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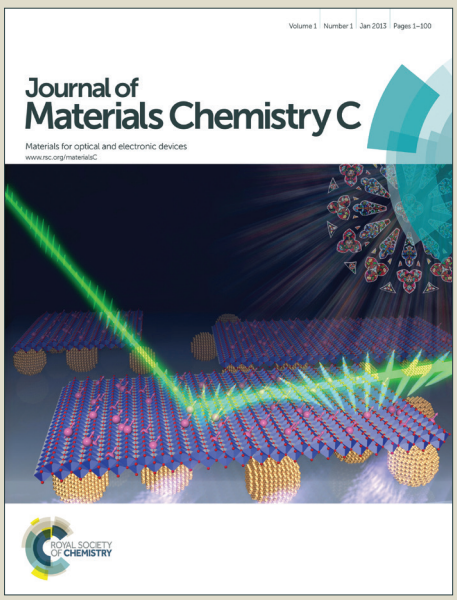

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Predicting low-k zeolite materials†

Roberta Poloni[a] and Jihan Kim*,[b]

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The IZA and the hypothetical pure-silica zeolite structures are investigated theoretically to identify optimal dielectric materials for semiconducting device applications. The dielectric constant, k, and the bulk modulus, B, are computed as second order energy-derivatives using a classical model. Six zeolites within the IZA database (JSR, IRR, OBW, BOZ, OSO, and NPT) exhibiting both ultra low-k (2.27, 2.33, 2.34, 2.37, 2.39, and 2.49, respectively) and relatively large bulk modulus are suggested as promising candidates. Finally, many hypothetical zeolite structures are predicted to out-perform the aforementioned six structures, enhancing the pool of structures that can be used for low-k dielectric materials.

With the persistent size reduction in the microelectronic devices, it is becoming imperative to manufacture insulating materials that can separate the conducting parts from one another to avoid unwanted effects like crosstalk noise and power consumption. As such, new dielectric materials that can replace the traditional silicon dioxide need to satisfy $k < k_{SiO_2} = 3.9$. Development efforts are ongoing to find new classes of low dielectric constant (low-k) materials that can easily be integrated into a conventional manufacturing process. A widely adopted approach to reduce k is to introduce porosity into silica. The presence of void space can allow materials with k in the ultra-low range (i.e. $k \leq 2.5$). Accordingly, several porous and mesoporous silica based materials have attracted much attention in this respect[1–4]. An alternative related approach is to use the inherent porosity found in many zeolites. Since zeolites possess attractive properties such as chemical and structural stability, they can serve as promising insulating materials as long as they can be mass-produced and easily integrated into the conventional microelectronic devices technology. The dielectric properties of a few zeolites have already been reported, showing that ultra-low k values are possible for these meterials. For example, recent measurements reported k values of 1.62, 2.01 and 2.13 for LTA, FER and MFI, at 2 GHz[5,6], placing these materials among the best candidates for ultra-low k materials. Also, several metal-organic frameworks have been computationally investigated in this respect[7]. In the past, there have been work investigating the relationship between k-value and various properties of porous materials (e.g. pore volume, size, shape)[2,8,9], with models being used to predict k at a given density[10]. However, to the best of our knowledge, a systematic work on a large number of zeolite structures aimed at identifing the optimal dielectric zeolite materials has not yet been reported.

In this Communication, we report large-scale computational screening results of 205 zeolite structures in the International Zeolite Association (IZA) database* and 1970 zeolite structures from the hypothetical zeolite database[11] to identify pure-silica materials that exhibit both ultra-low k (i.e. $k < 2.5$) values and an acceptable mechanical strength. In the past, we have performed similar computational zeolite screening studies for carbon capture[12] and methane mitigation[13] applications. The dielectric constant and the elastic properties are computed as second order derivatives of the total energy using GULP[14] with the zeolite model from Ref. 15. This model uses a two-body potential consisting of a long-range Coulomb term and short-range Buckingham-type potential plus a three-body bond-bending term to account for the directionality of the bonding between O and Si. A shell model is used to describe the polarization of the oxygen atoms. This model has been widely used to simulate various properties of zeolites, including dielectric properties[6,16,17]. Experimental studies have re-

