YbPO$_4$ Crystals Containing Tellurite Glasses

Muhammed Abul Hasnat

Master Thesis
April 2020
Department of Physics and Mathematics
University of Eastern Finland
Abstract

Yb$^{3+}$ doped glasses have the uses in many appliances like: solid-state lasers and laser amplifiers. Glasses with Yb$^{3+}$ doped crystals became more attractive because of their high absorption and emission cross sections, large gain bandwidth, and long lifetime. Inspired from that, the purpose of this thesis was to prepare and characterize tellurite glasses which contain YbPO$_4$ crystals. In this study, the crystals were added in the glass melt and also in the glass batch in order to prepare a glass with a large amount of YbPO$_4$ particles. The direct doping of particles method was used to add the particles in the glass melt. The process was optimized to balance the survival and dispersion of the particles using persistent luminescent (PeL) SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ particles (MPs). The doping temperature $T_{\text{doping}}$ was found at 575 $^\circ$C. The survival of the YbPO$_4$ particles in the glasses was confirmed using XRD and the emission spectra measured using excitation 900 nm and 960 nm. However, all the investigated glasses have some apparent crystallization after adding the YbPO$_4$ particles in the tellurite glass. The crystallization of the glass was related to the poor stability of the glass as evidenced using differential thermal analysis (DTA). The YbPO$_4$ particles are suspected to act as a nucleation agent.

Keywords: tellurite glasses; persistent luminescence; SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ microparticles; YbPO$_4$; direct doping method; crystals; glass; laser.
Acknowledgement

To my parents, family, wife and specially to my beloved daughter Rupkotha, thanks for the endless support and patience.

To Laetitia, Matthieu, Alexander, Mika and my research group, thanks for guided me whenever I needed.

Without the help and support of these people, I wouldn’t able to make this journey.

Tampere, the 11th of April 2020

Muhammed Abul Hasnat
1 Introduction

2 Theoretical background
  2.1 Glass ................................................................. 3
     2.1.1 Definition of glass ............................................. 4
     2.1.2 Glass formation ................................................. 4
  2.2 Tellurite laser glass .................................................. 6
     2.2.1 Glass formation ................................................. 6
     2.2.2 Laser glass ..................................................... 9
     2.2.3 Crystal containing glass ...................................... 10
  2.3 Application of Yb$^{3+}$-containing glasses .............................. 12

3 Experimental procedures
  3.1 Glass preparation ..................................................... 14
     3.1.1 Batch calculation ................................................ 14
     3.1.2 Persistent luminescent particles and YbPO$_4$ crystals ....... 15
     3.1.3 Glass melting .................................................... 15
  3.2 Spectroscopic properties ............................................. 16
     3.2.1 Spectroscopic properties of PeL glasses ..................... 16
     3.2.2 Spectroscopic properties of Yb$^{3+}$ doped glass based materials 17
  3.3 SEM coupled with EDS .................................................. 18
  3.4 XRD ................................................................. 20
3.5 Thermal properties ................................................. 21

4 Result and discussion ........................................... 24
  4.1 Optimization of the direct doping ............................... 24
  4.2 YbPO$_4$ containing glasses ..................................... 33
    4.2.1 YbPO$_4$ particles in tellurite glass melt ................. 33
    4.2.2 YbPO$_4$ particles in tellurite glass batch ................. 37

5 Conclusions ......................................................... 41

References ............................................................ 43
Tellurite glasses offer good features in terms of optical, mechanical, and processing properties, which makes it interesting for applications in the field of photonics. Tellurium dioxide (TeO₂) glass has a good thermal mechanical resistance, a high refractive index, a low phonon energy, a high stability against crystallization, and a high solubility of RE ions compared to other glasses [1]. In the 70s and 80s, lots of researches were focused on tellurite glasses. RE doped tellurite glasses showed some remarkable physical and optical properties in number of researches [1, 2]. These glasses can be used, for instance, in solid state laser. Such glasses can used in light emitting diodes, optical fiber, laser amplifiers and many other applications in telecommunication, science and medical field.

Development of glass-based materials with improved spectroscopic properties can be attained by controlling the site of RE ions. As rare earth doped crystals were found to exhibit enhanced spectroscopic properties compared to glasses [3], crystals containing glasses have been of great interest. Crystals can be added in the glass melt but as explained in [4], the crystals can dissolve in the glass during the melting. In order to increase the number of crystals in the glass, the crystals can be added in the glass melt using the direct doping process as reported in [5]. The goal of this work was to process glasses containing YbPO₄ crystals by adding the crystals of RE element in the glass melt and in the glass batch.

This thesis includes a chapter on background on laser glasses and crystals containing glasses. The state of research on various applications of Yb³⁺-doped tellurite glasses is also summarized. Chapter 3 describes in details the preparation of the YbPO₄ and YbPO₄-containing tellurite glasses. In addition, equipment and their
working principles, used to study the YbPO$_4$-containing tellurite are also summarized. X-ray powder diffraction (XRD), micro-Raman experiment, scanning electron microscope (SEM), emission spectra measurement, differential thermal analysis were used to characterize the spectroscopic properties and to verify the survival of the particles of YbPO$_4$-containing glasses. The results of these measurements are presented in Chapter 4 along with discussion based on the analysis of the results. The final chapter presents the conclusions and suggestions for future studies.
Chapter II

Theoretical background

The background chapter focuses on the some basics about glass, specially lasing tellurite glass, and direct doping method, the technique used in this study for the preparation of particles containing glasses. This chapters ends with a summary on the various applications of Yb$^{3+}$-doped materials.

2.1 Glass

The first glass making was invented in Egypt at 7,000 BCE. Some sources say that glass making was first found in Mesopotamia back in 3,600 BCE, even though some claim that it might be the one of copies of glass from Egypt. Some archaeological proof also shows that, at 2,000 BCE, first real glass was made in Syria. Most of the archaeological evidences suggest that first glass was made at least 4,000 years ago. Until the late Bronze Age glass goods were a kind of luxury. [6]

Glass was known as “mysterious” materials until the last century due to some difficulties of managing its properties. From that point of view, glass was studied and analyzed to discover its properties and its relationship with its composition with the intention to unveil the mystery. It is well known that a tiny variation in the synthesis process can cause enormous changes in final feature of the glass. P. W. Anderson once said “the deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition” [7]. Glass has many applications nowadays including in the field of optics, fiber optic communication, electronics, lasers, and many bio-medical applications [7,8].
2.1.1 Definition of glass

By the definition of Shelby, J.E [9] “glass is an amorphous solid completely lacking long range, periodic atomic structure, and exhibiting a region of glass transformation behavior” [9]. Optical glass can be defined as optically homogeneous glass, without faults like bubbles or unmelted grains [10].

