

## THE SYSTEM $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ : 90 YEARS OF RESEARCH, BUT DO WE REALLY KNOW EVERYTHING ?

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In their landmark paper from 1925 MOREY & BOWEN presented the first comprehensive description of the phase relationships and melting behavior of the compounds belonging to the ternary system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ . Due to its fundamental importance for many fields of industrial inorganic chemistry and technical mineralogy this system has been in the focus of a large number of subsequent studies dealing with both basic and applied aspects of silicate science (SEGNIT, 1953; SHAHID & GLASSER, 1971; WILLIAMSON & GLASSER, 1965; ZHANG et al., 2011). After more than 90 years of research activities one should assume that no problems remain to be solved.

In the course of an ongoing project on the high-temperature chemistry of compounds in the systems  $\text{M}_2\text{O}-\text{RO}-\text{SiO}_2$  (M: Na, K; R: Ca, Sr, Ba) we realized that even for the most intensively studied Na-Ca-silicates suspicion has to be attached not only to what concerns their melting characteristics but also to what concerns the number of existing phases. Despite the compounds whose existence has been unequivocally proofed by a combination of chemical analysis and crystal structure determination there is still a large number of phases mentioned in the literature which, at best, have been characterized by unindexed powder diffraction patterns. Furthermore, in many cases even the compositions have not been thoroughly studied after synthesis. This information, however, is definitely of great importance when dealing with volatile components such as  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  at temperatures above  $1000^\circ\text{C}$ .

We were able to demonstrate that  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ , for example, which has been first synthesized via hydrothermal methods by ARMBRUSTER & RÖTHLISBERGER (1990) can be also obtained under dry conditions using  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$  as educts. Therefore, the ternary phase diagram, where this compound has not been taken into consideration, has to be revised. In-situ high-temperature powder diffraction experiments were used to determine the thermal expansion tensor of  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$  between ambient temperature and  $1100^\circ\text{C}$ . Furthermore, the crystal structure of a new high-temperature polymorph of the compound has been determined.

Finally, comprehensive synthesis experiments using solid state reactions as well as re-crystallization studies from glasses revealed that several previously described sodium calcium silicates such as  $\text{Na}_8\text{Ca}_3\text{Si}_5\text{O}_{17}$ ,  $\text{Na}_2\text{Ca}_3\text{Si}_2\text{O}_8$  and  $\text{Na}_2\text{CaSi}_5\text{O}_{12}$  could not be reproduced indicating that a question mark has to be put on their existence.

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