† Electronic Supplementary Information (ESI) available: DFT calculations of dielectric constant and bulk modulus, box plot of the dielectric constant computed for the 1200 hypothetical zeolite structures, dielectric constant of the hypothetical zeolite structures with framework densities < 1300 kg/m^3, table with the high frequency and static dielectric constant and the bulk modulus for the 205 IZA zeolite structures. See DOI: 10.1039/b000000x/

[a] *Laboratoire de Science et Ingénierie des Matériaux et Procédés (SIMaP), CNRS UMR5266, Grenoble-INP, BP 75, 38402 Saint Martin d'H'ères Cedex, France; E-mail: roberta.poloni@simap.grenoble-inp.fr*
[b] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Korea*

* www.iza-online.org/

ported the dielectric constant for a few pure silica zeolites studied here, such as MFI, ITW, FER, STT, CHA, LTA, and BEA[5,6,18]. However, a meaningful comparison with our data cannot be performed since the measurements were executed at frequencies between 1 MHz and 8 GHz, far above and below, respectively, the static (i.e. zero-frequency) and high-frequency limits employed here. Instead, we compute the static dielectric constant values of a few selected IZA structures using density functional perturbation theory and find reasonable agreement with the values from GULP (results shown in Table S1†). Similarly, the reliability of our classical model to describe the mechanical properties of pure silica zeolites is demonstrated by the reasonable agreement found between the computed bulk modulus and the values obtained using density functional theory, as shown in Table S2†.

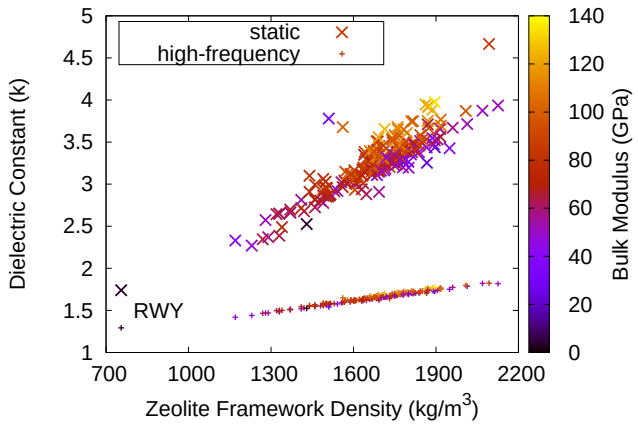

Fig. 1 The static and high frequency dielectric constants for the 205 IZA zeolites are plotted as a function of the framework density.

Figure 1 shows the static and the high frequency k values for the 205 IZA zeolites as a function of the zeolite framework density (FD). As expected, the zeolites with the lowest k-values tend to have smaller FD. The correlation between k and FD becomes weaker for the static frequency values, indicating the sensitivity of the ionic contribution to the structural topology. Given the relatively low operating frequencies in current microprocessors, the static dielectric constant is viewed as a more reasonable approximation than the infinite frequency limit. Therefore, in what follows we focus on the static dielectric constant data. From Figure 1, a large spread in the k-values for structures that possess similar FD can be observed, indicating that FD alone is not sufficient to fully predict k. While k has been shown to correlate with pore volume[2,8,9], we did not find meaningful correlation between k and pore volume for zeolites that possess similar FD. Instead, we found that for the IZA structures, materials that possess large bulk moduli tend to have larger k-values at similar FD (color-coded in Figure 1). Inspection of several zeolite structure with similar FD reveals that high k values are found for structures with evenly distributed silicon and oxygen framework atom, while low-k values correspond to zeolites with localized regions of both dense and sparse framework atoms (large pores separated by homogeneous networks). As an example to illustrate this finding, the unit cell of zeolites MTN (FD: 1710 kg/m^3, k: 3.66) and SOS (FD: 1690 kg/m^3, k: 2.91) are shown in the the SI (Figure S2†). This analysis suggests that, apart from the overall FD, the local density of the silicon/oxygen atoms can impact the dielectric properties significantly.

