Advanced Low Gravity Characterization and Liquid-phase Synthesis of Non-equilibrium and Glassy Oxides

PROPOSED RESEARCH PLAN

Submitted to NASA Biological and Physical Sciences Division

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This plan lays out research priorities and a path towards implementing key elements of the NASA Biological and Physical Sciences Division program to address basic and applied scientific research and development opportunities and problems identified in the recent Decadal Survey. The research plan supports both fundamental discovery and applied/commercial development of space-based materials.

Keywords: Non-equilibrium liquids, oxide glass, properties, structure, modeling, containerless

Executive Summary

Materials processing in space and the investigation, development and commercialization of non-equilibrium materials and glasses are key aspects of NASA's BPS mission. The MATRICES project recommended by the Decadal Survey panels calls out key aspects that support development of new materials in space. These areas directly serve NASA space exploration mission and lay the basis to commercialize high value or enabling materials that can be produced in low gravity. The proposed program builds on a strong foundation to advance:

- Fundamental understanding of the principles of developing new non-equilibrium materials in space.

- Models of glass processing, structure and properties needed to develop new commercial products and products needed to enable NASA's exploration mission.

- Training, skill and workforce development in an area that is essential to meeting NASA's mission and relevant to next generation industrial glass development and utilization.

1. Relevance and Background

Cover of the recent Decadal Survey report [1].

The recent National Academy of Sciences, Engineering and Medicine Decadal Survey of Biological and Physical Sciences (BPS) report "Thriving in Space" identified eleven key scientific questions [1]. These questions will drive NASA's BPS program over the next 10 years. In the materials area, "What are the fundamental laws that govern the behavior of systems that are far from equilibrium?" was identified as an important basic and applied research question that can be addressed effectively using reduced gravity experiments as a major component of the program. The proposed research program directly approaches the topic as it relates to the prototypical non-equilibrium materials – supercooled liquids and glasses. The program focuses mainly on metal oxide based materials that are relevant to both space exploration and high value add commercial oxide glass and ceramic products [2,3].

The Decadal Survey recommends a broad materials research program that will underpin NASA's space exploration mission, address fundamental scientific questions, and lay the basis for developing commercial materials products. The use of reduced gravity will enable novel processes that exploit the control of heat and mass transport in liquids that are only possible in space. The proposed research program directly addresses several areas cited in the MATRICES project topic areas:

- Glasses and other amorphous materials made in space. Amorphous materials could be cooled sufficiently fast to avoid nucleation and crystallization. Containerless processing avoids nucleation owing to contamination of the container surface.
- Material behavior during processing in reduced gravity. Processing within this context may include extraction, refinement, manufacturing, and reuse/recycling.
- Phase change processes could include studies that can take advantage of a quiescent environment that promotes both mass and thermal diffusion that may lead to different morphologies of bubble nucleation distribution as well as growth.

- Combined measurements including properties.
- Effects of gravity on nucleation, growth, phase transformation, and the evolution of microstructure.
- New materials synthesis routes enabled by the space environment.

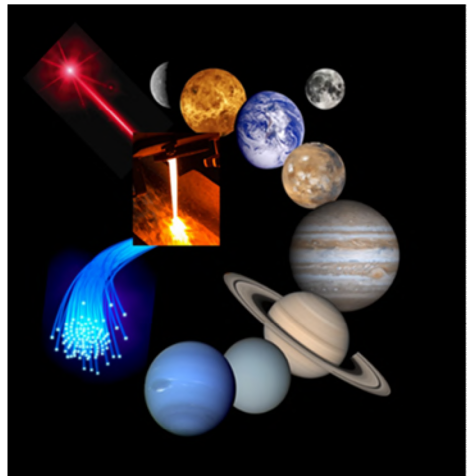


Image adapted from NASA/JPL.

The research will investigate materials processing in non-equilibrium and reduced gravity conditions. Materials of major interest lay the foundation for production of strategically (in terms of space exploration) and commercially valuable new glass products by non-equilibrium processing. Glasses lend themselves to additive manufacturing. This is an area currently being developed for fabrication of materials in space both for re-use and utilization of local resources [4,5]. Utilizing and recycling the resources is essential to sustain human missions and ultimately develop habitation.

Oxide materials are ubiquitous and abundant in nature. Much like Earth, the accessible surfaces of any planet that humans are likely to visit will be composed mainly of metal oxide-based regolith and/or water. Learning to harvest and use these materials in the local gravity and atmospheric conditions is an essential step to sustaining life and thriving in space.

