CHAPTER - III

Study of Single Crystal of Potassium Nickel Bromide Monohydrate

Introduction

Compounds of composition $A_mB_{n+p}Cl_{2n}H_2O$ were $A$ stands for alkali metal (Li, Na, K, Rb, Cs etc.), $B$-second group element (Cr, Fe, Mn, Ni, Co, Cu, Cd, Zn etc.) and $C$-a halogen atom (mostly F and Cl and sometimes Br), $m$, $n$ and $p$ are numbers and generally $m = 1$ or $2$, $n = 3$ or $4$ and $p = 0$ or any integer, have attracted the attention of various investigators [1-15].

Generally, studies have been done on crystal and magnetic structures, electron distribution density, structural and magnetic phase transition, relaxation effects and dichroism etc. Much work has been done on KNiF$_3$ [16] and KNiCl$_3$ [11-14] due to their interesting properties. The majority of the fluorides adopt the cubic perovskite structure [17, 18]. In both fluorides and chlorides mixed cubic-hexagonal stackings have been observed. Bromides and iodides [7] in so far as they exist crystallize in the structure types adopted by the chlorides.

A search of literature did not show any work on the compound potassium nickel bromide (KNiBr$_3$·H$_2$O). Therefore, it was thought worthwhile to work on this compound by x-ray diffraction and electron paramagnetic resonance.
Experimental details

The crystals of KNiBr₃·H₂O were grown from aqueous solutions of NiBr₂ and KBr in equimolar ratio by slow evaporation method at room temperature. For electron paramagnetic resonance (EPR) work a little amount of MnBr₂ (0.5 wt%) was added to the mother solution. Transparent crystals with well developed faces were grown in a few days. The crystals were tested for the percentage of constituents present in them. The constituents tested in KNiBr₃·H₂O are potassium, nickel and water of hydration. Potassium was estimated by systronic flame photometer with potassium filter, nickel by EDTA titration method using PAN indicator and H₂O was estimated with the help of rapid oxygen method. The estimated percentage are as follows:

\[ K = 11.0\% \]
\[ Ni = 16.5\% \]

and one molecule of H₂O per formula unit. The rest belongs to promine. These estimates satisfy the chemical formula of the compound as KNiBr₃·H₂O. The infrared spectrum of KNiBr₃·H₂O showing absorption by water of hydration is shown in Fig. 1.

Powder pattern and single crystal x-ray studies were carried on Radon House x-ray diffraction unit with unfiltered radiation from a Cu-target working at 30 kV and 15 mA. The powder pattern was taken by crushing the crystals into fine powder. The rotation photographs of the crystal were taken.
Fig. 1. I.R. spectrum of KNiBr$_3$·H$_2$O crystal.
by rotating the crystal about the three crystallographic axes a, b and c.

Diffractogram (powder) of KNiBr$_3$H$_2$O was recorded by crushing the crystals into fine powder and the specimen was prepared in the form of a flat faced briquet of powder on x-ray diffractometer (PW 1140.90) having Cu-target with nickel filter at 35 kV and 20 mA.

Electron paramagnetic resonance spectra were recorded by X-band EPR JEOL spectrometer at room temperature. One of the spectra which was of maximum spread was also recorded at liquid nitrogen temperature (LNT). As the crystal axes were identified by x-ray, the angular variation study was done by rotating the crystal when the magnetic field was in ab, bc and ac crystallographic planes.

The density of the crystals was measured by liquid (benzene) displacement method and it was found to be 2.435 gm/cc.

Results and discussion

In the diffractogram and powder pattern the low angle lines are doublet which suggests that most probably the system is monoclinic. After this speculation, rotation photographs were taken about various axes. After much trial and error, these directions were located which could be taken as coinciding with the crystallographic axes of a monoclinic system. The angle between two directions was found to be 99.7° and the
third was perpendicular to these two. If three directions are found to coincide with a, b, c axes, then the lattice constants are found to be

\[ a = 6.00 \, \text{Å} \]
\[ b = 21.28 \, \text{Å} \]
\[ c = 15.12 \, \text{Å} \]

and \( \beta = 99.7^\circ \).

The angle \( \beta \) was further confirmed by taking rotation photograph when the crystal was rotated along [101] axis. The layer line spacing along [101] gave an identity period corresponding to 17.18 Å which is justifiable by simple geometry. On the basis of density measurement and lattice constants the crystal has 8 formula units per unit cell.

The rotation photographs of the crystal by rotating it along a, b, c axes and along [101] axis are shown in Figs. 2, 3, 4 and 5 respectively.

The cell constants reported here are the refined values obtained by the powder pattern analysis.

