Internal force constants in GVFF model collected in Table 2 are compared with the results reported by others.[1-a] It is apparent from Table 2 that the agreement is satisfactory. It is also obvious that all the force constants show decreasing tendency in the order $NCl_3 > PCl_3 > AsCl_3 > SbCl_3$. An inspection of the results further shows that the variation in the stretching and bending force constants is smaller than that in the interaction force constants. This can be explained on the basis that for $NCl_3$ and $PCl_3$ where $m_x < m_y$, mass coupling will be more than for $AsCl_3$ and $SbCl_3$ where $m_x > m_y$.

A comparative study of the bond polarizability derivatives and stretching force constants (Table 2) for the trichlorides of VA group elements shows that the trends of variation of the two parameters are opposite in nature. The average value of the product of the bond polarizability derivatives ($\bar{\alpha}'$) and stretching force constants ($f_r$) comes out to be 7·183. Deviations of the product of $\bar{\alpha}'$ and $f_r$ for $NCl_3$, $PCl_3$, $AsCl_3$ and $SbCl_3$ from the average value of their products are respectively 0·018, 0·620, 0·000 and −0·649. Since the average of the deviations is very very small, we conclude that the bond polarizability derivative of a bond is inversely proportional to its stretching force constant.


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## Crystal Growth of Transition Metal Oxides from Potassium Pyrosulphate Flux


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Crystals of some transition metal oxides viz. NiO, ZnO, $Fe_2O_3$ and $Mn_3O_4$ have been grown from a $K_2S_2O_7$ flux. The crystals are found to be shiny, flaky and of 1 mm size.


Recently crystals of a number of materials are being grown by the flux method.[1] This has been mainly possible because of the fact that some flux material could be used to grow crystals of a wide variety of materials, e.g. PbO and $PbF_2$. In this note, we report the use of $K_2S_2O_7$ as a useful flux material for the growth of single crystals of a number of transition metal oxides.

In a typical experiment about 2 g of the oxide was mixed thoroughly with about 50 g of $KHSO_4$ or $K_2S_2O_8$ both of which on heating get converted to $K_2S_2O_7$. The mixture is heated, in a platinum vessel covered with a lid, to 1000°C in a box-type furnace with good controls. The operation should be done in a fume cupboard with good exhaust system to drive away the $SO_2$ evolved on heating. The melt is soaked at 1000°C for 5 hr. Then it is cooled down at the rate of 5°C/hr to 800°C and then to room temperature at the rate of 100°C/hr. During this period $K_2S_2O_7$ decomposes to $K_2SO_4$ according to

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_2$$

The $K_2SO_4$ is leached with warm water and crystals are separated.

The physical characteristics of the crystals of the oxides grown by this method are presented in Table 1, and photographs of some of the crystals are shown in Fig. 1.

A few experiments were carried out to throw some light into the basic processes involved in the crystal growth. The details and conclusions are as follows:

1. The end product of heating of $K_2S_2O_7$ at 1000°C is $K_2SO_4$. The conversion of $K_2S_2O_7$ to $K_2SO_4$ is complete in about 5 hr.

2. A few experiments carried out with $K_2SO_4$ as the starting flux material, keeping other experimental conditions the same, yielded no crystal.

3. A mixture of $K_2SO_4$ and iron sulphate [$Fe_2(SO_4)_3$] was heated to 1000°C and allowed to remain at that temperature for 5 hr. During this period iron sulphate decomposes to give iron oxide, $Fe_2O_3$ and $SO_3$. When the mixture was cooled at the rate of 5°C/hr to 800°C and then rapidly to room temperature, flaky single crystals of $Fe_2O_3$ were obtained. The crystal size was 0·2 mm which is much smaller than those obtained when $KHSO_4$ was used as the starting flux material.

From the above results it is obvious that $SO_2$ present in the system facilitates the formation of a solution of oxide in the melt. More studies are required to ascertain its role.

There are very few flux inclusions in the crystals. The maximum amount of $K_2SO_4$ present in these crystals is 0·1%.

Some other advantages of $K_2S_2O_7$ flux are as follows:

1. Irrespective of the composition of the melt, the oxide is the only stable crystallized phase. No other unwanted compound is formed.

Table 1—Physical Characteristics of Transition Metal Oxide Crystals Grown from $K_2S_2O_7$ Flux

| Oxide | Appearance | Size |
|---|---|---|
| NiO | Shining, greenish yellow flaky crystals | ~ 1 mm |
| ZnO | mixture of yellowish white flaky crystals and | ~ 1 mm |
| | hollow cylindrical crystals | ~ 5·15 mm (length) ~ 0·5 mm (diam.) |
| $Fe_2O_3$ | reddish brown, shining flaky crystals | ~ 1 mm |
| $Mn_3O_4$ | dark red, shining flaky crystals | ~ 1 mm |

Note: The identification of the oxides was confirmed by powder pattern and chemical analysis.


Fig.1—Photographs (×23) of crystals prepared from $K_2S_2O_7$ flux: (a) nickel oxide, (b) manganese oxide ($Mn_2O_4$).

