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Synthesis of 11 Å Al-substituted tobermorite from trachyte rock by hydrothermal treatment

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Abstract

The alkaline hydrothermal activation of trachyte rock led to synthesis of technologically important 11 Å tobermorite. Tobermorite synthesis was studied by X-ray diffraction, scanning electron microscopy and ^{29}Si and ^{27}Al high resolution magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. The influence of the reaction conditions such as different temperatures (150–170 °C), times (5–20 h) as well as different Ca/Si ratios of 0.6, 0.9 and 1.3 on tobermorite formation were investigated. The results showed that the main rock constituents were completely converted into a well crystallized Al-substituted 11 Å tobermorite when hydrothermally activated with 3.0 M NaOH under the optimum hydrothermal conditions of 170 °C for 20 h and using Ca/Si and Al/Al + Si ratios of 0.9 and 0.17, respectively. The local structure of the synthesized tobermorites as determined by MAS-NMR spectroscopy implied an alumino-silicate mean chain length of 5.9 units with 79% of the interlayer cross-links which are of ≡Si–O–Al≡ configuration. The present results show that trachyte rock could be considered as a new economic resource for synthesizing Al-substituted 11 Å tobermorites.

Keywords: Al-substituted tobermorite; Trachyte; Hydrothermal synthesis; ^{29}Si and ^{27}Al MAS-NMR spectroscopy

1. Introduction

Tobermorites are layered calcium silicate hydrate minerals with an ideal $Ca_5Si_6O_{18}H_2\cdot 4H_2O$ composition [1]. Natural tobermorites are found as veins or filling amygdales in hyper-alkaline, hydrothermal environments as the alteration products of basic igneous rocks by hydrothermal fluids [2,3]. Tobermorites are commonly used as autoclaved concretes, which serve as non-asbestos, heat insulating and fire-resistant building materials as well as adsorbents for organic or inorganic effluents [4,5]. They can also be used as cation exchangers in the decontamination of radioactive species from low-level nuclear wastes [6–12]. Synthetic tobermorites have been discovered by Komarneni et al. [9] and Komarneni and Roy [13] as a new family of cation exchangers with an intermediate cation exchange and selectivity properties between those of clays and zeolites. The coupled substitution of [$Al^{3+} + Na^+$] or [$Fe^{3+} + Na^+$] for Si^{4+} in the synthetic forms results in selective ion exchange properties for heavy metals such as Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+} and Cs^+ from aqueous solutions [7,9] that are superior to zeolites.

The natural, orthorhombic, rarely monoclinic 11 Å tobermorite is the most technologically important mineral of the tobermorite family [2,14]. Its ideal layer structure consists of an infinite layer of seven-coordinated Ca–O polyhedra linked on both sides to wollastonite-like silicate chains in an arrangement parallel to the *b*-axis, and stacked in the *c*-axis direction (Fig. 1) [15]. The vicinity of the interlayer forms a channel running along the *b*-axis direction where exchangeable calcium ions and water molecules are accommodated [16–19]. Tobermorite minerals are named according to their *c*-axis length which mainly depends on the number of water molecules per formula unit. Accordingly, the approximate *d*-spacing of the (0 0 2) Bragg reflection (i.e. the basal spacing) of 11 Å tobermorite lies

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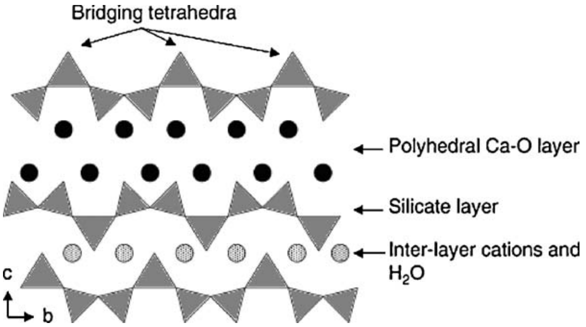

Fig. 1. Structural projection of 11 Å tobermorite in the *bc*-plane, showing the dreierkette chains of tobermorite where the silicate tetrahedra share O–O edges with the central Ca–O layer [15].

in the range of 11.2–11.7 Å. The deviation from the ideal structure is due either to breaks in the silicate chains which cause extensive layer stacking, or due to some compositional variation such as the coupled isomorphous replacement of up to 15% Al^{3+} for Si^{4+} with spontaneous OH– for O^{2-} substitution and/or additional interlayer calcium or alkali ions [7,8,20–22].

