

TABLE 1 — SOLUBILITY DATA OF COBALTOUS OXIDE

Molarity of solution of CoO <i>M</i>	5+log <i>S</i>	Original <i>pH</i> value	Original <i>pOH</i>
$1.25 \times 10^{-3}$	2.0969	6.9	—
$3.5 \times 10^{-4}$	1.5441	7.5	—
$4.5 \times 10^{-5}$	0.6532	8.6	—
$1.5 \times 10^{-5}$	0.1761	9.12	—
$1.2 \times 10^{-5}$	0.0792	10.02	—
$1.1 \times 10^{-5}$	0.0414	10.4	—
$5.0 \times 10^{-6}$	-0.3010	10.8	(3.2)
$7.0 \times 10^{-6}$	-0.1549	11.0	(3.0)
$5.2 \times 10^{-5}$	0.7160	12.12	(1.88)
$1.33 \times 10^{-4}$	1.1239	12.6	(1.4)

hydroxide occurs at *pH* 10.1. Below this point the oxide dissociates mainly as a base. From the solubility data of cobaltous oxide in solutions of different  $[H^+]$  below the isoelectric point, one can obtain information as to the most probable mode of ionization of the hydroxide in solution. The completion of reaction between the base of a divalent metal and an acid implies that the [metal ion] in solution will be proportional to  $[H^+]^2$ . Generally, the solubility will be proportional to  $[H^+]^n$ , where *n* is the number of OH<sup>-</sup> ions provided by the prevailing base.

Above the isoelectric point, CoO is expected to dissociate as an acid and its solubility will be proportional to  $[OH^-]^{n'}$  where *n'* is the number of H<sup>+</sup> ions furnished by the prevailing acid. The values of *n* and *n'* can be evaluated as follows:

Let us consider Eqs. (2) and (3)

$$S = K[H^+]^n \quad \dots(2)$$

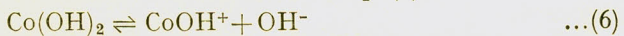
$$S' = K'[OH^-]^{n'} \quad \dots(3)$$

where *S* and *S'* are the solubility in g moles of the oxide per litre of solution and *K* and *K'* are constants. Taking the logarithm of both sides of each equation we get Eqs. (4) and (5)

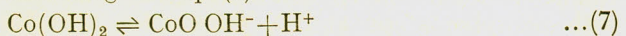
$$-\log S = -\log K + n \text{ pH} \quad \dots(4)$$

$$\text{and } -\log S' = -\log K' + n' \text{ pOH} \quad \dots(5)$$

This implies linear relations between  $-\log S$  and *pH*, or  $-\log S'$  and *pOH* with slope equal to *n* and *n'* respectively. It is observed that the plot of  $-\log S$  versus *pH* for *pH* values 6.9, 7.5, 8.6 and 9.12 is linear with a slope = 0.94 which is very near to unity, indicating that cobaltous oxide ionizes in accordance with Eq. (6)



The plot of  $-\log S$  versus *pOH* for *pOH* values 1.4, 1.88, 3.0 and 3.2 is also linear with a slope = 0.88 which is again very near to unity indicating that on the alkaline side of the isoelectric point, cobaltous oxide dissociates as a weak monobasic acid according to Eq. (7)



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### Structural Studies in the System

#### $(\text{Li}_{0.5}\text{Ln}_{0.5})\text{TiO}_3^*$

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**Structural characteristics of a new type of perovskites with the general formula  $\text{Li}_{0.5}\text{Ln}_{0.5}\text{TiO}_3$  where Ln = a rare earth cation or  $\text{Y}^{3+}$ , are reported. All the compounds except the La compound have the orthorhombic distorted perovskite structure.**

**P**EROVSKITE like compounds of the type  $\text{ABO}_3$  can be obtained with A and B ions having ionic radii within fairly wide limits<sup>1</sup>. The same structure type can be found in solid solutions of the type  $\text{A}(\text{B}_i\text{B}_j)\text{O}_3$  (ref. 2),  $(\text{A}_i\text{A}_j)\text{BO}_3$  (ref. 3), and even in the quaternary system  $(\text{A}_i\text{A}_j)(\text{B}_i\text{B}_j)\text{O}_3$  (ref. 4). In most of these systems the ions A and the B are divalent and tetravalent respectively. We have earlier reported<sup>5</sup> on the formation of  $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and its solid solution with  $\text{BaTiO}_3$ . The present note deals with the structural studies of similar systems obtained by replacing La with other lanthanide ions and  $\text{Y}^{3+}$ .

