

Mechanoluminescence of ferroelectric crystals

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Abstract. Mechanoluminescence spectra of triglycine sulfate, guanidine aluminium sulfate, rochelle salt, diglycine manganous chloride dihydrate, lithium ammonium tartate monohydrate and potassium dihydrogen phosphate crystals resemble the discharge spectra of nitrogen gases. Glycine silver nitrate, thiourea, ammonium sulfate and azobenzene crystals, the structure of which is centrosymmetric at room temperature, do not show mechanoluminescence. Following the role of crystal structure, the mechanoluminescence excitation is discussed on the basis of the piezo-electrification of the new surfaces created during fracture of the crystals.

Keywords. Mechanoluminescence; triboluminescence; luminescence; ferroelectricity; crystal fracture; high pressure phenomena.

1. Introduction

Mechanoluminescence (triboluminescence) is a type of luminescence produced during mechanical action on solids. Most of the crystals show mechanoluminescence (ML) only during their fracture. However, crystals of impurity-doped zinc sulphides and coloured alkali halides show ML in their elastic, plastic and fracture regions (Meyer *et al* 1970). The crystals of certain rare earth oxides also exhibit ML in their plastic and fracture regions (Williams and Turner 1979). Because of the complexity of crystal fracture, relatively less progress has been made on the investigation of ML (Zink 1978).

We have been interested in the correlation between the ML and piezoelectric behaviour of crystals (Chandra and Shrivastava 1978). The present paper reports on the ML of certain ferroelectric crystals and shows that the crystal structure plays a fundamental role in the ML excitation.

2. Experimental

Single crystals of rochelle salt, potassium dihydrogen phosphate and ammonium sulfate were grown from the supersaturated solution of the reagent grade materials. The crystals of guanidine aluminium sulfate, triglycine sulfate, diglycine manganous chloride dihydrate, glycine silver nitrate and lithium ammonium tartrate monohydrate were obtained from the aqueous solution which contained stoichiometric quantities of the constituent materials. The crystals of thiourea and azobenzene were grown by

the slow evaporation of their solution in methanol and acetone respectively. For the determination of the ML spectra the crystals were fractured in a glass vial with a stainless steel rod. The spectra of the light emitted as a result of the application of the mechanical stress were measured using EMI9558RF photomultiplier tube and Bausch and Lomb 1 m excitation monochromator following the method of Hardy and Zink (1976). For the measurement of the ML activity, the crystals of a particular size were fractured into crumbled masses by dropping a load of 800 g from a height of 4 cm. The intensity of ML was monitored by an IP21 photomultiplier tube connected to a ballistic galvanometer. When the crystals of small cross-section area as compared to the light-sensitive area of the photomultiplier tube, are crushed close (1.5 cm) to the photomultiplier tube, the ML intensity measured in terms of the galvanometer deflection will be proportional to the total intensity of ML. Thus the ML activity per gram mole can be determined relatively from the intensity of ML for a given mass of the crystals. It is well known that after a particular size, the total intensity of ML increases directly with the mass of the crystals (Chandra and Zink 1979). The piezoelectricity of the crystals was tested by the method described in an earlier paper (Chandra and Shrivastava 1978). All measurements were made at the room temperature.

3. Results and discussion

Figure 1 shows the ML spectra of triglycine sulfate crystals. It is seen that the ML

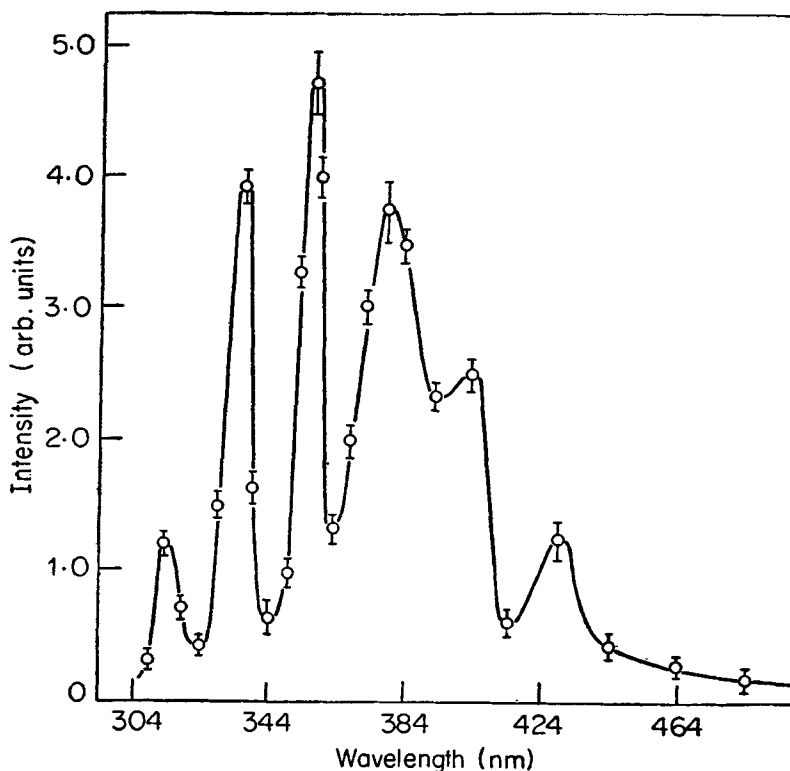


Figure 1. Mechanoluminescence spectra of triglycine sulfate crystals.

