



# Understanding the AC conductivity and permittivity of trapdoor chabazites for future development of next-generation gas sensors



H el ene Bordeneuve<sup>a,1</sup>, Dominic J. Wales<sup>b,1,2</sup>, Andrew J.W. Physick<sup>b</sup>, Huan V. Doan<sup>c,d</sup>, Valeska P. Ting<sup>c</sup>, Chris R. Bowen<sup>a,\*</sup>

<sup>a</sup> Department of Mechanical Engineering, University of Bath, Claverton Down, Bath, Somerset, BA2 7AY, UK

<sup>b</sup> Department of Chemical Engineering, University of Bath, Claverton Down, Bath, Somerset, BA2 7AY, UK

<sup>c</sup> Department of Mechanical Engineering, University of Bristol, Bristol, BSS 1TR, UK

<sup>d</sup> Department of Oil Refining and Petrochemistry, Faculty of Oil and Gas, Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem, Hanoi, Viet Nam

## ARTICLE INFO

### Keywords:

Chabazites  
Conductivity  
Permittivity  
Zeolites  
Trapdoor

## ABSTRACT

Synthetic K<sup>+</sup> chabazite (KCHA), Cs<sup>+</sup> chabazite (CsCHA) and Zn<sup>2+</sup> chabazite (ZnCHA) have been synthesized and investigated in order to relate the differences in their crystalline structures to their thermal stability, moisture content and frequency dependent alternating current (AC) conductivity, permittivity and phase angle at a range of temperatures. The materials are shown to exhibit the universal dielectric response, which is typical of materials consisting of both conductive and insulating regions. Due to the presence of porosity, the three chabazites were hydrated significantly at room temperature and so the dehydrated state was achieved by heating the chabazites to high temperatures to ensure that all different energetic types of water were removed. Cation migration activation energies for KCHA (0.66 ± 0.10) eV, CsCHA (0.88 ± 0.01) eV and ZnCHA (0.90 ± 0.01) eV were determined during the cooling cycle from the fully dehydrated state to provide an accurate measurement of the activation energies. Good thermal stability of the materials was observed up to 710 °C and below 200 °C the electrical properties can be strongly influenced by hydration level. Overall, it was determined that when either hydrated or dehydrated, KCHA had the highest conductivity and lowest cation migration activation energy of the three studied chabazites and thus has the most promising electrical properties for potential use as a gas sensing material in next-generation electrical-based gas sensors.

## 1. Introduction

Zeolites are porous aluminosilicate minerals with large extra-framework sites that can incorporate both exchangeable cations and water molecules [1]. They are described by the simplified formula M<sub>2/n</sub>O-Al<sub>2</sub>O<sub>3</sub>ySiO<sub>2</sub>wH<sub>2</sub>O where *n* is the charge of the cation M and *w* is the amount of water contained in the voids [2]. In addition, some of the Si and Al atoms can be replaced by atoms of other elements that form tetrahedral TO<sub>4</sub> units; examples include Ti and B [3]. These materials are used in many industrial processes for adsorption, catalysis, ion exchange or as molecular sieves [4]. Zeolites have also been used as the active gas detecting element in a wide range of detector and/or sensor systems [5].

Chabazite (CHA) zeolites form one of the 82 accepted zeolite mineral topologies [6], and is an abundant natural mineral, but can also be readily synthesized [7]. The chabazite framework consists of an

ordered arrangement of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra forming three different types of rings, as shown in Fig. 1a, which shows four (4MR), six (6DR), and eight-membered rings (8MR). Double 6-rings (6DR) are arranged in layers in an ABC sequence and linked by tilted 4-rings [8].

The favoured positions of different cations in chabazite results in different properties for the different cation forms of chabazite, which makes chabazite materials attractive for several processes and applications. For example, in CsCHA, the Cs<sup>+</sup> cations can act as selective aperture ‘trapdoors’, which have been successfully utilised for gas and gaseous isotope separations [9–11]. This selective ‘trapdoor’ behaviour in chabazite is a potentially attractive functional attribute in a gas selective material for sensing applications.

