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# The steric influence of extra-framework cations on framework flexibility: An LTA case study

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## Abstract

The theoretical extent of framework flexibility of Zeolite A (LTA) in response to the steric and geometric effects of different Si/Al compositions and extra-framework cation content has been explored using GASP software. Flexibility windows and compression mechanisms for siliceous LTA and aluminosilicate Na-LTA, Ca-LTA and K-LTA have been modelled. As expected, relatively small cations in the zeolite pores have little effect on the range of flexibility observed. Aluminosilicate LTA, Na-LTA and Ca-LTA frameworks exhibit identical flexibility windows and these frameworks also follow the same compression mechanisms. The introduction of larger K<sup>+</sup> ions, however, results in greater steric hindrance. This restricts the flexibility of the framework and alters the compression mechanism to accommodate these larger cations. It is shown that the limits of the flexibility window of Zeolite A are dependent on framework aluminium content and extra-framework cation size.

## Introduction

Zeolites are microporous aluminosilicate materials with uniform pore systems. They exhibit high thermal stabilities and are excellent molecular sieves, solid acid catalysts and ion exchange materials. As a result of their unique properties, zeolites are widely used in industrial applications, from adsorption to catalysis. [1–3] The preparation and optimisation of existing zeolites is a highly active field and a number of synthesis methods have been developed, including methods making use of naturally occurring precursors such as kaolin, and waste-stream materials such as coal fly ash. These alternative feedstocks for zeolite synthesis contain impurities such as calcium, potassium, magnesium, and

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iron for example, which may influence the zeolite crystallisation process. [3–9] Cations are known to play an essential part in the zeolite crystallisation process and influence the type of zeolite structure formed. This is due to the limited structure directing effect of cations in aqueous solutions. [10,11] Monovalent cations, such as sodium and potassium, and divalent cations, such as calcium, are capable of serving a charge-balancing function in the aluminosilicate zeolite structure. Sodium cations are commonly used for charge-balance during zeolite synthesis, and are said to direct the formation of certain building units during crystallisation. For example, Zeolite A (**LTA**) is preferentially synthesised using sodium cations that easily permit the formation of sodalite and *lta* cages along with double four ring (*d4r*) units. Calcium, on the other hand, is known to significantly retard the crystallisation of zeolites and is typically referred to as a “structure-breaking” cation. Potassium has a similar “structure-breaking” effect during the synthesis of some zeolites, but it also exhibits a “structure-directing” effect during the synthesis of zeolites with larger pores, for example **KFI**, **LTL** and **MER**. [10–13]

Furthermore, exchanging these cations in zeolite frameworks can significantly alter the pore sizes and accessible void space for adsorbed molecules. This, in turn, leads to zeolites with different diffusion and molecular sieving properties. Zeolite A is commercially available in different ion-exchanged forms, Zeolite 4A (Na-**LTA**), Zeolite 5A (Ca,Na-**LTA**) and Zeolite 3A (K,Na-**LTA**). These cations vary in their number and ionic radii and this affects the free-diameter of the pores. Zeolite A (4A) typically has an effective pore diameter of  $\sim 4$  Å. Calcium-exchanged zeolite 5A has a larger effective pore diameter of  $\sim 5$  Å, as the divalent calcium ion is comparable in size to sodium but only half as many calcium ions are required for charge balance. Potassium-exchanged zeolite 3A has a much smaller pore diameter of  $\sim 3$  Å due to the larger size of the monovalent potassium ion. These unique pore dimensions have made cation-exchanged zeolite A materials highly desirable for applications in gas adsorption, separation and purification processes [4,14,15]. Zeolite A (**LTA**) has cubic symmetry and an ordered arrangement of silicon and aluminium ions in the framework, with an overall Si/Al ratio of 1. [2,15,16]

