Chapter 4.
Quantitative Analysis of Rare Earth Doped Phosphate glasses

Abstract

Rare earth elements are widely used in modern optoelectronic devices due to their special optical properties. These elements are doped in different host matrices and are characterized using various methods to study their optical emissions. In the present study, elemental compositions of synthesized rare earth doped phosphate glasses are determined using a home built Laser-Induced Breakdown Spectroscopy (LIBS) system. LIBS spectra of these rare earth (samarium (Sm), thulium (Tm) and ytterbium (Yb)) doped glass samples of known composition are recorded. Major atomic emission lines of Sm, Tm and Yb found in LIBS spectra are reported. By considering the atomic emission line of phosphorous (P) as an internal standard, calibration curves were constructed for all the rare earth elements. Analytical predictive capability of LIBS was studied further using leave-one-out method. Better correlation obtained between measured and actual concentration ratio confirms that LIBS technique has great potential for quantitative analysis of rare earth elements in glass matrix.
4.1 Overview

Phosphate glasses are extensively studied in material science with various possible compositions to investigate their applicability in nuclear waste management [1], tissue engineering [2], photonics [3], optoelectronics [4], etc. Phosphate glasses possess special physical properties like low glass transition temperatures, low melting temperature and high thermal expansion coefficient [5,6]. Hence, its usefulness in several areas is growing over the period of time.

Several papers have reported investigation of rare earth elements (REEs) in various matrices using LIBS technique. Quantitative analysis of analyte of interest can be carried out by calibration based [7] and calibration free LIBS approaches [8,9]. Using LIBS technique, Unnikrishnan et al. have used a calibration based method to carry out the quantitative analysis of five different concentration of La and Nd in (La\(_{1-x}\)NdY\(_2\)O\(_2\)S samples [7]. Regression coefficients of 0.98 and 0.99 were reported for Nd and La respectively. Determination of lanthanides is essential in ensuring the quality of nuclear fuel materials and also in many areas of research. In similar lines, Alamelu et al. have used the LIBS technique to determine the REEs such as Sm, Eu, and Gd present at trace levels [10]. The detection of these elements at trace level was carried out with an accuracy of 5%. Abedin et al. also studied the detection of REEs using LIBS in naturally occurring minerals [11]. Authors have presented the qualitative analysis of number of REEs such as Ce, La, Pr, Nd, Y, Sm, Gd, Dy and Yb present in the sand samples. In addition to this, using LIBS, the qualitative analysis of Nd, Er, Eu and Ho is reported in oxyfluoroborate optical glasses [12]. Along with this, they have also characterized the plasma parameters such as electron density and plasma temperature. Furthermore, the authors have demonstrated the potential of LIBS technique to detect heavy elements (Ba, Ca, Eu, Er, Nd, and Ho) as well as light elements (B, O, and F) present in the optical glasses. In addition to the above mentioned applications, REEs are widely used to manufacture the consumer needs such as magnets, phosphors and also in many other related components. In line with this, a recent study has explored the prospects of LIBS technique for the qualitative analysis of Gd, Nd and Sm in such consumer electronics [13].

REE doped phosphate glasses have various important applications in the field of photonics. They are widely used as optical amplifiers, three-dimensional displays, infrared-to-visible up-converters, gain medium in solid-state lasers etc. To name a few, Sm doped glasses can be
used in undersea communications, optical storage devices, fluorescent devices etc. [14,15].
 Further work on trivalent Tm/Yb co-doped phosphate glasses have been carried out for the investigation of up-conversion emission materials [16]. Hence, it’s worth pursuing an extensive study on these trivalent REEs (Sm, Tm and Yb) doped glasses due to its vast applications.

It is of great importance to pay our attention to a very recent work (described above) where the authors clearly indicated the dearth of work on quantitative analysis of REEs [13]. It’s worth noting at this point that the fluorescence efficiency as well as non-radiative relaxation rates of a material is depending on the concentration of REEs [6]. It is evident from the literature that majority of the work done so far in this field was dedicated for the qualitative analysis of REEs. Hence, a quantitative analysis of REEs plays a major role in the characterization of such in house/prepared samples. In view of the above-mentioned circumstances, the current study aims to demonstrate the potential of LIBS technique to perform qualitative as well as quantitative analysis of prepared rare earth doped phosphate glasses. Further, to the best of our knowledge, this is the first report on quantitative analysis of rare earth elements in phosphate glass matrix.

