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Triboluminescence of Inorganic Sulfates

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A survey is made of the triboluminescence (TL) of 45 common inorganic sulfates. All the noncentrosymmetric crystals show TL, and all the crystals not exhibiting TL are centrosymmetric. The TL spectra of all of the crystals except $Ce_2(SO_4)_3{\cdot}8H_2O$ show that the emission originates from the second positive group of molecular nitrogen. In $Ce_2(SO_4)_2{\cdot}8H_2O$ crystals, the TL spectrum resembles the photoluminescence spectrum. TL appears concurrently with the sudden force decreases in the fracture region of the force vs. compression curve of the crystals. This fact suggests that the motion of cracks and thereby the creation of new surfaces are responsible for the excitation of TL. The TL activity per mole of the triboluminescent crystals varies over 3 orders of magnitude. It is concluded that, for the inorganic crystals, both piezoelectricity and other processes of charging the newly created surfaces may cause the TL excitation.

Introduction

Triboluminescence (TL) is the emission of light caused by the application of mechanical energy to solids. A surprisingly large number of inorganic salts and organic molecular crystals are triboluminescent. In spite of the large total number of triboluminescent materials, quantitative spectroscopic and mechanistic studies of only a limited number of organic molecular crystals have been reported.[2]

The most successful studies of TL have been those designed to specify the excited state origins. A large variety of excited states give rise to TL.[2] The two most common are emission from nitrogen molecules and fluorescence or phosphorescence from the molecules comprising the crystals. These types of emission can occur individually or jointly.

Quantitative methods of measuring the intensities of TL and the dynamics of the emissions have recently been reported.[3] Only organic molecular crystals have been studied to date. In those systems, the rise and decay of the TL is governed by the motion of mobile fractures in the crystals. Because of the complexity of the process of crystal fracture, it is not yet possible to specify the details of the factors which are responsible for the excitation.

A quantitative investigation of the spectroscopy and dynamics of the TL of simple inorganic salts was undertaken in order to determine the excited-state origins of the luminescence, the stress–strain relationships when TL occurs, the intensities of the TL, and the dynamics of TL in ionic crystals. In a survey of readily available metal sulfate salts, 36 were triboluminescent. We report here the results of spectroscopic and mechanical investigations of these crystals.

Experimental Section

Crystals of all the substances listed in Table I with the exceptions of Ag_2SO_4, $Al_2(SO_4)_3{\cdot}18H_2O$, $Ce(SO_4)_3{\cdot}8H_2O$, $Cr_2(SO_4)_3{\cdot}xH_2O$, $ZrSO_4{\cdot}4H_2O$, $BaSO_4$, $SrSO_4$, and $CaSO_4{\cdot}2H_2O$ were grown from aqueous solutions of the reagent grade materials. Some of the mixed crystals were grown from an aqueous solution which contained appropriate quantities of the constituent materials. $ZrSO_4{\cdot}4H_2O$ crystals were obtained from the slow evaporation of a solution of $ZrSO_4$ in dilute H_2SO_4. Ag_2SO_4 crystals were obtained from the slow cooling of the melt. Crystals of $Al_2(SO_4)_3{\cdot}18H_2O$ and $Cr_2(SO_4)_3{\cdot}xH_2O$ were chosen directly from those supplied by Mallinckrodt Chemical Works. The crystals of $Ce_2(SO_4)_3{\cdot}8H_2O$ were chosen from those supplied by the G. Frederick Smith Chemical Co. $BaSO_4$, $SrSO_4$, and $CaSO_4{\cdot}2H_2O$ crystals were chosen from the minerals barite, celestite, and gypsum, respectively.

The simultaneous measurements of the TL vs. compression curves of single crystals were carried out by using the method described previously.[3] In this method, the crystals were compressed by a table-model Instron testing machine, and the TL intensity was monitored by an IP28 photomultiplier tube. The TL vs. compression and force vs. compression curves of the crystal were determined at a compression rate of 1.69×10^{-3} mm/s.

The instrument used for the determination of both the TL intensity and the mechanical characteristics of TL is based on an air-driven steel piston.[3] A Hewlett-Packard velocity transducer (Model LV Syn $6LV_1$) is attached to the piston to measure the velocity. The calibration constant of the velocity transducer is 0.238 V cm^{-1} s. The crystal is placed on a Lucite or quartz plate inside a vertically adjustable sample holder below the piston. The luminescence is monitored from below the transparent plate by using an IP28 photomultiplier tube (response time 7 μs) connected to a Tektronix 564 dual-beam storage oscilloscope. The piston is released to start the experiment and then moves under the force of the compressed gas. The velocity of the piston can be increased to ca. 500 cm/s by increasing the pressure up to 400 psi. To trigger the oscilloscope, we covered the crystal with thin aluminum foil which is connected to one terminal of a 1.5-V battery through a resistance. The other terminal of the battery is connected to the piston. When the piston touches the aluminum foil on the crystal, the pulse which appears across the resistance triggers the oscilloscope. The rise and decay of luminescence and the velocity of the piston are recorded simultaneously. The total intensity of the TL, determined from the area below the TL intensity vs. time curve, is measured with a planimeter. The compression of the impact instrument is 0.32, 0.52, 0.63, and 0.76 mm for impact velocities of 63, 210, 315, and 378 cm/s, respectively. The time duration of TL produced during the motion of a single crack is determined by using another photomultiplier tube with a response time of 100 ns.

