Synthesis and Characterization of \( \text{K}_2\text{SiF}_6 \) Hexafluorosilicate

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Abstract. Hexafluorosilicates such as \( \text{K}_2\text{SiF}_6 \) (Hieratite) exists in nature as minerals. The common formula is \( \text{M}_2\text{SiF}_6 \) where \( \text{M} \) represents alkali ion. All the alkali fluorosilicates including \( \text{K}_2\text{SiF}_6 \) decomposes in the temperature range of 300 to 700 °C with SiF\(_4\) as residual product. SiF\(_4\) has an important application in the solar cells fabrication industry. Due to low thermal stability, it is difficult to prepare these complex fluorides by the conventional methods. Hence, a one step simple wet-chemical route was adopted. Confirmation of successful precipitation of \( \text{K}_2\text{SiF}_6 \) during our process of synthesis was done by using various analysis techniques. Results obtained through XRD, EDAX and SEM measurements are reported and discussed here in brief.

Keywords: Hexafluorosilicate, Synthesis, Precipitation, XRD, EDAX, SEM.

1. Introduction

\( \text{K}_2\text{SiF}_6 \) is a complex fluoride which belongs to a type of compounds collectively called as hexafluorosilicate. Main formula for these fluorides is \( \text{M}_2\text{SiF}_6 \) where \( \text{M} \) represents an alkali ion. Alkali fluorosilicate \( \text{K}_2\text{SiF}_6 \) decomposes in the temperature range of 300 to 700 °C with SiF\(_4\) as residual product. The reaction commences as: \( \text{K}_2\text{SiF}_6 \rightarrow 2\text{KF} + \text{SiF}_4 \). Its low decomposition temperature makes it major source of fluorine and silicon in chemical processing factories. SiF\(_4\) has an important application in the solar cells fabrication industry. Also more recently, \( \text{K}_2\text{SiF}_6 \) was used in producing tubular \( \text{SiO}_2 \) by hydrothermal reactions [1]. Hexafluorosilicates are significant in geological research since, \( \text{K}_2\text{SiF}_6 \) also known by the names Demartinite and Hieratite exists in nature as minerals. \( \text{K}_2\text{SiF}_6 \) “Hieratite” is properly used in the manufacture of special glasses, enamels and ceramic materials [2].

More recently, \( \text{Mn}^{4+} \) activated \( \text{K}_2\text{SiF}_6 \) phosphor finds huge applications as a red component in warm-white LED’s used in smart phones, tablets and televisions [3-6].

Week thermal stability of hexafluorosilicates makes difficult to prepare these fluorides via conventional solid state diffusion method. Solid state reaction methods needs very high temperatures for diffusion of initial reactants and require huge apparatuses. Hence, another simple method of synthesis was attempted as \( \text{K}_2\text{SiF}_6 \) is insoluble in water and therefore can be precipitated.

2. Synthesis

Reagents used were of the Analytical grade. Desired amount of potassium carbonate (\( \text{K}_2\text{CO}_3 \)) was thoroughly mixed with silicic acid (\( \text{SiO}_2\cdot\text{H}_2\text{O} \)). Hydrofluoric acid HF(48%) was poured drop wise in the aq. solution of potassium carbonate and silicic acid, till effervescence due to decomposition of carbonate
and evolution of CO₂ stops. This process was done at room temperature. Water formed in the reaction and excess HF was slowly evaporated off on a hot plate. The whole procedure was done in a PTFE beaker. Resulting mass was dried and used in further experiments.

3. Results and Discussion

“X-ray diffraction patterns were recorded on a Rigaku MiniFlex II diffractometer. Elemental and morphological studies were performed on scanning electron microscope (SEM, VEGA MV2300T/40) operated at 20.0kV voltage.”

3.1. X-Ray Diffraction (XRD) Analysis

Fig. 1 shows the XRD pattern of K₂SiF₆ (as prepared sample without any thermal treatment). Stick pattern of ICDD 85-1382 is also shown for the comparison. Excellent match is seen. Cubic form of K₂SiF₆ is thus obtained by the simple wet chemical synthesis.