Natural tobermorites are usually more highly crystalline than synthetic ones; however, their rare occurrence is the main reason for the production of synthetic alternatives. Synthetic 11 Å tobermorites and their Al- and Fe-substituted forms have been readily synthesized under saturated steam or hydrothermal conditions at temperatures between 80 and 225 °C from a range of starting materials including various mixtures of the following: lime, zeolites, quartz, gibbsite, cement, clays, fly ash, sodium silicate and aluminum chloride; and more recently, a number of industrial by-products [7,21,23,24]. Al-substituted 11 Å tobermorite has been synthesized from newsprint recycling residue comprising gehlenite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$), β-dicalcium silicate (Ca_2SiO_4) and anorthite ($CaAl_2Si_2O_8$) under hydrothermal conditions at 100 °C for 1–2 days in the presence of NaOH [23,25]. In a recent study, hydrothermal alkaline activation of oil shale fly ash converted it to mainly 11 Å tobermorite after 24 h treatment under hydrothermal conditions at 160 °C in the presence of NaOH. Tobermorite fibers 40–100 μm in length and 0.1–1 μm in diameter were hydrothermally synthesized at 200 °C for 5 h, using a solution containing silicate ions and Ca(II)–EDTA complex precursor [26]. The starting Ca/Si molar ratio did not greatly influence the phase and morphology of tobermorite but determined its final composition.

Recently microwave heating has been used in tobermorite synthesis to increase the kinetics of crystallization [12]. A highly crystalline Al-substituted tobermorite with high cesium ion selectivity was rapidly synthesized in 2 h at 180 °C under microwave heating, from two zeolites (natural phillipsite and Linde 3A zeolite), calcium oxide, sodium silicate, aluminum chloride and sodium hydroxide.

As mentioned above, there is a notable relation between basic volcanic rocks and the formation of natural tobermorites [27]. Therefore, natural rocks with their great economic potential were used in this work to reduce the cost of production by substituting them for chemical reagents in the synthesis of tobermorites. Tobermorite synthesis as proposed in this paper refers to mineral crystallization by a facile chemical treatment of natural alkali aluminosilicates derived by direct alkali-solution hydrothermal treatment of an inexpensive alkali volcanic rock (trachyte). Trachyte rocks are a group of fine-grained, generally porphyritic, extrusive igneous rocks consisting of alkali feldspar (usually sanidine) and minor mafic minerals as the main components, and possibly a small amount of sodic plagioclase [28].

2. Experimental

2.1. Chemicals and materials

The trachyte was supplied as igneous extrusive hand specimens (Ward's Catalog Reference #47-8273) by Ward's Natural Science Establishment, Inc., Rochester, NY, USA. The other chemicals used in the synthesis were NaOH pellets (Baker analyzed ACS reagent grade, 98.6% NaOH + 0.4% chloride), and ACS reagent grade $Ca(OH)_2$, 98+% (Aldrich Chemical Company, Inc.).

2.2. Synthesis

Fig. 2 shows the flow chart for tobermorite synthesis from trachyte. The trachyte powder of particle size <63 μm was treated with 3.0 and 5.0 M NaOH solutions. The calculated amount of calcium hydroxide was then added, based on the Ca/Si ratio of the C–S–H formula of tobermorite. The batch constituents were stirred for 30 min to form the raw slurry (RS) used to obtain the tobermorite phase. This slurry was placed in a 125 ml Parr-type vessel lined with Teflon and heated at temperatures between 150 and 170 °C for times of 5–20 h. The solid product was collected, washed with distilled water, centrifuged several times and dried overnight for phase characterization.

2.3. Characterization

The chemical composition of trachyte was measured by X-ray fluorescence (XRF) using an AXIOS WD-XRF Sequential Spectrometer (Panalytical, 2005). The end window Rhodium (Rh) anode tube was operated at up to 60 kV and current up to 160 mA at a maximum power level of 4 kV. Phase identification was carried out by XRD Scintag diffractometer; model XDS 2000 with Ni-filtered Cu Kα radiation. The patterns of all synthesized phases were recorded in the range of 4–45° 2θ and compared to the following JCPDS data base reference cards; 97-045-1480, 97-007-3393 and 97-004-0315 for 11 Å tobermorite [$Ca_5Si_6(O,OH,F)_{18}\cdot 5H_2O$], Al-substituted tobermorite [$Ca_{4.9}(Si_{5.5}Al_{0.5}O_{16.3})(OH)_{0.7}(H_2O)_5$] and sodalite [$Na_8(Al_6Si_6O_{24})$], respectively. The morphology and particle size was observed by scanning electron microscopy, Philips XL30 with an attached EDX unit, using an accelerating voltage of 30 kV, magnification 10× up to 400,000× and resolution for W (3.5 nm). The ^{27}Al and ^{29}Si MAS-NMR (magic angle spinning nuclear magnetic resonance) spectra were acquired at 11.7 T using a Bruker Avance 500 spectrometer and 4 and 5 mm Doty MAS probes spun at 10–12 kHz for Al and 6 kHz for Si. A 1 μs