CHAPTER 2

EXPERIMENTAL TECHNIQUES
2.1. INTRODUCTION

In this chapter, the detailed description of the methods used in the preparation and characterization of Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ ions in fluorophosphate glasses under ambient conditions are presented. The optical properties of Ln$^{3+}$-doped materials are influenced by the constituents of glass composition, dopant ions concentration, structure, optical quality, thermo-optical, thermo-mechanical and chemical durability. As described earlier, the glass is formed due to the sudden cooling of melts below their freezing point without crystallization.

2.2. GLASS PREPARATION

Various techniques that can be used for the preparation of glasses as reviewed by Zarzycki [1] are:

i) Thermal evaporation  
ii) Sputtering  
iii) Glow-discharge decomposition  
iv) Chemical vapour deposition  
v) Melt quenching technique  
vi) Gel-desiccation  
vii) Electrolytic deposition  
viii) Chemical reaction  
ix) Reaction amorphization  
x) Irradiation  
xi) Shockwave transformation  
xii) Shear amorphization

Among all the techniques, the well established and versatile technique used for the production glass is the melt quenching technique.

2.2.1. Melt quenching technique

The usual way of obtaining a glass is by the fusion of one or more raw materials, using the conventional melt quenching technique. When the rate of cooling is sufficiently fast to bypass crystallization, the disordered state of the liquid melt is retained in the form of solid state.

The batch composition of high purity chemicals were thoroughly grinded in an agate mortar with a pestle and the homogeneous mixture was collected in a platinum crucible. The mixture was heated inside an electric furnace around 1100-1200 °C for 60-90 min. and then air quenched by pouring it onto a thick polished/uncontaminated brass mould as shown in Fig. 2.1. The glasses were annealed at a temperature slightly lesser than the glass transition temperature ($T_g$) to remove the thermal strains. The samples were polished before measuring their optical properties.
2.3. CHARACTERIZATION TECHNIQUES

2.3.1. Physical properties

The physical properties such as density, concentration, refractive index and optical path length are important to characterize the Ln$^{3+}$-doped glasses.

2.3.1.1. Density

The densities ($d$) of the glasses were determined by the Archimedes’ method using water as an immersion liquid by the following formula,

$$d = \frac{w_1}{w_1 - w_2} \times d_w,$$

(2.1)

where $w_1$ = the weight of the glass sample in air,

$w_2$ = the weight of the glass sample in water,

and $d_w$ = density of water and taken as 1.00 g/cm$^3$.

2.3.1.2. Concentration

The concentrations ($C$, in mol/lit) of the dopant ions in the glasses were found from the expression,

$$C = \frac{y}{MW} \times \frac{d}{x} \times 1000$$

(2.2)

where $y$ = weight of the RE compound,

$x$ = total weight of the chemical composition

$d$ = density of the glass

and $MW$ = molecular weight of the RE compound.
2.3.1.3. Refractive index

Refractive indices (n) of the glasses were measured using an Abbe refractometer at a wavelength of sodium yellow line (589.3 nm) and 1-bromonaphthalene (C₁₀H₇Br) as a contact liquid with an accuracy of 0.001.

2.3.2. Characterization of the host

For the better understanding of structural, thermal and vibrational characteristics of the host and its influence on the photoluminescence properties of the Ln³⁺ - doped glasses the X-ray diffraction (XRD), differential thermal analysis - thermal gravity analysis (DTA-TGA), FTIR and Raman spectral measurements were performed for the undoped host glass.

2.3.2.1. X-ray diffraction

X-ray diffraction studies are of immense help in understanding the structure of metals, polymeric materials and other solids. The arrangement and spacing of atoms in crystalline materials can be directly deduced from the diffraction studies.

In the present study, the X-ray diffraction pattern of the undoped PKAlCaF glass recorded at room temperature with X'PERT PRO X-ray diffractometer using CuKα (1.5406 Å) radiation in the range of 2θ = 10°–80° is shown in Fig. 2.2. The broad scattering at lower angles, indicates typical long range structural disorder which confirms the amorphous nature of the host glass.