One can say that glass is produced when the fluid is cooled sufficiently quickly and does not offer time for crystalline structure to precipitate. Glass has a vast variety of properties depending upon the composition, but commonly glasses are solid, light transparent, comparatively resistant to high temperature and recyclable. [11]

2.1.2 Glass formation

The glass formation from any liquid can be described by the changes in the volume or enthalpy as a function of temperature as presented in Fig. 2.1 [9].

![Figure 2.1: Volume or enthalpy versus temperature curve. [9]](image)

The materials having the glass transition proprieties could be considered as glass materials. Any liquid might have capitalization or form supercooled liquid without crystallization, when the temperature is reduced after melting. Meanwhile, when a liquid is cooled down very slowly underneath the melting temperature, it turns to crystal if the kinetics promote the nucleation of the crystalline phase, thus volume or enthalpy starts to fall rapidly at this point [9]. The rate of nucleation and growth
of crystals depends on both the viscosity of the supercooled liquid along with the free energy difference of glass and crystal [12]. However, if the liquid is cooled down while preventing crystal nucleation, it converts to supercooled liquid. When the temperature decreases further, the glass structure starts to rearrange without any abrupt changes in volume or enthalpy due to irregular structural rearrangement of the molecules.

Fundamentally, the glass network consists of three components: network modifiers, network forming ions, and intermediate oxides as shown in Fig. 2.2 [13].

![Network modifier, Network forming ion, Bridging oxygen, Non-bridging oxygen](image)

**Figure 2.2:** Structure of tellurite glass with main components of the network. [13]

Network former ions contain components such as tellurium dioxide (TeO$_2$) in tellurite glasses. In these cases, the glass network is formed by Te making ionic bonds with oxygen bridging. Network modifiers are responsible for rearranging the structure, ionic bonds of oxygen bridging can turn into non-bridging modifiers in the glass structure. Intermediate oxides may act as network former ions or network modifiers by entering the network and maintaining backbone structure. However, they can form a network on their own. [13]

Crystals have distinct internal structures, resulting in a unique pattern in X-ray diffractogram that could be utilized to distinguish the particular material as shown in Fig. 2.3 (a), taken SiO$_2$ as an example.

As shown in Fig. 2.3 (b), glasses have an interconnected structure within the blocks, hence no long-range order. Glass in respect of both number of coordinators
Figure 2.3: Atomic structure: (a) crystalline structure of SiO$_2$ (b) amorphous structure SiO$_2$ and (c) structure with a network modifier. [12]

and the inter-atomic distances are unequal. Normally, most of the oxides are able to form amorphous solid. In addition strong bonds are formed randomly arranged through components called network formers. However as shown in Fig. 2.3 (c) most of the bonds can be changed by different elements, known as network modifiers that change the glass properties by occupying thermodynamically stable structural sites.

2.2 Tellurite laser glass

The study was focused on Yb$^{3+}$ doped tellurite glass-based materials, which has good potential uses in laser glasses.

2.2.1 Glass formation

Tellurium dioxide glass has good thermal mechanical resistance, high refractive index ($n = 2.6$ at 480 nm), low phonon energy (at around 700 cm$^{-1}$), high stability against crystallization and high solubility of RE ions compared to other glasses. These advantages make TeO$_2$ a prosperous glass in the field of optics, fiber optic communication, electronics, lasers, art, various glassware, lighting and many prospering appliance in medical technology. [1]

As shown in Fig. 2.4, tellurite glass is formed by tellurite units linked by oxygen
Stanworth et al. showed that tellurium has an electronegativity value of 2.1 at Pauling scale, indicating that tellurium oxides or tellurite can form glasses back in 1952 [15]. In another experiment 1956, Brady demonstrated that tellurium oxides could form glass when adding Li₂O by studying the structure and the distribution of electrons using X-ray analysis [16]. In 1977 at Seventh International Conference on Amorphous and Liquid Semiconductors in Edinburgh, Flynn et al. declared that, TeO₂ − V₂O₅ glass can act as a semiconductor. Depending on its composition, the glass can have a good DC conductivity with constant activation energy of 0.25 eV to 0.34 eV, which is much better than phosphate glasses [17]. Mochida et al. in 1978, inspected the formation of metal oxides containing tellurite glass in the glass system MO₁/₂ − TeO₂ (where M is Na, Li, K, Ti and Ag) and MO − TeO₂ (where M is Ba, Be, Cd, Mg, and Zn). Table 2.1 provides details such as the higher limit and lower limit of secondary materials of tellurite glasses [1, 18].

In 1980s the famous Japanese electronics company, Matsushita Electric Industrial Co. now known as Panasonic Corporation, started a successful project on tellurite glasses to be used as optical disk system to store data. They also attained the restoring capability with mixing of indium and germanium in tellurite glass system. This data erasable optical disk offered the possibility to rewrite the data many times. It was accepted as a great milestone in information technology as it had the option to huge amount of storage size compared to a regular floppy disk. On the
Table 2.1: Table of upper and lower limit of secondary materials of tellurite glass. [1]

<table>
<thead>
<tr>
<th>Second material</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol%</td>
<td>mol%</td>
</tr>
<tr>
<td>LiO$_{1/2}$</td>
<td>20.0</td>
<td>46.3</td>
</tr>
<tr>
<td>NaO$_{1/2}$</td>
<td>10.0</td>
<td>46.3</td>
</tr>
<tr>
<td>KO$_{1/2}$</td>
<td>2.5</td>
<td>34.6</td>
</tr>
<tr>
<td>AgO$_{1/2}$</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>TiO$_{1/2}$</td>
<td>5.0</td>
<td>59.6</td>
</tr>
<tr>
<td>BO</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>MgO</td>
<td>10.1</td>
<td>40.4</td>
</tr>
<tr>
<td>BaO</td>
<td>2.5</td>
<td>35.8</td>
</tr>
<tr>
<td>CdO</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>9.2</td>
<td>40.0</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>8.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Dy$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Gd$_2$O$_3$, Ho$_2$O$_3$, La$_2$O$_3$, Lu$_2$O$_3$, Sc$_2$O$_3$, Yb$_2$O$_3$</td>
<td>8.0</td>
<td>26.0</td>
</tr>
</tbody>
</table>

consequences, the Japanese material scientist Y. Mizuno discovered that, tellurite glass system with 85% of TeO$_2$ with the combination of 5% of ZnO and 10% of CdO could be useful to build a material for recording device with bigger memory. [1,19]

