The Proposed Crystallization Behavior of the TeO_2-Nb_2O_5-Bi_2O_3-Er_2O_3 Glass Ceramic System

By

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The road to completing this thesis began quite a long time ago, though its actual inception was fairly recent. When I began my time at Alfred University I was entered as a mechanical engineer, I went through all of the first year courses, and then got to our explorations in the second semester. I took the one on mechanical engineering first, I found myself becoming increasingly disinterested as the class went on, disillusioned with mechanical engineering. Then, I took the ceramics exploration, and it clicked. At the beginning of the next semester after the summer, I signed the paperwork and changed my major, and found my home in the world of materials science. Ceramic engineering immediately became something I was deeply interested in, I approached all the relevant coursework with gusto and a desire to learn. My excitement grew more and more as I realized how much of an active field the discipline is, the opportunities for research and discovery at every turn. This was the first key moment in how I came to my thesis.

While my love for ceramic engineering grew, I also continued to cultivate my long held interest in physics, taking a physics course in every semester up until my senior year, where my workload finally caught up with me. Those classes broadened the scope of what I knew significantly, deepening my understanding of everything, from basic kinematics and Newtonian physics, to complex glassy structures and the fundamentals of the universe. As I progressed through my major coursework I increasingly realized just how closely linked the disciplines of materials science and physics are, they influence each other in incredible ways. Without physics we wouldn't understand half of what happens in materials science, and without materials science, we wouldn't have discovered half the things in physics. This is hyperbolic, of course, but it got me thinking in a major way about what I would like to do in the future, as I knew I would like to research something that synthesized my love for physics and my love for ceramics, so bridging the gap was crucial. This was the second key moment in how I came to my thesis.

Finally, the summer before my senior year I stayed in Alfred for a research assistant position, working with my advisor, Dr. Wu, and his research team. The whole lab was working on a variety of

different materials, ranging from magnesia compounds, to yttria alumina garnet, but there was one thing that tied them all together; optical transparency. This immediately fascinated me, as all the materials being worked with were polycrystalline ceramics, which in my understanding were inherently opaque. I understood that single crystal materials could be transparent, I knew that glasses could be transparent, but the notion that genuine ceramic materials could be transparent drew me in. I began doing background research immediately, learning what I could from Alfred's substantial pool of research, along with articles that Dr. Wu sent me, and then found what I would like to do. Working with optically transparent ceramics bridged the gap between physics and ceramic engineering in a beautiful way, and provided me with an opportunity to do unique and valuable research. In particular, I was going to be working with glass ceramics.

Glass ceramics are an interesting group of materials, as they combine useful properties of both ceramics and glasses, because they are sort of both. There is a long held, and humorous, debate between ceramic engineers and glass scientists, which is if a glass is a failed ceramic, or if a ceramic is a failed glass. Glasses and ceramics are cousins of sorts, made from the same basic materials, silica, alumina, various fluxes, and the major difference arises in their microstructure. Glasses have no long range order, having the same basic structural units as a ceramic, but disordered and amorphous, with no crystallinity. Conversely, ceramics are all long range order, having repeating structural units that form crystal structures, which in turn form individual grains that make up the larger structure. In either case, they are formed at extremely high temperatures, but how that microstructure forms is critically determined by how they are heated or cooled. Ceramics have to be formed using a careful heating schedule, as the crystals that form are dependent on what temperatures you use, and their size depends on how long you hold them at a particular temperature. Glasses on the other hand, are melted at temperatures significantly higher than ceramic firing, and have to be formed using a careful cooling schedule, which is to say, quickly. As I mentioned before, glasses are characterized by their amorphous

structure, but nature likes order, which for the materials used is a crystalline structure. To keep glass from crystallizing, you have to cool it sufficiently fast so that it doesn't have the time to crystallize, keeping it locked in that amorphous state. This is where glass ceramics come in, and turn that long held debate on its head. Glass ceramics are formed by producing a glass, then reheating above its glass transition temperature, causing it to crystallize in such a way that you can have a combination of the two materials. In the case of my thesis, the goal was to determine how that crystallization occurs for a very particular glass ceramic system, and how a number of factors can affect that.

