Hydrothermal Synthesis and Characterization of Sodium Dititanium Triphosphate

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Sodium dititanium triphosphate has been synthesized hydrothermally from the Na_2O–TiO_2–P_2O_5–P_2O_5–H_2O system, and characterized by *X*-ray powder diffraction and Raman and IR spectroscopy.

$NaTi_2(PO_4)_3$, which has a NASICON-type structure (space group $R\bar{3}c$) with a three-dimensional network of PO_4 tetrahedra corner-shared with TiO_6 octahedra, has been prepared previously by melting together $NaPO_3$ and TiO_2,[1] and by other solid-state reactions.[2] However, there have been no reports of a hydrothermal synthesis. We report here a novel method, hydrothermal crystallization, for the synthesis of $NaTi_2(PO_4)_3$.

Hydrothermal crystallization of $NaTi_2(PO_4)_3$ was carried out in a stainless steel autoclave with a Teflon liner under

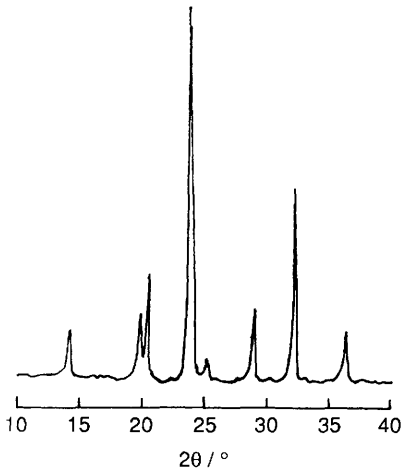

Figure 1. *X*-Ray powder diffraction pattern of the product.

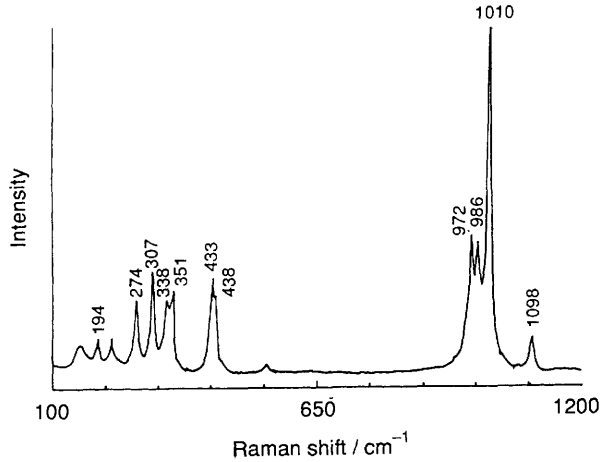

Figure 2. Raman spectrum of the product.

autogenous pressure. TiO_2 (anatase), 85% orthophosphoric acid, and NaOH solution (2 M), a mineralizer, were mixed in the molar ratio 4 Na_2O : 0.5 TiO_2 : 12 P_2O_5 in the Teflon liner. The autoclave was sealed and heated in an oven at 250 °C for 5—7 days. After cooling, the product was filtered, washed with distilled water, and dried at ambient temperature. The crystalline product was identified by means of *X*-ray powder diffraction and IR and Raman spectroscopy.

The *X*-ray powder diffraction pattern of the product (Figure 1), recorded with a Rigaku D/MAX-IIIA diffractometer using Cu-K_α (λ = 1.5418) radiation, is similar to that of $NaTi_2(PO_4)_3$ obtained from solid-state reactions by others.[3] The product is free of TiO_2 and other impurities. The Raman spectrum (Figure 2) was recorded on a Ramanor SPEX 1403 double spectrometer with an argon-ion laser (488.0 nm line, 100 mW). The spectrum is unique and quite characteristic of $NaTi_2(PO_4)_3$[4] with a strong peak at 1010 cm^{-1}, and weaker peaks at 432—194 cm^{-1}. The IR spectrum shows absorption bands at 500—660 cm^{-1} and 900—1200 cm^{-1}, which are attributed to PO_4 bending and stretching vibrations. The absorptions at 1645 and 3450 cm^{-1} could be assigned to the vibrations of water and $(OH)^-$,[1] respectively.

DTA–TG (differential thermal analysis–thermogravimetric analysis) shows that $NaTi_2(PO_4)_3$ synthesized hydrothermally was stable at 1200 °C. TG curves show that 7.8% of the weight is lost continuously when the sample is heated from room temperature to 1200 °C. After heating, the water bands disappear in the IR spectrum. Therefore it seems that $NaTi_2(PO_4)_3$ synthesized hydrothermally contains a small amount of water which is probably zeolitic in nature.[5]

In summary, a new method for the synthesis of $NaTi_2(PO_4)_3$ by hydrothermal crystallization is reported. The product is the same as that of the solid-state reaction and contains a little zeolitic water.

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