Table 1. Mechanoluminescence activity of ferroelectric crystals

Crystal	Space group		Transition temperature (°C)	Reference	Piezo-electricity at 27°C	Mechanoluminescence	Normalised ML activity/g mol with respect to that of triglycine sulfate crystals
	Para-electric	Ferro-electric					
Triglycine sulfate	$P2_1/a$	$P2_1$	47	Ikeda <i>et al</i> (1962)	+	+	1.00
Guanidine aluminium sulfate	$P6_3$	$P3m$	200	Holden <i>et al</i> (1955, 1956)	+	+	1.05 ± 0.06
Rochelle salt	$P2_12_12_1$	$P2_1$	24, -18	Zhadnov (1965)	+	+	0.48 ± 0.03
Diglycine manganese chloride dihydrate	—	$P2_1$	55	Pepinsky <i>et al</i> (1957)	+	+	0.24 ± 0.02
Lithium ammonium tartrate monohydrate	$P2_12_12_1$	—	-167	Zhadnov (1965)	+	+	0.34 ± 0.02
Potassium dihydrogen phosphate	$F4d2$	$Fdd2$	-140	Zhadnov (1965)	+	+	0.013 ± 0.003
Glycine silver nitrate	$P2_1/a$	—	-55	Hoshino <i>et al</i> (1957)	—	—	0.00
Thiourea	$Pnma$	—	-105	Soloman (1956)	—	—	0.00
Ammonium sulfate	$Pnma$	—	-49.5	Matthias and Renneka (1956)	—	—	0.00
Azobenzene	$P2_1/a$	—	—	Brown (1966); Mitsui <i>et al</i> (1976)	—	—	0.00

+ Present; - Absent

spectra correspond to the second positive group ${}^3\Pi_u \rightarrow {}^3\Pi_g$ of molecular nitrogen (Herzberg 1950). The ML spectra of guanidine aluminium sulfate, rochelle salt, diglycine manganous chloride dihydrate and lithium ammonium tartrate monohydrate crystals, are also similar to those of triglycine sulfate crystals. As the ML intensity of potassium dihydrogen phosphate crystals is very weak, it was not possible to take the complete spectra. However, the test with filters suggests that the ML spectra of potassium dihydrogen phosphate crystals also correspond to the second positive group of molecular nitrogen.

Table 1 shows that the crystals whose structure is centro-symmetric at room temperature, do not show ML.

The appearance of ML only during crystal fracture and its origin from excited molecules of nitrogen suggest that the mechanism of excitation may involve creation of charged surfaces during fracture followed excitation of nitrogen molecules by electrons accelerated between the surfaces (Chandra 1978; Walton 1977). Since the ML appears only in non-centrosymmetric crystals (table 1), the charging could be related to their piezoelectric behaviour. The electric field between the newly created surfaces can be estimated from the following consideration of Langevin's model of the creation of oppositely charged surfaces during the movement of a crack in a piezoelectric crystal (Langevin 1913).

When a stress is applied to a piezoelectric crystal, its one surface along the direction of the stress becomes positively charged and the other surface becomes negatively charged. During the movement of a crack, the crystal begins to separate into two parts. Due to the piezoelectric behaviour, the newly created surface towards the positively charged surface of the unbroken crystal is negatively charged and the newly created surface towards the negatively charged surface of the unbroken crystal is positively charged. Thus an intense electric field is generated between the newly created and oppositely charged surfaces at fracture. For the simplification of the problem, let us make certain assumptions: (i) that the piezoelectric constant d remains unchanged up to the fracture stress σ_f of the crystal, (ii) that the stress near the tip of the mobile crack acts along the polar direction of the crystal and (iii) that the stress near the tip of the crack is not relaxed before the discharge of the intervening gases. Then the charge density ρ of the newly created surfaces near the tip of the mobile crack will be $d \sigma_f$. For triglycine sulfate crystals d_{22} at the room temperature is $16.7 \times 10^{-12} \text{ CN}^{-1}$ (Ikeda *et al* 1962) and the fracture stress estimated from 1/30 of the Young's modulus (Ikeda *et al* 1962) is $3.8 \times 10^8 \text{ Nm}^{-2}$. Thus the charge density of the newly created surfaces of triglycine sulfate crystals will be $6.3 \times 10^{-3} \text{ cm}^{-2}$. The electric field between the charged surfaces will be, ρ/ϵ_0 , that is $7.1 \times 10^8 \text{ Vm}^{-1}$, where ϵ_0 is the permittivity constant. This electric field is sufficient to initiate gas discharge at atmospheric pressure which needs a field around $3 \times 10^7 \text{ Vm}^{-1}$. As such the rough estimation supports the possibility of ML excitation as a result of the piezoelectrification of the new surfaces created during fracture of the crystals. Similarly, the ML in guanidine aluminium sulfate and diglycine manganous chloride dihydrate crystals can also be understood. Lithium ammonium tartrate monohydrate, potassium dihydrogen phosphate and rochelle salt (above 24°C) crystals are piezoelectric only under torsion, hence, the appearance of ML in these crystals suggests that there is sufficient torsion near the tip of the mobile crack which produces the necessary charge on the newly created surfaces of the crystals.

We have found the gas discharge ML in triglycine sulfate, diglycine nitrate and diglycine manganous chloride dihydrate crystals above their Curie temperatures. This shows the presence of some non-centrosymmetric phase even at temperatures higher than the Curie temperature. The ideas on the effects of temperature on the ML of ferroelectric crystals will be explored fully in a subsequent paper.

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