In particular, I intended to work with a tellurite glass ceramic, formed using tellurium dioxide, niobium pentoxide, bismuth(III) oxide, and erbium(III) oxide as a dopant. Tellurite glasses are notable for their infrared light transparency, and some degree of visible light transparency, and past research has indicated that this is equally true for a fully crystallized version of the same material. This crystallization was performed using an extremely rapid heat treatment, and done at a relatively high temperature considering the material used. As a result, the way in which this material crystallizes is little understood, and what factors impact crystallization have not been studied. To achieve this, I designed my methods to dramatically slow down crystallization, and varied the level of dopant added, so as to determine its role in the growth of crystals in the material. The use of this material, and other tellurite glasses, is typically in optics systems, medical devices, and most interesting to me, lasers. This is why erbium was chosen as the dopant, as it is a laser active ion, meaning that a certain group of its electrons can be charged with energy by a particular wavelength of light. In turn, those charged electrons can be hit by that same wavelength of light, and emit a photon from losing that energy they gained, while the other original photon continues to travel. This means you get two photons for the price of one, this process is called optical amplification, and is the basic principle behind all laser systems. Crystalline structures can enhance this effect, as the crystal matrix improves the materials ability to transfer energy because of its enhanced order, as such, it is beneficial to have an optically transparent ceramic be the host for a laser

active ion. The problem then becomes that crystalline structures can scatter light, if the crystals are the wrong size, hence why I chose to study the crystallization behavior of this material. Understanding how this material crystallizes gives a window in to improving this system through a number of means. For example, if my hypothesis of the erbium dopant acting as a nucleation site is correct, then the capabilities can be dramatically enhanced by using the dopant to crystallize the material, while increasing the amount of light it could output. If my prediction that the crystals had a linear pattern of growth, then the fraction of crystal could be tailored to a particular application, assuming that it's beneficial to do so. Unfortunately, I was unable to provide any evidence for any of the predictions I set out to explore.

There are setbacks in any project, this is a given, nothing goes perfectly, there are issues with equipment, a failed sample here or there, your X-ray diffraction data doesn't save, you forget to turn on the spectrometer before you go to lunch, these things happen. What generally doesn't happen is a globe spanning pandemic that locks down the entire country and causes massive quarantine efforts. To further enhance just how complicated my situation became, I live in New York City. This completely derailed my thesis, I no longer had access to the furnaces needed to produce the glass, the spectrometers needed to analyze the optical properties, the X-ray diffractometer needed to determine the crystal structures, or the scanning electron microscopes needed to determine the size of the crystals. I had no data, no experiment performed, to talk about. However, I did have a significant pool of articles, a well thought out methodology, and a number of predictions that can be supported with evidence. To this end, my thesis changed from what I had hoped, to what it needed to be under the circumstances. I was no longer doing an experiment, but a literature review. After a good deal of consultation with my advisor, I created something that was a rough approximation of what I had hoped to produce. In many ways, writing this literature review was significantly harder than doing the experiment itself. I have always been a hands on kind of person, I like working in a lab setting a great

deal, preparing samples, using instruments, analyzing data, those are my wheelhouse. Since this thesis was designed around experimentation and obtaining data, that made writing about it in an abstract sense much more difficult. The system used in this paper isn't widely used, unlike say yttria alumina garnet, its new and novel, which is what drew my interest in the first place. Unfortunately, this meant I didn't have fifty odd years worth of research on the particular composition I was using to reinforce my predictions. However, fortunately there are many systems similar to it, tellurite glasses and glass ceramics have existed for some time now, and many of the principles applied in other studies still work here. This literature review caused me to use my critical thinking abilities in a way that I didn't think I had to, and in this way, it was a positive experience. I have no doubt that the acutely bizarre circumstances this thesis was written under have given me the ability to produce future work that is even better than if this hadn't happened in the first place.

The writing of this would never have been possible if it weren't for the people I worked with over the years. My professors over the years have given me invaluable experience, without them I would have never developed the skills used to produce this work. My knowledge of ceramic engineering was nonexistent before I came to Alfred, and the expert tutelage of the ceramic engineering departments faculty are what gave me the ability to understand how the crystallization process would work, how the glass would be made, how every aspect of the experiment would function. My knowledge on the theoretical background for much of this materials potential applications would be minimal were it not for the physics department, who cultivated a desire to know more about the way in which the basic units of the universe works. Finally, I would like to thank the honors program, the courses I took over the years brought so much joy into my education, while providing depth and knowledge. They may not have been vital to my education as an engineer, but they did keep me sane through the years, which is a well known problem amongst engineers. Humor aside, I sincerely thank Alfred's faculty for everything they have done for me, and for the opportunity to produce this work.

Acknowledgements

Thank you Dr. Wu, your assistance and support has been invaluable.

Thank you to all of my professors over the years, you have all had an impact on me and put me on the path I'm on today.

Thank you to my dear friends, you are the finest people I have the pleasure of knowing, and while our time has been cut short, the measure of your effect on me is infinite.

