Synthesis and Characterization of Yttrium based Luminescent Materials

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Abstract. NaYF₄ is well known and most promising upconversion yttrium based fluoride phosphor till date. Fluoride synthesis is rather tricky due to their peculiar physico-chemical properties. Fluorides are highly susceptible to hydrolysis. This is detrimental to the luminescence. Conventional method for preparing complex fluoride compounds is solid state reaction which is a tedious task. In recent years, many new methods such as wet chemical synthesis have been suggested for these novel materials. These new syntheses provide more milder and efficient ways of materials preparation. Here, preparation of two luminescent hosts NaYF₄ and KYF₄ was attempted via Wet-Chemical synthesis. Among these, NaYF₄ could be successfully prepared, whereas synthesis of KYF₄ was partially successful. Formation of these compounds was confirmed by various measurements. Photoluminescence was obtained for Ce³⁺ doped NaYF₄.

Keywords: Fluorides, Phosphors, Photoluminescence, Synthesis

1. Introduction

In the recent years number of yttrium based fluorides are reported as solid state lasers, upconversion and VUV materials. The examples include fluorides of the type MYF₄ where M= Li, Na, K etc. Pol and Rao[1] have described the synthesis of the compound NaYF₄ through a chemical reaction using NaF and YCl₃ as starting materials. More recently, NaYF₄ has been also synthesised via few new novel methods such as hydrothermal [2], solvothermal [3] etc. Interesting phosphors result when small amounts of rare earth activators are incorporated into the NaYF₄. NaYF₄ :Nd³⁺ is known to be potential host since tunable laser action in infrared region is reported in 1969 [4]. It is one of the efficient material for infrared to visible upconversion when activated with Yb³⁺, Er³⁺ since 1972 [5, 6]. Many studies have been carried out in recent years. NaYF₄ :Yb, Er [7-16] has emerged as a most desirable upconversion fluoride material.

Other efficient UC materials are NaYF₄ :Tm³⁺, Yb³⁺ [17-28], NaYF₄ :Yb³⁺, Ho³⁺ [29-31], NaYF₄ :Yb³⁺, Tm³⁺ /Er³⁺/Eu³⁺ [32], NaYF₄ :Yb³⁺ [33], NaYF₄ :Nd/Yb [34,35] and NaYF₄ :Ce³⁺, Tb³⁺ [36,37]. Also, interesting properties have been observed in nanocrystals of doped NaYF₄ [38-41]. NaYF₄ is also useful in bioimaging [42].

The structure of the fluorides NaLnF₄ (Ln=Y–Lu) was first described by Burns in 1965[43] and subsequently confirmed[44]. At ambient temperature and pressure, NaYF₄ exists in two polymorphs [45], the hexagonal type structure and the cubic (fluorite type) one, depending on the synthesis method. The space group for NaYF₄ is P-6 and the unit cell dimensions are a = 5.967 Å and c = 3.523 Å. Each unit cell contains 1.5 formula units, so that the compound may be written as NaLn(Na½Ln½)F₆ to indicate that three cation sites exist, one occupied fully by Ln³⁺ (1a), one occupied randomly by ½ Na⁺, ½ Ln³⁺ (1f) and the third occupied fully by Na⁺ (2h). Sites 1a and 1f both have C3h symmetry and are nine fold
coordinated, whereas site 2h has C3 symmetry. The rare earth ion should be accommodated in both sites 1a and 1f, the number of Ln$^{3+}$ ions in site 1a and 1f being twice that in site 1f. Crystal structure of NaYF$_4$ is given in the Figure 1.

![Figure 1: Crystal structure of Hexagonal-type NaYF$_4$.](image)

The alkali metal-rare earth fluoride systems generally have complex phase diagrams\[46\] which make it difficult to obtain well-crystallized single-phase materials. The transition in NaYF$_4$ between hexagonal and cubic phases occurs at 691°C.

### 2. Experimental
NaYF$_4$ was synthesized by using wet chemical synthesis. All the reagents used were of the Analytical Reagent grade. Freshly prepared aqueous solution of NaF was used. Chloride salts of Y$_2$O$_3$ and Ce$_2$(CO$_3$)$_3$ were prepared by dissolving in dil. HCl. NaF was taken in 10 time’s excess than the stoichiometric ratio. Both the solutions were heated to 85°C. At 85°C, solution of YCl$_3$ and CeCl$_3$ was added slowly into the solution of NaF, yielding NaYF$_4$ precipitate. The resultant precipitate was filtered, washed and dried under the fan. The dried powdered was collected and used for subsequent experiments. KYF$_4$ was prepared in a similar way.

