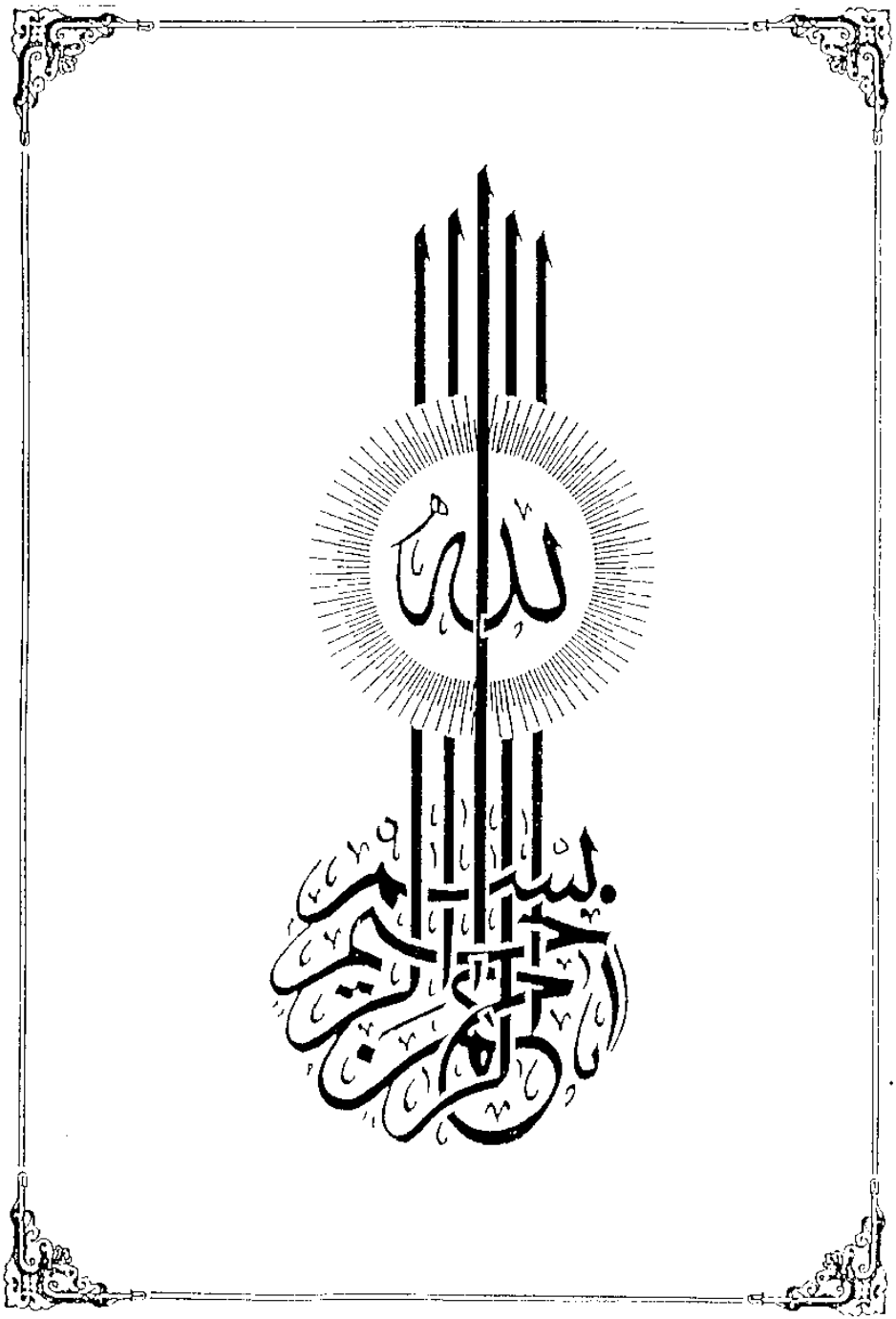

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SUMMARY

S U M M A R Y

Ferroelectric crystals exhibit strong anomalies in many of their physical properties such as dielectric constant, electrooptical coefficients, piezoelectric coefficients, and eleastic constants, such crystals have very large dielectric constant, and their large piezoelectric coefficients make them particularly suitable as transducers and resonators in place of quartz.

Triglycine sulfate crystals (TGS) are famous ferroelectrics which have high pyroelectric coefficient which enhanced them to be used as sensor elements for IR radiation, which has a great importance in military and agricultural applications as well as in medicine.

For there reason, this work was carried out to study the effect of adding some divalent or trivalent ions to the solution of grown TGS crystals to reveal some details about their behaviour in persue of some dopants for enhancing their efficiency as infrared detectors as well as inducing some special properties for the use in other applications.

Some physical properties of single TGS crystals pure as well as doped with Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}

and Cr^{3+} grown under identical conditions were studied. The spontaneous polarization, P_s and the coercive field E_c were studied as a function of temperature. The dielectric constant ϵ_{22}, the A.C. electrical conductivity σ_{22}, the pizoelectric constant d_{zz}, and the temperature of phase transition were studied in details.

It was found that the addition of such ions affected considerably the physical constants measured for pure TGS crystals. The degree of variation changed from one dopant to the other. There is no single dopant which affects all the measured physical properties towards the ideal behaviour. The variation in the physical properties of TGS is attributed to deformation, caused by the dopant, in the ferroelectric structure of the TGS lattice. The size of such deformed structures depdns on the nature of the incorporated ion.