In 1985, H. Burger et al. showed that tellurite glass can be a good transmitter in the range of visible spectral region and infrared region. Earlier on 20$^{th}$ century, number of companies started to make tellurite based fiber optics. Tellurite glass provides better reliability than other glass fiber, it has the ability pump the light at 980 nm to 1480 nm. Additionally, this glass has good bend strength and good photoluminescence spectra compared to other fibers like silica or fluoride. [20]

Marinov et al. in 1988 was able to process rare earth oxides containing tellurium dioxide (TeO$_2$) with the composition 85TeO$_2$ - 5R-O and 95TeO$_2$ – 15R-O (in mol%) used for making thin film (where, R-O is a rare-earth oxides.). Marinov et al. found that heat treatment changes the absorption coefficient ($\alpha$) and the refractive index
(n) of the film. They testified sub-oxide thin film can be excited by a laser excitation at $\lambda_{exc} = 830 \text{ nm}$. Their study shows that, rare earth oxides containing tellurite films are can be used as a media optical information system. [21]

In this study, the glass with the composition of 70TeO$_2$ - 20ZnO - 10Bi$_2$O$_3$ (in mol%) was investigated. A complete crystallization study of glasses in this glass system can be found in [22]. The 70TeO$_2$ - 20ZnO - 10Bi$_2$O$_3$ glass was reported to be thermally stable and fiber could be drawn from this glass [23]. In addition tellurite glasses are able of integrating large amounts of RE ions into the glass as reported in [24].

### 2.2.2 Laser glass

Photonic glasses are used for waveguide glasses with gradient-refractive index, photosensitive/photochromic glasses, nonlinear glasses, magneto-optical glasses, and especially laser glasses. Laser glasses contain rare earth ions. Rare earth materials are a metal assembly typically found in the lanthanide series, as shown in Fig. 2.5.

![Figure 2.5: Periodic table highlighted with RE materials.][25]

These rare earth (RE) ions are interesting as their electron structure provides various functional fluorescent states allowing wide scope of engagements in science for medical and communication purposes. Rare earth materials such as erbium, ytterbium, holmium, thulium are used to make solid state lasers. [12]

If an external pump light excites an RE-ion, the electrons are transferred to an excited state from the base. Therefore, these rare earth doped laser glasses emit high power at around 1 $\mu$m in the case of ytterbium, at around 1.5 $\mu$m for erbium and at around 2 $\mu$m for holmium. Erbium and ytterbium ions are popular doping materials for this fiber laser and also for fiber amplifiers. [26]
Yb\(^{3+}\) ion is one of the prominent RE ions used in laser and laser amplifiers. As shown in Fig. 2.6, 980 nm laser is typically used as a light source to excite electrons from \(^2\!F_{7/2}\)-energy level to \(^2\!F_{5/2}\)-energy level leading to emission at around 1 \(\mu m\).

![Energy levels diagram](image)

**Figure 2.6:** Schematic of Yb\(^{3+}\) energy levels. [27]

The absorption and emission cross-section of Yb\(^{3+}\) can be determined form the \(^2\!F_{5/2} - ^2\!F_{7/2}\) transition.

### 2.2.3 Crystal containing glass

It is accepted that the spectroscopic properties are determined by the ion’s crystal field, which is determined by the surrounding atoms and bonds. Therefore, one can expect to be able to improve the spectroscopic properties of RE doped glasses by controlling the site of the RE. In crystalline structures, the local environment for rare earth ions are well established, allowing only certain transitions to exist in rare earth ions. Therefore, glass-ceramics has been of great affection to the researchers as compared to glasses, they can exhibit improved spectroscopic properties if the RE-ions are sited in the crystals with a specific composition. [28]

The first glass-ceramic was invented in the 1960s [29]. According to Deubener et al. [30], “Glass ceramics are inorganic and non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction of crystallized material may vary from 1% to almost 100%.”

There are two main criteria to fulfill for the glass ceramics to be promising materials for photonics: 1) glass ceramic needs to be transparent at the targeted wavelength and 2) crystals should precipitate in the volume of the glass and should contain the rare-earth ions [31].
Glass ceramics can be made in a two-step of heat treatment: nucleation phase and growth phase, which is demonstrated in Fig. 2.7 [31].

![Diagram of crystal nucleation and growth.](image)

**Figure 2.7**: Diagram of crystal nucleation and growth. [31]

Nucleation is a process during which a crystal starts to crystallize. Nucleation rate and growth of the crystals depends on temperature and time. Nucleation also have some kind of dependency on nucleating agent applied to the glass. Differential thermal analysis (DTA) can find the glass transition and crystallization temperatures by which it is possible to define heat treatment process. If the nuclei radius is greater than the critical radius of nuclei, crystal growth can be initiated immediately after the nucleation. The crystals can develop only from nuclei in the metastable zone of supercooling. However when the glass is cooled down from high temperature and being heat treated at metastable zone of supercooling no nuclei and no crystal can developed. [32]

For the nucleation phase, the glass is maintained at a high temperature for overcoming Gibbs free energy $\Delta G$, and to form nuclei. Meanwhile, to overcome the $\Delta G$ is quite important in order to maintain a perfect size of nucleus. This step is followed by the growth phase. The temperature is increased to grow the nuclei into crystals. [31]

As not all glasses can be processed into transparent glass ceramics with RE doped crystals in the volume of the glass using a heat treatment [9], crystals containing glasses perhaps prepared by adding RE doped in the glass. These RE doped crystals can be added in the glass batch earlier to the melting. However, as explained in [33],
the crystals can dissolve during the melting of the glass. To limit the dissolution of the crystals, the crystals can be added in the glass melt as illustrated in Fig. 2.8 [33]. This technique is known as the direct method. In this method, the crystals are added in the glass batch after melting. The temperature at which the crystals are doped (doping temperature) and the dwell time before quenching the glass should be optimized to balance the survival and dispersion of the crystals in the glass, as explained in [5]. One should point out that 30% to 60% of crystals can dissolve in the glass [34]. As explained in [35], the survival of the crystals depends not only on the melting conditions but also on the composition of the glass and crystals.

