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STATIC AND DYNAMIC PROPERTIES OF AMORPHOUS MATERIAL DERIVED FROM ZEOLITE ZSM-5

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Introduction

Motivation

Study of zeolite-based amorphous materials are important for technological applications:

- **Catalysis** [1]
- **Ion-exchange** [2]
- **Ceramic Chemistry** [3]

Method

- **Molecular dynamics** using BKS **interaction potentials** [4] with **canonical** ensembling.
- **System size**: 3456 and 1152 atoms for static and dynamic properties, respectively.
- **Structure generation**: Silicious crystalline configuration was heated to temperatures T = 4700 K, 4800 K, 4900 K and 5000 K, then equilibrated and finally quenched to T = 300 K followed by equilibration of 3×10^5 time steps with each **time step** of 2 fs.
- Stored expected minima were quenched to zero temperature using a combined **steepest-descent-conjugate-gradient algorithm** and used for analysis of structural and vibrational properties.
- Extent of amorphization was quantified as **percentage of energy crystallinity** (PEC) [5], i.e.,

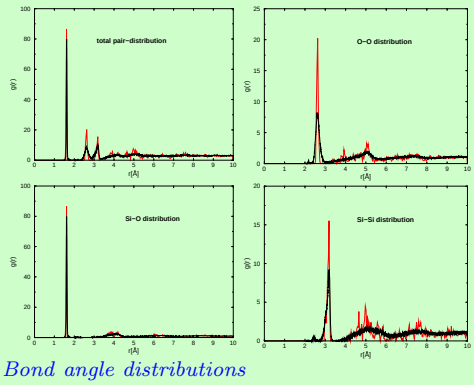
$$PEC = \frac{E_{amorphous} - E_{configuration}}{E_{amorphous} - E_{crystalline}} \times 100$$

- $E_{amorphous}$ =-16.9 eV/atom represents the energy per atom of the maximum amorphized structure obtained in our simulation.

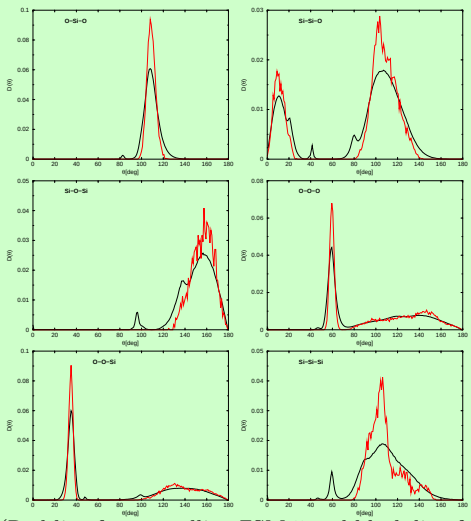
Results

Static Properties [5]

Pair-distribution functions



Bond angle distributions



(Red line for crystalline ZSM-5 and black line for the amorphous form derivedfrom it).

- Slightly distorted SiO_4 tetrahedra are the basic units.
- Connectivity: Mainly corner sharing and a small percentage of **edge sharing** were observed.

Internal surface area (ISA)

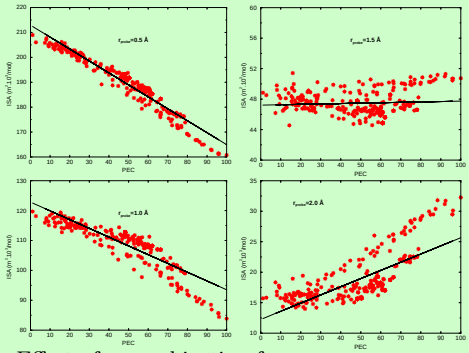
- We model the system as an ensemble of intersecting hard spheres with radii depending on the coordination number (CN).

Atomic/ionic radii R_{coord} (in Å) for O and Si.

CN	R_{coord}(O)	R_{coord}(Si)
0	1.52	2.10
1	1.435	1.64
2	1.35	1.18
3	0	0.72
4	0	0.26
5 and higher	0	0

- ISA was determined using the **probe-atom model**.

$$ISA = \frac{1}{M}\left(\sum_{i=1}^{N} 4\pi[R_{coord}(i) + r_{probe}]^2 \frac{p_i}{p}\right)$$



- Effect of amorphization for:

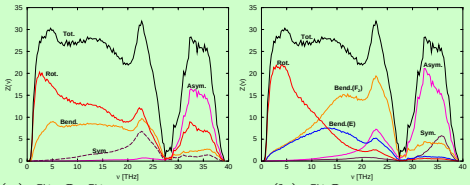
Large probe radii: ISA decreases due to the reduction in the number of large pores.

Small probe radii: ISA increases due to increase in under-coordination and increasing tendency to convert large rings into smaller rings.

Dynamic Properties [6]

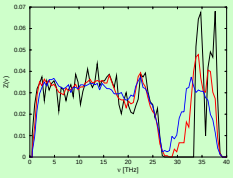
Relative contribution of motions of structural subunits to vibrational density of states (VDOS)

- VDOS were obtained by diagonalization of the dynamic matrix.
- Two basic subunits Si-O-Si and SiO_4 with the approximate local point group symmetries C_{2v} and T_d, respectively, were considered.
- In order to investigate atomic motions for different eigenmodes, projections of eigenvectors onto the various vibrational modes of structural subunits were performed.



(a) Si-O-Si (b) SiO_4

Effect of extent of amorphization on VDOS



(Black line refers to the VDOS for the crystalline ZSM-5 and the red line for the structures with PEC of 70 % and the blue line for the structures with PEC of 50 %).

- Amorphization leads to broadening of high-frequency peaks and shifts peaks towards low frequency with a narrowing of the band gap.

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