The pure phases were prepared by the high temperature solid state reaction of the constituents ( $\text{Ln}_2\text{O}_3$  were better than 99% pure, BARC products while  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  were both AR grade samples) at 1100-1300°. The time of reaction was between 10 and 12 hr, and intermittent X-ray patterns of the reaction products showed that only monophasic systems were present. The X-ray diffraction patterns of the products were taken on a Philips PW 1010 diffractometer using Mo/Cu  $K_\alpha$  radiation filtered suitably. The *d* values were calculated accurately to  $\pm 0.2\%$  and the patterns indexed since the same were isomorphous with known structures. The densities were determined pycnometrically using  $\text{CCl}_4/\text{water}$ . These suggested a value of *Z* = 1 for

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TABLE 1—UNIT CELL PARAMETERS OF THE  $(\text{Li}_{0.5}\text{Ln}_{0.5})\text{TiO}_3$  COMPOUNDS

Compound	$R_A$ (Å) (effective)	$a$ $b$ $c$			$V$ (Å <sup>3</sup> )	$b/a$
		(Å)				
$\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$	0.840	5.44	5.57	7.75	235.1	1.02
$\text{Li}_{0.5}\text{Sm}_{0.5}\text{TiO}_3$	0.820	5.39	5.59	7.71	232.3	1.03
$\text{Li}_{0.5}\text{Gd}_{0.5}\text{TiO}_3$	0.810	5.34	5.61	7.67	230.2	1.05
$\text{Li}_{0.5}\text{Dy}_{0.5}\text{TiO}_3$	0.795	5.30	5.59	7.62	226.9	1.05
$\text{Li}_{0.5}\text{Y}_{0.5}\text{TiO}_3$	0.765	5.25	5.58	7.54	218.3	1.11

the La compound and 4 for the rest. The unit cell parameters for the different compounds are shown in Table 1. It can be seen that all the compounds exhibit an orthorhombic distortion of the  $\text{ABO}_3$  cubic perovskite structure, in contrast to the cubic structure reported for the La compound<sup>5</sup>. It is also seen that the orthorhombic distortion in terms of  $b/a$  goes on decreasing with increasing  $\text{Ln}^{3+}$  size. The effective ionic radii of the A site ions decrease with the decreasing  $\text{Ln}^{3+}$  ionic size (ionic size of  $\text{Li}^+$  ion is constant). Increase in  $b/a$  with decreasing effective ionic radii of the A-site ions is contradictory to normal behaviour. However, as expected, Table 1 shows that the cell volume decreases with decrease of the effective radius of the ion at A site.

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#### Emission Spectra of Isomeric Trifluoromethylbenzonitriles

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Phosphorescence and total emission spectra of isomeric trifluoromethylbenzonitriles have been recorded at liquid nitrogen temperature (77°K). A complete vibrational analysis of the bands observed is given and assignments are discussed. Relative quantum yields of fluorescence and phosphorescence are discussed. Life-times of phosphorescence emission are estimated from the decay curves.

PHOSPHORESCENCE emission<sup>1-7</sup> of benzene has been studied by numerous researchers. It shows well-resolved vibronic structure and is a classical example of both a spin and symmetry forbidden transition.

From the vibrational analysis of emission spectrum, it has been concluded that in benzene the basic structure of both fluorescence and phospho-

rescence involves one quantum of a non-totally symmetric  $e_{2g}$  motion (606  $\text{cm}^{-1}$ , mode 6 for fluorescence and 1595  $\text{cm}^{-1}$ , mode 8 for phosphorescence) over which quanta of a totally symmetric  $a_g$  vibration (the 990  $\text{cm}^{-1}$ , mode 1) are superposed. However, the phosphorescence shows more extensive fine structure than fluorescence.

In this paper total emission spectra and phosphorescence of isomeric trifluoromethylbenzonitriles (*o*, *m* and *p*) have been recorded at liquid nitrogen temperature and a complete analysis of the bands observed and other assignments are given. Relative quantum yields of fluorescence and phosphorescence are also given. Phosphorescence spectra of benzonitrile and its derivatives were studied by Takei and Kanda<sup>8</sup>, Faure<sup>9</sup> and LeBel and Laposa<sup>10</sup>.

Solutions of appropriate concentrations were prepared in ethanol and taken in a quartz cylindrical tube of about 3 mm diameter. The sample tube was connected to a vacuum system through a stopcock. It was immersed in liquid nitrogen and evacuated. The sample tube was warmed to room temperature in vacuum after closing the stopcock. This process was continued for thorough degassing until a clear glass with no apparent cracks was obtained. The sample tube was mounted in a quartz dewar containing liquid nitrogen and the dewar was placed between the choppers of a phosphoscope. Light from a 200 watt xenon arc coming through the sample was focussed on the slit of the medium quartz Hilger spectrograph. Phosphorescence spectra were photographed after choosing the proper chopper speed. The exposure times were of the order of 1 to 3 hr. Iron and copper arcs were used for standard wavelengths. Band positions were calculated using comparator and microphotometer traces. Microphotometer traces were obtained for the comparison of relative band intensities.

Total emission spectra were recorded on Aminco-Bowman spectrophotofluorometer with the same arrangement without the phosphoscope. X-Y recorder was used to record the photomultiplier output against wavelengths.

For obtaining phosphorescence life-times, the Aminco-Bowman spectrophotofluorometer was used with phosphoscope and X-Y recorder, together with an arrangement for cutting off the exciting radiation.

**Phosphorescence\***—Phosphorescence spectra of isomeric trifluoromethylbenzonitriles are in the same

\*All band positions, separations and vibration frequencies are in  $\text{cm}^{-1}$ .