The steric effect that extra-framework cations have on the flexibility of a zeolite framework may provide some insight into their structure-directing or structure-breaking role during synthesis. Geometric simulation is an effective way to model the geometry of a zeolite framework and explore its flexibility. GASP (Geometric Simulation of Structural Polyhedra) software makes use of template based geometric simulation [17,18], modelling the framework as an assemblage of tetrahedral units connected by freely flexible joints, and neglecting long-range electrostatic and dispersion reactions while enforcing steric exclusion at close range. This approximation recognises that the energy cost of distortions in inter-polyhedral geometry is much lower than the energy cost for intra-polyhedral distortions. GASP has been used to investigate the flexibility windows of a range of zeolites, as well as the influence of different types of extra-framework content (for example charge-balancing

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cations and solvent molecules) on the flexibility of specific zeolite frameworks. [19–24]. In an investigation of the influence of sodium hydroxide and sodium bromide syntheses on the flexibility of sodalite (SOD) frameworks, no significant steric hindrance from sodium cations was found, while the steric effect of the large Br<sup>-</sup> ion was considerable. [23] However, the steric influence of different cations on one particular zeolite framework simulated by GASP has not been reported to date. Therefore we present this paper based on a model zeolite framework (LTA) with ordered aluminium atoms containing three different types of extra-framework cations; (1) monovalent sodium, (2) divalent calcium and (3) monovalent potassium.

## Methodology

The flexibility window of LTA zeolites was simulated using GASP software, to determine the effect of extra-framework cation type on the flexibility window limits of zeolite A. The flexibility window is the range of cell parameters within which the polyhedra in the structure can in principle be free of any distortion from ideal tetrahedral geometry, being limited in expansion by the extension of bonds and in contraction by contacts among framework oxygens. GASP software makes use of input structures in CIF file format containing a unit cell in P1 symmetry. In this study, we used a 2.2.2 supercell of the siliceous LTA framework based on an LTA CIF file obtained from Baerlocher and McCusker, Database of Zeolite Structures. [25] Similarly, a 2.2.2 supercell of the dehydrated, ordered aluminosilicate LTA framework was used for simulations of the empty aluminosilicate LTA framework and the aluminosilicate LTA framework with extra-framework cation content based on a refined structure for dehydrated zeolite NaA reported in the literature. [26] The 2.2.2 supercell structures were generated to enable visualisation of the  $\alpha$  cage in the LTA framework. The input structures of the cubic LTA framework structures used for GASP simulations were prepared using the starting cell parameters described in Table 1.

Table 1: The starting cell parameters and T-O bond lengths used for the GASP simulation of cubic LTA framework.

Framework	Starting cell parameter (Å)	T-O bond length (Å)
Siliceous LTA	23.838	1.61
LTA (Si/Al ratio = 1)	24.555	1.68
LTA (Si/Al ratio = 1, Al-O bar)	24.555	1.61 (Si-O) 1.75 (Al-O)
Na-LTA	24.555	1.68
Ca-LTA	24.555	1.68
K-LTA	24.555	1.68

In each case, the steric radii of framework elements Si, Al and O were set as 0.26, 0.40 and 1.35 Å, respectively. The Pauling hard-sphere ionic radii of extra-framework cations Na, Ca and K reported as 0.95, 0.99 and 1.33 Å were used,

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respectively. [27] Since the geometric simulation considers extra-framework objects purely as steric objects, without electrostatic effects, empty and filled aluminosilicate frameworks can be investigated and compared directly. The empty, ordered aluminosilicate LTA framework was investigated using two approaches. The first is to apply a tetrahedral template to every T site with an averaged T-O bond length of 1.68 Å. The second is to retain Al-Si ordering in the framework with an Si-O bond length of 1.61 Å and an Al-O bond length of 1.75 Å, and to apply Al-O bar constraints which permit small variations in the O-Al-O angles [23]. The cation site occupation per unit cell for different extra-framework cations in the dehydrated LTA framework assigned according to literature [28–29] is summarised in Table 2.

Table 2: The cation sites occupation in the LTA frameworks Na-LTA, Ca-LTA and K-LTA used for the GASP simulation of cubic LTA framework.