2.3.2.2. Thermal analysis

The TGA–DTA thermographs of the PKAlCaF host glass scanned between 30 and 1300 °C at a heating rate 10 °C /min are shown in Fig. 2.3. The DTA curve exhibited a weak endothermic peak at 480 °C, corresponding to the glass transition (Tg) temperature. An exothermic peak due to crystallization (Tc) and an endothermic peak (Tm) owing to the melting temperature of the glass are observed at 660 and 960 °C respectively. It has been proved that for thermally stable glass forming systems, the Hruby’s parameter, \[ K_{gl} = \frac{T_c - T_g}{T_m - T_g} \], value should be > 0.1. For the present PKAlCaF glass, the ΔT and K_{gl} values are found to be 180 °C and 0.6, respectively, which indicates the good glass forming tendency and thermal stability of the present glass.
Fig. 2.2. X-ray diffraction trace of undoped PKAlCaF host glass

Fig. 2.3. DTA-TGA curves of PKAlCaF glass

The TG profile revealed that, the weight loss in the precursor chemical mix is a two-step process in the temperature range of 30 °C - 1300 °C. In the first step, the
initial weight loss of samples has been observed between 30 °C and 206 °C due to the 
decomposition of the water present in the chemical mix and the observed weight loss 
has been formed to be around 5%. No appreciable weight loss has been noticed in the 
sample in the temperature range of 206 °C – 1200 °C and there-after a sudden 
decrease in the weight has been attributed to phase changes due to melting of the 
chemicals mixed in the sample preparations.

2.3.2.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy has been widely used for the 
identification of functional groups in organic, inorganic and biological compounds. In 
the present investigation, FTIR spectum was recorded with a resolution 1 cm⁻¹ in the 
400-4000cm⁻¹ range using Perkin-Elmer Paragon 500 FTIR spectrometer. Fig. 2.4 
shows the FTIR transmittance spectrum of undoped glass consisting of ten bands 
centered at 540, 612, 744, 786, 920, 1132, 1394, 1630, 2365, 2965 and 3443 cm⁻¹. The 
characterization of FTIR peaks has been summarized as follows:

Fig. 2.4. FTIR spectrum of PKAlCaF glass

(a) The peaks at 540 and 612 cm⁻¹ are assigned to the vibrations of P-O bonds.
(b) The peaks at 744 and 786 cm⁻¹ are due to the symmetric stretching vibrations of 
P-O-P group, while the 920 cm⁻¹ band corresponds to asymmetric stretching 
vibrations.
(c) The peaks at 1132 cm\(^{-1}\) and 1394 cm\(^{-1}\) are assigned to PO\(_3\) and PO\(_2\) asymmetric stretching vibrations [2].

(d) The peaks at 1630, 2365 and 2965 cm\(^{-1}\) are related to the stretching vibrations of P-O-H groups [3].

(e) The broad band centered at 3443 cm\(^{-1}\) may be due to the air moisture during the preparation of KBr pellets for IR measurements, which belongs to symmetric stretching of O-H or H-O-H groups [4-5].

### 2.3.2.4. Raman analysis

The vibrational properties of the PKAlCaF host glass has been studied through the Raman spectrum shown in Fig. 2.5. The spectrum revealed seven characteristic bands at 335, 543, 625, 728, 1075, 1135 and 1284 cm\(^{-1}\), which are ascribed to characteristic phosphate group vibrations. The two bands at 1135 cm\(^{-1}\) and 1284 cm\(^{-1}\), correspond to the symmetric and asymmetric stretching vibrations of non-bridging oxygen atoms bonded to phosphorous atoms (O-P-O) in the Q\(^2\) phosphate tetrahedron, respectively [6-11]. The Raman line at 1075 cm\(^{-1}\) is due to the asymmetric stretching mode of P-O-P groups linked with small meta-phosphate groups [10-11]. The band at 728 cm\(^{-1}\) is assigned to the vibrations of P-F chain formation [12-14], while the weak band at 625 cm\(^{-1}\) belongs to Al\(_2\)O vibrations [15]. The band at 543 cm\(^{-1}\) corresponds to the bending vibrations of O-P-O units and PO\(_2\) modes [8] and the relatively strong band at 355 cm\(^{-1}\) is due to alkali-oxides (such as K\(_2\)O and Na\(_2\)O) [16].

