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Non-Traditional Oxide Glasses via Rapid Quenching

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We demonstrate the use of rapid quenching as a method to produce novel oxide glasses not containing traditional glass formers. A splat quench technique was developed to produce glasses in the binary La2O3-Ga2O3 and ternary La2O3-Ga2O3-(Ta or Nb)2O5 materials system in significantly larger sizes than other techniques allow. The glass forming regions of these systems using the splat quench techniques were experimentally determined. The mechanical, thermal, and optical properties of these glasses were measured and the effects of chemistry determined. Glass formability was improved while maintaining mechanical and optical properties through the use of network modifiers. We also demonstrated the doping of active rare earth components into these glass compositions.

This report presents research conducted by Optical Sciences code 5620 for the development of novel oxide glasses with greatly improved mechanical and thermal properties for us in the UV to mid-IR spectra.

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CONTENTS

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EXECUTIVE SUMMARY

We demonstrate the use of rapid quenching as a method to produce novel oxide glasses not containing traditional glass formers. A splat quench technique was developed to produce glasses in the binary La_2O_3-Ga_2O_3 and ternary La_2O_3-Ga_2O_3-(Ta or Nb)$_2O_5$ materials system in significantly larger sizes than other techniques allow. The glass forming regions of these systems using the splat quench techniques were experimentally determined. The mechanical, thermal, and optical properties of these glasses were measured and the effects of chemistry identified. Glass formability was improved while maintaining mechanical and optical properties through the use of network modifiers. We also demonstrated the doping of active rare earth components into these glass compositions.

This report presents research conducted by Optical Sciences code 5620 for the development of novel oxide glasses with greatly improved mechanical and thermal properties for us in the UV to mid-IR spectra.

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NON-TRADITIONAL OXIDE GLASSES VIA RAPID QUENCHING

1. INTRODUCTION

Non-Traditional Oxide Glasses (NTOGs) are a promising new category of glasses that don't follow Zachariasen's rules for glass formation. Zachariasen's rules for glass formation list conditions generally needed for oxide glasses: no oxygen atom may be linked to more than 2 cations, cation coordination number is 3 or 4, oxygen polyhedral share corners and not edges or faces, and at least three corners are shared. These new glasses differ primarily in their lack of the traditional glass network formers. Significant interest has been shown in glasses based on Ga_2O_3, La_2O_3, Ta_2O_5, and Nb_2O_5[1-3] due to their high refractive index, infrared transparency, strong luminescence, and crack resistance. These systems have a high tendency to crystallize due to the lack of network formers in sufficient quantity. Consequently, this places severe restrictions on scaling to large sizes. To date, exotic approaches have been used in order to make these glasses, albeit in small sizes. The most common method for producing glasses in these systems is a process called aerodynamic levitation. [1,4-6] This process has been successful in producing small quantities of glasses in these system by suppressing crystallization by rapid cooling and removing nucleation sites. This process limits the size of samples to 1-3mm balls limiting any useful application.

In recent studies glasses based on the binary (Ga_2O_3-La_2O_3) and the ternary (Ga_2O_3- La_2O_3- Ta_2O_5); (Ga_2O_3- La_2O_3- Nb_2O_5) glasses have been shown with wideband transparency, high refractive index, and improved thermal stability. [1,4] The improved thermal stability of these glasses shows promise that glasses can be produced using other processing methods that allow for larger sizes.

In this report we describe our methods and results for producing and characterizing these glass compositions fabricated within the Optical Sciences Division of the US Naval Research Laboratory. We developed a new process for compositions of these NTOGs that allows for much larger sizes to be produced than current containerless processing methods. We were able to map the glass forming region of this new process of both binary and ternary compositions based on Ga_2O_3-La_2O_3. We then characterized the mechanical, thermal, and optical properties of these glasses. We also demonstrated new multi-component glasses with greatly improved thermal stability while maintaining their superior properties. Doping of NTOGs with Er_2O_3 was also successfully shown highlighting the potential for use in active applications, potentially leading to high-power solid-state lasers.