2. The flux is non-volatile. More studies are under way to use $K_2S_2O_7$ for the preparation of crystals of other oxide materials.

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## Force Constants of Some $XY_4$ Molecules by Modified Redington & Aljibury Method

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To calculate the parameter $\phi$, the Redington and Aljibury method [*J. molec. Spectrosc.*, **37** (1971), 494] has been reformulated by choosing the triangular $L$-matrix ($L_{12} = 0$) as the initial $L$-matrix instead of $L_0 = A\,\Gamma^{1/2}$, as given in the original method. Force constants for halides of Sr, Ge, Sn, Ti, Zr, and Hf and, those of $CH_4$, $GeH_4$ and $SnH_4$ have been calculated in this formalism. The possibility of using the formalism to indicate the correct siga of $\phi$ is indicated.

In one of our recent calculations[1] on the parametric representation method developed on the basis of $L$-matrix approximation[2] we have indicated the importance of pre-knowledge of the sign of parameter $\phi$ when mean amplitude of vibration is to be used as additional vibration data. To obtain this information we thought it worthwhile to reformulate the Redington and Aljibury method[3] using the triangular $L$-matrix ($L_{12} = 0$) as the initial $L$-matrix. This approximate method is chosen in preference to other methods because of the fact that the constraint proposed on the basis of virial theorem in this method of calculation is a distinctly different condition from $L_{12} = 0$. Therefore, $\phi$ calculated by this formalism may indicate the correct sign, which will remove the ambiguity arising in exact force field studies using the mean amplitude of vibration. This formalism was used to calculate the force constants of halides of Si, Ge, Sn, Ti, Zr and Hf and, those of $CH_4$, $GeH_4$ and $SnH_4$. The calculated values of force constants of these molecules along with the observed frequencies and the values of $\phi$ are given in Table 1.

The following features regarding our calculated values of force constants are worth-noting:

(1) The parameters calculated in this formalism have been found to be close to zero.

(2) The calculated values of $\phi$ for Ge and Si show good agreement with those of the exact values obtained in the previous calculations.[1]

(3) The values of $\phi$ for the halides of Ti, Zr, Hf, Ge and Si turn out to be almost the same (1°~2°).

Table 1—Force Constants (in mdyne/Å) of Some $XY_4$-Type Molecules

| Molecule | Vibrational frequency, $cm^{-1}$ | | $\phi$ deg | $F_{33}$ | $F_{34}$ | $F_{44}$ |
|---|---|---|---|---|---|---|
| $CH_4$ | 3008·75 | 1298·3 | 1 | 4·80 | 0·037 | 0·417 |
| $SiF_4$ | 1031·8 | 389·35 | 4 | 5·69 | 0·150 | 0·433 |
| $SiCl_4$ | 619·0 | 212·3 | 5 | 2·47 | 0·097 | 0·218 |
| $SiBr_4$ | 494 | 133·6 | 3 | 1·99 | 0·152 | 0.166 |
| $SiI_4$ | 404 | 88·8 | 5 | 1·12 | 0·0512 | 0 125 |
| $GeH_4$ | 2195·0 | 846·0 | 0 | 2·81 | 0·00732 | 0·205 |
| $GeF_4$ | 821·6 | 271·0 | 1 | 5 56 | 0·0809 | 0·273 |
| $GeCl_4$ | 453·0 | 172 | 2 | 2·50 | 0·0814 | 0·173 |
| $SnH_4$ | 1961·0 | 698·0 | 0 | 2·26 | 0·00313 | 0·141 |
| $SnCl_4$ | 408·2 | 126·1 | 1 | 2·44 | 0·0329 | 0·105 |
| $TiCl_4$ | 498 | 136 | 1 | 2·53 | 0·0671 | 0 0962 |
| $TiBr_4$ | 393 | 88 | 1 | 2·16 | 0·0742 | 0·0762 |
| $ZrCl_4$ | 418 | 113 | 1 | 2·33 | 0·0282 | 0·0784 |
| $ZrBr_4$ | 315 | 72 | 1 | 2·073 | 0·0329 | 0·0583 |
| $ZrI_4$ | 254 | 55 | 1 | 1·62 | 0·0424 | 0·045 |
| $HfCl_4$ | 390 | 112 | 1 | 2·47 | 0·0112 | 0·0918 |
| $HfBr_4$ | 273 | 71 | 1 | 2·16 | 0·02059 | 0·0677 |
| $HfI_4$ | 224 | 63 | 2 | 1·86 | 0·0740 | 0·0740 |

It was observed by Ramaswamy *et al.*[4] that the method ia its original form ($L0 = A\ f^{1/3}$) gives results as good as the exact force field for the boron trihalides. In the present calculation, the force constants are also satisfactory. This makes us hopeful to use the present formalism in extracting the true signs of $\phi$ at least for those types of molecules for which $\phi$ shows a similar trend. This can he used in choosing the correct $\phi$, calculated from mean amplitude of vibration, when two values of $\phi$ are obtained with equal magnitude and opposite sign.[1]

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