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Abstract

The goal of this paper is to propose a method of determining the crystallization behavior of the TeO_2-Nb_2O_5-Bi_2O_3-Er_2O_3 glass ceramic system. The polycrystalline form of this material created from the parent glass is of great interest for applications in fiber optics and laser systems, as it fluoresces in the short infrared wavelength range, and exhibits high optical gain. Understanding the crystallization kinetics of this material through a slowed nucleation and growth process will grant insight into the ideal process for optimizing the microstructure. Two separate parent glasses will be prepared, one containing 0.8 mol percent of the erbium dopant, and one containing 1.2 mol percent. The parent glasses would be produced by melting high purity powders at 850 °C, with crystallization subsequently occurring at 400 °C for intervals of 2 hours, ranging from 2 hour to 10 hour annealing times. Analysis would be conducted using scanning electron microscopy (SEM) for crystallite size determination, spectroscopy to determine transmittance in the short IR range, and X-ray diffraction (XRD) to determine crystal content and structure. It is predicted that crystal growth will follow a linear pattern as a function of time, with the dopant ions serving as nucleation sites, resulting in the two compositions having different percentages of crystallinity. This paper synthesizes prior research to support these predictions as well as detail the optical and structural properties of the proposed material.

Introduction

Optically transparent ceramics are a group of novel materials, having unique and useful properties that bridge the utility of ceramic and glass material. The most common route of forming optically transparent ceramics is through the sintering of raw powder materials and carefully controlling the heating schedule to ensure that grain sizes remain small. This forming route proves to have a number of issues, as a misstep during the production process can result in porosity and impurities trapped in the grain boundaries, providing scattering centers. This renders the final material useless, as it loses the desired optical transparency. Producing an optically transparent ceramic through the use of a glass ceramic is particularly attractive as it solves this issue. Starting from a parent glass made produced using typical glass forming processes, a controlled crystallization process through annealing is performed to produce a fully dense polycrystalline ceramic. The benefits of producing a crystalline body through this route are numerous, crystal structures have significantly enhanced thermal stability, improved mechanical strength, and the final ceramic material has very little to no porosity, due to its origins as a glass.[1] As such, glass ceramics show great promise for use in optics applications since there are few scattering centers, due to the lack of porosity and inclusions at the grain boundaries.

These properties make optical gain media a primary application for optically transparent ceramics, as they can be doped with heavy lanthanide elements to produce a medium for stimulated emission. Out of the lanthanide ions with potential in this application, erbium is particularly promising. Erbium has a wide array of excitation wavelengths, its emission spectrum has significant utility in medical device applications, as well as already serving a crucial role in fiber optic applications.[2] Broadly speaking, lanthanide dopants present in the matrix have unpaired electrons present in their f orbitals, which do not interact with the host lattice. As a result, these electrons are free to be interacted with by photons. A specific wavelength of light, corresponding to the energy level of the electron, can be used to bring these f orbital electrons into an excited state. Subsequent interactions with photons of that

wavelength can cause that electron to be brought down from the excited state, resulting in a photon being emitted. By using a particular wavelength, it is possible to pump the gain medium with enough energy to bring a majority of the electrons into the excited state. The excited electrons then decay, and due to interaction with the incident photons, emit a photon of the same wavelength. This is the principle behind a laser, as the optically pumped gain medium transmits photons, while emitting photons through stimulated emission, drastically increasing the light output.[3]

Recently, tellurite-based glasses and glass ceramics have become particularly attractive in this application, due to their transparency through the infrared region, and their extremely high refractive indices. Additionally, tellurite glasses exhibit low melting temperatures, and while TeO_2 on its own is not an ideal glass former, the addition of other oxides allows it to readily form a glass.[4] This makes tellurite-based glasses an ideal candidate suited for use in infrared optics applications, as the production of the optics is relatively easy to perform, and is easily scalable.

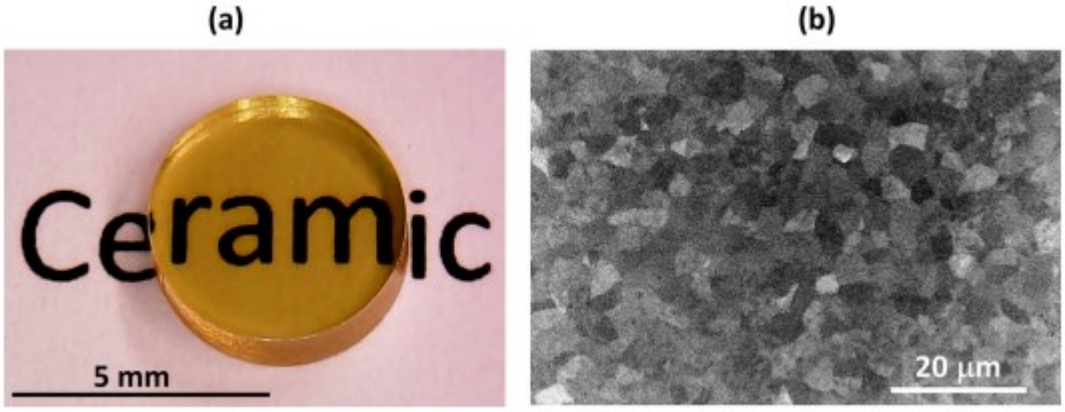

Figure 1: Undoped fully crystallized parent glass ceramic, from prior research conducted by Dolhen et. al. a) Typical sample transparency expected from this system, b) SEM imaging displaying the fully crystalline microstructure predicted to form.

