Glass- Crystallisation Synthesis and Characterisation of the New Strontium Silicate Compound Sr2Si3O8

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Abstract

Glass-crystallisation has proved to be an innovative technique in the synthesis of new metastable oxides with interesting properties. Using it the discovery of the novel phase 'Sr2Si3O8' in the SrO-SiO2-Al2O3 ternary diagram was made possible. Computational prediction, based on probe structure energy calculations, of stable compositions aided the discovery of this phase by allowing a focused and accelerated approach to be adopted when examining the ternary diagram.1,2 Variable temperature X-ray diffraction (VTXRD) was used to find the optimum synthesis conditions of this previously undiscovered phase; glass crystallisation with a heat treatment of 850∘C for 12h. Synthesis of this composition was also later achieved by aerodynamic levitation (ADL), although not to as high a degree of crystallinity. Even though the initial precursor glass composition contained aluminium, the crystal structure (solved from PXRD and neutron diffraction) showed it to be Al-free, with the remaining non-crystallised glass being Al-rich, as confirmed by multi-nuclear MAS-NMR and TEM-EDX. The crystal was found to have a monoclinic, $P21/c$, unit cell, with corner sharing SiO4 units forming Zwier ribbon chains in-between 7- or 8- coordinated Sr sites. Comparison with the known phase, Ba2Si3O8, showed the structures to be similar but not isostructural with the difference being a cooperative twisting of Sr2Si3O8's external SiO4 chains creating distorted hexagonal rings.3 Attempts at synthesising the Sr2Si3O8 phase without aluminium in the glass matrix were discouraging as while the sample's crystalline phase fraction was high, in excess of 85%, the peak widths were broad compared to the aluminium containing analogue. High energy ball milling of the glass was tried to help solve this issue by reducing particle size and therefore encouraging surface crystallisation, however while it did reduce the optimum synthesis temperature to 800∘C it did not reduce Bragg peak widths. Same group elements, barium and calcium, were then tried as dopants and nucleating agents such as ZrO2, AgNO3 and Au were independently added to the glass in the hopes of improving stability and crystallinity, thus allowing detailed microstructural analysis under TEM measurement conditions. Differential scanning calorimetry (DSC) analysis proved to be in good agreement with the VTXRD results of all the samples and appeared to show two types of behaviour. Both the dopants and nucleating agents decreased the crystalline phase

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fraction, however while the former also increased peak widths the latter decreased it. This result was unexpected as it was thought that an increase in peak resolution would also lead to an increase in crystalline phase fraction, hence the need for SEM and TEM microstructure analysis to determine the cause. The discovery of metastable Sr2Si3O8 has proven that glass-crystallisation and other innovative synthesis methods, can be harnessed to computational approaches to isolate new materials even in well explored phase diagrams. The main aim of this project is the exploration of other complex phase diagrams by these methods, like the CaO-SiO2-Al2O3 system, to discover new compounds with potentially useful properties.

References

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