INTRODUCTION

I. INTRODUCTION

I.1 General Features of Ferroelectricity:

A ferroelectric crystal is that type of crystal which exhibits an electric dipole moment even in the absence of an external electric field. In the ferroelectric state the center of positive charges does not coincide with the center of negative charges. The macroscopic structure of a ferroelectric crystal consists of domains; within which the polarization has a specific direction which varies from one domain to another. The ferroelectric properties disappear above a critical temperature T_c called curie temperature, below which the crystal is ferroelectric, while above it the crystal becomes paraelectric i.e. ordinary dielectric. The dielectric constant of a ferroelectric crystal, in most cases, exhibits a peak at the curie temperature. Similar anomalous behaviour is found in particular in the piezoelectric and elastic properties. (All ferroelectrics are necessarily piezoelectrics, but not all piezoelectrics are ferroelectrics).

Ferroelectric cystals show also hysteresis effects in the relation between dielectric displacement and electric field. This behaviour is mostly observed near the curie temperature.

The phenomenological theory of ferroelctrics and its application are described in several publications and monographs (1-4). Among the well known representatives of ferroelectric crystals, that -so far- have been studied, are Rochelle salt, Barium titanate, Potassium dihydrogen phosphate and other related isomorphous salts. Table (I.I) shows some ferroelectric materials with their characteristic T_c and the value of the spontaneous polarization at certain temperature.

Ferroelectrics exhibit, strong anomalies in many of their physical properties, such as dielectric constant, electrooptical coefficients, piezoelectric coefficients, elastic constants, ...etc. Some of these properties are actually used to build special devices. For example, the very large value of the dielectric constant of some ferroelectrics makes them useful -in ceramic form- as high capacitance condensers, while their large piezoelectric coefficients make them particularly suitable as transducers and resonators in place of quartz. More over, some ferroelectrics, e.g. TGS, have high, pyroelectric coefficients which enhanced the use of such materials as sensor elements for IR radiation (5). This has a great importance in remote sensing in military and agricultural applications as well as in medicine (thermography).

Table (I.I): Ferroelectric crystal data.

		T_c, °K	P_s(esu), at T °K	
Rochelle salt group	NaK $(C_4H_4O_6).4H_2O$	297 (upper) 255 (lower)	800	278°K
	Nak $(C_4H_2D_2O_6).4O_2O$	308 (upper) 251 (lower)	1100	279
	$LiNH_4(C_4H_4O_6).H_2O$	106	660	95
KDP group	KH_2PO_4	123	16000	96
	KD_2PO_4	213	13500	--
	RbH_2PO_4	147	16800	90
	RbH_2AsO_4	111	--	--
	KH_2AsO_4	96	15000	--
	KD_2AsO_4	162	--	--
	CsH_2AsO_4	143	--	--
	CsD_2AsD_4	212	--	--
Perovskites	BaTi	393	78000	296
	$SrTiO_3$	32	9000	4
	WO_3	223	--	--
	$KNbO_3$	712	90000	523
	$PbTiO_3$	763	150000	300
Limenite (approx.)	$LiTaO_3$	-	70000	720
TGS group	Tri-glycine sulfate	322	8400	293
	Tri-glycine selenate	295	2600	273

I.2 Triglycine sulfate crystals (TGS)

I.2.1 Crystal structure:

Triglycine sulfate $(NH_2\ CH_2\ COOH)_3\ H_2\ SO_4$ is a relatively young member of the fast-growing family of ferroelectric crystals. It has drawn the attention of many researchers since its ferroelectric behaviour was discovered by Matthias et al.(6) in 1956. It exhibits ferroelectric properties at room temperature, and can be grown easily from aqueous solution into large crystals with good quality. Ferroelectricity occurs also in two isomorphous crystals with triglycine sulfate namely, triglycine selenate (6) (TGSe) and triglycine fluoberyllate (7) (TGFB).

The peak value of the dielectric constant of TGS crystal at the transition temperature is very large and the spontaneous polarization decreases slowly with temperature and show no discontinuity at the transition temperature, indicating that the phase transition of triglycine sulfate is a typical second order phase transition.

Crystallographic data for triglycine sulfate were first reported by Wood and Holden (8) as follows

a= 9.15 A° , b= 12.69 A°

c= 5.73 A° , B= 105°

According to Wood and Holden the ferroelectric properties occur along the direction of the two-fold polar axis which is the monoclinic b-axis. The phase above the transition temperature for these crystals belongs to the point groups C_{2n}=2/m, and space group $P_{2_1/m}$, therefore it has a center of symmetry. In most ferroelectrics the structure symmetry is lowered by passing through the transition point to low temperatures, which is the case in TGS. Below the transition temperature, the spontaneous polarization occurs parallel to the ferroelectric b-axis and thus the mirror plane disappears and the point group becomes C_2=2 and space group P_{2_1}, which means that crystals of TGS have monoclinic symmetry both above and below the transition.

Figure (1.1) shows the morphology of TGS. The crystals have a good cleavage plane parallel to the (010) plane normal to the ferroelectric axis. The reference system of coordinates generallY adopted is that proposed by Konstantinova et. al.(9) and is shown in Fig.(1.2); the y-axis is parallel to the polar axis, the z-axis is parallel to the natural edge which forms an angle of 150° with predominant (C) faces of the crystals and the x-axis is perpendicular to y and z to form a right handed system.