The TL spectra were taken by using the methods described previously.[4] The photoluminescence (PL) spectra of the crystals were obtained on a Spex Fluorolog spectrofluorometer. No corrections for the response characteristics of the instruments were made. All the TL and PL spectra were obtained at room temperature.

Results

The triboluminescent sulfate crystal, their TL intensities, and their crystallographic space groups[5–39] are given in Table

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(2) (a) Zink, J. I. *Acc. Chem. Res.* **1978**, *11*, 289. (b) Walton, A. J. *Adv. Phys.* **1977**, *26*, 887.

(3) Chandra, B. P.; Zink, J. I. *Phys. Rev. B* **1980**, *21*, 816.

(4) Hardy, G. E.; Zink, J. I. *Inorg. Chem.* **1976**, *15*, 3061.

(5) (a) Ivanov, V. I. *Acta Crystallogr.* **1966**, *21*, A55. (b) Rennetier, G.; Rossberg, M. *Bull Soc. Chim. Fr.* **1965**, 102.

(6) Larson, A. C. *Acta Crystallogr.* **1965**, *18*, 717.

(7) Margulis, T. H.; Templeton, D. H. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1962**, *117*, 344.

(8) Cavalca, L.; Nardelli, M. *Gazz. Chim. Ital.* **1952**, *82*, 1394.

(9) Klug, H. P.; Alexander, L. *J. Am. Chem. Soc.* **1940**, *62*, 1492.

(10) Pannetier, G.; Gaultier, M. *Bull. Soc. Chim. Fr.* **1966**, 188.

(11) Beevers, C. A.; Lipson, H. *Proc. R. Soc. London, Ser. A* **1934**, *146*, 570.

(12) Larson, A. C. *Acta Crystallogr.* **1965**, *18*, 717.

(13) Lipson, H.; Beevers, C. A. *Proc. R. Soc. London, Ser. A* **1935**, *148*, 664.

(14) Gattow, V. G.; Zemann, J. *Z. Anorg. Allg. Chem.* **1958**, *293*, 233.

(15) Franke, W.; Henning, G. *Acta Crystallogr.* **1965**, *19*, 870.

(16) Ogg, A. *Philos. Mag.* **1930**, *9*, 665.

(17) Hartman, D.; Woensdrejt, C. F. *Acta Crystallogr.* **1964**, *17*, 779.

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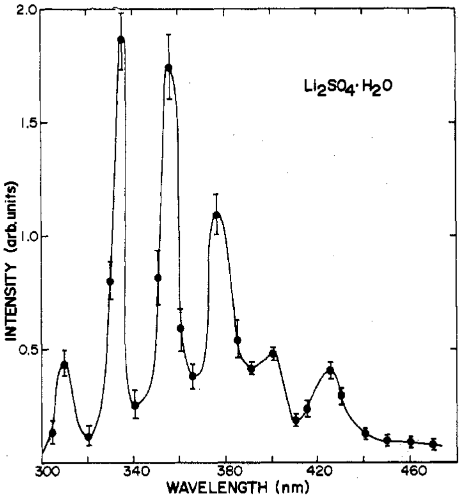

Figure 1. Triboluminescence spectrum of $Li_2SO_4·H_2O$ crystals.

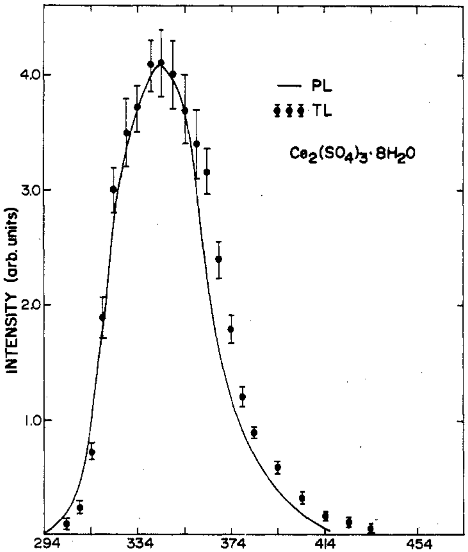

Figure 2. Triboluminescence and photoluminescence spectra of $Ce_2(SO_4)_3·8H_2O$ crystals.

