

Cation substitution and strain screening in framework structures: The role of rigid unit modes

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Abstract

We use a combination of real-space geometric algebra and reciprocal space dynamical matrix analyses to study the effect of cation substitution on the framework geometries of β -quartz, cordierite and leucite. We show that the geometric stress associated with the substitution in these framework silicates is absorbed by rigid-unit type motion of those coordination polyhedra near the substitution site. We find that the inherent flexibility of these structures enables screening of geometric stress, such that the associated energy cost is minimal and unlikely to influence substitution patterns.

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1. Introduction

Cation substitution is a phenomenon observed repeatedly throughout both naturally occurring and synthetic framework materials; in particular, Al-substituted (‘stuffed’) silicates and zeolites are a class of materials of great importance to the earth sciences. The substitution patterns exhibited by these materials are varied, and can involve order (or disorder) on multiple length scales. However, some empirical rules do emerge. For example, the ‘Al-avoidance rule’ reflects the observation that Al atoms rarely substitute the centres of connected $[\text{SiO}_4]$ tetrahedra in framework silicates. In general, such rules are qualitatively explained in terms of two balanced effects. The first considers the electrostatic interaction

between substituted centres; for example, the $[\text{AlO}_4]$ coordination polyhedra in siliceous frameworks bear a negative charge, and so the substitution of adjacent coordination polyhedra carries with it a large electrostatic energy cost. The second is a geometric effect, which accounts for the strain introduced by the associated change in metal–oxygen bond lengths.

Taken at face value, the suggestion that one can minimise the geometric strain associated with Al-substitution by maximising the number of Al–O–Si linkages seems a natural assumption. However, the manner in which such geometric strains propagate throughout the crystal lattice, and their effect on possible substitution patterns are non-trivial issues. To address these, it is important to explore the way in which framework structures respond to the introduction of substitutional centres. Such a response will necessarily depend on the inherent flexibility of the framework; i.e., the degree to which the framework can distort with minimal energy cost.

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A simple and surprisingly effective interpretation of framework flexibility is that given by the Rigid Unit Mode (RUM) model. In this picture, the metal coordination polyhedra within the framework are viewed as rigid units, connected to form the required framework topology. The physical significance of the model lies in the observation that the forces required to deform coordination geometries are significantly greater than those required to rotate and/or translate coordination polyhedra relative to each other. The various combinations of translations and rotations of the rigid units that preserve the framework topology, such as the octahedral rotation mode in perovskite (Fig. 1), are consequently likely to dominate the dynamical behaviour of the material. Indeed, those phonon modes that can be described in this way (termed RUMs) often occur at very low energy (typically 0–2 THz) and so dictate many physical properties of the materials in which they exist. The model has enjoyed much success in explaining a range of phenomena, including the existence and nature of phase transitions (Hammonds et al., 1996) and anomalous thermal expansion behaviour (Heine et al., 1999; Welche et al., 1998).

In this paper, we show that the topologies of a number of framework structures are capable of accommodating cation substitution without significant deformation of individual coordination polyhedra. In particular, the associated geometric ‘stress’ can be absorbed by the rotations and/or translations of the neighbouring coordination polyhedra. The same inherent framework flexibility that gives rise to RUM-type vibrational motion is shown to allow cation substitution with a small geometric energy cost.

Our analysis involves the use of two methods: firstly, a recently developed geometric algebra approach that quantifies the influence of rigid-unit motion on atomistic configurations; secondly, a novel dynamical

matrix method that determines the flexibility of each framework with respect to changes in size (‘breathing’) of the coordination polyhedra. We present results for three representative silicate structures: β -quartz, cordierite and leucite.

2. Geometric algebra analysis

Despite the obvious usefulness of the RUM model in determining the dominant reciprocal-space influences on framework structures, the active phonon modes in a real material do not in practice fall neatly into a family of RUMs that dominate all motion, and another family of non-RUMs with minimal effect on atomic displacements. Instead, any mode can include components of either type of motion, with the relative proportions varying primarily as a function of mode frequency. As such, atomistic configurations – ‘snapshots’ of instantaneous atomic positions within a material – will reflect the influence of both RUM- and non-RUM-type phonon modes.

To quantify these contributions, a real-space analysis of RUM fluctuations based on the technique of geometric algebra (GA) has recently been developed (Wells et al., 2002) and has been implemented by the program GASP (Wells et al., 2004; Wells, 2004). It allows us to determine the extent to which atomistic configurations can be described in terms of RUM displacements, by decomposing the atomic displacements into rigid-unit translations, rotations and distortions.

The approach compares the polyhedral geometries within a given structure, before and after introduction of the defect. Let A denote any one polyhedron in the initial configuration and A' the corresponding polyhedron in the defective structure. If A and A' are superposed such that their centres coincide, there will be a mismatch between each vertex Q of A and the

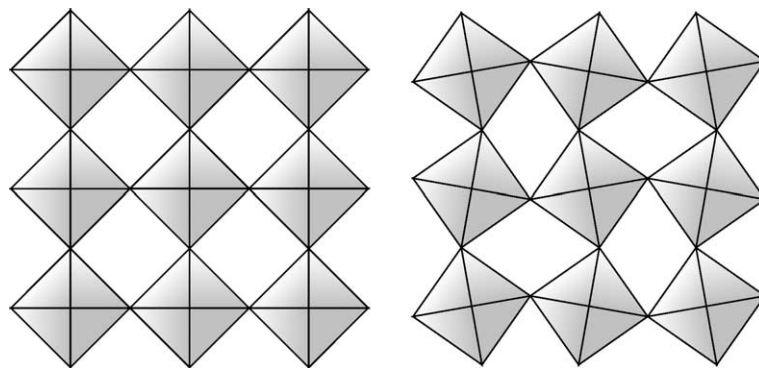


Fig. 1. Illustration of a rigid unit mode in the perovskite structure. The mode involves counter-rotation of successive coordination octahedra about an axis perpendicular to the page, and preserves the integrity of all coordination polyhedral geometries.

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