This proposed study concerns itself with an Erbium doped tellurite glass ceramic system, combining the advantages of tellurite glasses with the beneficial properties of the compositions crystalline form. Literature regarding systems similar to the proposed composition has determined its properties in its glassy and fully crystalline forms, however the crystallization behavior of such systems is not well understood. The impact of crystallization as a function of time has not well been explored, leaving the mixed phases in between the two endpoints an unknown phenomenon, additionally, the rate of crystal growth is completely undetermined. It is understood that the material can fully and congruently crystallize, but where those crystallites are nucleated and grown from is still unknown.

Therefore, a methodology has been proposed to discern the nature of the nucleation and growth of crystallinity, and the associated optical and structural properties. First and foremost is reducing the temperature of the annealing process, as to dramatically slow the process of crystallization, allowing for the way in which this material crystallizes to be better understood. Secondly, controlling the concentration of erbium to determine the dopant's role as a nucleation site within the glass body. This is advantageous as the role of the dopant in crystallization has not been explored. Improving the understanding of how this glass ceramic forms, and how to best control the microstructure, is hugely beneficial to producing the optimal material tailored for individual applications. This study seeks to propose a methodology for determining the crystallization behavior of the TeO_2-Nb_2O_5-Bi_2O_3-Er_2O_3 glass ceramic system, as well as predict its structural and optical properties, through a synthesis of prior research regarding similar tellurite glass ceramic compositions.

Methods

The parent glasses would be prepared from 75% TeO_2, 12.5% Nb_2O_5, (12.5-x)% Bi_2O_3, and x% Er_2O_3, on a mol percent basis. Two different dopant concentrations would be used, one concentration of 1.2 mol percent, and one concentration of 0.8 mol percent. The melts would be formed by heating the

raw materials in a platinum crucible at 850 C, in air. Once the melt is formed, it would be held at that temperature for one hour, being mixed occasionally to ensure the homogeneity of the glass[5]. Once the melts are fully formed, the melts would be poured into five small pucks of equal diameter on a preheated block to quench the material, to ensure a glassy structure. Once cooled, the samples would be annealed just below T_g at 380 °C to relieve internal stresses and fully relax the structure, using a slow heating and cooling rate to ensure that thermal shock is not induced. The fully relaxed parent glass would then be annealed at 400 C for a range of times to induce crystallization, beginning at 2 hours, increasing by 2 hour increments, for a total of 5 samples ranging from 2 to 10 hour annealing times.

Data collection would be performed in a very particular order, beginning with spectroscopy. Spectroscopic analysis requires no specialized preparation techniques, the glass would simply be mounted and subject to FTIR spectroscopy for infrared range analysis. Additionally, UV-Vis spectroscopy would be performed for visible and NIR range analysis. Subsequently, the samples would be prepared for scanning electron microscopy. Each sample would have its surface polished to produce a suitable surface for SEM analysis, utilizing diamond polishing fluids, then selectively etching the surface of the samples to highlight crystalline features. Subsequently the samples would then be sputtercoated with gold nanoparticles to ensure proper conductivity for imaging. SEM analysis would be conducted using backscattered electron imaging, to optimally obtain crystallographic information. Once SEM analysis is complete, the samples would be ground down to a fine to prepare for use in X-ray diffraction (XRD) analysis. Scans would be conducted using CuKα radiation, from a range of 20 to 80° 2θ. The result would then be matched to known stick patterns in the ICDD database, with gold selectively removed from the pattern matching via chemical filter, to eliminate identification due to the presence of gold nanoparticles from SEM preparation.

Predicted Crystallization Behavior

Predicted results pertaining to crystal growth are largely dependent on annealing time, given that each sample is annealed at a constant temperature, time becomes the most important factor in the final crystallite size. A study performed by Hu et. al[6], on a different composition, containing ZnO rather than Nb_2O_5, with an exact composition of 75% TeO_2-x% Bi_2O_3-(25-x)% ZnO. This indicated that crystal growth was predominantly a function of time held at temperature. Crystallization was performed at a temperature of 335 C at times of 2, 7, 11, 17, 22, 30, or 64 hours. Crystallite size in this study was sufficiently small, ranging from 700 nm to 8 μm depending on the annealing time, with a demonstrably linear trend in crystallite size (Figure 2).