Frame-work	M <sup>n+</sup> Radius (Å)	Site I	Site II	Site III	Total M <sup>n+</sup> /unit cell
Na-LTA	0.95	8	4	-	12
Ca-LTA	0.99	6	-	-	6
K-LTA	1.33	8	4	-	12

## Results

### 1.1 Siliceous LTA and ordered LTA (Si/Al = 1)

The flexibility windows of the siliceous LTA framework and the empty aluminosilicate LTA framework with Si/Al ratio of 1 were simulated using GASP software. Results for siliceous LTA (grey) and aluminosilicate LTA (orange) are depicted in Figure 1. Black data points represent the starting input structures. The flexibility window limits of LTA (siliceous and aluminosilicate) framework structures are summarised in Table 3.

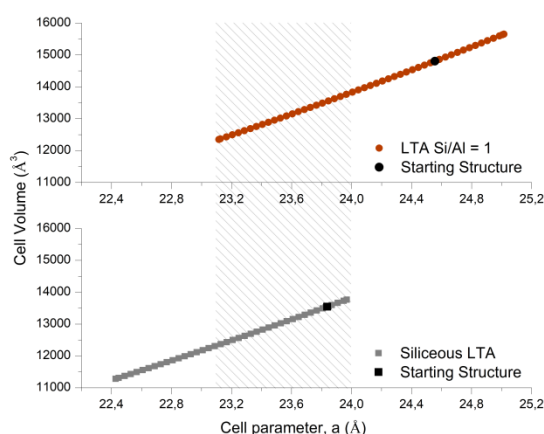


Figure 1: GASP simulated flexibility windows of siliceous LTA and aluminosilicate LTA

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Table 3: Starting cell parameters and flexibility window limits of the cubic **LTA** framework (siliceous and Si/Al ratio = 1) simulated using GASP.

Framework	Starting cell parameter, $a$ (Å)	Lower window edge (Å)	Compressed cell volume (Å <sup>3</sup> )	Upper window edge (Å)	Expanded cell volume (Å <sup>3</sup> )
Siliceous <b>LTA</b>	23.838	22.428	11282	23.968	13769
<b>LTA</b> (Si/Al = 1)	24.555	23.115	12350	25.015	15653
LTA (Si/Al = 1, Al-O bar)	24.555	22.635	11597	25.275	16146

The siliceous **LTA** framework exhibited a flexibility window ranging between  $a = 22.428$  Å and  $23.968$  Å, corresponding cell volume values are listed in Table 3. Illustrations of the **LTA** flexibility window limits are depicted in Figure 2; where the **LTA** framework is depicted as the (a) compressed structure, (b) starting structure and (c) expanded structure, with silica tetrahedra represented in grey. The starting structure for siliceous **LTA** lies on the upper edge of the flexibility window, as is typical for a relatively open zeolite framework structure. Both expansion and contraction alter the profile of the 8-ring windows, from an octagonal shape at starting conditions towards a more square profile.

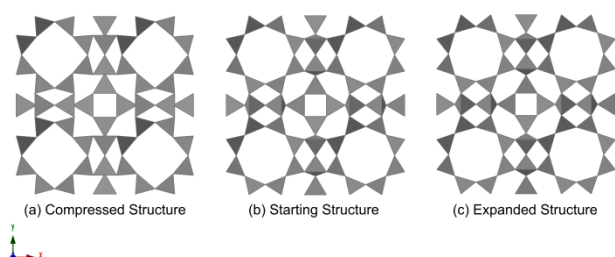


Figure 2: Flexibility window limits of the **LTA** framework, with grey silica tetrahedra.

Aluminosilicate **LTA** (Si/Al ratio = 1), simulated using tetrahedra with an averaged T-O bond length of  $1.68$  Å, exhibited a flexibility window between  $23.115$  Å and  $25.015$  Å, as depicted in Figure 1. The shaded area depicted in Figure 1 represents the overlapping regions of the flexibility windows of siliceous **LTA** and aluminosilicate **LTA**; the upper region of the flexibility window of siliceous **LTA** corresponds to the lower region of the flexibility window of aluminosilicate **LTA**. This is due to the incorporation of aluminium into the **LTA** framework giving a longer typical T-O bond length. However, the overall theoretical compression mechanism of siliceous and aluminosilicate **LTA** frameworks were the same. The 8 ring windows in the aluminosilicate **LTA** framework were distorted upon compression in a similar manner as observed for the siliceous **LTA** framework, as depicted in Figure 3.