The powder pattern of the crystal was recorded both by Debye-Scherrer camera and diffractometer, as shown in Figs. 6 and 7 respectively. The data from the Debye-Scherrer pattern and diffractogram are the same but the diffractogram data were finally taken for analysis because of better resolution and better estimates of intensity.
Fig. 2. Rotation photograph of NKiBr$_3$.H$_2$O crystal by rotating it along a-axis.
Fig. 3. Rotation photograph of KNiBr$_3$.H$_2$O crystal by rotating it along $\mathbf{b}$-axis.
Fig.4. Rotation photograph of KNiBr$_3$.H$_2$O crystal by rotating it along $c$-axis.
Fig. 5. Rotation photograph of KNiBr$_3$·H$_2$O crystal by rotating it along [101] axis.
Fig. 6. Powder diffraction pattern of KNiBr$_3$.H$_2$O crystal. Prominent lines marked.
Fig. 7. Diffractogram (Powder) of KNiBr$_3$.H$_2$O crystal. Lines have been marked.
Powder pattern analysis of KNiBr$_3$·H$_2$O is presented in table 1. In table 1, the first column indicates intensity, second, observed Sin$^2\theta$ values, third, calculated Sin$^2\theta$ values and the fourth, indices of reflections. As seen from table 1, there is close resemblance between the Sin$^2\theta$ observed and Sin$^2\theta$ calculated for all the diffraction lines. It indicates that the system, axial lengths and the interaxial angles have been determined correctly.

Non-extinction conditions show that the space group of the crystal is P2$_1$/n. The following observations support this.

i) There is no restriction on hkl reflections.

ii) In oko reflections, everytime we have k = 2n as in the lines with Sin$^2\theta$ obs. = 0.0210 and 0.1317.

iii) a. In okl reflections, k+1 = 2n as in the lines with Sin$^2\theta$ obs. = 0.0162, 0.0315, 0.0365, 0.0643, 0.1317, 0.1421.

b. In hko reflections, h+k = 2n, no such reflection was found here.

c. In hol reflections, h+1 = 2n as in the line with Sin$^2\theta$ obs. = 0.0347.

It has been possible here to determine the crystal system and space group of KNiBr$_3$·H$_2$O. Location of the atomic positions inside the unit cell by structure factor analysis
Table 1. X-ray diffraction data for KNiBr$_3$·H$_2$O (P2$_1$/n).

<table>
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<tr>
<th>Intensity observed</th>
<th>Sin$^2$$\Theta$ observed</th>
<th>Sin$^2$$\Theta$ calculated</th>
<th>hkl</th>
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FOOT NOTE: s (strong), ms (medium strong), w (weak) and vw (very weak).
still remains a problem to be solved.

Since all the three crystallographic axes are known, therefore, it is easy to mount the crystal to record the EPR spectra at different angles. Angular variation studies were made by rotating the crystal when the magnetic field is in ab, bc and ca plane. The angular variation studies show very interesting features. When the magnetic field direction was 25° away from the axis 'a' in ab plane a clear 30 lines Mn²⁺ spectrum of maximum spread was observed. This gives the Z-axis of the magnetic vector. Fig. 8 shows the EPR spectrum of Mn²⁺ doped KNiBr₃.H₂O along BNZ axis. The fine structure components loose intensity and ultimately vanish one by one starting from the higher field components when we go away from Z-axis on either sides. Some representative spectra are shown in Fig. 9. When the magnetic field is rotated by 90° from Z-axis, all the fine structure splitting vanishes and almost a straight line was observed(Fig. 9f).

The emergence of a weak spectrum in the region about 90° from Z-axis in ab plane where the main spectrum disappears, is probably due to another magnetic site for Mn²⁺ in the lattice. The spectrum in the ac plane is almost the same as in ab plane. In bc plane the spectrum does not show any unusual characteristics. Similar spectral behaviour has been observed in many compounds such as NiK₂(SO₄)₂.6H₂O [19], Ni(NH₄)₂(SO₄)₂.6H₂O [20], Ni(CH₂)₆(NO₃)₂ [21] and NiSO₄.7H₂O[22]
Fig. 8. EPR spectrum of Mn$^{2+}$ doped KNiBr$_3$·H$_2$O single crystal along $\vec{b}||Z$ axis in ab plane.
Fig. 9. EPR spectra of Mn$^{2+}$ doped KNiBr$_3$·H$_2$O single crystal in ab plane, when $\mathbf{B}$ is a) $10^\circ$ away from Z-axis b) $20^\circ$ away from Z-axis c) $30^\circ$ away from Z-axis d) $50^\circ$ away from Z-axis e) $70^\circ$ away from Z-axis f) $90^\circ$ away from Z-axis.
by various workers. They have attributed the disappearance of signal due to broadening for various reasons as exchange broadening (isotropic and anisotropic), dipolar interaction, cross relaxation etc.