2. APPROACH

2.1 Glass Production

Glasses were produced using traditional melt processing and casting. Target compositions were batched and mixed from high purity powders of Ga_2O_3, La_2O_3, Ta_2O_5, Nb_2O_5, Er_2O_3 and K_2CO_3. The powders were weighed to the target concentration and mixed for 12 hours utilizing a bottle shaker. Glasses were melted using a bottom loading furnace in air with a platinum crucible. Melts were further homogenized using stirring while at temperature.

NTOGs typically require high cooling rates to prevent crystallization from occurring when cooling from the melt. To produce larger sizes of NOTGs a combination of stamping and quenching was used to provide adequate cooling rate in the cast samples. This splat quenching method utilized copper quench

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plates cooled to liquid nitrogen temperature, shown in Figure 1, provides sufficiently high cooling rate to produce a bulk glass from the melt. This allows for glass samples to be produced in larger sizes up to 50mm in diameter and 1-3mm in thickness which is unobtainable from other methods such as the aerodynamic levitation process.

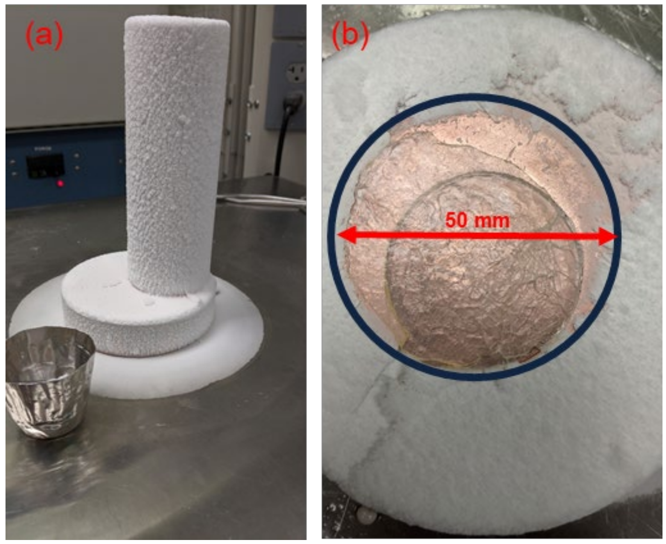

Fig. 1 — (a) Splat quench setup using liquid nitrogen cooled plates. (b) NTOG samples produced using setup from (a).

The glass forming region in the binary (Ga_2O_3-La_2O_3) and the ternary (Ga_2O_3- La_2O_3- Ta_2O_5); (Ga_2O_3-La_2O_3- Nb_2O_5) systems was mapped using this rapid quenching process. Additions of potassium carbonate, as a source for potassium oxide, were utilized to stabilize the glass allowing for compositions to be cast without high cooling rates. Glasses were annealed near the glass transition temperature to relieve any residual stresses resulting from the quenching. Erbium oxide was utilized to dope glass compositions for active glasses.

2.2 Characterization of Glass Compositions

Compositions that successfully produced glasses were characterized to provide an understanding of the mechanical, thermal, and optical properties. Hardness and fracture toughness were calculated from micro-indentation. Micro-indentation was done with a Leco LM 248AT using a vickers indenter and a test load of 200gf. Hardness was averaged over 10 indents per sample. Thermal analysis was done using a TA Instruments SDT Q600 to provide both glass transition and crystallization temperature. Samples were tested from room temperature to 1300°C and heated at a rate of 10°C/min. Optical analysis was done to determine the transmission characteristics and dispersion of the glass. Transmission spectra was collected using a Cary UV-Vis Spectrophotometer and an Analect FTIR. This allowed for measuring the transmission from 0.25-8µm wavelength. Dispersion was measured for select compositions using a Woolam IR-VASE Ellipsometer in the wavelength range of 1.5-9µm.
Glass compositions doped with erbium were further characterized by fluorescence measurements. Doped samples were pumped using a 980nm laser to confirm the presence of the erbium.