![Diagram of crystal containing glass using the direct doping method](image)

**Figure 2.8:** Process of crystal containing glass using the direct doping method. [33]

It is therefore, vital to optimize the direct doping process when preparing new glass-es. Persistent luminescent (PeL) microparticles (MPs) such as SrAl₂O₄ : Eu²⁺, Dy³⁺ MPs have been used for the optimization of the process [34]. These MPs exhibit green PeL after UV charging. However, an increase in the doping temperature and in the dwell time results to a decay in the PeL, which can be related to the dissolution of the MPs in the glass occurring through a glass preparation process. Phosphate and silicate glasses were successfully prepared with PeL after optimization of the process [34].

### 2.3 Application of Yb³⁺-containing glasses

In the past few decades, many Yb³⁺ doped glasses showed some attractive features over optical and mechanical properties. In gain media, Yb³⁺ doped glasses usually
allow high-power operation, broad emission spectrum, high emission cross sections, high thermal conductivity and large gain bandwidth [36]. Rare earth ions can act as activator ions in various glass composition. As an activator ions Yb$^{3+}$ ion is known for its brilliant properties like: absorption band from 850 nm to 1080 nm, emission band from 900 nm to 1200 nm, long fluorescent lifetime from 0.4 to 1 ms [37, 38]. Therefore, Yb$^{3+}$ crystal containing glasses are used for many optical applications, e.g., amplifiers in optical fiber communication, ultrafast optics, and solid state laser.

Tellurite glass can be doped with number of RE ions, which was found useful in optical laser and amplifier. As an example, Yb$^{3+}$ doped tungsten-tellurite glass showed promises as a gain medium for lasers and amplifiers [24]. The optical quality and solubility of Yb$^{3+}$ containing tellurite glasses are relatively high, which make it more attractive for laser applications. The spectroscopic and lasing properties mainly depends on energy level configuration, meanwhile Yb$^{3+}$ containing tellurite are glasses with high energy level configuration meaning they have good spectroscopic and lasing properties. Furthermore, Yb$^{3+}$ doped tellurite glasses can find in many applications like: light emitting diodes, solid-state lasers and laser amplifiers. [38]
This chapter mainly describes the techniques used to prepare and characterize the tellurite glasses.

3.1 Glass preparation

In this project, YbPO$_4$ containing glasses with the composition 70TeO$_2$ - 20ZnO - 10Bi$_2$O$_3$ (in mol%) were prepared using melting process. The YbPO$_4$ crystals were added: 1) in the glass melt (technique known as direct doping method) and 2) in the glass batch earlier to the melting.

3.1.1 Batch calculation

The average molar mass of the glasses has been calculated using the general Eq. 3.1,

$$M_{\text{glass}} = \sum x_i M_i,$$

where, $M_{\text{glass}}$ is the average molar mass of the glass, $x_i$ the fraction of the component and $M_i$ the molar mass of the component.

The number of moles of the glass ($n_{\text{glass}}$) is calculated using the Eq. 3.2,

$$n_{\text{glass}} = \frac{m_{\text{glass}}}{M_{\text{glass}}},$$

where, $m_{\text{glass}}$ is the target mass of the glass.

Hence, the number of moles of each compound ($n_i$) is defined by Eq. 3.3 and the mass of each compound ($m_i$) by Eq. 3.4,

$$n_i = x_i n_{\text{glass}},$$

$$m_i = n_i M_i.$$
3.1.2 Persistent luminescent particles and YbPO₄ crystals

Persistent luminescent (PeL) particles were used for the optimization of the direct doping process of the glasses as in [33]. The particles were SrAl₂O₄ : Eu²⁺, Dy³⁺ MPs from Jinan G.L. New Materials, China, YG – 101.

The other particles were YbPO₄ crystals which were obtained from aqueous solution according to the following reaction:

\[
2\text{YbCl}_3 + 3(\text{NH}_4 )2\text{PO}_4 + m\text{H}_2\text{O} \rightarrow 4 \times \text{NH}_2\text{O}(\text{ppt}) \rightarrow 6\text{NH}_4\text{Cl} + \text{H}_3\text{PO}_4
\]

Yb(III)Cl₃ × 6H₂O (99.9 %, Aldrich) and (NH₄)₂HPO₄ (>99 %, Aldrich) were used for the synthesis.

The as-prepared YbPO₄ × NH₂O powder was calcinated at 1200 °C for 2 h. During this step the YbPO₄ × NH₂O transforms to water-free YbPO₄ crystalline phase (xenotime) and the size of individual crystals increases. The average size of the crystallites after the calcination is about 200 nm.

3.1.3 Glass melting

The particle-containing glasses were prepared using the direct doping method and by adding the particles in the glass batch with composition 70TeO₂ - 20ZnO - 10Bi₂O₃ (in mol%). TeO₂ (Sigma Aldrich, 99 %), Bi₂O₃ (Sigma Aldrich, 99.99 %), ZnO (Sigma-Aldrich, ≥ 99.5 %) were the starting raw materials.

The series of particle containing glasses were prepared using the direct doping process. The 6 g batches were melted for 5 min at 850 °C in normal atmosphere. Then, the temperature was reduced prior to adding the YbPO₄ particles. This temperature is called the doping temperature, T_doping. After 20 min at this doping temperature (T_doping), the particles were added into the glass melt. The glasses were pitched onto a brass mold 3 min after adding the crystals and finally annealed for 4 h at 40 °C beneath the glass transition temperature to eliminate any residual stresses from the quench.

\[ m_i = n_i M_i. \] (3.4)
For the optimization of the process, PeL particles were used. As explained in [35], it is possible to track the degradation of the particles during the preparation of the glass due to the corrosive behavior of the glass melt from the losses in the spectroscopic properties of the glasses. Therefore, 0.5 wt% of the particles with PeL were added at different $T_{doping}$ in the glass melts in order to find out the relation between the PeL loss and the doping parameters. The doping temperature was varied between 550 °C and 650 °C. The dwell time was fixed at 3 min.