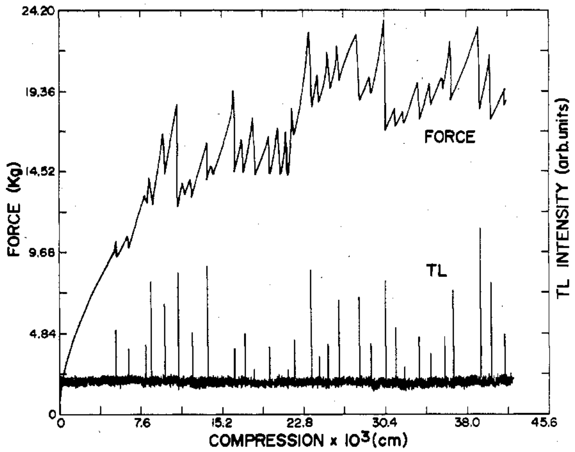

Figure 3. Triboluminescence vs. compression curve and force vs. compression curve of a single crystal of $CuSO_4·5H_2O$ (size of crystal = 11 × 7 × 4 mm^3).

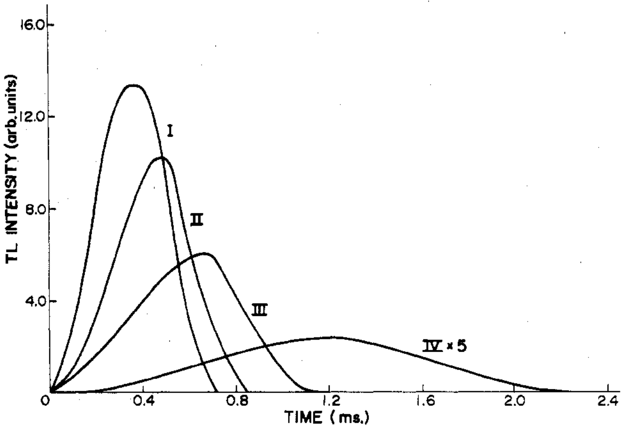

Figure 4. Time dependence of TL in 3.5 × 3.0 × 2.3 mm^3 $CuSO_4·5H_2O$ crystals at impact velocities of (I) 378, (II) 281, (III) 170, and (IV) 25.5 cm/s.

I in order of decreasing TL intensity. All the piezoelectric crystals show TL, and all the crystals not exhibiting TL are nonpiezoelectric. Some of the nonpiezoelectric crystals also show TL with intensities similar to those of the piezoelectric crystals.

The TL spectrum of $Li_2SO_4·H_2O$ crystals is shown in Figure 1. The TL spectra of all of the other sulfate crystals studied, with the exceptions noted below, are identical with Figure 1. The TL spectra correspond to those of the second positive group ($^3\Pi_u \rightarrow {}^3\Pi_g$) of molecular nitrogen.[40,41] The spectra of $ZnSO_4·7H_2O$, $MgSO_4·6H_2O$, $MnSO_4·H_2O$, and $Al_2(SO_4)_3·18H_2O$ crystals could not be taken because the TL intensity is too low. The TL spectrum of $Ce_2(SO_4)_3·8H_2O$ crystals, in contrast, is different as shown in Figure 2. The TL spectrum and the photoluminescence spectrum are almost the same. Note that the TL intensity on the long-wavelength side of the peak is larger than that in the PL spectrum. No nitrogen emission TL was found in $Ce_2(SO_4)_3·8H_2O$ crystals. The photoluminescence in $Ce_2(SO_4)_3·8H_2O$ crystals was assigned to the 5d → 4f transition.[42] Because of the similarity

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(18) James, R. W.; Wood, W. A. *Proc. R. Soc. London* **1925**, *109*, 598.
(19) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1478.
(20) Donnay, J. D. H.; Ondik, H. M. "Crystal Data Determinative Tables"; U.S. Department of Commerce, National Bureau of Standards, and Committee on Powder Diffraction Standards: Washington, DC, 1973; p H207.
(21) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 728.
(22) Menary, J. W. *Acta Crystallogr.* **1935**, *8*, 840.
(23) Hofmann, W. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1931**, *78*, 279.
(24) Bacon, G. F.; Gardener, W. E. *Proc. R. Soc. London, Ser. A* **1958**, *246*, 78.
(25) Jellinek, F. *J. Inorg. Nucl. Chem.* **1960**, *13*, 329.
(26) Zachariasen, W. H.; Zieger, G. E. *Z. Kristallogr. Kristallgeom., Kristallphys., Kristallchem.* **1931**, *81*, 9.
(27) Hill, W. H.; Hendricks, S. B. *Ind. Eng. Chem.* **1936**, *28*, 441.
(28) Beevers, C. A.; Lipson, H. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1932**, *82*, 297.
(29) Le Fur, Y.; Coing-Boyat, J.; Bassi, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1966**, *262*, 632.
(30) Bechman, R.; Taylor, R. "Piezoelectricity"; Her Majesty's Stationary Office: London, 1957; p 346.
(31) Ide, K. H. *Naturwissenschaften* **1938**, *26*, 411.
(32) Baur, W. H. *Acta Crystallogr.* **1964**, *17*, 1167.
(33) Stranz, H. "Mineralogische Tabellen", 3rd ed.; Akademie Verlagsges: Berlin, 1957; p 201.
(34) Sutor, D. J. *Acta Crystallogr.* **1959**, *12*, 72.
(35) Tutton, A. E. H. *Philos. Mag.* **1930**, *9*, 667.
(36) Traill, R. J. *Am. Mineral.* **1952**, *37*, 8394.
(37) Herrmann, H.; Ilge, W. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1931**, *80*, 402.
(38) Staritzky, E.; Singer, J. *Anal. Chem.* **1956**, *28*, 553.
(39) Blandin, J.; Rerat, B. *C. R. Hebd. Seances Acad. Sci.* **1956**, *242*, 1740.
(40) Herzberg, G. "Molecular Spectra and Molecular Structure", 2nd ed.; Van Nostrand: New York, 1950; Vol. I, p 324.
(41) Longchamhon H. *Bull. Soc. Fr. Mineral.* **1925**, *48*, 130.