3. EXPERIMENTS

3.1 Determination of Glass Forming Region

Samples were produced from the binary Ga_2O_3-La_2O_3 system ranging from 20-50 mol% La_2O_3. In the ternary system compositions were tested in the range of 25-60 mol% Ga_2O_3, 25-50 mol% La_2O_3 and10-20 mol% (Ta or Nb)$_2O_5$. These compositional ranges were selected based on success at producing glass in levitation techniques as well as furnace temperature limitation (1800°C) being able to melt the samples. The results of selected compositions from the glass forming study using splat quenching are shown below in Table 1.

Table. 1 — Selected NTOG compositions showing limits of glass forming region using splat quenching.

Sample ID	Ga_2O_3	La_2O_3	Ta_2O_5	Nb_2O_3	K_2O	Rapid Quench Results
NTOG-14	76.9	23.1				**Glass**
NTOG-21	71.9	28.1				**Glass/Crystalline Mix**
NTOG-20	81.9	18.1				**Crystalline**
NTOG-26	66.9	33.1				**Crystalline**
NTOG-19	45	55				**Did Not Melt**
NTOG-28	60	30	10			**Glass**
NTOG-29	60	30		10		**Glass/Crystalline Mix**
NTOG-30	30	50	20			**Glass**
NTOG-33	30	50		20		**Glass/Crystalline Mix**
NTOG-31	61.1	33.15		5.75		**Crystalline**
NTOG-32	25.5	53		21.5		**Crystalline**
NTOG-36	60	30	5	5		**Crystalline**
NTOG-37	30	50	10	10		**Crystalline**
NTOG-40	60	25	10		5	**Glass**
NTOG-42	60	25		10	5	**Glass**
NTOG-38	60	20	10		10	**Glass**

The glass forming region using the splat quench method in the binary Ga_2O_3-La_2O_3 system was found to be limited to compositions from the eutectic point at 23.1 mol% La_2O_3 to 28.1% La_2O_3. The glass forming region was much larger in the ternary system Ga_2O_3 - La_2O_3 - Ta_2O_5 but was still a reduced area compared to the glass forming region demonstrated using levitation techniques. The ternary system Ga_2O_3- La_2O_3- Nb_2O_5 was partially crystalline in all samples produced using the splat quench technique. Replacing small quantities of La_2O_3 with K_2O (5-10 mol%) was shown to greatly improve stability of the glass to the point that it could be cast without the liquid nitrogen quench plates or the stamping. Figure 2 below shows a piece of the stabilized NTOG-40 from casting that was 2mm thick and over 25mm in diameter.

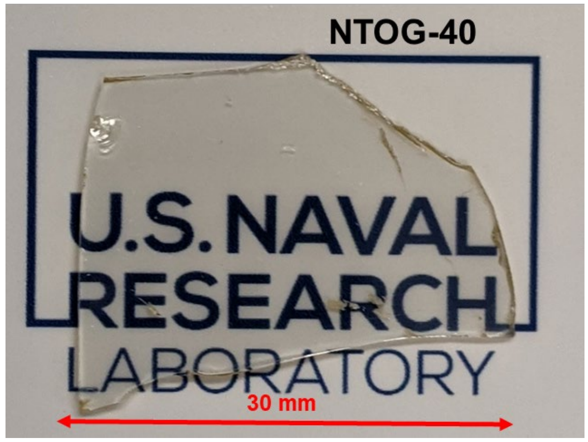

Fig. 2 — Sample of NTOG-40 cast into a thin sheet without rapid quenching.

3.2 Mechanical Properties of Glasses

Micro-indentation testing was done to provide Vickers hardness values for all glass compositions. Indentation tests were done on both annealed and unannealed glass samples. Testing on unannealed glass had limited results due to the high incidence of cracking during indentation. The unannealed glass showed significantly higher hardness and behaved like tempered glass. Vickers hardness values are summarized below in Table 2.