The glass with the composition (68.8TeO$_2$ - 19.68ZnO - 9.84Bi$_2$O$_3$ - 1.58Yb$_2$O$_3$(in mol%)) was also prepared to be used as a reference. The amount of Yb$_2$O$_3$ corresponds to the amount of Yb$_2$O$_3$ in the YbPO$_4$ crystals containing glass, prepared with 5 wt% of YbPO$_4$. Yb$_2$O$_3$ (Sigma Aldrich, 99.99 %) was used as the Yb$^{3+}$ precursor. The glass was melted at 850 °C for 5 min. After quenching, the glass was then annealed for 4 h at 40 °C under the glass transition temperature of the glass.

### 3.2 Spectroscopic properties

The spectroscopic properties were measured for both the persistent luminescence and YbPO$_4$ particles doped glasses.

#### 3.2.1 Spectroscopic properties of PeL glasses

The PeL mechanism of SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ is outlined in Fig. 3.1 [39].

![Figure 3.1: Current model of PeL mechanism.][39]
The excited energy in PeL materials is discharged from traps with thermal energy. UV irradiation results in Eu$^{2+}$ photo-excitation to one of its excited state 4f$^6$5d$^1$ from the 4f$^7$ ground layer. Excited state overlays with the SrAl$\text{2}$O$_4$ conduction band, which permits easy discharge of some electrons directly from a 4f$^6$5d$^1$ level or helped by thermal energy ($kT$) to the SrAl$\text{2}$O$_4$ conduction band. The electrons can move easily in the conduction band until returning to the center of europium. They are stuck near to the ground of the conduction band. When the charging source is switched off, the discharging process starts and the stuck electrons discharge back to the conduction band. This is accompanied by non-radiative transition (within the 4f$^6$5d$^1$ states) and, finally, the Eu$^{2+}$ radiative relaxation (from the lowest 4f$^6$5d$^1$ state) that creates the persistent luminescent signal. [39]

Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier (PMT) was used to measure the PL and PeL spectra of the SrAl$\text{2}$O$_4$: Eu$^{2+}$, Dy$^{3+}$ containing glasses at room temperature. For PeL measurements, the samples were irradiated for 5 min at room temperature with a compact UV lamp (UVGL-25, 4 W, $\lambda_{exc}$ = 254 nm) and the collection time of the spectra was set to 1 min after stopping the irradiation. The PL ($\lambda_{exc}$ = 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis) was measured using a CCD camera (Avantes, AvaSpec HS-TEC).

These two spectra were measured in a collaboration with Dr. Mika Lastusaari at Turku University (Finland).

### 3.2.2 Spectroscopic properties of Yb$^{3+}$ doped glass based materials

This technique is based on photon absorption and the creation of electronic excitation as light carves on a material. The electrons can go back to the ground state (relaxation) emitting light. When relaxation occurs, light is emitted and is referred to as photoluminescence (PL). The emitted light can be collected producing an emission spectrum. The PL intensity gives the proportion among radiated and non-radiated recombination. PL depends on excitation wavelength. The required instrumentation is quite simple and is composed of an optical source and a spectrometer, as shown in Fig. 3.2 [40].
In this project, three different equipment were used:

- Spectro 320-131 Vis-NIR emission spectrometer (Instrument Systems, Germany) was used to measure the emission spectra of the inspected glasses at room tem-temperature using. The glasses were crushed into powder in order to compare the in-tensity of emission between samples. The excitation was achieved by means of a monochromatic single-mode fiber pigtailed laser diode (CM962UF76P-10R, Ocla-ro) temperature tuned to 960 nm wavelength.

- FLS1000, Edinburgh Instrument was used with an excitation at $\lambda = 900$ nm in order to measure the shape of the emission band.

- The micro fluorescence spectroscopy was done using an inVia Qontor confocal Ra-man microscope (Renishaw, Gloucestershire, UK) using a $\lambda = 405$ nm and $\lambda = 532$ nm lasers to register Eu$^{2+}$ and Eu$^{3+}$ emission respectively.

### 3.3 SEM coupled with EDS

Scanning electron microscope (SEM) was used to analyze the PeL particles at the surface of the glasses. The electron bombardment is used either to induce a secondary electron or to reflect the original electrons into backscattered electrons:

- Secondary electrons are created with the assistance of inelastic scattering between a K-shell electron and electron beam. Beam electron influences and discharges an electron from nearest shell to the nucleus. These discharged electrons have a lower energy than the electron beam. Because of such a low
energy, they do not penetrate far in the sample and, which is ideal to studying sample topology.

- Backscattered electrons are electrons from the beam, which travel through an elastic scattering with nucleus core of the atoms of the sample. The scattering is elastic since the kinetic energy and electron velocity do not change. The scattering probability is proportional to the atomic mass. Backscattered electrons are therefore used in the calculation of the sample composition. These backscattered electrons are gathered and estimated to get data on the sample structure and topology.

Fig. 3.3 is a schematic of an SEM column. The electron gun produces the electrons. Magnetic coils coordinate and collimate the electron beam. The electron beam impacts the samples and the different types (secondary or back-scattered) electrons are collected by the detector. All processes take place in vacuum. [41]

![Figure 3.3](image.png)

**Figure 3.3:** Schematic diagram of the SEM electron column. [41]

Energy-dispersive X-ray spectroscopy (EDS) was used to investigate the composition of the glasses and particles. EDS is method of characterizing the atomic
composition of a sample using the element specific Kα and Kβ X-ray emission lines. X-rays can be generated along with the creation of secondary electrons. An electron hole at ground state is formed, causing an electron from higher shells to fill it and in the process, to emit an X-ray photon of characteristic energy. These X-rays are identified and measured to map the elemental composition of the sample. [19]

The scanning electron microscope (Leo 1530 Gemini, Zeiss) in conjunction with energy dispersive X-ray analyzer (Oxford Instruments X-ACT) was used in this study. To enhance the resolution, the samples were coated with carbon. Particles were searched at the surface. When found, they were imaged and their composition was analyzed with an EDS line. Composition is given with an accuracy of (±1.5 mol%).

3.4 XRD

X-ray powder diffraction (XRD) is a technique used to analyze crystalline materials. XRD is grounded on constructive interference of x-rays, which can be scattered from atoms placed at parallel crystal planes. Basically, this method exploits the unique diffraction patterns produced by the intensities and spatial distributions of elastically diffracted X-rays from the sample.

