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FELLOWSHIP FINAL REPORT

Mechanisms of glass crystallization analyzed by electron backscatter diffraction (EBSD)

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REPORT INFO

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ABSTRACT

This Le Studium Fellowship was used to analyze the crystal growth in levitated melts. Furthermore, methodical questions concerning the method EBSD as well as XRD were addressed. Finally, the literature concerning oriented surface nucleation in glasses was completed.

1- Introduction

The goal of this Le Studium fellowship was to improve the knowledge in the field of glass crystallization mechanisms and develop innovative glass ceramics in collaboration with M. Allix at the CEMHTI laboratory on the CNRS campus in Orléans. As the access to a functioning EBSD system was severely limited because the intended analysis system was not delivered during the stay, this Le Studium research fellowship was also used to address alternative topics of interest to the wider scientific community. Altogether four topics were considered:

a) The possibility of mis-indexing during EBSD analysis due to EBSD-pattern superposition, an aspect of interest to the EBSD-community.

b) Crystal growth in levitated melts in the Ga_2O_3-La_2O_3 system, i.e. addressing the primary goal of the fellowship.

c) Oriented surface nucleation in inorganic Glasses, reviewing the work of 10 years towards this fundamental aspect of glass-crystallization and discussing possible causes for this yet unexplained effect.

d) Experimental measurements to determine the information depth significant to XRD in the Θ-2Θ setup. This method has been established for many years and is widely applied, but experimental confirmation of its information depth stated in the literature has not been provided. This is especially relevant when analyzing compact samples with layers of different crystal phases or crystallographic textures.

2- Experimental details

a) Individual EBSD-patterns indexed as ZnY_2O_4 in a Y_2O_3 matrix were analyzed in detail. For further details, please see Ref. [1].

b) Cross sections of three beads crystallized during the cooling after levitation melting were analyzed by EBSD to determine which mechanisms of crystallization occurred.

c) The entire work concerning oriented nucleation in glasses was reviewed and two models of possible causes for this effect are formulated and discussed. See Ref. [3].

d) A thin layer of µ-cordierite crystals was produced in a glass. Then the sample was flipped upside down and embedded in a polymer matrix. Subsequently, the glass layer was carefully thinned while performing repeated XRD-scans. The thickness of the glass layer through which the first signal of the crystallized layer could be obtained logically represents the minimum information depth significant to XRD in a material of this density. It is correlated to the calculations of the information depth so as to determine the correct cut off value for the latter. This cut off value allows any user to calculate the approximate information depth of XRD in any material of a known density.

3- Results and discussion

a) All analyzed EBSD-patterns indexed as ZnY_2O_4 were found to in fact be superpositioned EBSD-patterns of Y_2O_3. The existence of ZnY_2O_4 could not be verified by neither EBSD, EDXS nor XRD. This possible artifact must be considered when performing EBSD-measurements across grain boundaries. For further details, please see Ref. [1].

b) A opaque bead primarily contained dendritic $LaGaO_3$. A transparent but polycrystalline bead showed the desired phase $Ga_3La_2O_{7.5}$ crystallized in a thermal gradient. Another transparent bead showed only a single crystal orientation in the analyze cross section, indicating is crystallized via flash crystallization.

While these three very different results from one experimental procedure indicate that more control over the process must be gained, the third bead proved the possibility of producing single crystals of several mm diameter via levitation melting. This means levitation melting can be used to produce single crystals for e.g. optical components, a hypothesis long held by M. Allix and finally proven.

c) Oriented nucleation seems to rather be the norm in surface crystallizing glasses than the exception. Hence assuming random nucleation in the classic nucleation theory for glasses is incorrect. Fundamentals of glass crystallization must be reconsidered taking this into account. For further details, see Ref. [3].

d) The significant information depth of XRD using K_α radiation in the Bragg-Brentano setup for a material of the density 2.59 g/cm^3 is most probably larger than 48 µm but smaller than 118 µm. 48 µm corresponds to of 67% the penetration depth of this radiation under an entry angle of 90°. This cut off value enables to calculate a minimum significant information depth of XRD for any material using any X-radiation.

4- Conclusion

a) ZnY_2O_4 was not detected and the literature concerning this phase is very questionable. EBSD data must always be treated with care, misindexing due to EBSD-pattern superposition can occur in the applied software.

b) Levitation melting can lead to various microstructures. More control over the process must be gained to increase the reproducibility of the process. The potential for producing single crystals via levitation melting is proven.

c) Oriented nucleation seems to be the norm during the surface crystallization of glasses instead of the random nucleation previously assumed.

d) The significant information depth of XRD is most likely larger than 48 µm for the chosen material. Hence it is significantly larger than usually assumed.

5- Perspectives of future collaborations with the host laboratory

The performed work concerning the crystallization of levitated melts enabled to develop clear steps that are now being taken to evolve the experimental setup with the goal of producing single crystals via aerodynamic levitation. This work increased the knowledge concerning the abilities but also limitations of the method EBSD in the local group.

Further collaborative work concerning the crystallization of glasses and melts in similar samples is possible.

6- Articles published in the framework of the fellowship

a) W. Wisniewski, P. Švančárek, M. Allix: Attempting to Verify the Existence of ZnY_2O_4 using Electron Backscatter Diffraction (EBSD), *ACS Omega* **2020**, *5*, 17576-17581.

b) W. Wisniewski, M. J. Pitcher, E. Veron, J. Fan, V. Sarou-Kanian, F. Fayon, M. Allix: Macroscopic Orientation Domains grown via Aerodynamic Levitation - a Path towards Single Crystals, *Cryst. Growth. Des.* submitted 2021.

c) W. Wisniewski, C. Rüssel: Oriented Surface Nucleation in Inorganic Glasses - A Review, *Progr. Mater. Sci.* **2021**, *118*, 100758.

d) W. Wisniewski, C. Genevois, E. Veron, M. Allix, Experimental Evidence concerning the Significant Information Depth of X-Ray Diffraction (XRD) in the Bragg-Brentano Configuration, *ACS Advances* submitted 2021.

7- Acknowledgements

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8- References

[1] W. Wisniewski, P. Švančárek, M. Allix: Attempting to Verify the Existence of ZnY_2O_4 using Electron Backscatter Diffraction (EBSD), *ACS Omega* **2020**, *5*, 17576-17581.

[2] W. Wisniewski, M. J. Pitcher, E. Veron, J. Fan, V. Sarou-Kanian, F. Fayon, M. Allix: Macroscopic Orientation Domains grown via Aerodynamic Levitation - a Path towards Single Crystals, *Cryst. Growth. Des.* submitted 2021.

[3] W. Wisniewski, C. Rüssel: Oriented Surface Nucleation in Inorganic Glasses - A Review, *Progr. Mater. Sci.* **2021**, *118*, 100758.

[4] W. Wisniewski, C. Genevois, E. Veron, M. Allix, Experimental Evidence concerning the Significant Information Depth of X-Ray Diffraction (XRD) in the Bragg-Brentano Configuration, *ACS Advances* submitted 2021.