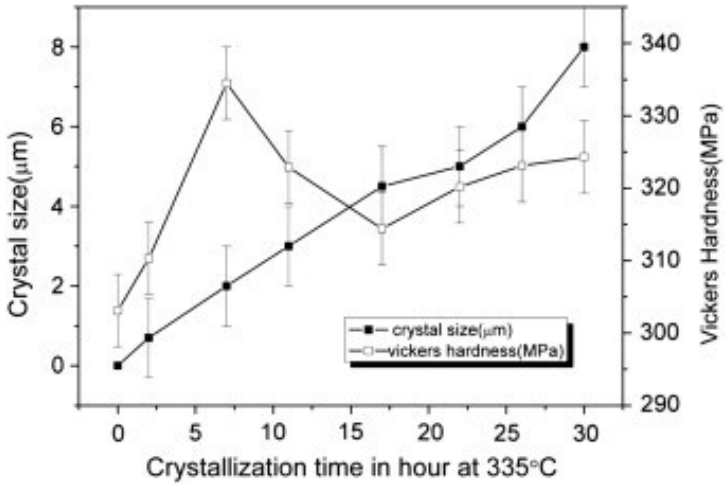

Figure 2: Growth curve from Hu et. al, demonstrates linear growth of crystallites as a function of time, at a maximum of 8 μm at 30 hours.

The volume fraction of crystallinity in this study is relatively low, never becoming a fully crystalline body, reaching a maximum volume fraction of approximately 7% crystal at the 30 hour mark. It is worth noting that temperature is also a contributing factor of how the crystalline structure forms, as the temperature affects the type of polymorphs that form.

A study conducted by Bertrand et. al sought to achieve a fully crystalline body, using a near identical composition to the parent glass proposed in this study, only lacking the erbium dopant.[5] This study used a significantly faster crystallization process, running at a higher temperature of 510 °C for 90 minutes, resulting in a fully crystalline body being produced. This process yielded small crystallite sizes, on a scale comparable to the size of the crystals produced at the 30 hour mark from the study discussed previously. Bertrand's study concluded that the crystalline form precipitated within the parent glass was a cubic structure with the composition $Bi_{0.8}Nb_{0.8}Te_{2.4}O_8$, this is the crystalline form expected to form in this proposal as well (Figure 3).

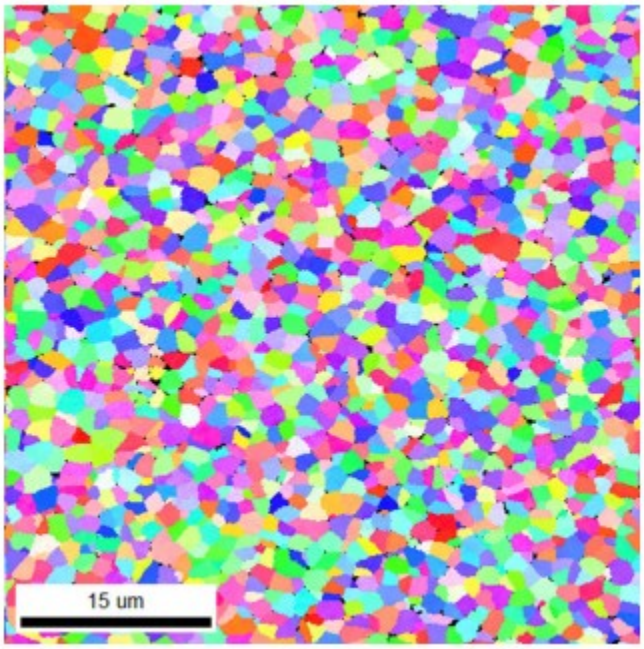

Figure 3: EBSD Map of undoped glass ceramic from Dolhen et. al, crystallite sizes range from 3 to 5 µm. Dark spots represent residual glassy phase.

Taking into consideration the results of the literature discussed, reducing the temperature of the crystallization process while increasing the time should allow for similar results to be achieved in terms of crystallite size. The time consideration is of critical importance as it would give a clear indication of this glass ceramic's crystallization behavior, it is expected based on the ZnO composition

that the proposed composition will exhibit linear crystallization behavior. The decreased temperature consideration adapted from Hu et. al will increase the time required for full crystallization, however, this increased time will enable clear construction of a crystallization curve for the parent glass.

Erbium Dopant Role in Nucleation

The inclusion of the erbium dopant is essential for the utility of the glass ceramic system as an optical material, as it results in the fluorescence of the material. In addition to erbium's important optical properties, it is predicted that the dopant will contribute to the crystallization behavior of the parent glass. A study performed by Zhang et. al[7] on fluoride tellurite glass ceramics with the composition $75TeO_2$-$15BaF_2$-$15YF_2$, co-doped with 5% Er_2O_3 and 5% Yb_2O_3, determined that dopant ions were present in the crystalline matrix. This is evident as the partially crystallized glass ceramics studied had increased luminescence in comparison to the parent glass, as the crystal structures cause a decrease in phonon energy. This decrease in phonon energy allows for the dopant ions to fluoresce with less energy input. This behavior indicates that the dopant ions were incorporated as part of the nucleation and growth process, if the ions were present exclusively in the glass phase, due to a substitution mechanism not having time to occur, this measured increased luminescence would not occur.