![Fig. 2.5. Raman spectrum of the PKAlCaF glass.](image-url)
It is known that the phonon energy of the host can be defined as the highest intents vibrational energy, which can be measured from the Raman spectrum. From Fig. 2.4, it is found that the maximum phonon energy of the host glass is $1135 \text{ cm}^{-1}$, which plays a major role on the emission properties of the luminescent ions.

2.3.3. Absorption spectra

Optical absorption spectra of Ln$^{3+}$-doped glasses were recorded using Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer [17]. The photograph of the instrument and its block diagram are shown in Figs. 2.6 & 2.7, respectively. The technical specifications of the spectrophotometer are shown in Table 2.1.

Two radiation sources, namely deuterium lamp (DL) and halogen lamp (HL), cover the working wavelength range of the spectrophotometer. For operation in the near infrared (NIR) and visible (Vis) regions, source mirror M1 reflects radiation from the halogen lamp onto mirror M2. At the same time, it blocks the radiation from the deuterium lamp. For operation in the ultraviolet (UV) range, mirror M1 is raised to permit radiation from the monochromator slewing.

Radiation from the respective source lamp is reflected from mirror ‘M2’ via mirror ‘M3’ through an optical filter on the filter-wheel (FW) assembly to mirror ‘M4’. The filter wheel is driven by a stepping motor to be in synchronization with the monochromators. Depending on the wavelength being produced, an appropriate optical filter is located in the beam path to pre-filter the radiation, before it enters into the monochromator. Filter changes automatically during monochromator slewing.

Fig. 2.6. Photograph of Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer.
Fig. 2.7. Block diagram of Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer.

From mirror ‘M4’, the radiation is reflected through the entrance slit of monochromator ‘I’. All slits are located on the slit assembly (SA). The radiation is collimated at mirror ‘M5’ and reflected towards the grating table ‘G1’. Depending on the current wavelength range, the collimated beam strikes either the UV/Vis grating or the NIR grating. The radiation is dispersed at the grating to produce the spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting this segment to mirror ‘M5’ and then through the exit slit. The exit slit restricts the spectrum segment to a near monochromatic radiation beam. Grating position changes automatically during monochromator slewing.

The exit slit of monochromator ‘I’ serves as the entrance slit of monochromator ‘II’. The radiation is reflected via mirror ‘M6’ to the appropriate grating on grating table ‘G2’ and then back via mirror ‘M6’ through the exit slit to mirror ‘M7’. The rotational position of grating table ‘G2’ is synchronized to that of grating table ‘G1’. The radiation emerging from the exit slit exhibits high spectral
purity with extremely low stray radiation content. In the UV/Vis and NIR ranges a choice is provided between a fixed slit width, a servo slit and a slit program. When the servo slit is selected, the slit widths change automatically during scanning to maintain constant energy at the detector.

**Table 2.1. Technical specifications of Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer.**

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
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<tbody>
<tr>
<td>Principle</td>
<td>Double-beam, double-monochromator, ratio-recording UV/Vis/NIR spectrometer with microcomputer electronics and are controlled by personal computer</td>
</tr>
<tr>
<td>Optical system</td>
<td>All reflecting optical system are SiO₂ coated holographic grating monochromator with 1440 lines/mm UV/Vis blazed at 240 nm and 360 lines/mm NIR blazed at 1100 nm with littrow mounting</td>
</tr>
<tr>
<td>Detectors</td>
<td>UV/Vis - Photomultiplier R6872</td>
</tr>
<tr>
<td>Source</td>
<td>Pre-aligned tungsten halogen and deuterium lamps</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>175-3300 nm</td>
</tr>
<tr>
<td>UV/Vis resolution</td>
<td>≤ 0.05 nm</td>
</tr>
<tr>
<td>NIR resolution</td>
<td>≤ 0.20 nm</td>
</tr>
</tbody>
</table>

From mirror ‘M7’, the radiation beam is reflected via toroid mirror ‘M8’ to the chopper assembly ‘C’. As the chopper rotates, the mirror segment, window segment and two dark segments are brought alternately into the radiation beam. When a window segment enters the beam, radiation passes through to mirror ‘M9’ and is then reflected via mirror ‘M10’ to create the reference beam ‘R’. When a mirror segment enters the beam, the radiation is reflected via mirror ‘M10’ to form the sample beam ‘S’. When a dark segment is in the beam path, no radiation reaches the detector, permitting the detector to create the dark signal.