In our simulations of the IZA structures, zeolite RWY has been identified as having the lowest k-value of 1.74, which is not surprising given its extremely low FD[19]. In order to find zeolite structures with even lower k, we enlarged the set of zeolite structures to include over 136000 methane-accessible hypothetical structures generated by Deem and coworkers[11]. The methane-inaccessible structures are predicted to possess large k values due to their high FD and neglected in our analysis. To expedite calculations, 1200 zeolite structures from a wide range of FD were selected as representative test cases. The spread in the k-values increased for larger FD with k values of 2.62±0.09 at FD = 1285-1315 kg/m^3 to 4.26±0.21 at FD = 2285-2315 kg/m^3 (shown as box plot in Figure S3†). At high FD, the spread in the k-values is not large enough such that the best materials could be found in those structures.

Accordingly, simulations were conducted on the 770 zeolite structures with the lowest FD (i.e. FD $<$ 1300 kg/m^3) in order to find the zeolites with the lowest k. Within the IZA database, only five zeolites (i.e. RWY, IRR, JSR, OBW, and BOZ) have FD $<$ 1300 kg/m^3. Similar to the case for the IZA data set, a general positive correlation between k and FD is observed for these hypothetical zeolite structures (shown in Figure S4†).

For practical application purposes, the best materials need to possess both low-k values and high mechanical strength. As such, we computed the bulk modulus for the lowest FD zeolite structures using GULP, with the results shown in Figure 2. Together with the five zeolites which have FD $<$ 1300 kg/m^3 and ultra low-k, we have also included in Figure 2 zeolites JST, OSO, and NPT within the IZA database which have $k \leq 2.5$. The simulation results indicate that zeolites RWY and JST possess poor mechanical strength with a computed bulk modulus of 3.2 GPa and 4.1 GPa, respectively. The remaining zeolites

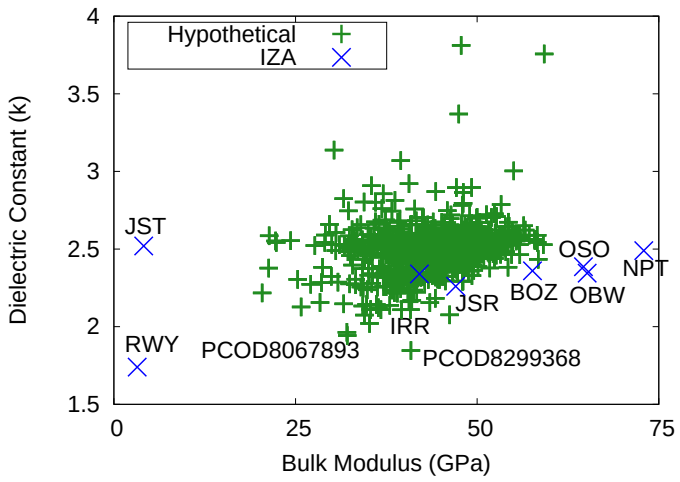

Fig. 2 Dielectric constant plotted as function of the bulk modulus for the low density zeolites. 770 structures in the hypothetical zeolite database with FD < 1300 kg/m^3 and the eight IZA structures with the lowest k values are included as data points.

all possess a much larger bulk modulus and thus, hundreds of structures with $k < 2.5$ are suitable as excellent candidate materials. Among the IZA structures, zeolites JSR, IRR, OBW, BOZ, OSO, and NPT are identified as promising structures that possess both ultra low-k (2.27, 2.33, 2.37, 2.34, 2.38, and 2.49) and high bulk modulus (47.0, 42.1, 65.1, 57.6, 64.6, and 72.9 GPa) values. Within the hypothetical zeolite database, we also identified two structures, PCOD8299368 and PCOD8067893, with k < 2 (1.85 and 1.94). The results here indicate that the choice for the optimal low-k materials can change depending on the requirement imposed on the mechanical strength. As such, the data generated from large-scale analysis can serve as an useful guideline for future experimental efforts when it comes to synthesizing pure-silica insulating zeolite materials. The dielectric constant and the bulk modulus values of the 205 IZA structures are shown in Table S3†.

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