A similar study performed by Yu et. al[8] on another oxyfluoride tellurite system, with the composition $71TeO_2$-$18ZnO$-$7ZnF_2$-$3YF_3$-$1ErF_3$, found similar results in terms of fluorescent properties. The parent glass compositions were annealed at 345 °C for 10 hours. After the initial annealing, samples were treated using different time and temperature schedules. One sample group was treated at 375 °C for 2 hours, another group treated at 375 °C for 3 hours, and the last group treated at 380 °C for 3 hours. Crystallite sizes after the second heat treatment averaged 50 nm, 51 nm, and 55 nm respectively. Fluorescence data on these compositions indicated that the crystalline phase had increased fluorescence lifetimes and intensity, with times of 5.36 ms, 5.52 ms, and 5.36 ms respectively, in

comparison to the lifetime of 4.96 ms for the parent glass. Additionally, XRD data recorded that all samples, across temperature and time intervals, indicated the crystalline structures contained Erbium, forming a crystalline phase of $Er_2Te_5O_{13}$ (Figure 4).

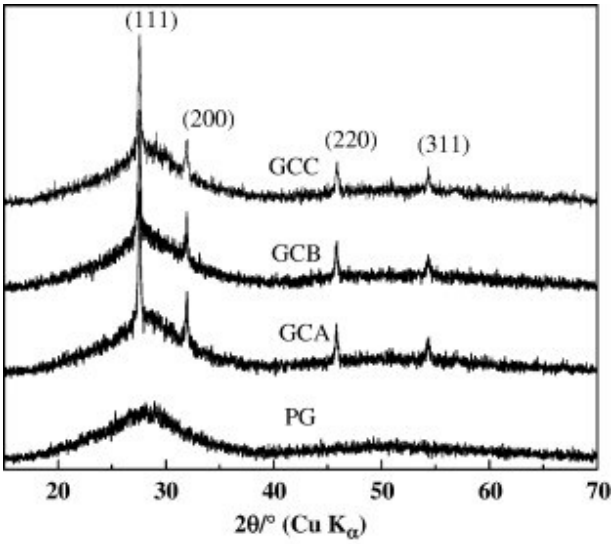

Figure 4: X-Ray diffraction data from Yu et. al, presence of an amorphous hump indicates residual glassy phase, crystalline peaks are attributed to $Er_2Te_5O_{13}$.

The fluorescence data from this study supports the conclusion drawn by the study conducted by Zhang et. al, as well as XRD data providing confirmation that Erbium is present in the crystal structure. The presence of erbium in the crystal structure of this composition strongly suggests that erbium will be present in the structure of the proposed system, in the form of $Er_{0.8}Nb_{0.8}Te_{2.4}O_8$.

The studies conducted by Zhang et. al and Yu et. al provide significant insight into the role of the dopant in the crystallization process, as both studies reach similar conclusions. The compositions used in both studies displayed improved luminescence properties upon crystallization, as a result of the dopant ions being incorporated in the crystal matrix. This indicates that the dopant ions are not trapped in the grain boundaries of the crystalline phase, as is the typical case for impurities in ceramics, but that they are included in the crystal structures themselves. Additionally, the property of enhanced luminescence

occurs in all crystallized samples in both studies, regardless of time and temperature. This provides further evidence that the dopant ions are included in the initial formation of the crystalline phase, as opposed to inclusion through a substitution mechanism. The literature then strongly supports the theory that dopant ions are a factor in the nucleation and growth of the crystalline phase in the glass. The demonstrated enhancement of luminescence is a direct result of the dopant being included in the crystalline phase, and enhancement through all time and temperature variables indicates that the dopant is present from initial crystallization. Overall, it is predicted that the erbium dopant will serve as a nucleation site for crystalline growth, resulting in a greater degree of crystallinity in the samples containing the higher dopant concentration.

Predicted Optical Properties

The optical properties of the glass ceramic are of immense importance, as they determine its potential applications and provide insight into its structural properties. As discussed in the previous section, the luminescent properties of similar systems are directly affected by the crystalline phase of the glass ceramic, however it is not just emissive optical properties impacted by the crystalline phase. The crystalline phase of tellurite glass ceramics have similar properties to the parent glass, in particular, the refractive index (RI) of the crystalline form as it is very close to the RI of the parent glass. The study performed by Bertrand et. al found that the refractive index of the undoped parent glass used in the proposed study had a refractive index of n= 2.17±0.05, and the fully crystallized glass ceramic had a refractive index of n= 2.24±0.05, assessed at a wavelength of 1064 nm.[5] The glass ceramic system proposed in this study is expected to have similar properties, given that the dopant added does not affect the refractive properties of the parent glass, as indicated by the study performed by Dolhen et. al.[9] This study was performed on an identical composition using a neodymium dopant and concluded that the refractive index of the neodymium doped material was identical to that of the undoped material.