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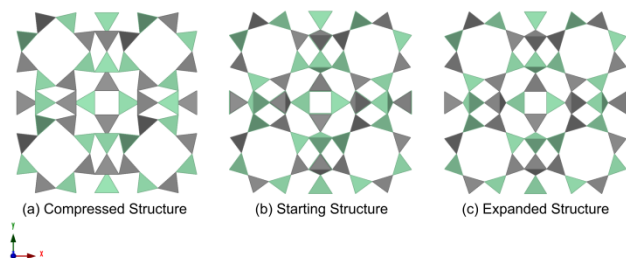


Figure 3: Flexibility window limits of aluminosilicate **LTA** framework (Si/Al ratio = 1), with grey silica tetrahedra and green alumina tetrahedra.

We have additionally investigated the fully ordered **LTA** framework using shorter Si-O and longer Al-O bond lengths, following a previous investigation of the flexibility window in ordered sodalite [23]. As in that case, we find that if tetrahedral constraints are applied to both Si and Al sites, the structure cannot be geometrically relaxed to ideal tetrahedral geometry, and no flexibility window can be defined. The framework can be relaxed using ‘softer’ Al-O bar constraints, which permit the O-Al-O angles to vary slightly within the limits imposed by the steric radii of the oxygens. Using this approach, a slightly wider flexibility window is obtained, as shown in Table 3, but the character of the compression mechanism is essentially the same. For ease of comparison to the siliceous case, we concentrate on the model using averaged bond lengths.

## 1.2 M-LTA (M = Na, Ca or K extra-framework cations)

Three types of cation sites are common for the **LTA** framework, as depicted in Figure 4. Site I represents cations positioned near/in the centre of the 6-ring of sodalite cages, Site II represents cations positioned (slightly off-centre) in the 8-ring window of  $\alpha$  cages and Site III represents cations positioned opposite the 4-rings on the interior of  $\alpha$  cages. Site I and II have relatively high occupancies of 0.97 and 0.24, respectively, while Site III has a site occupancy of 0.07. The dehydrated Na-**LTA** framework contained a total of 12 sodium cations per unit cell, with cation site I filled with 8 sodium cations and site II filled with 4 sodium cations. Potassium cations fill the same cation sites. However, the **LTA** structure containing calcium cations had 6 cations per unit cell only, occupying the site I position. [28–30]

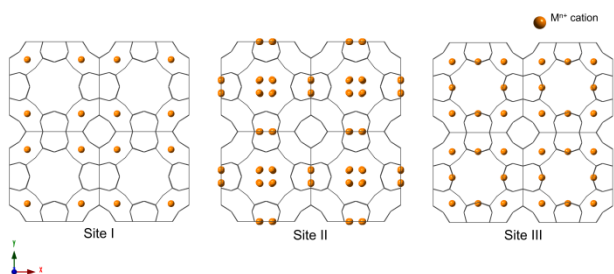


Figure 4: Common cation sites in the **LTA** framework

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The flexibility window of aluminosilicate **LTA** frameworks with extra-framework cations (sodium, calcium and potassium) was simulated by GASP. [28] The cation site and content per unit cell for each aluminosilicate **M-LTA** framework is specified in Table 2. Flexibility windows of the aluminosilicate **M-LTA** frameworks simulated using GASP are depicted in Figure 5, with the compression and expansion limits of each **M-LTA** framework summarised in Table 4.

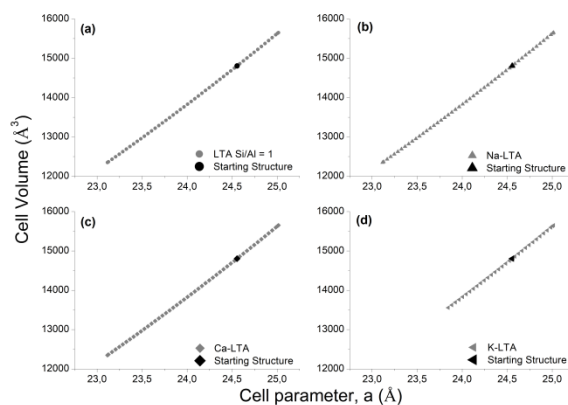


Figure 5: GASP simulated flexibility windows of **M-LTA** (b)-(d) compared to aluminosilicate **LTA** without cation content (a).

