



Dehydration process and transient channel deformations of slightly hydrated boron leucite: An “*in situ*” time-resolved synchrotron powder diffraction study

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ABSTRACT

The step by step thermal dehydration process of slightly hydrated boron leucite $K_{16}[B_{16}Si_{32}O_{96}]$, was studied *in situ* by synchrotron radiation powder diffraction. A time-resolved experiment was performed using a translating imaging plate system. Rietveld refinements were carried out on 41 consecutive powder patterns in the 25–940 °C temperature range. Results show that temperature-induced transformations can be schematized into two main steps. In the 25–565 °C temperature range, the symmetry remained cubic *I*-43*d* and the unit cell parameter increased with an increase in temperature. The migration of H₂O molecules through the [1 1 1] channels during dehydration determined an opening of the six-member ring apertures which was as wide as possible and, at the same time, a narrowing in the eight-ring along [1 1 1]. This process was accomplished by a twisting in the tetragonal prism, constituting a leucite framework, which led to an opposed tilting in the tetrahedra connecting the prisms. Above 565 °C, a continuous structural transformation led to a displacive polymorphic transition. Rietveld structure refinement of the unit cell parameters showed a remarkable change, thus indicating an *I*-43*d* → *Ia*-3*d* change in symmetry. This was associated with a relaxation in the continuous structural distortions of the leucite framework and the T–O–T and O–T–O angles indicated the formation of more regular apertures.

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1. Introduction

The response of zeolites to heating is not only of academic significance but also of potential industrial importance. A number of factors contribute to macroscopically observable thermal effects such as the evolution of H₂O and encapsulated organic species, variations in unit-cell volume and structural breakdown or modification [1,2]. These effects, which modify pore and channel geometry, affect the absorption and diffusion of molecules in zeolites and microporous catalysts, and consequently the catalytic properties of materials [3]. When boron ions are incorporated into the tetrahedral framework sites of zeolites, selective heterogeneous catalysts are produced (which are referred to as “boralites” or “borosilicates”). In comparison to zeolites, boralites display lower thermal stability and framework deboronation often occurs during the calcination steps which are required to eliminate organic molecules trapped within their pores [3].

The structure of leucite, which shows an ANA-type zeolitic framework, has been the subject of extensive research, due to its

displacive tetragonal to cubic transition, Al and Si ordering on T-sites and its ferroelastic and dielectric properties [4,5]. The structure of analcime, leucite and analogue materials have been extensively studied by several authors [6–11]; comprehensive summaries of structural investigations have been reported by Henderson and Taylor [12], Hazen and Finger [13], and Palmer et al. [11].

Leucite frameworks can be built using six-membered tetrahedra rings connected through distorted four-rings to form chains along the *b* axis [14] which are common to the ANA group of zeolites [14,15]. Two different types of channels exist: larger channels which are made of highly distorted eight-membered rings along [1 1 0], and smaller channels which are defined by six-membered rings along the [1 1 1] direction of the cubic lattice. Cavities in ANA consist of three distorted prismatic cages which are delimited by 4-, 6- and 8-member tetrahedral rings.

The major differences between the analcime and leucite stems are due to the type and distribution of extraframework ions. In analcime Na, cations occupy the centre (*S* site) of each prismatic cage and are coordinated by two water molecules (*W* site) and four framework oxygens. The water molecules in analcime occupy the same structural positions in the [1 1 1] direction as the K ions in leucite, whereas the analcime Na positions fill sites that are vacant in leucite. Analcime is a zeolite-type hydrous mineral; its

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stoichiometric water content is >8.0 wt.%, whereas, leucite is essentially anhydrous (a so-called ‘nominally anhydrous mineral’, NAM), in agreement with its origin as an early crystallizing volcanic mineral.

However, minor but significant amounts of water have been detected in leucite from Vesuvius and Roccamon-fina volcanic centres [16]. Recently, Della Ventura et al. [17] reported on a single-crystal FTIR spectroscopic study of many leucite samples deriving from different occurrences and localities in the volcanic Alban Hills area (Latium, Italy). Their FTIR spectra clearly indicated that almost all the examined samples contained hydrous components in the form of structurally-bound water molecules.

Leucite structures are extremely tolerant towards ionic substitutions [12,18,19], and it is its considerable structural flexibility with respect to changing composition, temperature, and pressure that makes leucite of particular interest from a crystal–chemical viewpoint.

The hydrothermal synthesis of a fully B-substituted ANA-type zeolite structure was achieved by Millini et al. [20] who demonstrated the possibility of completely replacing Al with B in the analcime framework by hydrothermal synthesis. The same authors performed a Rietveld refinement on their sample in the *Ia-3d* topological symmetry, concluding that boron-substituted analcime was actually isostructural with leucite rather than with analcime. This result was at variance with the previous structural analysis reported by Ihara and Kamei [21] who solved and refined the structure of K-boroleucite crystals in the *I-43d* space group. The latter space group was also used by Mikloš et al. [22] for the refinement of their $K(BSi_2O_6)$ boroleucite.