A schematic diagram of an X-Ray spectrometer is shown in Fig. 3.4.

![Figure 3.4: Schematic of an X-Ray spectrometer.](image)

Bragg’s Law can be used to explain how X-rays are diffracted by a crystal. The
constructive interference happens using the following equation,

\[ m\lambda = 2\sin\theta, \quad (3.5) \]

where, \( d \) is the distance between two crystal planes, \( \theta \) is the angle of incidence relative to crystal plane, \( m \) is an integer and \( \lambda \) is the wavelength of the X-ray. In XRD, generated X-ray passes through filters and collimators and reaches the sample, usually crushed into powder, at an angle \( \theta \). The diffracted X-rays are then gathered in a detector at angle \( 2\theta \) to meet the Bragg condition. The diffraction pattern is collected as a function of the angle of incident. A unique pattern is produced for crystalline materials. This spectrum can be compared to an archive of known patterns to determine the composition of an unknown sample.

In this study, the Panalytical EMPYREAN multipurpose X-ray diffractometer with an iron filtered cobalt K\( \alpha \) radiation (\( \lambda = 0.178897 \) nm) has been used. The samples were crushed into powder and spread over a “zero-background holder” Si-plate for the measurement of the XRD spectra.

### 3.5 Thermal properties

The thermal properties of the glass with the 70TeO\(_2\) - 20ZnO -10Bi\(_2\)O\(_3\) (in mol\%) composition were measured using a differential thermal analyzer (DTA). The main components in a DTA device are illustrated in Fig. 3.5.

![Figure 3.5: Schematic of a DTA.](image)
DTA allows the determination of characteristic temperatures in the thermal cycle of the glass, such as the melting point ($T_p$), the crystallization ($T_x$), and the glass transition ($T_g$). The DTA machine is composed of a sample holder, thermocouples, furnace temperature controller and data recording system. One can place the desire sample and the reference. Furnace is used to rise up the temperature. When the sample is heated, it undergoes a phase transition as a function of temperature. The fundamental of DTA is from the temperature difference $\Delta T$ between the sample and the reference under an organized cooling or heating system as a function of temperature. There are two types of processes in DTA: endothermic and exothermic processes. Endothermic process occurs when the sample temperature is less than that of the reference, thus $\Delta T$ is negative and the process can be associated to the absorption of heat by the sample. Whereas exothermic process occurs when the sample temperature is greater than that of the reference, thus $\Delta T$ is positive and the process can be related to the release of heat by the sample.

An example of thermogram is presented in Fig. 3.6.

![Thermogram of the tellurite glass, taken as an example.](image)

Figure 3.6: Thermogram of the tellurite glass, taken as an example.

$T_g$ is the glass transition temperature, $T_x$ the onset of the crystallization and $T_p$ the crystallization temperature. The $T_g$ is usually determined as the inflection point of the first endothermic peak also attained by taking the minimum of the first derivative of the DTA curve, while $T_p$ is taken at the maximum peak of the
exotherm. $\Delta T$, the temperature difference between $T_x$ and $T_g$, gives information about the thermal stability of the glass against crystallization.

In this study, the measurement was performed using DTA 449 F1 Jupiter (Netzsch-Geratebau GmbH, Selb, Germany) placing 30 mg of sample’s powder in a platinum crucible and heated up from room temperature to 600 °C, at 10 °C/min, in nitrogen atmosphere. All measurements were done with a precision of ± 3 °C.
In this chapter, the preparation and characterization of novel particles containing tellurite glasses are presented and discussed. The glasses were prepared applying different methods detailed in the previous chapters optimized to our particular case, in order to obtain Yb$^{3+}$ doped tellurite glasses with enhanced spectroscopic properties.

4.1 Optimization of the direct doping

The YbPO$_4$ particles containing glasses were prepared by adding YbPO$_4$ particles in the glass melt using the direct doping method. To balance the survival and dispersion of the particles, two parameters were optimized,

- Doping temperature ($T_{\text{doping}}$): at the temperature when the particles were added.

- Dwell time before quenching the glass after adding the particles.

These two parameters are crucial to determine because the particles may endure corrosion and the luminescence can be lost.

To optimize the process, microparticles (MPs) with persistent luminescence (PeL) were used as in [44]. These particles were chosen as they exhibit green persistent luminescence after stopping UV charging. As explained in [5], a loss of the PeL, related to the decomposition of the PeL particles, is due to high doping temperature and long dwell time.

Here, 0.5 wt% of SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ microparticles were added in tellurite glass melt at doping temperature of 550 °C, 575 °C, 600 °C, 625 °C and 650 °C.
while dwell time was 3 min. The images of the glasses in daylight and after stopping the UV is presented in Fig. 4.1.

![Figure 4.1: Daylight image of MPs containing glass on the upper case and afterglow image of MPs containing glass on the lower case at different $T_{doping}$.](image)

Depending upon the doping temperature, green PeL can be identified from some of the glass, ensuring the survival of the PeL microparticles. However, when the doping temperature increases, the intensity of the PeL decreases. One can further notice the homogeneous PeL from the glasses indicating a homogeneous distribution of the particles.

The PeL and PL spectra were measured are presented in Fig. 4.2 (a) and (b), respectively.
**Figure 4.2**: (a) Normalized persistent luminescence spectra and (b) photoluminescence spectra of the glasses investigated and of the microparticles alone.

The PeL and PL spectra exhibit an emission band with a maximum at $\lambda = 525$ nm, which is characteristic of $4f^55d^1 \rightarrow 4f^7$ transition of Eu$^{2+}$ indicating that the Eu$^{2+}$ ions are located in one single site in the SrAl$_2$O$_4$: Eu$^{2+}$ microparticles. A small shift of the emission band to longer wavelength, independently of the $T_{doping}$, can be found after embedding the particles in the glass revealing minor changes in the site of Eu$^{2+}$ in the PeL particles after adding them in the glass. Surprisingly, no bands at 590 nm, 610 nm and 680 nm due to Eu$^{3+}$ can be seen in the PL spectra although these bands were detected in PeL phosphate glasses [35]. One should remind that the emission of Eu$^{3+}$ can be related to the decomposition of the particles, which leads to the diffusion of Eu$^{2+}$ and so to the oxidation of Eu$^{2+}$ to Eu$^{3+}$. Due to the loss in the PeL of the investigated glasses, decomposition of the PeL particles is expected to occur with the formation of Eu$^{2+}$. Compared to phosphate glasses, the PeL from the tellurite glasses is low and therefore, the emission from Eu$^{3+}$ is expected to be small.