A focused laser beam with spot size of few tens of microns on the surface of the target ensures the ablation and ionization of the sample for spectrochemical analysis. The integration time which is also known as gate width enables the collection of sufficient emission from the laser produced plasma. Further, the optimization of LIBS set-up for the laser wavelength and pulse energy is already discussed in Chapter 2. In line with this, the LIBS spectra were recorded at 0.7 µs gate delay, 5 µs gate width and 17.5 mJ laser energy. Every spectrum is recorded under similar experimental conditions for all glass samples. Each spectrum is contributed by 115 laser pulses and three such LIBS spectra were averaged to quantify the REEs. The present work involves the use of third harmonic Nd:YAG laser (355 nm) for the study of REEs. Several studies have been carried out to investigate the LIBS spectrum with respect to irradiation wavelengths. Kim Taesam and Yoon Yooneyol have performed experiments using fundamental (1064 nm), second harmonic (532 nm) and third harmonic (355 nm) wavelengths on copper target [17]. They observed better signal-to-background (S/B) ratios using 355 nm wavelength. Barnett et al., have used second harmonic and fourth harmonic (266 nm) laser sources and studied glass samples for forensic applications [18]. Their study revealed that the results obtained have better precision using 266 nm irradiation wavelength. Similarly, Cahoon et al., have studied the effect of 266 nm
and 1064 nm on glass samples for the same applications and they have also concluded that signal reproducibility was better using UV irradiation [19]. In all the above three cases the authors have reported the nature of craters formed on the target material. They reported that the material mass ablated using UV irradiation was more and the craters formed on sample surface were uniform. However, the craters formed using 1064 nm wavelength were not deep compared to 355 nm or 266 nm wavelengths. Insufficient mass ablation and non-uniform craters formed on a sample surface using 1064 nm laser radiation may not provide reasonable precision of LIBS measurements.

4.2 Sample Compositions

The procedure for the sample preparation is already given the section 2.2.3 of Chapter 2. The amount of individual element in the glass is given the following table.

Table 4.1: The composition of the rare earth elements in phosphate glass

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of elements in 1g of the sample</th>
<th>Concentration ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sm</td>
<td>P</td>
</tr>
<tr>
<td>1</td>
<td>0.029</td>
<td>0.294</td>
</tr>
<tr>
<td>2</td>
<td>0.056</td>
<td>0.285</td>
</tr>
<tr>
<td>3</td>
<td>0.133</td>
<td>0.260</td>
</tr>
<tr>
<td>4</td>
<td>0.241</td>
<td>0.223</td>
</tr>
</tbody>
</table>

4.3 Identification of Rare Earth Elements

The LIBS spectra recorded using echelle spectrograph coupled with ICCD camera normally covers a very broad spectral range of 250 nm to 850 nm enabling one to carry out efficient qualitative and quantitative analysis of given sample. The LIBS spectra recorded from Sm, Tm, and Yb doped phosphate glasses are compared with the National Institute of Standards and Technology (NIST) database for identification of atomic and ionic lines (Figure 4.1).

The LIBS spectra from analyte of our interest consist of large number of atomic and ionic lines. Hence, we have thoroughly investigated the spectrum of rare earths samples prior to the construction of the calibration curves for quantification of REEs. In principle, the strength/intensity of the characteristic emission lines of the specific element must be linearly proportional to the concentration of the element present in the sample. However, this assumption is not observed experimentally across all the range of concentrations for an analyte of interest and linearity of calibration curve is limited to certain levels, beyond which the emission lines get saturated. Pease Patrick has studied Al, C, Sr, Ti, and other elements in
fused glass samples for geological applications [20]. The concentrations of elements in fused glass samples exceed over 40% in their work and calibration curves obtained were found to be linear. The samples used in the present case have REEs with concentration from 1 to 10 mol.% and calibration curves were found to be linear. Usually, the characteristic emission lines may overlap with emission lines of other elements. This problem can be tackled by choosing an interference free spectral line of the element of interest. Therefore selecting suitable spectral lines of an element for quantitative analysis is indispensable during LIBS analysis.

**Figure 4.1:** The selected regions of LIBS spectra for (a) Sm (400 nm-500 nm), (b) Tm (350 nm-450 nm) and (c) Yb (350 nm to 400 nm and 650 nm 700 nm) of doped phosphate glasses containing both atomic and ionic lines of the doped rare earth elements.