X-ray diffraction patterns were recorded on a Philips PANalytical X’pert Pro diffractometer. Photoluminescence spectra were recorded on a Hitachi F-4000 spectro-fluorimeter with spectral slit width of 1.0 nm in the spectral range 220-700 nm. Scanning electron microscope images were taken on the SEM,VEGA MV2300T/40 operated at 20.0kV voltage.

### 3. Results and Discussion

#### 3.1. X-ray diffraction analysis

Figure 2 shows the XRD pattern for NaYF$_4$ prepared by wet chemical synthesis. It was found that the XRD pattern of ICDD 77-2042(NaYF$_4$) is identical to that of ICDD 89-5167(YOF). Therefore, it raised a confusion regarding the precipitated sample that whether NaYF$_4$ is formed or always YOF precipitates during the wet chemical synthesis.
Similar, type of confusion was raised when X-ray diffraction pattern of KYF₄ (our sample) prepared by same wet chemical synthesis was compared with ICDD 79-1688(KYF₄) and ICDD 89-5167(YOF) (Figure 3).

**Figure 2:** XRD pattern of NaYF₄ prepared by wet chemical synthesis, compared with ICDD 77-2042(NaYF₄) and ICDD 89-5167(YOF).

**Figure 3:** XRD pattern of KYF₄ prepared by wet chemical synthesis, compared with ICDD 79-1688(KYF₄) and ICDD 89-5167(YOF).
3.2. EDAX and SEM

Therefore, Energy dispersive x-ray analysis (EDAX) and scanning electron microscope (SEM) studies were carried out on both the compounds. Figure 4 represents the SEM image together with the EDAX spectrum of NaYF₄. Table 1, shows the weight% and atomic% of the constituent elements, respectively. When composition of elements in NaYF₄ compound were calculated separately, the values obtained for different constituting elements are Na = 16.66 At%, Y = 16.66 At% and F = 66.67 At%, which are found to be approximately nearer to the values observed during EDAX analysis (values given in table 1). Therefore, formation of YOF phase can be ruled out since, oxygen is present but in very less amount. This could be due to formation of some oxides at the surface of the material during the measurements. Ce is present in 0.06 At% in the sample.

Table 1 gives the experimental values of weight% and atomic% of the Na, Y and F present in our sample.

Hence, it can be said that NaYF₄ has been formed in our experiment. Figure 5 shows the SEM micrograph and EDAX spectrum of KYF₄ prepared by wet chemical synthesis.
Table 2, shows the composition of various elements as their atomic percent. When composition of elements in KYF₄ compound were calculated separately, the values obtained for different constituting elements are K = 16.66 At%, Y = 16.66 At% and F = 66.67 At%. But according to the values given in the table 2, oxygen (O) and potassium (K) are present approximately in same concentration, indicating that may be both KYF₄ and YOF are coexisting in our sample. Na is present as an impurity but in a very small amount.

Figure 5: represents the (a) SEM image and (b) EDAX spectrum.

Table 2 shows the observed weight% and atomic% values of the K, Y and F present in our sample.

Hence, a very good match between our sample NaYF₄ and ICDD file 77-2042 is seen. Thus confirming the formation of hexagonal NaYF₄.

Therefore from the above results, it can be concluded that NaYF₄ can be prepared by using simple wet chemical synthesis easily but it’s difficult to synthesize pure KYF₄ in the same way. SEM images show the formation of irregular particles of different shapes and sizes.

3.3. Photoluminescence in NaYF₄:Ce³⁺

Figure 6 represents the Ce³⁺ luminescence in NaYF₄. A broad emission band peaking at 315 nm is observed for 254 nm excitation. The excitation spectrum consists of a peak at 254 nm and a shoulder at 288 nm. Peaks of the curves appears little disturbing due to very high PL intensity. As prepared Ce-doped
sample showed luminescence. Luminescence study on KYF₄ was not attempted due to the doubt regarding the formation of phase pure compound.

![Figure 6](image_url)

**Figure 6**: PL spectra of NaYF₄:Ce(1%). (a) excitation at λ_em=315nm and (b) emission at λ_ex=254nm.

4. Conclusions

Two well-known host phosphors NaYF₄ and KYF₄ were attempted via simple Wet-Chemical process. XRD studies showed that XRD pattern of both the compounds matches well with another compound YOF which raised doubt regarding the successful formation of desired phases. Hence in order to eliminate this confusion, further studies such as EDAX and SEM were also done. The EDAX confirmed the formation of phase pure NaYF₄ whereas KYF₄ was contaminated with YOF.

As prepared Ce³⁺ doped NaYF₄ showed luminescence, hence avoiding the need of high temperature and time consuming reduction processes. Emission has been recorded at 315 nm for 254 nm excitation with very high intensity. PL measurements are in good agreement with the previous studies.

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