![XRD pattern comparison](image)

**Figure 1.** XRD stick pattern of K₂SiF₆ formed in our sample, compared with ICDD 85-1382.

3.2. Crystal Structure

Fig. 2 shows the crystal structure for K₂SiF₆. It crystallizes in cubic system which is its more stable form with space group O_h³ (Fm3m) with a lattice constant of a = 8.13 Å. The K⁺ ions are coordinated by 12-fold F⁻ ions. The Si⁴⁺ ions are surrounded by 6 F⁻ ions. The K – F distance is about 2.897 Å and that of Si – F is 1.683 Å. The SiF₆ octahedra lie on the cell edges and on the face-centers.
Figure 2. Crystal structure of K$_2$SiF$_6$ showing (a) cubic K coordinated unit cell, (b) hexagonal-SiF$_6$, Si coordinated by 6F$^{-}$ ions.

3.3. Energy Dispersive X-Ray (EDAX) And Scanning Electron Microscope (SEM) Measurements

Previous investigations of the thermal stability of K$_2$SiF$_6$ in dry air by Deadmore (1960) [7] revealed that at temperatures above 700 °C, a progressive conversion from K$_2$SiF$_6$ to K$_3$SiF$_7$ initiates. During this phase transformation, it loses SiF$_4$ until the composition K$_3$SiF$_7$ completes. Recently, Barve et al [8] carried out TGA/DTA and XRD studies on K$_2$SiF$_6$. Two DTA peaks are observed in the temperature range 100-500 °C. The first exothermic peak is observed at 270 °C with the onset at 150 °C, indicates the onset of phase change to K$_3$SiF$_7$. Also careful study of their XRD results with increasing temperature, showed that small amount of K$_3$SiF$_7$ phase exists even in the sample heated at 350 °C and increases further with the increase in temperature. These observations show that decomposition of K$_2$SiF$_6$ starts at 150 °C, itself. Hence due to its very low thermal stability, incorporation of divalent rare earth ions is also very difficult in order to study other physical properties such as luminescence.

Energy dispersive x-ray analysis (EDAX) has been performed on K$_2$SiF$_6$ in order to know the actual composition of various elements present in our samples. Two phases, K$_2$SiF$_6$ and K$_3$SiF$_7$ are known to exist. By measuring relative ratios of different constituent atoms, it may be possible to deduce which of these phases is formed in order to confirm the phase pure formation of K$_2$SiF$_6$ by precipitation. Fig. 3 shows EDAX spectrum of K$_2$SiF$_6$ together with experimentally observed values.
Figure 3. EDAX spectrum of K$_2$SiF$_6$

The relative ratios of various atoms for two phases and experimentally observed values are given in the Table 1.

Table 1: Results of EDAX analysis of K$_2$SiF$_6$ compound.

| Atom percent: | K   | Si  | F   |
|---------------|-----|-----|-----|
| K$_2$SiF$_6$  | 22.22 | 11.11 | 66.7 |
| K$_3$SiF$_7$  | 27.2 | 9.1  | 63.6 |
| observed      | 30.18 | 9.5  | 60.32 |

| Atomic ratio: | Si | K | F |
|---------------|----|---|---|
| K$_2$SiF$_6$  | 1  | 2 | 6 |
| K$_3$SiF$_7$  | 1  | 3 | 7 |
| observed      | 1  | 3.17 | 6.34 |

EDAX results show that the composition is closure to K$_3$SiF$_7$. However, XRD pattern shows good match with K$_2$SiF$_6$. The discrepancy could be due to excess KF adsorbed on K$_2$SiF$_6$ particles. 

Fig. 4 shows SEM images where (a) shows the image taken at a resolution of 200μm, (b) at 50μm and (c) at 100μm. It can be concluded that the precipitates are particles of irregular shape and are of about 50 μm size.
Figure 4. SEM images of K₂SiF₆, (a) shows the image taken at a resolution of 200μm, (b) at 50μm and (c) at 100μm.

4. Conclusions

XRD results confirmed the formation of K₂SiF₆ hexafluorosilicate in our sample. However, EDAX measurements showed that the relative composition of different constituent elements appears more close to that of its high temperature phase K₃SiF₇. But XRD pattern shows no lines of such impurity present in XRD pattern of our sample. Hence, it could be concluded that this discrepancy could be due to excess KF adsorbed on K₂SiF₆ particles. Also, SEM images show that precipitated particles are of irregular shape and about 50 μm in size.

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