Table 4: Starting cell parameters and flexibility window limits of the cubic **LTA** framework (Si/Al = 1) simulated by GASP simulation with different extra-framework cations.

Framework	Starting cell parameter, a (Å)	Lower window edge (Å)	Compressed cell volume edge (Å <sup>3</sup> )	Upper window edge (Å)	Expanded cell volume (Å <sup>3</sup> )
<b>LTA</b> (Si/Al = 1)	24.555	23.115	12350	25.015	15653
<b>Na-LTA</b>	24.555	23.115	12350	25.015	15653
<b>Ca-LTA</b>	24.555	23.115	12350	25.015	15653
<b>K-LTA</b>	24.555	23.845	13558	25.015	15653

The flexibility window of **Na-LTA** and **Ca-LTA** frameworks was identical to that of the empty aluminosilicate **LTA** framework, as depicted in Figure 5 (a)-(c). The occupation of cation sites I and/or II by either sodium or calcium cations (as described in Table 2) did not have an effect on the theoretical compressibility of the **LTA** framework. A similar case was reported for sodium extra-framework cations in the **SOD** framework [23]. The ionic radius of sodium and calcium are both relatively small, therefore these cations were not expected to cause significant steric strain on the **LTA** framework. This is further illustrated in Figure 6 and Figure 7, which compare the starting **Na-LTA** and **Ca-LTA** structures to the compressed and expanded structures. It is clear that the compression mechanism – the pattern of collective rotation of polyhedra as the framework expands and contracts – is identical in these cases to that of the empty framework.

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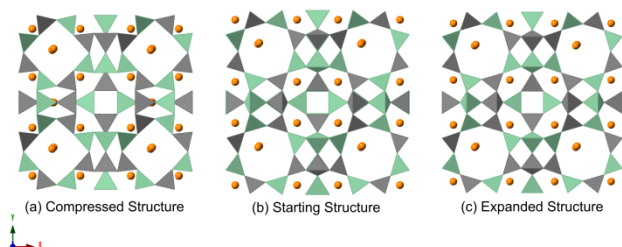


Figure 6: Flexibility window limits of aluminosilicate **LTA** framework (Si/Al ratio = 1) with sodium as extra-framework cation, grey silica tetrahedra and green alumina tetrahedra.

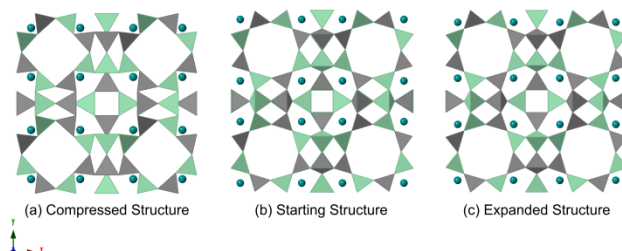


Figure 7: Flexibility window limits of aluminosilicate **LTA** framework (Si/Al ratio = 1) with calcium as extra-framework cation, grey silica tetrahedra and green alumina tetrahedra.

The **K-LTA** framework simulated by GASP exhibited reduced theoretical compressibility compared to **Na-LTA**, as depicted in Figure 5 (d). This is understandable in terms of the steric constraints imposed on the **LTA** framework as a result of the larger ionic radius of the potassium cation compared to sodium and calcium. The steric strain caused by potassium cations restricts the **LTA** framework flexibility and changes the theoretical compression mechanism of the **K-LTA**, as depicted in Figure 8. On compression, the framework displays a symmetry-breaking pattern of cooperative rotations, unlike that of the empty framework or the other ionic loadings, and the change in the 8-ring profile differs considerably from the previous cases; approaching a square or rhomboidal profile, with the square oriented differently with respect to the cell axes compared to the empty framework.