The radiation passing alternately through the sample and reference beams was reflected by mirrors ‘M11, M12, M13 and M11’, ‘M12’, ‘M13’, respectively. Mirror
‘M14’ is rotated to select the required detector. A photomultiplier tube (PMT) detector is used in the UV/Vis range, while a lead sulfide (PbS) detector is used in the NIR spectral range. Detector change is automatic during monochromator slewing.

At the cell plane, each radiation beam is approximately 12 mm height. The width of the radiation beams is dependent on the slit width. At a slit width of 5 nm, each radiation beam is approximately 4.5 mm wide. To permit minimum sample volumes to be measured in micro cells, the height of the radiation beam must be reduced in the active cell area. A common beam mask (CBM) is mounted between the slit assembly ‘SA’ and mirror ‘M7’. This mask restricts the cross-section of both the sample beam and the reference beam in the respective cell area. The radiation beam can be reduced from the maximum height of 11.7 mm to 0.0 mm in 50 steps. During all scanning operations, the monochromators stop slewing while a filter, source, or detector change is in progress. The spectrophotometer scans from higher to lower wavelengths. There is an optional depolarizing filter (DPF) accessory, which can be swung into the beam.

2.3.4. Excitation, emission and decay measurements

The excitation, emission and decay measurements were recorded on a JOBIN-YVON Fluorolog-3 spectrofluorimeter with a xenon arc lamp (450 W) as an excitation source in the steady state and a xenon pulsed lamp for decay time. The photograph of the spectrofluorimeter (JOBIN-YVON Fluorolog-3) as well as optical layout are shown in Figs. 2.8 & 2.9, respectively.

Fig. 2.8. Photograph of JOBIN-YVON Fluorolog-3 spectrofluorimeter.
2.3.5. NIR emission and decay measurements

The near infrared emission measurements of Nd$^{3+}$ and Er$^{3+}$ ions doped PKAlCaF glasses were recorded on Dongwoo Optron monochromator by using 808 and 980 nm diode lasers as exciting sources. The instrumental specifications are given in Tables 2.2 & 2.3. The photograph of the measuring setup and its schematic layout are shown in Figs. 2.10 & 2.11 respectively.
Fig. 2.10. Schematic layout for recording emission in NIR region

Fig. 2.11. Photograph of measuring setup for recording near infrared emission and decay
Table 2.2. *Certain specifications of monochromator DM511i.*

<table>
<thead>
<tr>
<th>MONOCHROMATOR SPECIFICATIONS</th>
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<tbody>
<tr>
<td><strong>Model No.</strong></td>
</tr>
<tr>
<td>Focal length</td>
</tr>
<tr>
<td>Resolution</td>
</tr>
</tbody>
</table>
| Grating ranges               | G1: 312-871 nm  
                                | G2: 730-1618 nm  
                                | G3: 1092-2428 nm |

Table 2.3. *Specifications of diode lasers*

<table>
<thead>
<tr>
<th>DIODE LASER SPECIFICATIONS</th>
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<tbody>
<tr>
<td><strong>MDL-H-808 nm</strong></td>
</tr>
<tr>
<td>Make:</td>
</tr>
<tr>
<td>Laser Diode model:</td>
</tr>
<tr>
<td>Wavelength:</td>
</tr>
<tr>
<td>Power O/P:</td>
</tr>
<tr>
<td>Transverse mode:</td>
</tr>
<tr>
<td>Operating Mode:</td>
</tr>
<tr>
<td>Beam divergence</td>
</tr>
</tbody>
</table>

| **SDL-980-LM-6000T**        |
| Make:                       | Shanghai Dreams |
| Laser Diode model:          | SDL-980-LM-6000T |
| Wavelength:                 | 980 nm          |
| Average Power:              | 4W, CW          |
| Transverse mode:            | TE00            |
| Operating Mode:             | CW              |
| Beam divergence             | < 2.5mrad       |
REFERENCES