Table I. Space Group and Triboluminescence Activity of Inorganic Sulfates

cryst	mass, mg	space group	ref	piezo-electricity[a]	tribolumi-nescence[a]	normalized TL activity/mol of cryst with respect to that of $Li_2SO_4 \cdot H_2O$ cryst[d]
$Ce_2(SO_4)_3 \cdot 8H_2O$	12	$Abm2$	5[b]	+	+	44.17 ± 2.11
$Li_2SO_4 \cdot H_2O$	19	$P2_1$	6	+	+	1.00 ± 0.04[c]
$Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$	10	$P2_1/a$	7	–	+	$(9.38 \pm 0.41) \times 10^{-1}$
$NaLiSO_4$	8	hexagonal?	8	?	+	$(5.80 \pm 0.20) \times 10^{-1}$
$NH_4Al(SO_4)_2 \cdot 12H_2O$	47	$H4_{1,3}$	9	+	+	$(4.34 \pm 0.21) \times 10^{-1}$
K_2SO_4	9.3	$Pnam$	10	–	+	$(4.23 \pm 0.19) \times 10^{-1}$
$CuSO_4 \cdot 5H_2O$	31	$P\bar{1}$	11	–	+	$(3.60 \pm 0.16) \times 10^{-1}$
$3CdSO_4 \cdot 8H_2O$	67	$C2/c$	12	–	+	$(2.63 \pm 0.12) \times 10^{-1}$
$AlK(SO_4)_2 \cdot 12H_2O$	13.6	$H4_{1,3}$	13	+	+	$(1.81 \pm 0.09) \times 10^{-1}$
$K_2Zn_2(SO_4)_3$	23.5	$P2_13$	14	+	+	$(1.71 \pm 0.07) \times 10^{-1}$
$NH_4Al(SO_4)_2$	51	$P32$	15	+	+	$(1.67 \pm 0.72) \times 10^{-1}$
Cs_2SO_4	8.5	$Pnam$	16	–	+	$(1.27 \pm 0.50) \times 10^{-1}$
$CoK_2SO_4 \cdot 6H_2O$	14	monoclinic?	17	?	+	$(9.37 \pm 0.41) \times 10^{-1}$
$AlK(SO_4)_2$	20	$P32$	15	+	+	$(7.19 \pm 0.32) \times 10^{-2}$
$Mg_2(NH_4)_2(SO_4)_3$	15	$P2_13$	14	+	+	$(6.46 \pm 0.30) \times 10^{-2}$
$SrSO_4$	58	$Pbnm$	18	–	+	$(5.89 \pm 0.54) \times 10^{-2}$
$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$	13	$P2_1/a$	19	–	+	$(4.94 \pm 0.23) \times 10^{-2}$
$Co_2K_2(SO_4)_3$	26	$P2_13$	14	+	+	$(4.84 \pm 0.21) \times 10^{-2}$
$KLiSO_4$	8	$P6_3$	20	+	+	$(4.38 \pm 0.19) \times 10^{-2}$
$(NH_4)_2Cd(SO_4)_2 \cdot 6H_2O$	19	$P2_1/a$	21	–	+	$(3.45 \pm 0.17) \times 10^{-2}$
$(NH_4)_2Li(SO_4)_3$	10	$P2_13$	14	+	+	$(2.87 \pm 0.12) \times 10^{-2}$
$Cd_2K_2(SO_4)_3$	73.5	$Fd3m$	14	–	+	$(2.48 \pm 0.13) \times 10^{-2}$
$LiNa_2(SO_4) \cdot 6H_2O$	41	$R3c$	8	+	+	$(2.40 \pm 0.11) \times 10^{-2}$
$FeNH_4(SO_4)_2 \cdot 12H_2O$	11	$H4_{1,3}$	22	+	+	$(2.28 \pm 0.06) \times 10^{-2}$
$K_2Fe_2(SO_4)_3$	84	$P2_13$	14	+	+	$(2.11 \pm 0.09) \times 10^{-2}$
$(NH_4)_2Cd(SO_4)_3$	46.5	cubic?	14	?	+	$(1.41 \pm 0.10) \times 10^{-2}$
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	23.6	$P2_1/a$	23	–	+	$(1.39 \pm 0.11) \times 10^{-2}$
$CrK(SO_4)_2 \cdot 12H_2O$	9	$H4_{1,3}$	24	+	+	$(1.24 \pm 0.70) \times 10^{-2}$
$BaSO_4$	102.5	$Pbnm$	25	–	+	$(9.31 \pm 0.53) \times 10^{-3}$
Na_2SO_4	11	$Fddd$	26	–	+	$(9.64 \pm 0.41) \times 10^{-3}$
$CaSO_4 \cdot 2H_2O$	18	C_2/c	27	–	+	$(8.47 \pm 0.49) \times 10^{-3}$
$BeSO_4 \cdot 4H_2O$	54.5	$I\bar{4}$	28	+	+	$(4.53 \pm 0.22) \times 10^{-3}$
$MnSO_4 \cdot H_2O$	87	$A2/a$	29	–	+	$(3.14 \pm 0.12) \times 10^{-3}$
$Al_2(SO_4)_3 \cdot 18H_2O$	60	?		?	+	$(2.90 \pm 0.13) \times 10^{-3}$
$ZnSO_4 \cdot 7H_2O$	74	$P2_12_12_1$	30	+	+	$(2.56 \pm 0.10) \times 10^{-3}$
$MgSO_4 \cdot 6H_2O$	39	$A2/a$	31	–	+	$(1.14 \pm 0.06) \times 10^{-3}$
$FeSO_4 \cdot 7H_2O$	73	$P2_1/c$	32	–	–	0.00
$CoSO_4 \cdot 7H_2O$	61	$I2/c$	33	–	–	0.00
$NiSO_4 \cdot 6H_2O$	82	$A2/a$	34	–	–	0.00
$(NH_4)_2SO_4$	53	$Pnam$	35	–	–	0.00
$(UO_2)SO_4 \cdot 3H_2O$	93	$Pbnm$	36	–	–	0.00
Ag_2SO_4	45	$Fddd$	37	–	–	0.00
$ZrSO_4 \cdot 4H_2O$	9[e]	$Fddd$	38	–	–	0.00
$Cr_2(SO_4)_3 \cdot 18H_2O$	60	?		?	–	0.00
$NH_4Ce(SO_4)_2 \cdot 4H_2O$	10[e]	$P2_1/a$	39	–	–	0.00