Previous studies [12,13] of several forms of ion-exchanged chabazite show that cations may be located at four different positions: one at the center of the 6DR prism (SI), one at the entrance of the 6DR prism, but displaced relative to the supercavity (SII), one in the supercavity at

\* Corresponding author.

E-mail address: [c.r.bowen@bath.ac.uk](mailto:c.r.bowen@bath.ac.uk) (C.R. Bowen).

<sup>1</sup> Joint first authorship: both authors contributed equally to this work.

<sup>2</sup> Current address: Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK.

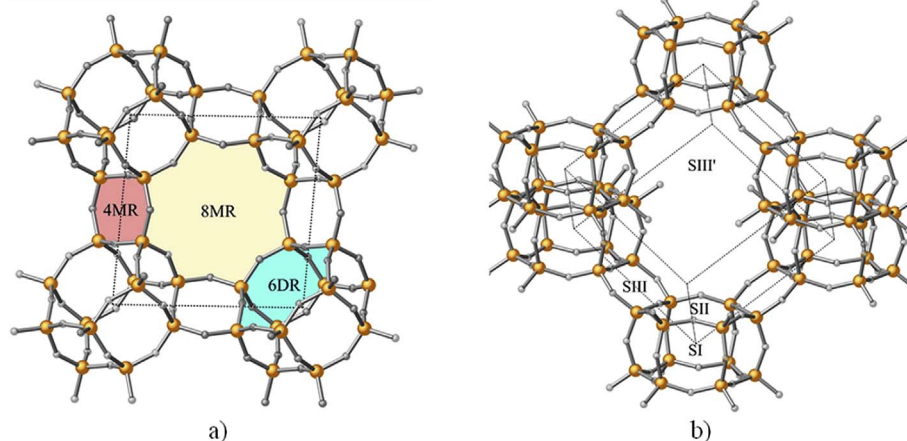


Fig. 1. Framework diagram of a chabazite zeolite. Orange = Si or Al, grey = O. a) The three different types of rings: 4MR = red, 6DR = blue, 8MRs = yellow. b) The four cation site preferences. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the four-ring window (SIII), and one in the eight-ring window of the channel (SIII'); these are shown in Fig. 1b.

In this paper we will examine synthetic chabazites containing  $K^+$ ,  $Cs^+$  and  $Zn^{2+}$ , therefore it is of interest to describe the position of these cations. At room temperature, in hydrated chabazites, the  $K^+$  cations are located in the SII positions and the  $Cs^+$  cations are bound primarily within the eight-member ring in the SIII' position [14]. According to density functional theory models,  $Zn^{2+}$  cations are more stable in the larger rings, with the  $Zn^{2+}$  cations located as six-membered rings as the most stable configuration [15]; the  $Zn^{2+}$  cations are likely to be more reactive in the small rings [15].

In addition, seven water sites are known. Previous electrical studies on zeolites have shown that the electrical conductivity, along with dielectric relaxation phenomena in zeolites, are strongly affected by the presence of adsorbed water [16–18]. However, after dehydration, it is expected that any measured conductivity will be due to the migration of interstitial cations, commonly alkali metal or alkaline earth metal cations [19–21]. This migratory cation behaviour is also expected to occur in chabazite, however, to the best of the authors' knowledge, few studies of the electrical properties of chabazites have been published [22–25]. For example, Beattie [20] examined a range of ion-exchanged chabazites based on the natural mineral of chabazite since it could not be synthesized at that time and an increase in activation energy with increasing ionic radii was observed, which ranged from  $\sim 0.65$  to  $0.8$  eV [20]. Barrer et al. [24] examined anhydrous and partially hydrated sodium chabazite, while Kjær et al. [25] examined sodium and lithium doped chabazites. Pressed powders of the material were used in all cases with metallic electrodes for electrical characterisation [20–22] and the measured activation energy was independent of pressing pressure [20]. There have been no such studies undertaken on the polycrystalline  $Zn^{2+}$  chabazite.