Table. 2 — Vickers hardness from micro-indentation using 200gf. *Unannealed hardness

Sample ID	Hardness* (kgf/mm^2)
NTOG-14 (Ga_2O_3-La_2O_3)	746 (1108*)
NTOG-21 (Ga_2O_3-La_2O_3)	724
NTOG-28 (Ga_2O_3- La_2O_3- Ta_2O_5)	747
NTOG-30 (Ga_2O_3- La_2O_3- Ta_2O_5)	739
NTOG-33 (Ga_2O_3- La_2O_3- Nb_2O_5)	698
NTOG-38 (Ga_2O_3- La_2O_3- Ta_2O_5-K_2O)	678
NTOG-40 (Ga_2O_3- La_2O_3- Ta_2O_5-K_2O)	705
NTOG-42 (Ga_2O_3- La_2O_3- Nb_2O_5-K_2O)	718

Hardness values were similar across all compositions with the hardness of the binary composition being the highest. All compositions demonstrated much higher hardness than the traditional glass compositions and even higher than chemical hardened glass such as gorilla glass (678 kgf/mm^2). The addition of K_2O while improving stability reduces the hardness of the glass minimally. In addition to the high hardness values NTOGs also demonstrated increased fracture toughness and resistance to cracking. This increased toughness is shown below in Figure 3. NTOGs are resistant to cracking at much higher force loads than silica glasses.

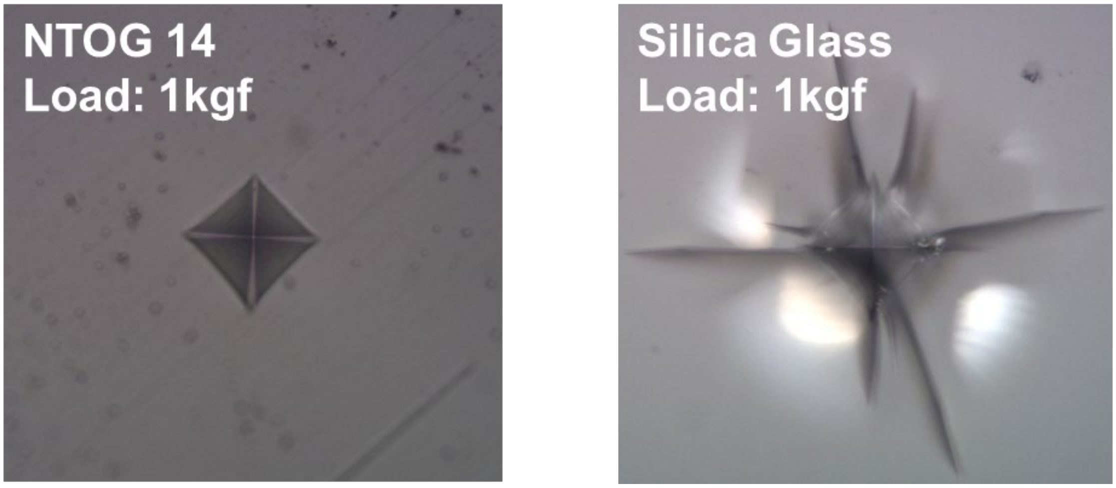

Fig. 3 — Micro-indentation marks comparing NTOGs (no cracking) to regular silica glass when done under high force loads

3.3 Thermal Properties of Glasses

Thermal analysis was carried out on small samples of each glass composition. Testing using the SDT allows for simultaneous DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) analysis to be carried out over the full temperature range tested. Samples were loaded in platinum test crucibles and heated at 10°C/min to 1300°C. NTOGs were shown to be thermally stable and have minimal decomposition up to 1300°C. The temperature difference between the glass transition and crystallization temperatures, represented as **ΔT,** is a measure of the stability of a glass composition. The thermal properties of the measured NTOG compositions is listed below in Table 3.