On Earth, oxide materials and glasses are high value enabling materials for a wide variety of human activities. The global annual market for glass products alone is ~$230B, growing at a CAGR of ~5% [6]. The enabling qualities of functional glasses in technology lead to enormous leverage in value by creating new products and capabilities. New types of glass have been transformational in optical communications, lasers, photonic devices, displays, medical, energy conversion and transportation applications. Expanding the range of compositions and capabilities of glass has a strong commercial pull and numerous benefits to terrestrial life. Glasses are easily recycled and can displace alternative materials in many applications. An increased fundamental understanding how glass materials can be synthesized and how new properties can be developed in space will underpin advanced models of glass production that provide competitive advantage and accelerate development of new products.

Investigation of liquid phase processing benefits greatly from the enhanced control of fluid motions that can only be achieved in reduced gravity. As pointed out in the Decadal Survey, gravity-induced buoyancy and flow can mask important effects that determine the behavior of liquid (molten) materials. These factors are particularly significant in relation to non-equilibrium materials. The properties and structure of non-equilibrium materials is largely determined by synthesis path and conditions. As a practical matter, processing materials in reduced gravity requires a sophisticated understanding of how materials and fluid mixtures respond in the quiescent conditions of space.

A unified model of glass formation will be a major step forward in understanding the vitrification process. Toward this goal, measurements on supercooled liquids as they cool and form glass are important to answer questions about the mechanisms of vitrification. Understanding the extent to which glass forming behavior can be predicted from liquid properties and structure will help to guide the focus of experimental research efforts to improve functional glass properties.

The research addresses process-property-structure measurement and modelling of a variety of both strong and fragile liquids [3]. Unveiling the temperature and composition dependence of viscosity, density and structure of supercooled liquids above the glass transition temperature is essential to understanding fragile liquids. Measurements of atomic structure and using fundamental (*ab-initio*) models constrained with measured data to test and optimize them, is a key element of the research.

Supercooling and supersaturation are frequently means by which a system enters non-equilibrium. The degree to which this occurs depends on avoiding nucleation of new phases. Supercooling/supersaturation is essential to form glass from liquid precursors. Containerless processing (“levitation”) can enable deep supercooling/supersaturation of liquids by eliminating extrinsic heterogenous nucleation [7,8]. This process enables investigation of supercooled liquids and often formation of glass or amorphous materials that cannot be made by other methods. Containerless techniques can help to reveal the structural pathways through a variety of cooling routes. These “extreme” glasses can serve as benchmarks for glass discovery. Understanding how the thermophysical and thermodynamic properties and the structure of liquids changes as a function of supercooling will support models of liquids [9,10]. For example, correlation of melt and solution properties and structure with process parameters can provide needed data for machine learning based design of functional materials. Ultimately an important goal would be the development of first principles predictive models of properties from atomic pair potentials [10].

Fluid immiscibility, or phase separation, can result in formation of coexisting liquids with different chemical composition and usually different density [11,12]. In addition to diffusion, the morphology of such mixtures depends on convective transport and density driven sedimentation. Inhomogeneities or phase separation may be useful if they can be introduced into a liquid or glass in a controlled manner to develop periodic differences in density, composition, refractive index or hardness. The degree to which fluid motion affects phase separation and the morphology of resulting products will be crucial for space-based materials processing. Understanding how phase separation affects the stability of glasses that are prone to surface (interface) crystallization is needed for future *in-situ* resource utilization. The behavior of dissolved and exsolved gases can also result in two phase mixtures. Flow and buoyancy can move gas bubbles in liquids, and the magnitude of motion affects the ability to remove unwanted gases (fining). Understanding these aspects of glass processing is particularly important for making materials in reduced gravity.

The proposed research project builds to some extent on prior work. This has shown the promise but limited access, few opportunities to make replicate measurements, and the small number of investigations have left important questions unanswered.

2. Goals

Major objectives of the research are to:

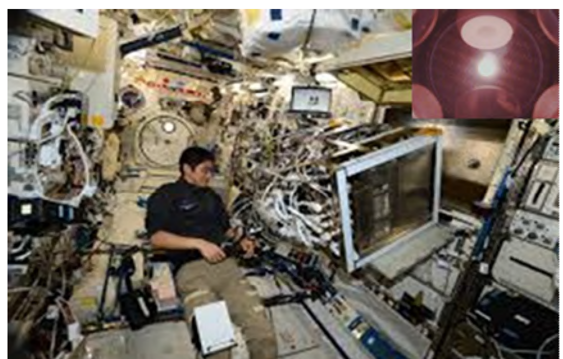
- Use low gravity containerless processing methods to synthesize and characterize melts and glass materials made from natural and artificial sources. The experiments will include measurements of thermophysical properties by using drop imaging and oscillation methods.

