Characterization of synthetic Cs-Li cancrinite grown in a butanediol-water system: An NMR spectroscopic and Rietveld refinement study

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ABSTRACT
A Cs-Li-analogue of cancrinite has been synthesized from tetraethoxysilane and Al sec-butoxide in a mixture of 1,3-butanediol and water. Cs and Li were introduced as hydroxides. Synthesis was done at autogeneous pressure and \( T = 473 \) K for 100 h. The synthesis product was characterized by powder X-ray diffraction, IR-spectroscopy, thermogravimetry, \(^1\)H, \(^6\)Li, \(^7\)Li, \(^129\)Cs, \(^27\)Al, \(^29\)Si MAS, and \(^{133}\)Cs CP/MAS NMR and Rietveld structure refinement. \(^29\)Si MAS NMR and \(^{27}\)Al MAS NMR spectroscopy show a framework with strong alternating order of the \( \text{SiO}_2 \) and \( \text{AlO}_4 \) tetrahedra and an Si/Al ratio of one. \(^6\)Li MAS NMR suggests the existence of two different signals that cannot be resolved in the \(^7\)Li MAS NMR spectrum. \(^{133}\)Cs MAS NMR shows only a single resonance. The thermogravimetric analysis reveals a continuous weight loss in several steps, indicating the evaporation of water of hydration. IR spectroscopy shows evidence for hydroxyl anions and water included in the cancrinite framework. The Rietveld structure refinement is consistent with a completely ordered aluminosilicate framework with an Si/Al ratio of one and the presence of both molecular water and hydroxyl groups in the hexagonal channel, a result different from the previously published structure. Cs is exclusively located in the \( \epsilon \)-cages; Li ions are located in the channels and are coordinated by water molecules.

INTRODUCTION
Cancrinite has the chemical formula \( \text{Na}_6\text{Ca}[\text{AlSiO}_4]_6(\text{CO}_3)^-\cdot 2\text{H}_2\text{O} \) and a structure composed of layers of six-membered rings called the secondary building units (Meier and Olson 1992). Its structure in the hexagonal space group \( \text{P}6_3 \) is characterized by the periodic arrangement of the \( \epsilon \)-cages forming an infinite one-dimensional twelve-membered ring channel with a diameter of 5.9 Å along the crystallographic \( c \)-axis (Meier and Olson 1992).

Synthetic analogues of cancrinite-group minerals have been prepared not only with carbonate (Barrer and White 1952) but also with other anions [e.g., selenate (Lindner et al. 1996) and nitrate (Barrer et al. 1970)]. An interesting fact is that the synthesis succeeds only in the presence of specific anions, preferably those with threefold symmetry. However, another approach is the use of a carefully selected combination of cations in which a large cation is combined with a small cation in the synthesis.

A well-studied combination of ions in synthesis is that of the large Cs cation with the small Li cation. Syntheses in aqueous solution at temperatures between 373 and 473 K were first done by Barrer and Sieber (1977) and later by Collella and de’Gennaro (1989). Reactants were pure Si and Al oxides, and Li and Cs hydroxides. The structure was characterized by Rietveld refinement using powder X-ray diffraction (XRD) data and chemical analysis (Norby et al. 1991), which showed that the Cs cations are located exclusively in the \( \epsilon \)-cages but the Li cations are in the channel. From the refined Si-O and Al-O distances (average 1.69 Å), they proposed that Al and Si were randomly distributed among the framework tetrahedra, although the \(^{29}\)Si MAS NMR spectra showed only a single line. In addition, the refinement had unusually high displacement factors for the framework atoms, especially Si and Al, and the residuals \( R(F^2) \), \( R_w \), and \( R_{wp} \) were above or equal to 0.1.

We have synthesized the Cs-Li-analogue of cancrinite with another approach using a mixture of 1,3-butanediol with 50\% by volume of water as a solvent. Tetraethoxysilane and Al sec-butoxide were used as silica and alumina sources, and Cs and Li hydroxides were used to introduce the cations. The synthesis product was extensively characterized by solid-state NMR spectroscopy and Rietveld refinement. We show from NMR spectroscopy that the aluminosilicate framework displays strong alternating Si/Al order, a pattern that is consistent with the structure refinement, which also suggests the presence of both molecular water and hydroxyl groups. The results differ from those of Norby et al. (1991) in these conclusions, but it should be noted that they followed a different synthetic approach starting from Al and Si oxide.

EXPERIMENTAL METHODS
Tetraethoxysilane (3.22 g, \( \text{C}_8\text{H}_{20}\text{O}_4\text{Si} \), TEOS; FLUKA 86578) and Al sec-butoxide (3.82 g, \( \text{C}_6\text{H}_{27}\text{AlO}_3 \), FLUKA 06190) were stirred together with 10 mL deionized water and...