Table 3 — Thermal Properties of selected NTOG compositions.

Sample ID	T_g (°C)	T_x (°C)	ΔT
NTOG-14 (Ga_2O_3-La_2O_3)	737	800	63
NTOG-21 (Ga_2O_3-La_2O_3)	737	806	63
NTOG-28 (Ga_2O_3- La_2O_3- Ta_2O_5)	772	902	130
NTOG-30 (Ga_2O_3- La_2O_3- Ta_2O_5)	864	995	131
NTOG-33 (Ga_2O_3- La_2O_3- Nb_2O_5)	831	927	94
NTOG-38 (Ga_2O_3- La_2O_3- Ta_2O_5-K_2O)	742	856	114
NTOG-40 (Ga_2O_3- La_2O_3- Ta_2O_5-K_2O)	756	888	132
NTOG-42 (Ga_2O_3- La_2O_3- Nb_2O_5-K_2O)	784	893	109

NTOGs made from the binary Ga_2O_3-La_2O_3 system showed lower T_g, T_x, and ΔT compared to other compositions. The low ΔT of these compositions greatly limits the workability of the glass and limits potential uses. The addition of tantalum oxide or niobium oxide increases all three values for the glass showing increased stability. The addition of potassium oxide to the glass results in reduction of both the T_g and T_x but maintains the ΔT. Additions of alkali oxides, a network modifier, creates non-bridging oxygens in the glass matrix resulting in lower glass transition temperatures. These network modifiers improve glass formability and workability. The higher ΔT present in the 3 and 4 component NTOGs greatly improves the workability of these glasses allowing for these glasses to be worked without devitrification.

3.4 Optical Properties of Glasses

Transmission spectra were collected from 0.25-8µm for all samples. The UV cutoff was determined around 0.33 µm for all compositions. All compositions also showed a small absorption band around 3µm which is indicative of OH groups in the glass. This is expected since the glass melting was not done in an inert environment and the OH impurity can be removed with processing. The IR cutoff for these glasses was dependent on composition and is shown for several compositions below in Figure 4.