The transmission properties of the crystalline form have been found to be comparable to that of the parent glass, though the crystalline phase exhibits slightly decreased transmittance, 75.76% for the parent glass, and 73.17 for the crystallized form.[9] This attributed to the differences in the refractive indices between the crystalline form and the parent glass, though the crystalline form maintains good transmission in the 3-5 µm wavelength range. Transmittance sharply decays below the 500 nm wavelength range, and decays more gradually past the 5 µm wavelength range (Figure 5).[5]

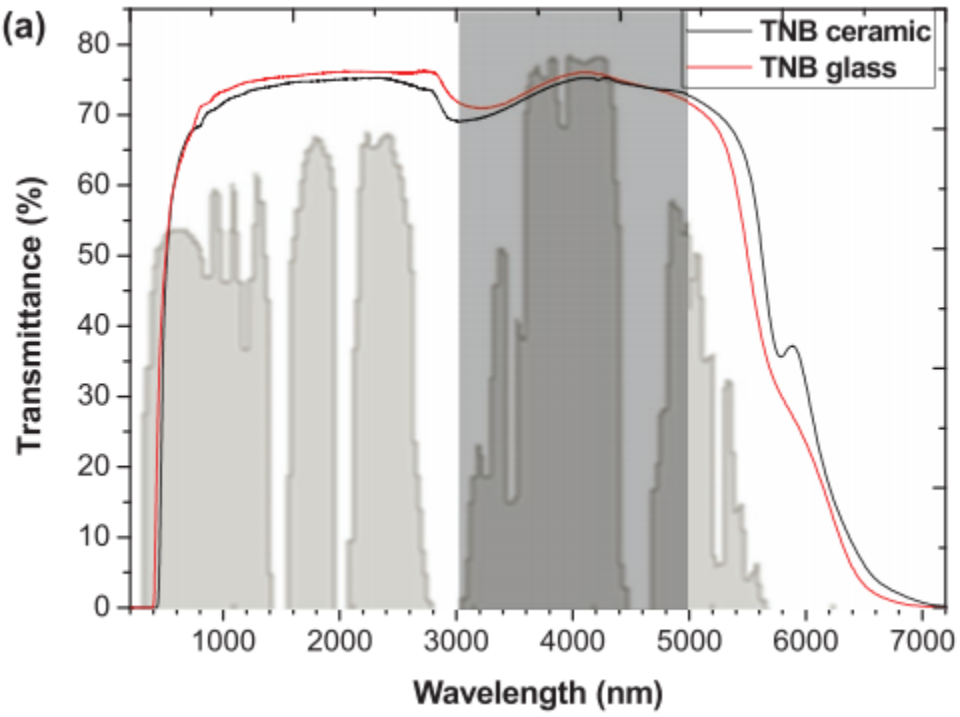

Figure 5: Transmission spectrum of undoped parent glass and glass ceramic. Shows strong transparency in the 3-5 µm wavelength range.

This is valuable as the proposed glass ceramic is designated for use in the mid infrared range, while maintaining optical transparency through a portion of the visual and NIR spectrum. This maintenance of transparency is due to the crystallite sizes being sufficiently small, and the lack of scattering centers present in the crystalline phase, however, this data was determined for an undoped

form of the parent glass. The presence of the erbium dopant should theoretically have little effect on the observed transmission properties, still allowing transmission in the ranges specified.

While maintaining transmission in those regions, the addition of the erbium dopant will cause the absorption spectrum of the glass ceramic to change significantly. Transitions within the f orbital will cause certain specific wavelengths to be strongly absorbed. A study performed by Kang et. al, using an erbium doped germanotellurite system, of the composition (59-x)% TeO_2-x% GeO_2-8% BaO-22% Li_2O-3% Er_2O_3, found that the characteristic absorption spectrum for erbium had peaks present at 524, 653, 800, 978, and 1535 nm, determined using FTIR spectroscopy (Figure 6).[10]