In this study, synthetic  $K^+$  chabazite (KCHA),  $Cs^+$  chabazite (CsCHA) and  $Zn^{2+}$  chabazite (ZnCHA) have been investigated in order to relate the differences in their crystalline structures to their thermal stability, and frequency dependent electrical properties as a function of temperature. KCHA and CsCHA were chosen as both exhibit selective aperture trapdoor behaviour for different gases [9]. ZnCHA was chosen to elucidate the effect of a divalent cation on the electrical properties of the chabazite and ZnCHA has also been demonstrated to exhibit greater  $CO_2/N_2$  selectivity compared to chabazites with other divalent counter cations [26]. This is ultimately to elucidate the suitability of these chabazites as potential gas selective/sensing materials, for example in ionic conductivity based gas sensors [27]. In particular, this work utilizes impedance spectroscopy, a technique which has been previously used to investigate long-range ionic conductivity of microporous materials and to screen porous materials for sensing applications, with a focus on the alternating current (AC) conductivity, permittivity and

phase angle of these chabazites, over a temperature range of  $30$  °C– $710$  °C [28,29]. It should be noted that it has been previously established, that neither the Si/Al ratio, nor the diameter of crystallites would result in the observed differences in conductivity of these zeolites [21,30,31].

## 2. Experimental section

### 2.1. Materials synthesis

Chemicals, materials and solvents were obtained from Sigma-Aldrich or Fisher Scientific and used as obtained, unless otherwise described.

The parent chabazite (KNaCHA) was synthesized from zeolite Y by heating 5 g of zeolite Y *in vacuo* at  $450$  °C for 6 h, at a heating rate of  $2$  °C  $min^{-1}$ .  $\sim 4$  g of dry zeolite Y was added to a solution of 31.6 mL  $H_2O$  and 4.3 mL KOH (45% w/v). The resulting mixture was agitated for 30 s before heating at  $95$  °C for 96 h. The overall gel composition was  $0.17 Na_2O:Al_2O_3:8 SiO_2:500 H_2O$ . The product was then washed with 500 mL distilled water and dried at room temperature to obtain the target KNaCHA chabazite [32].

A 2 g mass of the as-synthesized chabazite was then ion-exchanged with either 1 M KCl solution (80 mL), 1 M CsCl solution (80 mL) or 1 M  $ZnCl_2$  solution (40 mL) at  $70$  °C with stirring for 24 h to produce the K, Cs and Zn ion-exchanged CHA zeolites respectively. The products then were washed with water until the washings were at pH 7.

### 2.2. Materials characterisation

Powder X-ray diffractometry, for identification and phase purity determination, was performed using a Phillips SEI diffractometer with a  $CuK\alpha$  source ( $\lambda = 1.540598$  Å). Thermogravimetric analyses (TGA) was performed on a Setaram Setsys Evolution on sample masses of  $\sim 5$  mg. The samples were submitted to heating and cooling cycles from room temperature ( $\sim 21$  °C) to  $700$  °C at a  $5$  °C  $min^{-1}$  heating rate under a flow of air. Energy dispersive X-ray spectroscopy was performed using an Oxford INCA X-ray analyzer attached to a JEOL SEM6480LV scanning electron microscope.

In order to measure electrical properties, 0.5 cm diameter pellets consisting of the powders of the three chabazites were fabricated by compression for *ca.* 5 min at a pressure of  $1$  ton  $cm^{-2}$ . Electrical contacts were deposited onto both sides of the disks by gold sputter coating to a thickness of *ca.* 100 nm.

The complex impedance ( $Z^* = Z' + iZ''$ ) was measured in the frequency range  $0.1$  Hz– $1$  MHz using a Solartron 1260 Impedance analyzer with a 1296 Dielectric Interface, over a range of temperatures from room temperature ( $\sim 21$  °C) to  $710$  °C. Care was taken to ensure

Download English Version:

<https://daneshyari.com/en/article/6532401>

Download Persian Version:

<https://daneshyari.com/article/6532401>

[Daneshyari.com](https://daneshyari.com)