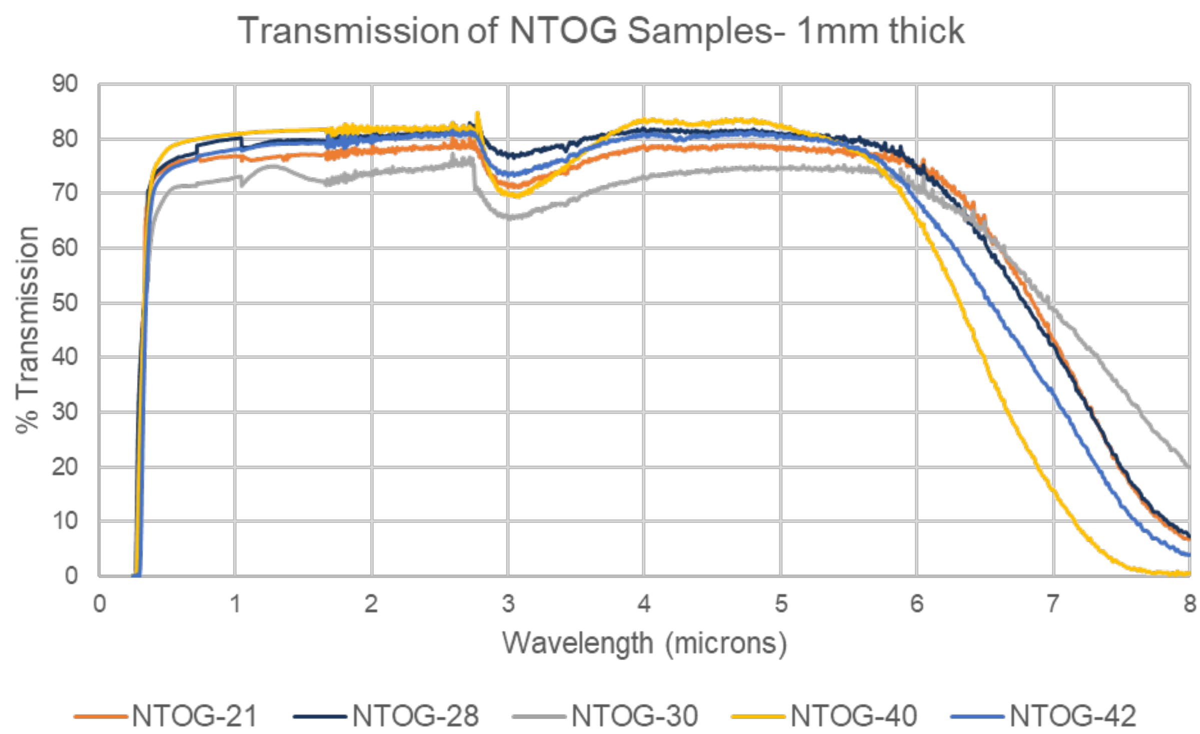

Fig. 4 — Transmission spectra of select NTOGs

The composition with the best IR cutoff was NTOG-30 which was the only composition where the primary component was La_2O_3. All NTOGs with Ga_2O_3 as the primary component had shorter IR cutoff windows which is expected due to the higher phonon energies in Ga_2O_3 rich compositions. Additions of Ta_2O_5, Nb_2O_5, and K_2O all further reduced the IR cutoff of the NTOGs. The refractive index in the visible region of the binary NTOGs were found to be in the range of 1.92-1.96 range while the NTOGs in the ternary system had indexes in the range of 1.95-2.2 range. Dispersion of NTOG-40 is shown below in Figure 5. NTOG-40 was shown to have high dispersion in both the near and mid IR regions.

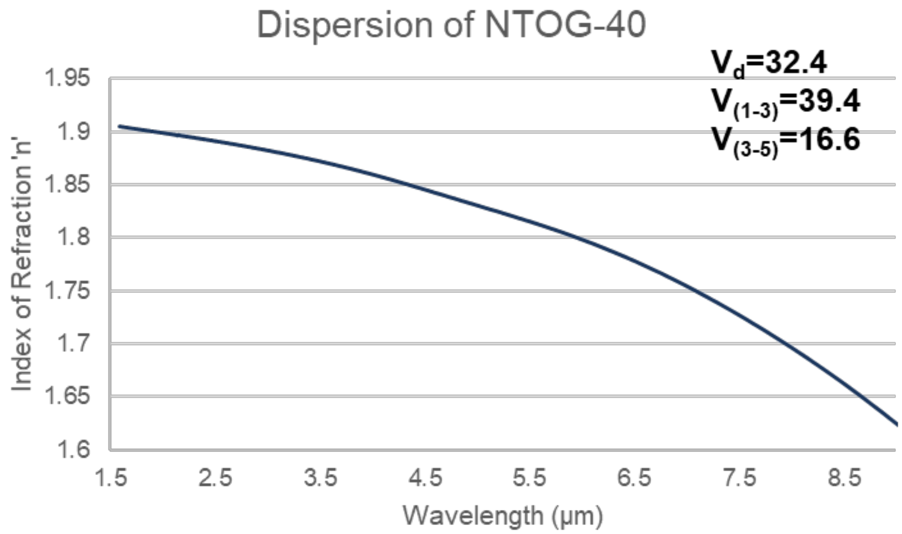

Fig. 5 — Index measurement of NTOG-40 ranging from 1.5-9μm

3.5 Rare Earth Doped Glasses

NTOGs have great potential as a host for rare earth doping due to the high concentration of La_2O_3. This provides sites for other rare earth ions to be incorporated into the glass structure. NTOG-14 with composition $23.1Ga_2O_3$-$76.9La_2O_3$ was successfully doped with Er_2O_3 being substituted in place of La_2O_3 at concentrations of 0.1, 0.5, 1, and 10 mol%. The 10% Er_2O_3 did not produce a glass upon quenching. The mechanical and thermal properties of these doped glasses did not change from the undoped composition and matched that of undoped NTOG-14. The transmission spectra of the doped glasses are shown below in Figure 6.