[a] + = present; – = absent. [b] The space group *Bmab* reported in ref 5b is inconsistent with its piezoelectric properties. [c] TL activity/mol of $Li_2SO_4 \cdot H_2O$ crystals normalized to that of sugar crystals, the standard used for N_2 emission TL, is 0.058 ± 0.004. [d] The upper limit for detection is about 10^{-4}. [e] Aggregate mass.

between the TL and PL spectra, the TL emission is assigned to the same transition.

The force vs. compression and the TL vs. compression curves of an $11 \times 7 \times 4$ mm^3 single crystal of $CuSO_4 \cdot 5H_2O$ are shown in Figure 3. The TL appears concurrently with the steps in the force vs. compression curve of the crystal, i.e., concurrently with fracture. All the other triboluminescent crystals also exhibit TL only during fracture.

The variation of intensity (I) of the TL with time in $CuSO_4 \cdot 5H_2O$ crystals for different impact velocities is shown in Figure 4. The peak in the TL intensity vs. time curve increases and shifts toward shorter times with increasing impact velocities. For a given impact velocity, the peak of the TL vs. time curve increases and shifts toward longer time with increasing size of the crystal. The plot of log (I/t^2) vs. t^2 is linear with a negative slope which suggests relation 1. The physical

$$I = I_0 t^2 \exp(-\gamma t^2) \qquad (1)$$

meaning of the parameters I_0 and γ will be discussed below. The slope γ increases with the impact velocity v and decreases with the thickness of the crystal.

The peak intensity I_m of the TL in a TL vs. time curve increases continuously with the impact velocity. However, the integrated intensity of TL, that is, the total light emitted at a given impact, increases and attains a saturation value for higher values of the impact velocity. Above a minimum size of the crystals, the peak of the TL intensity vs. time curve increases directly with the area of the cross section of the crystals, and the total intensity increases directly with the volume or mass of the crystals.

The relative intensity of TL per mole of crystal normalized to that of $Li_2SO_4 \cdot H_2O$ crystals is given in Table I. It is seen that the TL activity varies over 3 orders of magnitude. No significant changes in the TL activity are found with respect to the crushing direction of the crystal. The most intense TL is found in $Ce_2(SO_4)_3 \cdot 8H_2O$ crystals. No correlation of TL is found with the metallic character, acidity, basicity, size, or electronegativity of the cations in inorganic sulfates. The rise and decay time of TL due to the motion of a single crack is about 1 μs.

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(42) Hosina, T.; Kuboniwa, S. *J. Phys. Soc. Jpn.* **1971**, *31*, 828.

