THE BOSON PEAK IN PARTIALLY CRYSTALLINE MATERIALS DERIVED FROM ZEOLITE ZSM-5

A. B. Mukhopadhyay[1)], C. Oligschleger[2)] and M. Dolg[1)]

1) Institut für Theoretische Chemie, Universität zu Köln, Greinstr. 4, D-50939 Köln, Germany

2) Fachhochschule Bonn - Rhein - Sieg, University of Applied Sciences, von-Liebig-Straße 20, D-53359 Rheinbach, Germany

Introduction

Motivation

The **boson peak** (BP) is traditionally associated with a vibrational density of states exceeding the Debye value around 1 THz. The **origin** and **nature** of these vibrational excitations remains a subject of theoretical controversy.

Method

• **Molecular dynamics** using BKS **interaction potentials** [1] with **canonical** ensembling.

• **System size**: 3456 and 1152 atoms [2-3].

• **Structure generation**: The silicious crystalline configuration was heated to higher temperatures, then equilibrated and finally quenched to $T = 300$ K followed by equilibration.

• Stored expected minima were quenched to zero temperature using a combined **steepest-descent-conjugate-gradient algorithm**.

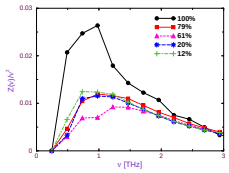
• Extent of amorphization was quantified as **percentage of energy crystallinity** (PEC), i.e.,

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

• For the detected local-minima the dynamic matrices were calculated and diagonalized in order to obtain eigenvalues (**square of eigenfrequencies**) and eigenvectors (**type of motion**).

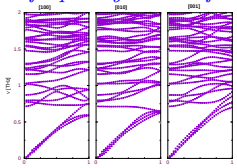
Results

Reduced density of states



Two distinct ranges of PEC exhibiting opposite behavior of the intensity of the BP with respect to amorphization: For structures with PEC of **above/below ≈60%**, intensity **decreases/increases**. We attempt an explanation in terms of **Maxwell counting of floppy modes**.

Low-frequency modes for crystalline structures:



Phonon dispersion curves along the symmetry directions of the orthorhombic unit cell of ZSM-5.

• The BP obtained around 1 THz is mainly due to the modes which are **optical** in nature.

• Experimental reduced specific heat for zeolitic systems [4]: A very intense hump for zeolites belonging to MFI and BEA in comparison to vitreous silica and cristobalite was associated with the presence of large 10-fold and 12-fold rings, respectively.

Distribution of coordination numbers in percent for **10% most active atoms** selected according to the magnitude of mass-weighted eigenvectors, in the modes belonging to the BP region.

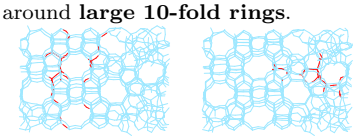
PEC	Si			O		
	= 4	> 4	< 4	= 2	> 2	< 2
100	1	-	-	99	-	-
79	7	0	0	89	0	4
61	14	0	0	81	0	5
20	17	0	1	59	1	23
12	17	0	2	55	1	25

Ring analysis depending on the extend of amorphization. The first line for each PEC gives **occurrence** of n-fold rings in percent. In the second line quantity $\rho = \bar{r}_{avg}/\bar{r}_{min}$, describes the **degree of puckering** of the rings. The numbers in parentheses in the first column represent the **average participation ratios** of the modes in the BP (0.5 THz - 1.5 THz) region.

PEC	n = 2	3	4	5	6	7	8	9	10
100 (0.45)	-	-	2.9	48.9	39.2	-	-	-	9.0
			1.01	1.06	1.13				1.09
79 (0.41)	1.0	2.6	9.0	37.7	33.4	8.2	2.4	1.9	3.8
	1.00	1.04	1.06	1.09	1.16	1.22	1.23	1.19	1.12
61 (0.40)	1.8	7.2	14.9	24.7	31.7	14.2	3.2	1.4	0.9
	1.00	1.09	1.10	1.20	1.37	1.22	1.22	1.22	1.28
20 (0.31)	3.9	11.8	16.4	25.7	26.6	10.7	2.8	1.4	0.7
	1.00	1.07	1.15	1.27	1.53	1.27	1.31	1.32	1.40
12 (0.27)	4.5	13.8	17.8	26.0	28.4	5.5	2.2	1.2	0.6
	1.00	1.15	1.21	1.32	2.78	1.30	1.47	1.46	1.54

Low-frequency modes for structures with PEC above ≈ 60%:

• The most active atoms are mainly located around **large 10-fold rings**.



(a) (b)

The active atoms shown by red lines of the modes at (a) 0.5 THz and (b) 1 THz in a structure with PEC of 73% in yz plane.

• For crystalline system the large 10-fold rings are quite regular. Amorphization causes drastic disappearance of these rings accompanied by a formation of other mismatched large rings.

• **Severe puckering** of the rings takes place and thereby reducing the possibility of having more regular and symmetric rings.

• **In the framework of floppy modes, the presence of large rings alone without the additional effect of symmetry cannot break the basic balance between the constraints and the degree of freedom and cannot give rise to floppy modes.**

• Therefore these modifications result in a reduction in the number of floppy modes and thereby decrease the intensity of the BP.

Low-frequency modes for structures with PEC below ≈ 60%:

• The possibility of having floppy modes due to the closed rings are low due to severe puckering.

• Tremendous **increase of the number of under-coordinated active atoms** is observed.

• These are related to non-bridging Si-O bonds and 'open rings'. The resulting reduced number of constraints leads to an increase of the number of floppy modes.

• The average participation ratio decreases drastically on amorphization, with the formation of highly localized modes.

• **The increased number of these localized floppy modes associated with under-coordinated centers causes the increased intensity of the BP for this range of PEC.**

Nature of the vibrational motions:

• Projections of eigenvectors onto the various vibrational modes of the ideal subunit SiO_4 with local point group symmetry T_d were performed.

• The main contributions result from rotational motions. For intermediate and low values of PEC the bending character contributes noticeably, indicating that distortions of the SiO_4 subunits are associated. **These floppy modes are not rigid unit modes in a strict sense.**

References

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