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# Searching for new crystalline compounds by combining glass-crystallisation synthesis with compositional prediction methods: the SrO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system as a test case

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## Abstract

The discovery of inorganic oxides with new compositions and crystal structures is important in many technological fields, because it can lead to new materials with improved performance, lower cost, better environmental sustainability or less reliance on strategically sensitive raw materials. However, progress in this field is not straightforward, firstly because conventional ceramic synthesis methods tend to disfavour the isolation of metastable products, obscuring a potentially vast pool of candidate materials, and secondly because there is an unapproachable number of element combinations for exploration, so that exhaustive trial-and-error synthesis approaches are impractical. These problems have driven interest in alternative oxide synthesis methods that operate at lower temperatures, bringing the domain of metastable oxides into reach, and in various computational approaches which identify promising targets for synthesis, thus focusing synthesis efforts only on the most interesting compositional regions.

In this context, glasses (and their parent under-cooled melts) can be considered as ideal precursors for exploratory oxide synthesis: they can be crystallised at substantially lower temperatures than the equivalent ceramic reaction, which allows metastable crystalline solids with unusual and surprising features to be isolated. For example, we recently showed that the crystallisation of YAG glass or melt below 1000°C permits highly nonstoichiometric derivatives such as Y<sub>3.4</sub>Al<sub>4.6</sub>O<sub>12</sub> to be isolated, which are totally inaccessible at the standard ceramic synthesis conditions of 1650°C.<sup>(1)</sup> When harnessed to apparatus such as laser-coupled aerodynamic levitation, a relatively wide range of compositions can be addressed that is not restricted to classic glass-forming systems. At the same time, computational tools based on crystal structure prediction have recently been developed to guide exploration of complex phase fields. In particular, the probe structure approach allows the identification of compositional regions that are most likely to yield stable crystalline compounds,<sup>(2)</sup> but it has previously only been deployed alongside ceramic synthesis methods. Here, I will describe how glass-crystallisation (as a non-equilibrium synthesis method) has been coupled to the probe-structure prediction method to isolate a new compound, Sr<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>, from the previously well-explored phase diagram SrO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, selected as a test case due to its

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large glass-forming domain and its ability to host functional properties such as luminescence phosphor hosts and transparent ceramics.  $\text{Sr}_2\text{Si}_3\text{O}_8$ , which adopts a distorted variant of the  $\text{Ba}_2\text{Si}_3\text{O}_8$  crystal structure, is the first example of a strontium silicate with an extended  $(\text{SiO}_4)$  network. In principle this methodology can be applied to other glass-amenable phase fields to find new crystalline compounds with interesting properties.

#### References

- (1) W. Cao, A. I. Becerro, V. Castaing, X. Fang, P. Florian, F. Fayon, D. Zanghi, E. Veron, A. Zandonà, C. Genevois, M. J. Pitcher and M. Allix, *Advanced Functional Materials*, 2023 (in press)
- (2) C. Collins, M. S. Dyer, M. J. Pitcher, G. F. S. Whitehead, M. Zanella, P. Mandal, J. B. Claridge, G. R. Darling and M. J. Rosseinsky, *Nature*, 2017, **546**, 280–284.

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