



Modeling short-range substitution order and disorder in crystals: Application to the Ga/Si distribution in a natrolite zeolite



Sylvian Cadars^{a,b,1,*}, Nak Ho Ahn^{c,1}, Kirill Okhotnikov^{b,1}, Jiho Shin^c, Aurélie Vicente^d, Suk Bong Hong^{c,*}, Christian Fernandez^{d,*}

^a Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 Rue de la Houssinière, BP32229, 44322 Nantes Cedex 3, France

^b CEMHTI CNRS UPR3079, Université d'Orléans, 1D, avenue de la recherche scientifique, 45071 Orléans cedex 2, France

^c Center for Ordered Nanoporous Materials Synthesis, School of Environmental Science and Engineering, POSTECH, Pohang 790-784, Republic of Korea

^d Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000, Caen, France

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ABSTRACT

Atomic substitutions are a central feature of the physicochemical properties of an increasing number of solid-state materials. The complexity that this chemical disorder locally generates in otherwise crystalline solids poses a major challenge to the understanding of the relationships between the structure and properties of materials at the atomic and molecular level. Strategies designed to efficiently explore the ensemble of local chemical environments present in disordered crystals and predict their signatures in local spectroscopies such as solid-state nuclear magnetic resonance (NMR) are therefore essential. Focusing on the Ga/Si disorder in the framework of rubidium-exchanged gallosilicate natrolite zeolite (Rb-PST-1) with a high Ga content (SiGa=1.28), we show how the structure-generation approach implemented in the new program *supercell* (Okhotnikov et al. [26]) provides an excellent basis for the understanding of complex experimental spectroscopic data. Furthermore, we describe how exhaustive explorations of atomic configurations can be performed to seek local structural ordering and/or disordering factors. In the case of Rb-PST-1, we more specifically explore the possibility to form and to detect the presence of thermodynamically unfavorable Ga-O-Ga connectivities. While particularly adapted to the description of dense materials, we demonstrate that this approach may successfully be used to reproduce and interpret the distributions of local structural distortions (*i.e.*, the geometrical disorder) resulting from the chemical disorder in systems as complex as microporous zeolites.

1. Introduction

The properties of an increasing number of advanced crystalline materials nowadays are directly related to the ability to adjust their compositions through atomic substitutions. In many cases these substitutions leave the long-range average structure essentially unchanged, with only systematic changes in the unit cell parameters that relate to the relative sizes of the substituted and substituent atoms and the amount of the latter, and sometimes a change in the system symmetry. In favorable cases, *i.e.*, when the atomic factors are sufficiently distinct, Rietveld refinements of (X-ray or neutron) diffraction data provide direct measures of the average composition at each mixed crystallographically distinct site. But diffraction data provide no or very limited information on the distributions of the substituents within the framework and the local structures around them. Considerable efforts have been devoted in the recent years to the

characterization of the local structures of such disordered crystalline systems with local spectroscopies, among which solid-state NMR has played a particularly important role [1,2]. This includes a broad range of materials and applications, from clays and other layered materials [3–7] to ceramics [8–11], battery materials [12,13], chalcogenide semiconductors for photovoltaics [14,15], and many others [16]. Most of these materials have in common the great extent of local structural complexity that the chemical disorder generates at the local level. This is primarily because any site surrounded by several sites of mixed composition within its first and/or second coordination shell(s) will give rise to multiple potential molecular motifs with different local signatures. In addition, these individual signatures are further broadened by longer-range compositional effects (typically substitutions within the third or fourth coordination spheres), but also by distortions of the local bond angles and distances; a short-range geometrical disorder arising from differences in the atomic radii and/or bonding

* Corresponding authors.

E-mail addresses: sylvian.cadars@cnrs-imn.fr (S. Cadars), sbhong@postech.ac.kr (S.B. Hong), christian.fernandez@ensicaen.fr (C. Fernandez).

¹ S.C., N.H.A., and K.O. contributed equally to this work.

properties of the atoms involved in the substitutions.

Both intermediate-range chemical disorder and short-range geometrical disorder give rise in local spectroscopies such as NMR to distributions of resonance frequencies that often cause strong spectral overlap and considerably complicate the interpretation of experimental spectra. The prediction of the spectroscopic response of such materials by means of electronic structure calculations therefore plays an essential role not only to assign the different spectral contributions to the structural motifs potentially present in the system, but also to understand the structural origins of the observed distributions of experimental parameters [1,17,18]. This ability has been exploited with considerable success in numerous solid-state NMR studies of amorphous materials [19–22] and crystalline materials with substitution disorder [8,10,16,23]. The latter include the use of a common approach which consists in building a small number of supercells based on several repetitions of the crystal unit cell, in which atoms are distributed randomly onto the disordered sites (possibly with some local preference rules). Except for few recent studies employing for example random-structure search [24] or similar strategies [25], this procedure has most often been performed “by hand”.

Very recently, some of us introduced a new program, called *supercell*, which provides all the necessary tools to perform efficient exhaustive explorations of the different atomic configurations that can be generated for a given supercell size, and then to conduct electronic calculations on small subsets of structures chosen on the basis of rational criteria [26]. While Ref. [26] was dedicated to a general description of the program, comparisons with other existing solutions [27–30] and its application to simple model systems, this article describes the first application of the *supercell* program to an important solid-state material science problem: the M(III)/Si(IV) disorder in the framework of silica-based zeolites. These microporous materials are one of many examples of systems where atomic substitutions give rise to numerous important properties. For example, the introduction of Ge precursors into the syntheses mixtures not only substitutes Si atoms but also directs the formation of novel zeolite framework types by favoring specific building units [31–33]. But the most common form of atomic substitutions used in zeolites is by far the substitutions of framework tetrahedral Si atoms by heteroatoms of lower valence states (the most common being Al), which introduce negative charges resulting in the formation of Brønsted and/or Lewis acid sites. The development of experimental approaches to characterize the distribution of these heteroatoms (Be, B, Al, Ga, Ge, etc.) over the available T-sites in zeolites has been and continues to be the focus of much research effort [34–41]. The degree of T-site ordering, in particular, is indeed one of the important factors that affect various physicochemical properties of zeolites, including their thermal stability, the cation exchange ability and water adsorption-desorption properties [42–46].