Three different types of experiments were done in order to probe the effect of chemical defects on TL excitation of the crystals. First, the TL activity was measured as a function of the number of crystallization of the crystals. Second, the TL activity was measured for the crystals synthesized by using different methods. Third, the TL activity was measured as a function of doping different amounts of various chemicals in the crystals.

The number of crystallizations does not affect the TL activity of $CuSO_4 \cdot 5H_2O$ and K_2SO_4 crystals. The TL activity of $CuSO_4 \cdot 5H_2O$ crystals synthesized from cupric oxide, cupric carbonate, and cupric acetate is nearly the same as that of the crystals grown from the chemical obtained directly from Mallinckrodt Chemical Co. The TL activity of K_2SO_4 crystals synthesized from potassium hydroxide, potassium carbonate, and potassium bicarbonate is nearly the same as that of the crystals grown from the chemicals supplied by J. T. Baker Chemical Co. No significant change in the TL activity of $CuSO_4 \cdot 5H_2O$ crystals was found when they were independently doped by $ZnSO_4 \cdot 7H_2O$, K_2SO_4, $CoSO_4 \cdot 7H_2O$, $AgNO_3$, and KCl between 100 and 10 000 ppm. Similarly the TL activity of K_2SO_4 crystals did not change when they were independently doped by Na_2SO_4, $ZrSO_4 \cdot 4H_2O$, $CoSO_4 \cdot 7H_2O$, KBr, and NaCl between 100 and 10 000 ppm.

Discussion

Spectroscopy of TL. Two independent types of TL emission were found. The most common emission is from nitrogen molecules. Second, one example of emission from a metal cation was found in the crystals of $Ce(SO_4)_3 \cdot H_2O$. None of the crystals exhibiting nitrogen emission TL are photoluminescent. The TL spectra show no evidence of emission other than that of nitrogen. The bands in the TL spectra are from the second positive group of N_2 and represent a vibronic progression from $\Delta\nu = 1$ at 316 nm to $\Delta\nu = -4$ at 429 nm.[40] These bands had previously been observed from copper sulfate and cadmium sulfate.[41] The second positive group of N_2 is a transition between two triplet excited states, ${}^3\Pi_u \rightarrow {}^3\Pi_g$ (Figure 1). The emitting state lies 11 eV (88 100 cm^{-1}) above the group state.[40] Thus the TL spectra demonstrate that a large excitation energy is involved.

Among the inorganic sulfates surveyed, only $Ce_2(SO_4)_3 \cdot 8H_2O$ crystals exhibit TL emission other than nitrogen emission. The TL emission resembles the photoluminescence emission which corresponds to a 5d → 4f transition, and it has decay time of 10^{-4} s.[42] From the similarity of the TL spectrum to the PL spectrum, the TL emission is assigned to the 5d → 4f transition. It is likely that other photoluminescent rare-earth sulfates will also exhibit metal-centered TL.

Dynamic Properties of TL. When single crystals of metal sulfates are subjected to strain, TL emission occurs only in the fracture region of the stress–strain curve as shown for copper sulfate in Figure 3. Thus, neither elastic nor plastic deformation is responsible for TL excitation. The "steps" in the force vs. compression curve shown in Figure 3 are caused by the movement of cracks in the crystal. The observation of TL *only* concurrently with the movement of cracks suggests that fracture and the concomitent creation of new surfaces in the crystal are responsible for the TL excitation.

In contrast, Alzetta et al. have reported that TL emission occurs in the elastic, plastic, and fracture regions during bending of plates of ZnS:Mn and colored alkali halide crystals.[43] For most of the substances studied to date, fracture is required.[3,44]

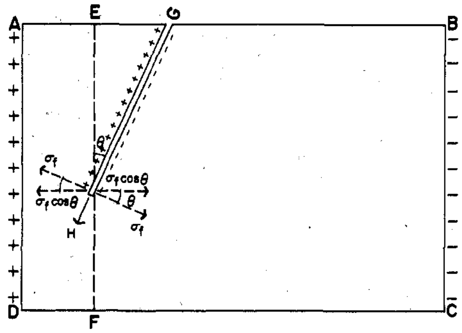

Figure 5. Generation of an electric field during movement of a crack in a piezoelectric crystal.

The rise and decay times of TL due to the motion of a single crack are in the microsecond range which is of the order of the time needed for a crack to move through crystals of the dimensions used. However, the time duration of a continuous TL pulse produced during massive fracture of a crystal is of the order of milliseconds and depends on the impact velocity of the crushing instrument. Thus, the continuous TL signal produced during crushing is the superposition of individual TL pulses produced during the motion of many cracks in the crystal. The time dependence of TL produced during impact of a piston with the crystal may thus be described in terms of the production and interaction of mobile cracks. From the movement and interaction of mobile cracks a quantitative expression for the time and impact velocity dependence of the transient intensity (I) was derived in a previous investigation[3]

$$I = \frac{\eta b V u^3 v^3 t^2}{h^3} \exp\left(\frac{-\beta u^2 v^2 t^2}{h^2}\right) \qquad (2)$$

where η is the normalization constant which takes into account the TL activity of the crystal, b is a proportionality constant, V is the volume of the crystal, h is the thickness of the crystal, t is time after the appearance of TL, v is the impact velocity of the piston on the crystal, u is a factor which takes into account the compression of the impact instrument, and β is related to the attrition coefficient of mobile cracks in the crystal.