### 4.4 Selection of Internal Standard

As discussed above, the variation in the spectral line intensity depends on ambient conditions, laser pulse energy, light coupling efficiency and ablated mass. There are certain ways through which the results from the LIBS can be improved, even though the physical properties of the
sample such as roughness, state of the matter (solid, liquid and gas) and inhomogeneity of elements affect the analytical performance. Hence selection of emission line of interest alone may not resolve the issue concerned with nonlinear behavior of spectral lines in complex samples [21]. To tackle this issue, many groups had proposed the use of an internal standard to improve measurement accuracy in such studies [22,23]. The internal standard normally will be a major atomic emission line in the observed spectrum and it should be unaffected by the presence of other spectral lines. Therefore, phosphorous (P) is the matrix element whose concentration is almost same across all the prepared/reference samples, is considered as an internal standard in the study. The availability of consistent emission lines of P in the region of 250 nm to 850 nm is scarce. As seen from the NIST database, P has large number of persistent atomic lines in UV region (165 nm to 255 nm) and near IR region (952 nm to 980 nm). Hence, one of the emission lines of P observed at 255.32 nm in our spectra is chosen as the internal standard for quantitative analysis of phosphate glasses. This spectral line selection is justified since 255.32 nm emission line of P was almost unaffected by other spectral lines. There are other strong atomic emissions to consider them as internal standard, like oxygen observed at 777.19 nm, 777.41 and 777.53 nm (triplet lines). The spectral line of H is at 656.28 nm and Na doublets lines are present at 588.99 nm and 589.56 nm respectively. However, these emission lines were circumvented to consider them as an internal standard mainly due to their poor reproducibility.

4.5 Quantitative Analysis of Rare Earth Elements

As mentioned earlier, in the present work, the feasibility of LIBS technique for quantitative analysis is demonstrated using calibration based approach. Calibration curves were plotted for different concentrations of Sm, Tm and Yb observed at 471.61 nm, 371.79 nm, and 679.96 nm respectively (Figure 4.2).

Here X and Y-axis represents concentration and intensity ratios of REE to an internal standard. Natural logarithms were used to represent X and Y scale and the use of the same has also been found in the followings works [7,24]. However, these counts can be also used directly without natural logarithms to obtain the calibration curves. Though there are reports [25] suggesting that the analytical performance of LIBS for glasses is relatively poor compared to other materials and the accuracy for such studies ranges from 5-20%. The correlation uncertainty (accuracy) obtained in this work between the measured and known concentration of REEs using LIBS technique was found to be promising. Correlation
coefficients (R²) values close to unity were obtained for spectral lines of Sm, Tm, and Yb. This result clearly indicates the analytical predictive capabilities of LIBS technique for quantitative analysis of rare earth elements.

Figure 4.2: Calibration plots constructed for Sm, Tm and Yb using characteristic emission line intensities

Quality of the calibration curves and analytical prediction skills of LIBS were further investigated by the method of cross validation (leave-one-out method) [26] for each reference (synthesized) samples. For this, calibration curves were again constructed using three reference elemental concentrations of the said samples and by leaving one concentration (regarding this as unknown) out of the model. Unknown concentration of the element in the sample was determined using LIBS emission intensity of the respective characteristic line of that element. To make this procedure clear, Sm has been taken as an example.

As mentioned already we have four different concentration of Sm (1%, 2%, 5% and 10%). Calibration plot was constructed using the measured LIBS intensity ratios of Sm/P for 2%, 5% and 10% concentrations leaving 1% concentration out. Then, the concentration of 1% sample (x, which is unknown in this case) can be predicted by knowing the LIBS intensity ratio of Sm/P for this sample (y), intercept (c) and slope (m) using, \( y = mx + c \). Similarly, calibrations curves of Sm were obtained for 1%, 5% and 10% leaving 2% (unknown), 1%, 2%, 10% leaving 5% (unknown) and 1%, 2%, 5% leaving 10% (unknown) respectively as shown in Figure 4.3. Similarly, the intensity ratios versus concentration ratio were also calculated for Tm and Yb which are shown in Figure 4.4 and 4.5.
Figure 4.3: Calibration curves of Sm using leave-one-out method for analytical prediction

Figure 4.4: Calibration curves of Tm using leave-one-out method for analytical prediction
Figure 4.5: LIBS calibration curves of Yb using leave-one-out method for analytical prediction

The LIBS measured concentration of the sample is assessed by comparing it with known concentration (synthesized). Accordingly, closer values of prediction indicate the success of the quantification technique. Correlation uncertainty (accuracy) can be calculated using the following formula.

\[
\text{Correlation uncertainty (\%)} = \frac{|C_k - C_m|}{C_k} \times 100
\]

where \(C_k\) is known concentration of the sample and \(C_m\) is measured concentration of the same.