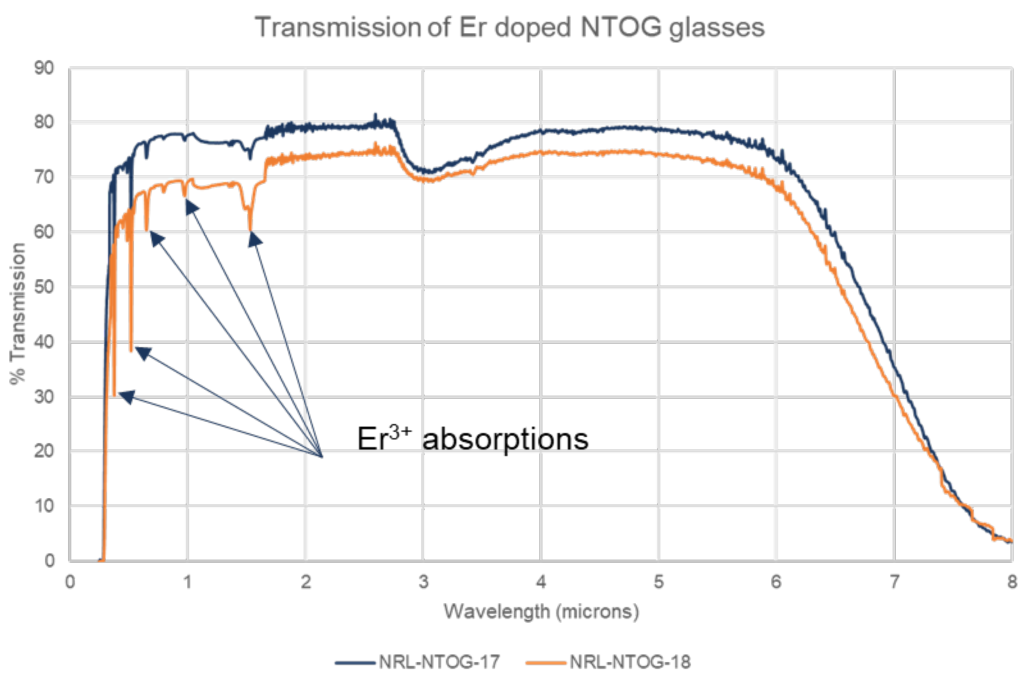

Fig. 6 — Transmission spectra of NTOG-17(0.1% Er_2O_3) and NTOG-18(1%Er_2O_3).

Transmission spectra showed absorption peaks corresponding to Er^{3+} with a clear concentration dependence. UV and IR cutoff were unchanged compared to the undoped glass composition. The active nature of the $Er^{3+}$was demonstrated by pumping the NTOG samples with a 980nm laser and observing the two-photon upconversion to generate green light. This is shown below in Figure 7.

