# A New Hydrothermal Route for the Preparation of $Na_4Zr_2(SiO_4)_3$

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$Na_4Zr_2(SiO_4)_3$ has been prepared hydrothermally from the reaction of $NaZr_2(PO_4)_3$ with $Na_2SiO_3$ under lower temperature and pressure conditions of crystallization than used previously, and identified by *X*-ray powder diffraction, and Raman and $^{29}Si$ MAS NMR spectroscopy.

$Na_4Zr_2(SiO_4)_3$ is the end member of the Nasicon family[1] ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$; $x$ = 0—3), in which $SiO_4$ replaces $PO_4$ completely, and has been synthesized by different methods. Hydrothermal preparations of $Na_4Zr_2(SiO_4)_3$ from the $Na_2O$–$ZrO_2$–$SiO_2$–$H_2O$ system have been studied by Alyamovakaya and Genet *et al.*,[2,3] but these were generally carried out at 300—600 °C with a pressure of >400 bar,[4] making it difficult to obtain a pure $Na_4Zr_2(SiO_4)_3$ phase.

Recently we have synthesized $NaZr_2(PO_4)_3$, the other end member of the Nasicon family, by hydrothermal crystallization at 250 °C. We thought that $Na_4Zr_2(SiO_4)_3$ could be obtained by substitution of $SiO_4$ for $PO_4$ in $NaZr_2(PO_4)_3$

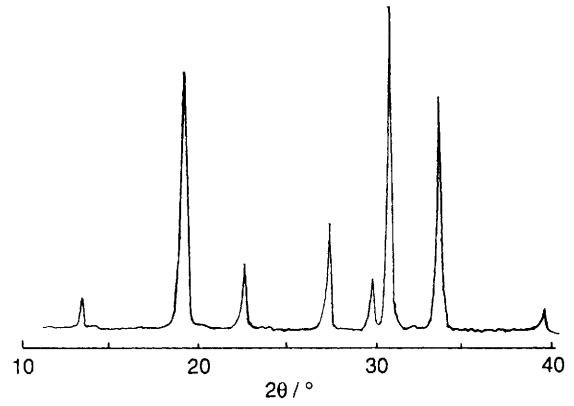


**Figure 1.** *X*-Ray diffraction pattern of $Na_4Zr_2(SiO_4)_3$ prepared from $NaZr_2(PO_4)_3$ (Cu-$K_\alpha$, λ 1.5418 Å).

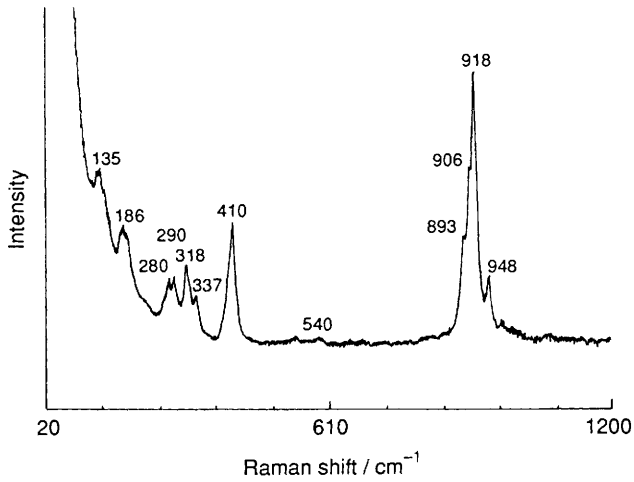


**Figure 2.** Raman spectrum of the product (excitation at 488.0 nm; 100 mW).

under conditions such that the content of zirconium was constant, and the reactions of $NaZr_2(PO_4)_3$ with $Na_2SiO_3$ in excess of NaOH under hydrothermal conditions have therefore been investigated. We now report the results of these experiments and the characterization of the product.

The hydrothermal reaction of $NaZr_2(PO_4)_3$ with $Na_2SiO_3$ was carried out in an autoclave with a Teflon liner. $Na_2SiO_3$ was dissolved in deionized water, and $NaZr_2(PO_4)_3$ and excess of NaOH were added. The ratio of $NaZr_2(PO_4)_3$ to $Na_2SiO_3$ was 1 : 3.5—4. The autoclave was *ca.* 60% filled so that the pressure reached *ca.* 120 atm. Heating at 290—300 °C for 48—72 h led to the main reaction (1) occurring. The products were filtered off washed, and dried in air.

$$NaZr_2(PO_4)_3 + 3\ Na_2SiO_3 + 6\ NaOH \rightarrow Na_4Zr_2(SiO_4)_3 + 3\ Na_3PO_4 + 3\ H_2O \quad (1)$$

*X*-Ray powder diffraction of the samples (Figure 1) gave the characteristic pattern of $Na_4Zr_2(SiO_4)_3$, which is identical to that published by Tran Qui *et al.*[5] The Raman spectrum of the products (Figure 2) was similar to that already published.[3] To investigate the state of silicon in the product, the high-resolution solid-state $^{29}Si$ magic-angle-spinning NMR spectrum was recorded (Bruker MSL-400 spectrometer; 79.46 MHz). The spectrum showed a single line at 88.6 ppm relative to $SiMe_4$, corresponding to that in previous work,[6] indicating that only substitution of silicon for phosphorus had occurred. All measurements have therefore confirmed that $Na_4Zr_2(SiO_4)_3$, prepared by the new hydrothermal route, is a stoicheiometric and pure compound.

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