In order to verify the presence of Eu$^{3+}$ in the tellurite glasses, micro-Raman spectrometer was used. This instrument allowed us to measure micro-luminescence properties of the glasses. Emission spectra were recorded using 405 nm and 532 nm excitation to detect Eu$^{2+}$ and Eu$^{3+}$ respectively are shown in Fig. 4.3.
Figure 4.3: Typical emission spectra for (a) Eu\textsuperscript{2+} and (b) Eu\textsuperscript{3+}.

The emission spectrum after 405 \textit{nm} excitation exhibits an emission band at 495 \textit{nm}, which can be attributed to the emission of Eu\textsuperscript{2+} according to [45], while the emission band after 532 \textit{nm} excitation exhibits an emission band at 612 \textit{nm} related to the emission of Eu\textsuperscript{3+} [45]. Optical images showing the location of the emission were recorded and the corresponding profile of the intensity of emission at 495 \textit{nm} and 612 \textit{nm} are presented in Fig. 4.4 for all the investigated glasses.
(a) $T_{doping} = 550 \, ^{\circ}\text{C}$

(b) $T_{doping} = 575 \, ^{\circ}\text{C}$

(c) $T_{doping} = 600 \, ^{\circ}\text{C}$

(d) $T_{doping} = 625 \, ^{\circ}\text{C}$
**Figure 4.4:** Optical images of the investigated glasses prepared using $T_{doping}$ (a) 550 °C, (b) 575 °C, (c) 600 °C, (d) 625 °C and (e) 650 °C and profile of emission measured using different excitation wavelength.
It is clearly shown that the grey spots in the optical images are the particles due to the high intensity of the Eu$^{2+}$ emission. Emission of Eu$^{3+}$ was detected in all the samples confirming that oxidation of Eu$^{3+}$ occurs also in the tellurite glasses. It can be noticed that the emission of Eu$^{2+}$ was detected only in the particles, while the Eu$^{3+}$ emission was detected mainly around the particles. The Eu$^{3+}$ emission decreases gradually with increasing of the distance from the particles confirming the decomposition of the PeL particles associated with the diffusion and oxidation of Eu$^{2+}$ in the glass.

In order to confirm the decomposition of the particles, the glasses were also analyzed using SEM (coupled with EDS). The glasses were polished so particles are at the surface. Fig. 4.5 shows the particles at the surface of the glasses and also the elemental composition across the particles.
(a) $T_{doping}$ 550 °C

(b) $T_{doping}$ 575 °C

(c) $T_{doping}$ 600 °C

(d) $T_{doping}$ 625 °C
Figure 4.5: SEM image of the MPs and SEM/EDS lines profiles giving the elemental distribution across the microparticle diameter and interface with glass composition at different $T_{doping}$ (a) 550 °C, (b) 575 °C, (c) 600 °C, (d) 625 °C and (e) 650 °C and profile of emission measured using different excitation wavelength.
The microparticles keep their composition in their center when the glasses are prepared using low doping temperatures. However, when preparing the glasses at more than 625 °C, the particles do not maintain their composition in their center. Additionally, leaching Sr and Al were observed from the microparticles into glass composition, when the doping temperature increases. This leaching of Sr and Al confirms the decomposition of the particles. The degradation of the microparticles that happens at the time the glass preparation can be associated with the diffusion of Al and Sr and most likely of Eu and Dy from the microparticles glass which decreases the PeL signal.

In summary, no changes in the morphology and the composition of the particles in the glass prepared using $T_{doping}$ at 550 °C and 575 °C were observed. During the melting process, the melt at 550 °C was found viscous during the quenching. Therefore, it was decided to continue the study with the $T_{doping}$ of 575 °C.

4.2 YbPO$_4$ containing glasses

The tellurite glass with the composition 70TeO$_2$ - 20ZnO -10Bi$_2$O$_3$ (in mol%) was prepared with YbPO$_4$ particles which were added in the glass melt and glass batch.

4.2.1 YbPO$_4$ particles in tellurite glass melt

2.5 wt% of YbPO$_4$ were added in the glass melt at 575 °C, the optimized doping temperature as described in the earlier section. After quenching, the glass is crystallized as shown in Fig. 4.6 (a). The crystallization of the glass cannot be related to the low quenching temperature as a particles free glass was prepared using the same melting process than the particles containing glass and no crystallization occurred. Therefore, the crystallization might be related to the presence of the YbPO$_4$ particles. Glasses were prepared with lower amount of YbPO$_4$ in order to prepare crystals-free glass. As shown in Figs. 4.6 (b) and (c), the glasses are still crystallized, the glass with the lowest amount of particles being the least crystallized clearly showing that the amount of crystallization depends on the 2.5 wt% of YbPO$_4$ added in glass melt.
The thermal properties of the particles free glass were measured. The onset of crystallization was found at 387 °C and the glass transition temperature at 330 °C indicating that the glass is a poor glass former due to the low difference in between crystallization temperature and glass transition temperature (57 °C). Massera et al. [22] reported a larger ∆T for the glass with the same composition. The different thermal properties of the tellurite glass may be due to the TeO₂ precursor used for the preparation of the glass, which is different from the one used by Massera et al. [22]. Nonetheless, it is possible that the YbPO₄ particles act as nucleation agents.

In order to find out the crystals in the glass, the XRD patterns of the glasses were measured and are depicted in Fig. 4.7.

Sharp peaks can be found in the XRD pattern of the glasses ensuring the existence of crystals in the glass. Some of the peaks can be related to the YbPO₄ particles confirming their survival but additional peaks are also present. These ex-
tra peaks can be related to Bi$_{0.33}$O$_{1.83}$Te$_{0.67}$ crystals. One can observe that the intensity of the peaks increases with the amount of YbPO$_4$.

Fig. 4.8 shows the normalized emission spectra obtained using 900 nm laser excitation.
The spectra exhibit an emission band with a maximum band at 975 \textit{nm} with a shoulder of 1000 \textit{nm}. One can see that an increase in the amount of YbPO$_4$ increases the intensity of the shoulder as compared to the band of 975 \textit{nm}. The investigated glasses exhibit different emission band compared to that of the particles alone and the intensity of the shoulder increases at 1000 \textit{nm} as the amount of YbPO$_4$ increases. These changes in the shape of the Yb$^{3+}$ emission may be related to radiation trapping or re-absorption as well as energy migration among the Yb$^{3+}$ ions as reported in [46].