The EPR spectrum along Z-axis is analysed by the effective spin-Hamiltonian

\[
H = \beta H \cdot g \cdot S_z + D [S_z^2 - \frac{1}{3} S(S+1)] + E (S_x^2 - S_y^2) \\
+ \frac{a}{6} [S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1) (3S^2 + 3S - 1)] \\
+ AS_z I_z
\]

where symbols have their usual meaning and \( S = I = \frac{5}{2} \) for \( \text{Mn}^{2+} \). On lowering the temperature of observation to LNT it is seen from the Z-axis spectrum (Fig. 10) that the intensity of the fine structure component on the higher field side is decreasing. Considering the general theory of change of intensity on lowering the temperature it can be inferred that the higher component belongs to \( \frac{5}{2} \rightarrow \frac{3}{2} \) and the lower most \( -\frac{3}{2} \rightarrow -\frac{5}{2} \), therefore, \( D \) must be taken as positive. In agreement with the usual practice that the hyperfine splitting constant \( A \) is negative in manganese complexes, the value of the spin-Hamiltonian parameters were found to be

\[
D = +276 \text{ gauss,} \quad A = -93.3 \text{ gauss,} \\
a = 7.8 \text{ gauss,} \quad E = 158 \text{ gauss} \\
g_z = 1.990.
\]
Fig. 10. EPR spectrum of Mn$^{2+}$ doped KNiBr$_3$·H$_2$O single crystal along B∥Z-axis in ab plane at LNT.
The large value of the rhombic component 'E' reveals the presence of very low symmetry of the Mn$^{2+}$ site.

The observed features in the EPR spectra can be explained as due to the magnetic interactions between Mn$^{2+}$ and the host ions Ni$^{2+}$ following Moriya and Obata [23] and Hutchings and Wolf [24]. In the spectrum of Mn$^{2+}$ in KNiBr$_3$·H$_2$O we find that the line widths of individual hyperfine components associated with various fine structure groups $+5/2 \leftrightarrow +3/2$ and $+3/2 \leftrightarrow +1/2$ are $13\pm 2$ gauss, while those for $-5/2 \leftrightarrow -3/2$ and $-3/2 \leftrightarrow -1/2$ are $24\pm 4$ gauss. The line width for the fine structure group $+1/2 \leftrightarrow -1/2$ is $19\pm 3$ gauss. The observed line widths with fine structure groups is different from that generally observed in diamagnetic hosts, which arises due to the broadening effects of the crystal field inhomogeneities [25]. Also the crystal field inhomogeneities generally cause a broadening of a few gauss only and their effect will not be perceptible on the much larger line width. The same type of line width variation as has been observed here has been reported by Chowdari [26] and Sharma [27] in the RT EPR spectra of Mn$^{2+}$ doped Cobalt and Nickel Acetate Tetrahydrate and Gd$^{3+}$ (S-state ion like Mn$^{2+}$) doped in some paramagnetic rare earth trifluorides. In principle, the study of widths and shapes of EPR lines can be used to obtain an understanding of the interactions between the various ions involved. For a multi-level ion, like Mn$^{2+}$, it is theoretically expected that the
line shapes will depend in a complicated way upon the relaxation transition probabilities between various levels [28]. The large line widths of Mn$^{2+}$ resonance lines are likely due to the fluctuating magnetic field created by the nickel magnetic moment. The complete broadening and disappearance of the well resolved 30 lines spectrum may be due to cross relaxation between Mn$^{2+}$ and Ni$^{2+}$ ions.

The magnitude of the g-tensor of Mn$^{2+}$ in KNiBr$_3$·H$_2$O along the principal Z-axis is less than the free spin g-value. The negative shift in the g$_z$-value is, most probably, due to Ni$^{2+}$, which produces a local static magnetic field at Mn$^{2+}$ ions.

As mentioned earlier that there is another spectrum seen in the region where the main spectrum does not exist and in the most favourable circumstances, its only three fine structure components are visible with relative separation of 760 gauss. This can be assigned to another magnetic site for Mn$^{2+}$ in the lattice. The probable site is K$^+$ and as this substitution is not favoured by charge compensation requirements, it is not populous. As the relative intensity of this component is very weak, this could not be further investigated.

**Conclusions**

The new crystal KNiBr$_3$·H$_2$O has been grown by slow evaporation technique of aqueous solution prepared by mixing NiBr$_2$ and KBr in equimolar ratio. The constituents have been tested
chemically and chemical formula verified. X-ray diffraction studies show that the crystal is monoclinic (P2_1/n) with lattice constants: \(a = 6.00 \text{ Å}, \quad b = 21.28 \text{ Å}, \quad c = 15.12 \text{ Å}\) and \(\beta = 99.7^\circ\). It has 8 formula units per unit cell.

EPR study shows that Mn\(^{2+}\) enters the lattice substitutionally and there is strong interaction between Mn\(^{2+}\) and the host Ni\(^{2+}\) ions resulting into large line width and unusual features in the EPR spectra.
References


