In-situ characterization of the High-Pressure High-Temperature synthesis of tetragonal Na_2Si_3

Leon SCHÜTTE (ICGM, France),
Doaa O. A. ALI (ICGM, France),
Rana GHANNAM (ICGM, France),
Dmitrii DRUZHBIN (ESRF, France),
Michael M. KOZA (ILL, France),
Jérôme ROUQUETTE (ICGM, France),
Mickaël BEAUDHUIN (ICGM, France),
Wilson A. CRICHTON (ESRF, France),
Romain VIENNOIS (ICGM, France)

Abstract

In a world of climate change and limited natural resources, the urgent need for sustainable energy technologies drives the search for novel functional materials made of abundant, non-toxic, and low-cost elements. In this context, sodium silicides are emerging as promising candidates for photovoltaics, energy storage, and thermoelectric applications. While the Na-Si phase diagram has been relatively unexplored, *in-situ* synchrotron techniques and high-pressure high-temperature (HP-HT) synthesis have enabled the search for additional phases. [1, 2]

At ambient pressure, NaSi is the only thermodynamically stable phase, but three metastable phases have also been reported: Type I clathrate Na_8Si_{46} and type II clathrate $Na_{x<24}Si_{136}$ consists of a framework of Si cages that are filled with sodium ions. The third known structure, $NaSi_6$, was first discovered by Kurakevych *et al.* through *in-situ* monitoring of high-pressure high-temperature (HP-HT) synthesis. [1, 2, 3]

We report the discovery of a new Na_2Si_3 phase, formed under HP-HT conditions in the large volume press (LVP) located at the ID06-LVP beamline (ESRF) and identified using *in-situ* synchrotron X-ray diffraction. Na_2Si_3 was formed using a 10/5 multianvil assembly near 5 GPa at around 510 °C and is recoverable to ambient pressure and temperature. Additionally, we have explored different HP-HT synthesis paths for Na_2Si_3.

Na_2Si_3 adopts a tetragonal structure composed of two-dimensional layers of silicon, separated by sodium ions. The bonding can be rationalized within the Zintl-Klemm framework with a formal charge distribution $(Na^+)_2(Si^0)(Si^-)_2$. *Ab initio* calculations confirmed this structure and predicted an indirect band gap of ~1.14 eV at ambient pressure, making Na_2Si_3 interesting for applications in photovoltaics and thermoelectricity. [4]

These findings highlight the importance of combining *in-situ* HP-HT experimentation with theoretical modelling to discover novel metastable materials.

[1] H. Morito, T. Yamada, T. Ikeda, H. Yamane, Journal of Alloys and Compounds. 2009, 480, 723-726.

[2] O. A. Kurakevych, T. A. Strobel, D. Y. Kim, T. Muramatsu, V. V. Struzhkin, Crystal Growth Des. 2013, 13, 303-307.

[3] C. Cros, M. Pouchard, P. Hagenmuller, J. Solid State Chem. 1970, 2-570-581.

[4] M. Redington, L. Schütte, D. O. A. Ali, D. Druzhbin *et al.*, submitted to Inorganic Chemistry, 2026.