Substitutional and thermal expansion in MAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6} aluminosilicates with keatite structure

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Abstract: A series of isostructural keatite-type MAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6} aluminosilicates with M\textsuperscript{+} ions ranging from H to K can be synthesized by low-temperature ion exchange. Because of its particular framework topology the keatite structure can accommodate large cations by c-axis expansion with concomitant slight a-axis contraction. This flexibility results from changes in T-O-T angles and finds its limit at the ionic size of K, Rb ions not even being incorporated in small quantities. From lattice constant variations the substitutional expansion coefficients are derived.

Structural modelling by Distance-Least-Squares (DLS) calculations shows that unacceptable framework deformation would result from substitution by ions larger than K. For the same reason, the thermal expansion of the MO\textsubscript{4} polyhedra is very restricted in KAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6}, leading to anomalous lattice thermal expansion. DLS calculations further reveal a close correlation between substitutional and thermal expansion in the keatite series. Anomalous bond lengths and anomalous thermal expansion occur in the MO\textsubscript{4} polyhedra of the ion-exchanged, unstable members of the series.

Key-words: keatite, aluminosilicates, ion exchange, thermal expansion, substitutional expansion.

Introduction

Keatite is one of the numerous polymorphs of SiO\textsubscript{2} with a tetrahedral framework. The high-temperature form of LiAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6} ("β-spodumen") is a stuffed derivate of keatite (Li & Peacor, 1968). It is technically important because of its very small thermal expansion which is used in Li-aluminosilicate glass ceramics (Beall & Duke, 1983). By a low-temperature ion exchange MAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6} phases having the same framework can be synthesized, with M\textsuperscript{+} ions ranging in size from H to K (Müller et al., 1988; Baumgartner & Müller, 1990). No p, T-field of thermodynamic stability exists for these phase. However, they only transform to more stable phase assemblages at rather high temperatures. Through the whole series, the lattice constants and structural parameters, particularly the (Al, Si)-O-(Al, Si) angles (called T-O-T angles below), are essentially linear functions of cation size.

In this paper we report on experiments to further expand the series of keatite-type MAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6} phases, on their lattice constants, thermal expansion coefficients, and, based on structural modelling, on relations between thermal and substitutional expansion.

2. Experimental procedures

Experimental details of the ion-exchange procedures have been described elsewhere (Müller et al., 1988; Baumgartner & Müller, 1990). Essentially, the starting material, LiAI\textsubscript{Si}\textsubscript{2}O\textsubscript{6}, is crystallized from glass, powdered and reacted with concentrated H\textsubscript{2}SO\textsubscript{4} at ~300°C to yield HAISi\textsubscript{2}O\textsubscript{6}. This form is then reacted with nitrates, e.g. NaNO\textsubscript{3}, at temperatures 10 to 20 K above their melting points. The framework topology remains intact during these processes and all the ion-exchange reactions can be reversed. Substitution by Cu\textsuperscript{+},

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