Table 4.2: Comparison of known and LIBS determined concentration ratios

<table>
<thead>
<tr>
<th>Intensity Ratios</th>
<th>Composition</th>
<th>1%</th>
<th>2%</th>
<th>5%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm/P (471.61 nm/255.32nm)</td>
<td>Known concentration</td>
<td>0.098</td>
<td>0.198</td>
<td>0.511</td>
<td>1.079</td>
</tr>
<tr>
<td></td>
<td>Predicted (LIBS) concentration</td>
<td>0.112</td>
<td>0.173</td>
<td>0.472</td>
<td>1.020</td>
</tr>
<tr>
<td></td>
<td>Correlation Uncertainty (%)</td>
<td>13.8</td>
<td>12.8</td>
<td>7.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Tm/P (371.79 nm/255.32nm)</td>
<td>Known concentration</td>
<td>0.110</td>
<td>0.223</td>
<td>0.574</td>
<td>1.212</td>
</tr>
<tr>
<td></td>
<td>Predicted (LIBS) concentration</td>
<td>0.126</td>
<td>0.203</td>
<td>0.561</td>
<td>1.333</td>
</tr>
<tr>
<td></td>
<td>Correlation Uncertainty (%)</td>
<td>14.8</td>
<td>8.5</td>
<td>2.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Yb/P (679.96 nm/255.32nm)</td>
<td>Known concentration</td>
<td>0.113</td>
<td>0.228</td>
<td>0.588</td>
<td>1.242</td>
</tr>
<tr>
<td></td>
<td>Predicted (LIBS) concentration</td>
<td>0.095</td>
<td>0.254</td>
<td>0.584</td>
<td>1.169</td>
</tr>
<tr>
<td></td>
<td>Correlation Uncertainty (%)</td>
<td>15.6</td>
<td>11.5</td>
<td>0.6</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Generally, it is expressed in percentages (%). Better analytical predictive models represent small values of correlation uncertainty. The same procedures are repeated for Tm and Yb samples to predict the unknown concentrations and its correlation uncertainty are tabulated in Table 4.2.

Figure 4.6 shows the correlation between measured and known (synthesized) concentration ratios of Sm, Tm and Yb with respect to the internal standard P. Excellent correlation (high $R^2$ values) inferred suggests the robustness of the LIBS technique for accurate and meaningful analytical prediction of complex samples like glasses. The limit of detection (LOD) helps in the evaluation of performance of the system used and it provides information about the minimum amount of analyte that can be detected. LOD calculated in the work is defined as the ratio of three times the standard deviation of the blank measurements to the slope of the calibration curve.

\[
\text{LOD} = \frac{3\sigma}{s}
\]

Where $\sigma$ represents standard deviation of background and $s$ is slope of the calibration curve. LODs found in our experiments are presented in Table 4.2.
### Table 4.3: Limit of detections for the three REEs

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>0.20</td>
</tr>
<tr>
<td>Tm</td>
<td>0.38</td>
</tr>
<tr>
<td>Yb</td>
<td>0.24</td>
</tr>
</tbody>
</table>

#### 4.6 Conclusion

REE oxide doped phosphate glasses were synthesized at four different concentrations. The quantitative analysis of REEs have been successfully performed using LIBS. The analytical performance of the LIBS technique has been assessed through the correlation coefficient of the linear fit ($R^2$) and found to be near unity (0.99). Results of the leave-one-out method adopted in this study are found to be promising for checking the analytical prediction of LIBS technique for complex samples like glass. Lower values of correlation uncertainty reported for Sm, Tm and Yb demonstrates the robustness of LIBS technique for the qualitative as well as the quantitative analysis of rare earth elements in glass matrices.
4.6 References


[15] G. Tripathi, V. K. Rai, and S. B. Rai, Optical properties of Sm\textsuperscript{3+}: CaO-Li\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}-BaO glass and codoped Sm\textsuperscript{3+}: Eu\textsuperscript{3+}, Applied Physics B \textbf{84}, 459 (2006).