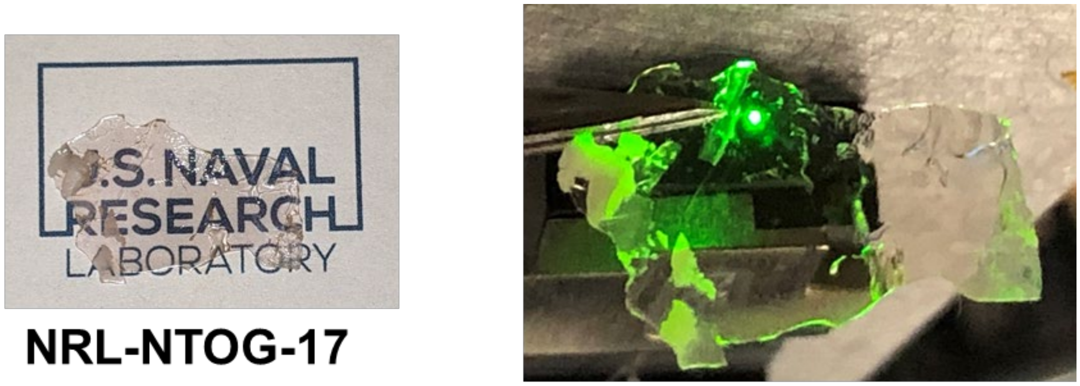

Fig. 7 — Sample of NTOG-17 showing clear pink hue indicating presence of Er^{3+} (left) and emission of green light when pumped with laser (right).

4. CONCLUSIONS

We demonstrated a rapid quench process for producing NTOGs in much larger sizes than have previously been produced. The glass forming region in both the binary (Ga_2O_3-La_2O_3) and the ternary (Ga_2O_3-La_2O_3-Ta_2O_5); (Ga_2O_3-La_2O_3-Nb_2O_5) systems was mapped for this rapid quench process. The mechanical, thermal, and optical properties of these NTOGs was characterized. These glasses possess a wide transmission window from UV to mid-IR (0.3-7µm), high temperature stability (>700°C), and robust mechanical properties with higher hardness than gorilla glass. New compositions of these NTOGs were developed with improved stability and the ability to be cast without the rapid quench process while maintaining their excellent mechanical and optical properties. We also demonstrated successful doping of NTOGs using several concentrations of Er_2O_3. These doped NTOGs showed successful 2-photon upconversion and generation of green light when pumped with a 980nm laser.

REFERENCES

1. Yoshimoto, Kohei, Atsunobu Masuno, Motoi Ueda, Hiroyuki Inoue, Hiroshi Yamamoto, and Tastunori Kawashima. "Low Phonon Energies and Wideband Optical Windows of La2O3-Ga2O3 Glasses Prepared Using an Aerodynamic Levitation Technique." *Scientific Reports* 7, no. 1 (March 30, 2017): 45600. https://doi.org/10.1038/srep45600.
2. Kokubo, T., Y. Inaka, and S. Sakka. "Glass Formation and Optical Properties of Glasses in the Systems (R2O or R'O)-Ta2O5□Ga2O3." *Journal of Non-Crystalline Solids* 80, no. 1–3 (March 1986): 518–26. https://doi.org/10.1016/0022-3093(86)90440-0.
3. Ma, Xiaoguang, Zhijian Peng, and Jianqiang Li. "Effect of TA 2 O 5 Substituting on Thermal and Optical Properties of High Refractive Index LA 2 O 3 – NB 2 O 5 Glass System Prepared by Aerodynamic Levitation Method." Edited by J. Mauro. *Journal of the American Ceramic Society* 98, no. 3 (March 2015): 770–73. https://doi.org/10.1111/jace.13384.
4. Yoshimoto, Kohei, Atsunobu Masuno, Motoi Ueda, Hiroyuki Inoue, Hiroshi Yamamoto, and Tatsunori Kawashima. "Thermal and Optical Properties of La 2 O 3 –Ga 2 O 3 – (Nb 2

O_5 or Ta_2O_5) Ternary Glasses." *Journal of the American Ceramic Society* 101, no. 8 (August 2018): 3328–36. https://doi.org/10.1111/jace.15484.

5. Benmore, C. J., and J. K. R. Weber. "Aerodynamic Levitation, Supercooled Liquids and Glass Formation." *Advances in Physics: X* 2, no. 3 (May 4, 2017): 717–36. https://doi.org/10.1080/23746149.2017.1357498.
6. Masuno, Atsunobu. "Functionalities in Unconventional Oxide Glasses Prepared Using a Levitation Technique." *Journal of the Ceramic Society of Japan* 130, no. 8 (2022): 563–74. https://doi.org/10.2109/jcersj2.22073.