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Synthesis, structure and ion exchange properties of 11 Å tobermorites from newsprint recycling residue

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Abstract

Al-substituted 11 Å tobermorites were obtained from stoichiometrically adjusted mixtures of newsprint recycling waste, sodium silicate and calcium oxide via hydrothermal synthesis at 100 °C. Hydrothermal processing in water yielded a highly crystalline 11 Å tobermorite product with a Cs^+ cation exchange capacity of 85 meq 100 g^{-1} and selective Cs^+ distribution coefficient of $\sim$5500 $cm^3\ g^{-1}$. Conversely, a product of inferior crystallinity was obtained from hydrothermal synthesis in alkaline liquor whose Cs^+ ion exchange capacity and selective Cs^+ distribution coefficient were found to be 66.3 meq 100 g^{-1} and $\sim$700 $cm^3\ g^{-1}$, respectively. Silicate chain configuration was found to have a modest impact on the number of cation exchange sites per unit cell, whereas the influence of structural defects on selectivity was more pronounced. The structures and ion exchange credentials of both 11 Å tobermorite products corresponded well with those of their essentially phase-pure counterparts.

Keywords: A. Ceramics; A. Layered compounds; B. Chemical synthesis; C. Nuclear magnetic resonance (NMR); D. Crystal structure

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1. Introduction

Tobermorites are rare naturally occurring calcium silicate hydrate minerals comprising a double Ca–O sheet bound by silicate chains in parallel arrangement to the *b*-axis direction [1–5]. Members of this family are characterised in terms of the length of their *c*-axis, which is dependent on the number of water molecules

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per unit formula. There are three principal polytypes of tobermorite, viz. 14, 11 and 9 Å, whose names are, accordingly, derived from the approximate *d*-spacing of their (0 0 2) Bragg reflections (i.e. their basal spacings). 12.6 and 10 Å tobermorite phases and clinotobermorite have also been reported [6–8].

Eleven angstrom tobermorite, $Ca_5Si_6O_{16}(OH)_2\cdot 4H_2O$, the most abundant and technologically significant polytype, is formed in alkaline hydrothermal media below ~200 °C. In addition to natural deposits, which generally arise from the action of hydrous fluids on basic igneous rocks, 11 Å tobermorite is found among the alteration products formed at the cement–rock interface of toxic and nuclear waste repositories and is the primary binder in autoclaved concrete and sand–lime masonry blocks [9–11].

To facilitate the description of the silicate structure of 11 Å tobermorite, notation will be used such that the symbol Q represents one $SiO_4{}^{4-}$ tetrahedron and the superscript denotes the number of other Q units to which it is bonded. Substitution of Q units by tetrahedra other than $SiO_4{}^{4-}$ will be indicated in parentheses, for example, a mid-chain $SiO_4{}^{4-}$ unit linked to one other $SiO_4{}^{4-}$ unit and one $AlO_4{}^{5-}$ unit would be represented thus, $Q^2(1Al)$.

The ideal structural unit of 11 Å tobermorite is an infinite layer of seven-coordinated Ca–O polyhedra linked on both sides to infinite Q^2 wollastonite-like silicate chains running parallel to the *b*-direction (Fig. 1) [2,3,5]. The layers are stacked in the *c*-direction creating an interlayer region, which accommodates labile calcium ions and water molecules. Paired silicate tetrahedra facing into the polyhedral calcium layer are referred to as 'non-bridging', whereas those tetrahedra which link the pairs together are termed 'bridging'. Two oxygen apices of each non-bridging silicate tetrahedron are associated with the wollastonite chain and the remaining two provide capping ligands for the 'structural' calcium polyhedra. Likewise, two oxygen apices of each bridging tetrahedron are linked into the silicate chain, however, only one oxygen apex is connected to the calcium layer, while the other terminates with a silanol (–OH) group.

Deviation from ideal structure and composition commonly arises in tobermorites from extensive stacking variations and crystallographic substitutions. For example, breaks in the silicate chains give rise to Q^1 units and Q^3 units are observed when displacement by $b/2$ enables bridging tetrahedra to condense across the interlayer. Many other mechanisms of displacement, tilting and twinning also introduce structural disorder [3,5]. Furthermore, coupled isomorphic replacements of up to 15% Al^{3+} for Si^{4+} with concomitant OH^- for O^{2-} substitution and/or additional interlayer calcium or alkali metal ions are widely reported and give rise to interesting ion exchange characteristics [12–19].

Al-substituted 11 Å tobermorites bearing labile interlayer alkali metal ions exhibit reversible cation exchange properties and are selective towards large less hydrated alkali and alkaline earth ions such as Cs^+ and Sr^{2+} [16–19]. This cation specificity is of particular relevance to the selective removal of radioactive species, $^{137}Cs^+$ and $^{90}Sr^{2+}$, during decontamination and treatment of low-level radioactive liquors. Despite the significance of this cation selectivity the influence of structural parameters such as degree of crystallinity and silicate chain configuration on the ion exchange properties of tobermorites has been overlooked.

Since the 1950s, synthetic 11 Å tobermorites and their Al- and Fe-substituted counterparts have been synthesised under hydrothermal conditions at temperatures between 80 and 225 °C from a range of parent materials including various mixtures of the following: zeolites, clays, lime, quartz, gibbsite, fly ashes, sodium silicate, aluminium chloride and, more recently, a number of industrial by-products [12–22]. Rapid microwave-assisted hydrothermal synthesis and mechanochemically activated synthesis have also been reported in recent literature [23,24].