The time dependence of TL, impact velocity dependence of TL, and dependence of TL on crystal size are similar for all the triboluminescent crystals listed in Table I. Equation 2 also describes the dependence of the slope of log (I/t^2) vs. t^2 curve on the impact velocity and the thickness of the crystal. As has been shown previously, the impact velocity dependence of the peak of the TL intensity vs. time curve and the total intensity of TL are quantitatively expressed by eq 2.

Mechanism of TL. The nitrogen emission TL of piezoelectric crystals can be explained by using Langevin's model of the creation of charged surfaces during movement of a crack in a crystal.[45] The mechanism by which an electric field is generated during propagation of a crack is shown in Figure 4. A rough estimation of the magnitude of the electric field near the tip of the mobile crack can be made for $Li_2SO_4 \cdot H_2O$ crystals where the values of the required constants are known. Three assumptions are required: first, that the piezoelectric constants remain unchanged up to the fracture stress of the crystal; second, that the stress near the tip of the crack is not relaxed before the TL excitation; third, that the charge development along the polar direction dominates the charge development along other directions. Let the direction of crack propagation make an angle θ with the normal EF to the polar

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(43) Alzetta, G.; Chudacek, I.; Scarmozzino, R. *Phys. Status Solidi. A* **1970**, *1*, 775.

(44) Wawner, F. E.; De Bolt, H. E.; Krukonis, B. J. *Silicon Carbide, Proc. Int. Conf., 3rd, 1973* **1974**, 464.

(45) Langevin, M. *Inst. Int. Chim. Solvay, Cons. Chim.* [*Rapp. Discuss.*] **1921**, 251.

direction AB of the crystal (Figure 5). Then the charge density of the newly created surfaces will be $d_{22}\sigma_f \cos\theta$, where d_{22} is the piezoelectric constant and σ_f is the stress needed to separate the crystal surfaces. The electric field between the newly created surfaces will be $(1/\epsilon_0)(d_{22}\sigma_f \cos\theta)$, where ϵ_0 is the permittivity constant.

For $Li_2SO_4\cdot H_2O$ crystals[46] d_{22} is $16.2 \times 10^{-12}(CN)^{-1}$, and the fracture stress σ estimated from $^1/_{30}$th of Young's modulus[47,48] is 1.77×10^8 N m^{-1}. θ is found to be 22 ± 2° by compressing a $Li_2SO_4\cdot H_2O$ crystal between the two jaws of a screw gauge. With substitution of the values of d_{22}, σ, cos θ, and ϵ_0, the calculated electric field between the newly created surfaces is 1.26×10^8 V m^{-1}. This electric field is larger than that required to initiate gas discharge at atmospheric pressure, 3×10^7 V m^{-1}.[49] Thus, the rough estimation supports the possibility of TL excitation as a result of the piezoelectrification of the new surfaces created during fracture of the crystals. It should be noted that certain crystals like $ZnSO_4\cdot 7H_2O$, $BeSO_4\cdot 4H_2O$, $(NH_4)_2Ni(SO_4)_3$, etc. are piezoelectric only under torsion. Hence, the TL excitation in these crystals due to the piezoelectrification will be possible only if the torsion near the tip of the cracks will be sufficient to produce the necessary charge on the newly created surfaces.

It follows from the piezoelectric origin of gas discharge TL that the TL activity is related to the charge density of the newly created surfaces. As the charge density may differ from crystal to crystal due to different piezoelectric constants, fracture stress, charge leakages, direction of crack propagation, etc., the differences in TL activities of the crystals are not unexpected. A possibility that the TL activity depends on the adsorption of nitrogen gas in the crystal can be ruled out. At atmospheric pressure, newly created surfaces of a crystal become covered with an adsorbed layer within about 10^{-7}–10^{-8} s.[50] The decay time of the TL from a single crack is longer, on the order of 10^{-5}–10^{-6} s. Thus, it is likely that the amount of nitrogen adsorbed on the crystal surface during fracture does not govern the TL intensity. Since $Ce_2(SO_4)_3\cdot 8H_2O$ crystals are piezoelectric, their TL excitation may be caused by piezo-induced electroluminescence. The electroluminescence may occur during the recombination of charges which are generated as a result of the high electric field.[51]

The appearance of TL in nonpiezoelectric crystals shows that other excitation mechanisms exist in ionic crystals. Three possible mechanisms are eliminated by the experimental results. Frictional electrification is eliminated because the TL intensity is independent of the materials used for crushing the crystals. Electrification caused by the separation of crystal regions of microscopically disturbed electrical equilibrium caused by chemical defects is not a general mechanism because the TL intensity is insensitive to the presence of dopants, number of recrystallizations, and the methods of crystal preparation for the crystals studied. Excitation by the motion of charged dislocations is ruled out because the TL intensity increases with decreasing temperature while the movement of dislocations is inhibited as the temperature decreases.