Fig. 4.9 shows the emission spectra of the glasses using 960 \textit{nm} excitation. The samples were crushed into the powder to compare intensity of emission.
Figure 4.9: Infrared Emission Spectra at $\lambda_{exc} = 960 \text{ nm}$ of YbPO$_4$ particles added in melt.

As expected, an increase in the amount of YbPO$_4$ particles increases the intensity of the emission.

4.2.2 YbPO$_4$ particles in tellurite glass batch

5 wt% of YbPO$_4$ were also added in the glass batch earlier to melting the glass. The glass was melted for 3 min at 850 °C. As shown in Fig. 4.10, the glass is fully and homogeneously crystallized after quenching.
**Figure 4.10:** Tellurite glass with YbPO$_4$ (5 wt%) particles added in the batch.

The XRD pattern of this glass is shown in Fig. 4.11.

**Figure 4.11:** XRD spectra of the glass (particles added in glass batch).
As for the previous glasses, sharp peaks can be seen in the XRD pattern of the glass, which can be attributed to YbPO\(_4\) and Bi\(_{0.33}\)O\(_{1.83}\)Te\(_{0.67}\) ensuring the survival of the YbPO\(_4\) particles during the melting process.

The emission spectrum of the glass after 960 nm excitation is presented in Fig. 4.12. Also shown is the emission spectrum of a Yb\(^{3+}\) doped tellurite glass within the same glass system used as a reference. The concentration of the Yb\(_2\)O\(_3\) in this glass corresponds to the amount of Yb\(_2\)O\(_3\) when adding 5 wt\% of YbPO\(_4\) in the tellurite glass.

![Emission spectra of the YbPO\(_4\) containing tellurite glass and of a standard Yb\(^{3+}\) doped tellurite glass (\(\lambda_{exc} = 960\) nm).](image)

**Figure 4.12:** Emission spectra of the YbPO\(_4\) containing tellurite glass and of a standard Yb\(^{3+}\) doped tellurite glass (\(\lambda_{exc} = 960\) nm).

It is clearly shown that the glasses exhibit different spectral shape indicating that Yb\(^{3+}\) ions are located in different sites in these glasses ensuring the survival of the YbPO\(_4\) particles. Moreover, the intensity of the emission from standard Yb\(^{3+}\) doped glass is slightly higher than that of the particles containing glass indicating that YbPO\(_4\) particles cannot be used in the tellurite glass with the composition 70TeO\(_2\) - 20ZnO -10Bi\(_2\)O\(_3\) (in mol\%) melted at 850 °C in order to prepare a glass with a strong emission at approximately 1000 nm.

It is possible that the low intensity of the emission can be related to a low amount of YbPO\(_4\) particles surviving the melting process.
In order to increase the amount of YbPO$_4$ particles surviving the melting process, a new glass was prepared with lower melting temperature. To reduce the melting temperature, the glass was first melted, then after annealing it crushed into powder. The YbPO$_4$ particles were then mixed with the glass powder. The mixture was melted at 650 °C for 3 min, quenched and annealed. The glass was completely crystallized. As performed previously, a particles free glass was prepared using the same melting process in order to verify if this melting procedure (low quenching temperature) leads to crystallization of the glass. After quenching, the particles-free glass was transparent, free of crystals, confirming that the crystallization occurring during the quenching of the particles containing glass is due to the presence of YbPO$_4$ crystals. The XRD pattern of this glass is shown in Fig. 4.13.

![XRD spectra of the glass (particles added in glass remelt).](image)

**Figure 4.13:** XRD spectra of the glass (particles added in glass remelt).

Like all the other glasses, sharp peaks are found in the XRD pattern of the glasses confirming the survival of the YbPO$_4$ particles and the precipitation of the Bi$_{0.33}$O$_{1.83}$Te$_{0.67}$ crystals. The characterization of the spectroscopic properties of this new glass is in progress.
In this thesis, YbPO$_4$ crystals containing tellurite glasses were prepared and characterized. The crystals were added in the glass melt using the direct doping method. The optimization of the direct doping method was done using persistent luminescent SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ particles. The doping temperature ($T_{doping}$) was defined at 575 $^\circ$C to balance the dispersion and survival of the particles. SEM coupled with EDS and microluminescence were used to analyze the survival of persistent luminescent. We found that the morphology and composition of the persistent luminescence particles changes as the $T_{doping}$ increases. In addition, when doping temperature is higher than 600 $^\circ$C particles endure corrosion losing their persistent luminescent properties. The doping temperature was defined at 575 $^\circ$C to continue the study.

Tellurite glasses were prepared by adding the YbPO$_4$ particles in the glass melt and in the glass batch. Survival of the particles was confirmed in the glasses but the glasses crystallized. In order to reduce the crystallization, different amount of YbPO$_4$ particles were added into the glass melt and we found that the crystallization level depended on the amount of YbPO$_4$ particles. The reason behind the crystallization of the glass, when adding the YbPO$_4$ particles, is due to the poor thermal stability of the glass matrix and YbPO$_4$ particles might act as nucleation agents. Differential thermal analysis (DTA) confirmed that this glass matrix is a poor glass former as evidenced by the low temperature difference between crystallization temperature and glass transition temperature (57 $^\circ$C). The survival of the YbPO$_4$ particles was ensured using XRD and also from the emission spectra measured using excitation at 900 nm and 960 nm excitation wavelengths. The XRD patterns exhibit sharp peaks confirming the survival of the YbPO$_4$ particles in all the
prepared glasses. Some changes in shape of the Yb$^{3+}$ emission was noticed, which might be related to re-absorption as well as energy migration among the Yb$^{3+}$ ions. However, no enhancement of the emission intensity was observed from the glass. In order to increase the intensity of the emission, a new glass was prepared using a lower melting temperature to increase the amount of the particles surviving the melting process.

The next steps would be to measure the spectroscopic properties of the newly prepared glasses and to estimate and compare the amount of YbPO$_4$ particles surviving in the various glasses. More importantly, the study should be repeated with a thermally stable tellurite glass.


[42] Hyperphysics, [http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html](http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html) (visited on 13.3.2020).