Concerning the effects of extraframework species on the stability of B-ANA-type structures, Millini et al. [20] also showed that in the presence of K^+ ions in the synthesis batch, the stoichiometry of the B-ANA-type structure is consistently close to the theoretical $K_{16}[B_{16}Si_{32}O_{96}]$ structure. Upon replacement of K^+ by other alkali metal ions, the formation of amorphous products was observed, while the addition of tetralkylammonium hydroxide did not influence the behaviour of the system [3]. The hydrothermal synthesis of boron-containing zeolites with a leucite structure and large

alkali cations, like potassium, rubidium or cesium, has been reported in the presence of organic cations by Di Renzo and co-workers [23]. These authors stated that the easy formation of borosilicates in the presence of the largest alkali cations was related to the organic-templated synthesis of borosilicate zeolites and confirmed the relevance of a hydrophobic effect in the insertion of boron in tetrahedral lattice sites.

As far as the thermal stability of these systems is concerned, Millini et al. [20] pointed out the lack of any signal as a result of trigonal boron species in the B MAS NMR spectra of the calcined material. This revealed the high thermal stability of their B-substituted K-leucite, which is unusual for borosilicates with zeolite structures. Mazza et al. [24] examined different samples prepared using a sol-gel preparation along the $K[Al_{1-x}B_xSi_2O_6]$ compositional junction with $0 \leq x \leq 1$ using XRD, DTA, FTIR, and dilatometry techniques. This work showed that by increasing the x value from 0 to 1 the samples crystallize, in a temperature range from 900 to 1250 °C, with tetragonal ($0 \leq x \leq 0.25$), cubic ($0.50 \leq x \leq 0.80$) and again tetragonal ($0.90 \leq x \leq 1.00$) symmetry. The above-mentioned authors concluded that all the phases derived from a cubic high-temperature form by means of a displacive phase transition.

The aim of the present work is to study the thermal behaviour of boron-substituted leucite, using Rietveld structure analysis of temperature-resolved powder diffraction data collected using synchrotron radiation. Such experimental conditions are ideal for the rapid collection of the diffraction data necessary to monitor each step of the dehydration process in detail.

2. Experimental

2.1. Materials

A powder sample of (B-LEU), $K_{16}[B_{16}Si_{32}O_{96}]$ B-leucite which was the same as was used for the X-ray powder diffraction study of Ref. [20], was selected for this experiment. As reported by Millini et al. [20], the B and K content were determined by ICP-AES using a Jobin Yvon 38II Plus spectrophotometer. TG and differential thermal analysis (DTA) measurements of the as-synthesized

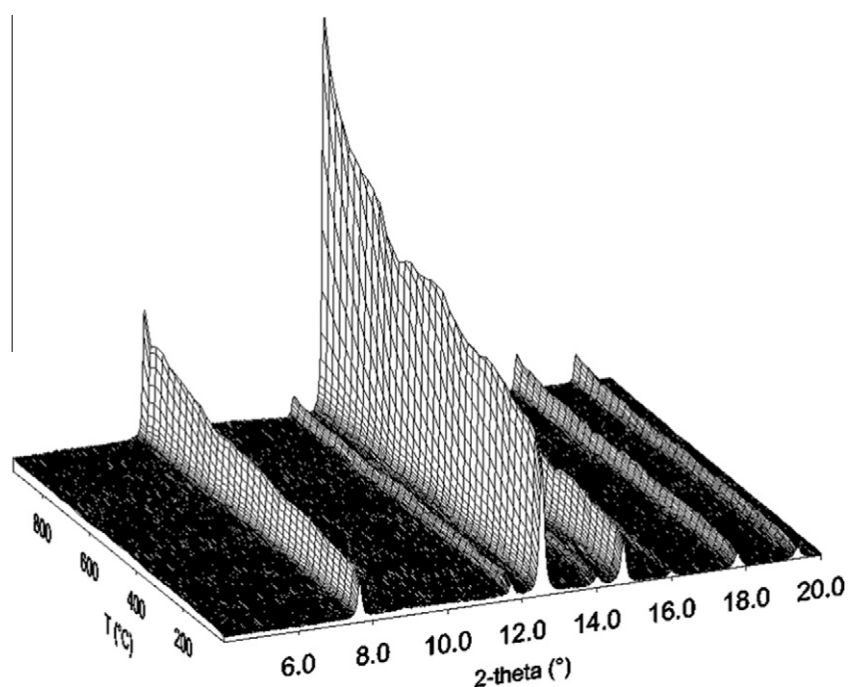


Fig. 1. Evolution of the XRPD patterns in the selected 5–20° 2θ interval as a function of the temperature during the *in situ* time-resolved experiment.

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