- Make ground-based measurements of melt and glass atomic structure and properties. Compare properties of Earth and space made glasses.
- Make ground-based measurements of the thermodynamic properties and energetics of Earth and space made glasses.
- Use models to correlate process-structure-properties to establish basis for development of new materials. Benchmark the models with measured data to establish reliability.
- Develop the basis for commercial applications of materials derived from space-based production and development of new materials. This will be done initially by demonstrating utility and then by developing intellectual property.

Results will be published in the open literature, used to develop intellectual property, and to develop the field and help to recruit students and workforce.

3. Implementation

A key element of the program is investigation of non-equilibrium states of matter (supercooled liquids, glasses, metastable crystalline and nanophase materials) at high temperatures. Prior art has established that containerless methods provide ideal conditions to investigate non-equilibrium liquids and to control melt chemistry at high temperatures [7,8]. Of the available containerless processing methods, electrostatic levitation (ESL) has significant advantages when compared to alternatives (*e.g.*, aerodynamic, acoustic, electromagnetic or optical levitation). ESL is already widely used for ground-based research on the thermophysical properties of metals (even molten tungsten has been successfully studied [13]), it is established for processing and measurements of thermophysical properties of liquid metal oxides on ISS. The pioneering work on ESL by Rhim, *et al*. [14] demonstrated levitation and property measurements on molten semiconductors. Other work has used ESL methods to investigate aqueous solutions and organic liquids [15].



The JAXA ELF instrument on the International Space Station. Inset shows an image of a levitated sample. Courtesy of JAXA.

An ESL in Low Earth Orbit (LEO) can effectively and inclusively serve the whole materials community. It will foster efficient discovery and enable rapid development of novel solutions to key problems in human exploration and commercial exploitation of space, including topics identified in the Decadal Survey report as both urgent and important.

The JAXA Electrostatic Levitation Furnace (ELF) has already been operated successfully on the ISS for several years [16]. During this time, a series of upgrades have been made to improve sample levitation performance, add imaging capabilities, and increase operational efficiency. The current life expectancy of the ISS is through ~2030. JAXA plans to continue operation of the current ELF instrument for the remaining life of ISS. JAXA is also evaluating operations beyond ISS, potentially using next generation LEO carriers that are being developed such as Axiom and Starlab.

During the ~7 years of remaining ISS operations, the ELF instrument will be systematically upgraded to provide additional capabilities and to tighten the specifications of existing capabilities. Timing and scope of any upgrades is dependent on funding levels and to an extent the demand from the scientific and commercial user communities. Upgrades under consideration include: (i) reducing the crew time needed to exchange sample holders (currently ~3 hours per exchange), (ii) improving the quality of sample imaging (particularly through the optical pyrometer), (iii) adding UHV/UHP gas handling for air-sensitive materials, (iv) adding a carbon dioxide heating laser to supplement the current diode laser beam heating [17], (v) modifying control capabilities to establish increased modulation of droplets, (vi) adding capabilities for *in-situ* optical property measurements, and (vii) providing operation in redox gases to precisely control (pO_2). Implementation of these upgrades will expand capabilities with minimal disruption of operations. By building on the successful and established ISS instrument platform, the work can be cost effective with relatively low risk and high potential payoff.

JAXA has an experienced and knowledgeable workforce who developed the ELF and took it from a concept to the current flight instrument. JAXA has a duplicate ELF instrument in their ground-based facility. This instrument is used for testing and development. Any upgrades that are developed will be tested and optimized before installation on the ISS unit. This approach effectively avoids the prohibitive cost of performing instrumentation engineering and development on ISS.

4. Outcomes

- Fundamental understanding of the principles of developing new non-equilibrium materials in space.
- Advances in models of glass processing, structure and properties needed to develop new commercial products and products needed to enable NASA's exploration mission.
- Training, skill and workforce development in an area that is essential to meeting NASA's mission and relevant to next generation industrial glass development and utilization.

5. Stakeholders

- NASA (and other participating space agencies, *e.g*. JAXA) by underpinning the BPS mission to develop technical approaches to sustaining human activities in space.
- Researchers in public and private universities by helping to attract and retain creative scientific talent needed to fulfil long term space missions, feed innovation in materials technology, and sustain the technology workforce of the future.
- Commercial materials manufacturers by developing workforce skillsets and discovering new scientific insight. Access to developing proprietary knowledge by investigating materials in reduced gravity.

Overall, the benefits of this will directly address BPS needs and mission, help to maintain US materials competitiveness, and advance the application of new materials in solving applied problems.

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