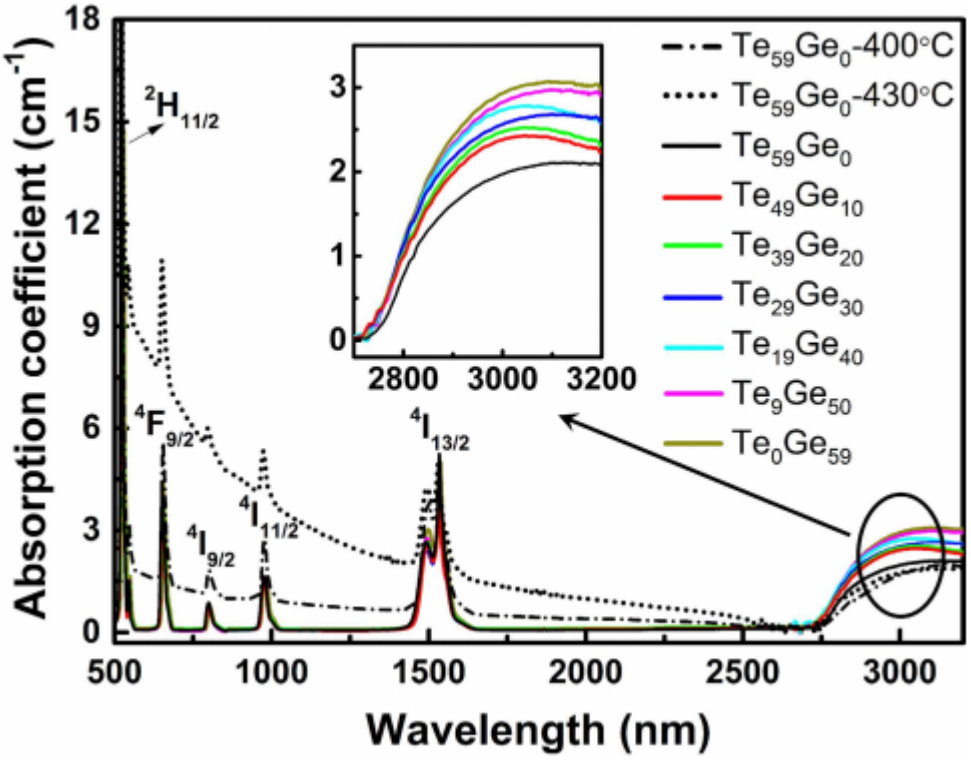

Figure 6: Absorption spectrum of Erbium(III) in germanotellurite system, hump at the far right is due to the host material, while characteristic peaks are present on the left.

These characteristic peaks are due to the aforementioned f orbital transitions, caused electrons moving from the ground state to the excited state. These characteristic peaks are expected to be found

in the proposed system as well. Additionally, the strength of these peaks will be strongly affected by the concentration of dopant present in the system. The lower dopant concentration samples would have decreased absorption for those specific wavelengths, conversely, the higher dopant concentration samples will have increased absorption. Therefore, the expected results for this line of experimentation will be that the refractive index will have little change across the range of degrees of crystallization, and the transmittance of the material will decrease slightly as the material becomes increasingly crystalline. Absorption is expected to remain the same throughout all degrees of crystallization, with the two different sample groups having distinct peak heights depending on the dopant concentration used.

Conclusions

The crystallization behavior of the glass ceramic system with the composition 75% TeO_2, 12.5% Nb_2O_5, (12.5-x)% Bi_2O_3, and x% Er_2O_3, is as of yet undetermined, however evidence strongly suggests that the crystallization behavior of this material will follow a linear pattern of growth, with nucleation occurring as a function of dopant concentration. Past research on similar compositions has indicated that these types of systems exhibit linear crystal growth, with the time required being a function of temperature. As such, reducing the temperature at which crystallization occurs, while increasing the time, should prove to be a reasonable methodology of accurately discerning the crystallization behavior of this glass ceramic system. The role of the erbium dopant in the nucleation process is likely to be significant, as other studies have indicated that the dopant is present from the beginning stages of crystal growth, supporting the idea that it is present during nucleation. Prior research indicates that the optical properties of the fully crystallized material will not differ greatly from those of the parent glass, though the added dopant will cause significant changes in the absorption spectrum of the material due to the f orbital transitions. Overall, the proposed system shows great promise and merits further research to improve the determination of its microstructural development and subsequent properties.

Future Research

Beyond the proposed methods and experimentation in this paper, it is worth performing a variety of follow up work based on the results of this work. First and foremost, once the emission spectrum for this material is determined, the most strongly absorbed wavelengths by the erbium dopant should be utilized for additional fluorescence spectroscopy. Results would allow for the emission spectrum of this particular glass ceramic to be accurately determined, as well as what wavelength would serve as an optimal pump source. This would in turn lead into the development of this material as a lasing medium. Once a high performing pump wavelength is established, it can be utilized to assess the lasing capabilities of this material. Knowing these properties would allow for the determination of the effect of this materials crystallinity on its viability as a laser source. If the hypothesis regarding dopant concentration and nucleation is found to be correct, further testing should be performed on modifying the dopant levels, raising the concentration incrementally to determine an optimal dopant level for ideal optical properties and the nucleation and growth of the crystal phase. Concerning the temperature and time dependence of this materials crystallization, in situ high temperature XRD should be performed using a series of temperatures near to the temperature proposed in this study. This will provide better indication the onset of crystallization and how the crystallization behavior varies near the temperature outlined in the methods. To summarize, there is substantial opportunity for follow up experimentation, and every avenue should be investigate in an effort to better understand the formation of this tellurite glass ceramic.

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