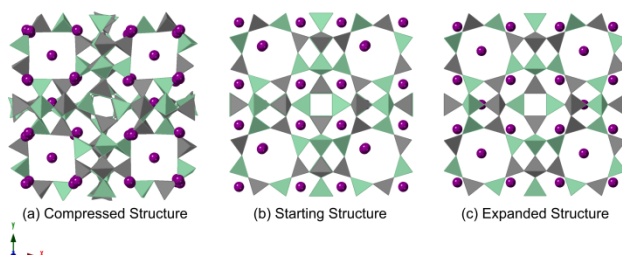


Figure 8: Flexibility window limits of aluminosilicate **LTA** framework (Si/Al ratio = 1) with potassium as extra-framework cation, grey silica tetrahedra and green alumina tetrahedra.

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## Discussion

Cations play an important role in the crystallisation of zeolite materials. They provide a moderate structure-directing role to guide the formation of a particular framework type, in addition to their role in charge balance. Correlations between the sizes of structural building units and the extra-framework cations which occupy them have been observed. It was reported that zeolite frameworks with cancrinite cages preferentially had potassium (or barium/rubidium) as extra-framework cations, while zeolite frameworks with sodalite or gmelinite cages preferentially had sodium cations as extra-framework species. [10] The results here show that small Na cations easily occupy cation sites I and II in Zeolite A. These correspond to the 6-ring windows of the sodalite cage and the 8-ring windows of the alpha cage, respectively. Furthermore, their presence in these sites does not sterically influence the compression mechanism or the extent of the flexibility window of the **LTA** framework. Potassium ions, however, have a much larger ionic radius and this affects both their sites in the framework and the compression behaviour. The framework flexibility is impeded due to steric hindrance. This results in a much smaller flexibility window being observed for **K-LTA**, and an altered compression mechanism. This implies that sodium ions also allow for more framework flexibility during the synthesis of Zeolite A and will more favourably guide its formation than potassium ions. The monovalent potassium cation is known to have a structure-breaking effect on the formation of certain zeolites due to the relatively larger ionic radius of potassium compared to the sodium cation. [10,12] However, in some cases potassium cations can serve as structure-directing agent. Zeolite frameworks **KFI**, **LTL** and **MER** are all synthesised using potassium. In some instances, a combination of both sodium and potassium cations is also required to promote the formation of different building units, notably for **FAU**, **OFF** and **PAU** syntheses. It is expected that the presence of two different cations in a framework will also affect the flexibility window limits. [2,4].

Calcium is typically referred to as a structure-breaking cation in the synthesis of many zeolites [10–13]. On the basis of the results here, the divalent  $\text{Ca}^{2+}$  ion does not affect the framework flexibility of zeolite A (as with the  $\text{Na}^+$  ion) since sterically the  $\text{Ca}^{2+}$  ion is similar in size to the  $\text{Na}^+$  ion. The structure-breaking effect of the  $\text{Ca}^{2+}$  ion may be attributed to the electrostatic effects of the divalent  $\text{Ca}^{2+}$  ion during zeolite crystallisation.

## Conclusion

The steric and geometric influence of extra-framework cations on the flexibility of the **LTA** framework has been investigated using GASP software. The siliceous and aluminosilicate **LTA** frameworks were modelled as empty structures, for comparison to the cation-containing **LTA** structures (**Na-LTA**, **Ca-LTA** and **K-LTA**). It is shown that the

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theoretical compressibility of the LTA framework is sensitive to the presence of framework aluminium. Larger Al ions result in longer Al-O bond lengths and more flexibility of Si-O-Si bridging angles. This creates a more open and more flexible framework. Extra-framework cations with relatively small ionic radii (such as sodium and calcium) have little influence on the theoretical compressibility of the zeolite framework. Larger potassium ions restrict the theoretical compressibility of the LTA framework and alter its compression mechanisms. We conclude that cation size, charge, and location can each separately play a significant role in the formation of an open, flexible zeolite framework.

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