The most attractive mechanism of TL excitation in nonpiezoelectric ionic crystals is fracture along planes of low Miller indices having opposite charges.[52] The separation of oppositely charged surfaces requires more energy than the separation of surfaces containing equal numbers of positive and negative ions. Thus the preferred macroscopic cleavage planes are electrically neutral. However, crystals having small anisotropic cohesive energies may not cleave perfectly along neutral planes and may yield a small fraction of charged surfaces at the microscopic level.[53] Because the field along such planes will be very high (10^{11} V m^{-1} for the 111 plane of NaCl), a small fraction of such surfaces will be able to produce significant excitation of nitrogen. Unfortunately, the details of the elastic properties of inorganic sulfate crystals are not known and further speculation is not warranted. It is interesting to note that, in alkali halide crystals where the elastic properties are known, there is an excellent correlation between them and TL activity.[53]

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Registry No. $Ce_2(SO_4)_3\cdot 8H_2O$, 10450-59-6; $Li_2SO_4\cdot H_2O$, 10102-25-7; $Mg(NH_4)_2(SO_4)_2\cdot 6H_2O$, 7785-18-4; $NaLiSO_4$, 13568-34-8; $(NH_4)Al(SO_4)_2\cdot 12H_2O$, 7784-26-1; K_2SO_4, 7778-80-5; $CuSO_4\cdot 5H_2O$, 7758-99-8; $3CdSO_4\cdot 8H_2O$, 7790-84-3; $AlK(SO_4)_2\cdot 12H_2O$, 7784-24-9; $K_2Zn_2(SO_4)_3$, 34377-66-7; $(NH_4)Al(SO_4)_2$, 7784-25-0; Cs_2SO_4, 10294-54-9; $CoK_2(SO_4)_2\cdot 6H_2O$, 10026-20-7; $AlK(SO_4)_2$, 10043-67-1; $Mg_2(NH_4)_2(SO_4)_3$, 27733-50-2; $SrSO_4$, 7759-02-6; $(NH_4)_2Ni(SO_4)_2\cdot 6H_2O$, 7785-20-8; $Co_2K_2(SO_4)_3$, 27733-52-4; $KLiSO_4$, 14520-76-4; $(NH_4)_2Cd(SO_4)_2\cdot 6H_2O$, 14767-05-6; $Cd_2K_2(SO_4)_3$, 27733-59-1; $FeNH_4(SO_4)_2\cdot 12H_2O$, 7783-83-7; $K_2Fe_2(SO_4)_3$, 27733-55-7; $(NH_4)_2Cd_2(SO_4)_3$, 13968-78-0; $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, 7783-85-9; $CrK(SO_4)_2\cdot 12H_2O$, 7788-99-0; $BaSO_4$, 7727-43-7; Na_2SO_4, 7757-82-6; $CaSO_4\cdot 2H_2O$, 10101-41-4; $BeSO_4\cdot 4H_2O$, 7787-56-6; $MnSO_4\cdot H_2O$, 10034-96-5; $Al_2(SO_4)_3\cdot 18H_2O$, 7784-31-8; $ZnSO_4\cdot 7H_2O$, 7446-20-0; $MgSO_4\cdot 6H_2O$, 17830-18-1; $FeSO_4\cdot 7H_2O$, 7782-63-0; $CoSO_4\cdot 7H_2O$, 10026-24-1; $NiSO_4\cdot 6H_2O$, 10101-97-0; $(NH_4)_2SO_4$, 7783-20-2; $(UO_2)SO_4\cdot 3H_2O$, 12384-63-3; Ag_2SO_4, 10294-26-5; $Zr(SO_4)_2\cdot 4H_2O$, 7446-31-3; $Cr_2(SO_4)_3\cdot 18H_2O$, 13520-66-6; $NH_4(Ce(SO_4)_2\cdot 4H_2O$, 10049-02-2.

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(46) Spitzer, F. *Electr. Commun.* **1951**, *28*, 300.

(47) Mason, W. P. "Piezoelectric Crystals and Their Applications to Ultrasonics"; Van Nostrand: New York, 1950; p 230.

(48) Cottrell, A. H. "Dislocations and Plastic Flow in Crystals"; Clarendon Press: Oxford, England, 1953; p 11.

(49) Thomson, J. J.; Thomson, G. P. "Conduction of Electricity through Gases"; Cambridge University Press: New York, 1933; p 487.

(50) Ponec, V.; Knor, Z.; Cerny, S. "Adsorption on Solids"; CRC Press: Cleveland, OH, 1974; p 19.

(51) Chandra, B. P.; Zink, J. I. *J. Chem. Phys.*, in press.

(52) Meyer K.; Ohrikat, D.; Rossberg, M. *Krist. Tech.* **1970**, *5*, 5.

(53) Chandra, B. P.; Zink, J. I., unpublished work.