Natrolite zeolites (framework type NAT) are particularly interesting examples in this respect, and the ability to characterize and control the T-site ordering, as well as the order-disorder transformation mechanism, have been investigated in these systems [45,47]. Several studies have shown in particular that solid-state ^{29}Si NMR spectroscopy provides direct insights into the degree of local ordering of the Al/Si and Ga/Si distributions in alumino- and gallosilicate NAT zeolites [37,43,48,49], respectively, the latter being the focus of the present work. In its simplest ordered form with a Si/M ratio of 1.5, where M is Al or Ga, the NAT framework structure gives rise to two well resolved and relatively sharp ^{29}Si NMR peaks, which relate to contributions of Si atoms surrounded by 2 or 3M atoms among their 4 next-nearest neighbors. The relative amounts of these species, which we denote here as Si(2Si, 2M) and Si(1Si, 3M) can therefore be quantified, along with the proportion of residual contributions from other Si species, whose amount relative to the two former species reflects the degree of T-site disordering [37,48]. In NAT zeolites this T-site ordering takes the form of preferential siting of Si atoms onto the site with the lowest multi-

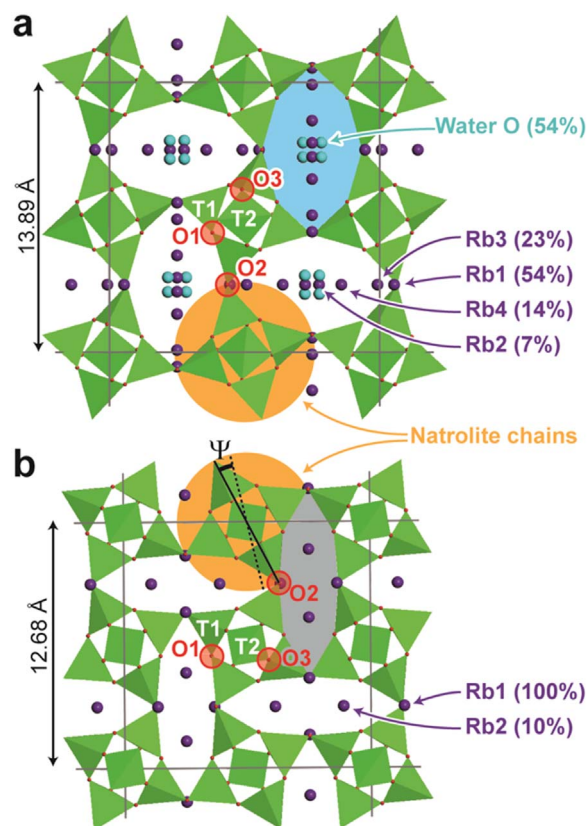


Fig. 1. Crystal structures of the (a) hydrated and (b) dehydrated forms of Rb-PST-1 ($I42d$ space group) determined from synchrotron powder X-ray diffraction data. TO_4 tetrahedra with mixed Ga/Si composition on the T-site are shown in green. Rb atoms are shown in purple and water O atoms in pale blue. The closing and opening of the channels upon dehydration and rehydration, respectively, are driven by rotating in the ab -plane of the natrolite chains (highlighted in yellow) with the T–O2–T bond angle that plays the role of a hinge. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

plicity (labeled T2 in the present work; Fig. 1), which has a pure Si composition in fully ordered, NAT. The other T-sites in the NAT framework show different situations, depending on the degree of Si/M ordering. In ordered NAT zeolites, which are characterized by an orthorhombic structure (space group $Fdd2$, no. 43), they are split into two distinct T-sites with equal multiplicities: one with Si and the other with M, which are partially substituted by small amounts of M and Si, respectively, in the presence of a slight disorder. In NAT zeolites with heavy T-site disorder, characterized by a tetragonal symmetry ($I42d$, no. 122), this second type of T-sites is merged into a single crystallographic site denoted as T1 in the present work (Fig. 1). Both T1 and T2 sites have a mixed Si/M composition (and become particularly difficult to distinguish by ^{29}Si NMR) in this disordered form. Table S1 in Supporting information summarizes this description and the correspondence between the ordered and disordered forms of the natrolite family of zeolites, as well as the labeling used here and in the literature.

PST-1 is a synthetic potassium gallosilicate natrolite with unusually low Si/Ga ratio of 1.28, compared to typical synthetic gallosilicate NAT materials with Si/Ga ratios over 1.5. This low Si/Ga ratio suggests that Ga–O–Ga bonds may form as a result (or as a cause) of the strongly disordered T-site distributions observed by ^{29}Si NMR. This work focuses more specifically on the Rb^+ -exchanged form (Rb-PST-1) of PST-1, as this form presents three different oxygen sites compared to 5 in the potassium form. This structure is studied with a combination of ^{29}Si and ^{17}O NMR experiments, and density functional theory (DFT) modeling performed based on structural models generated with the *supercell* program. The application of this general strategy for the modeling of substitution disorder in crystals to the case of the Rb-PST-

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