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Vibrations induced by different charged oxygen vacancies in quartz-like GeO_2

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ABSTRACT

We have studied local configurations and vibrations of oxygen vacancies in different charged states in α-quartz GeO_2 by computer simulation. First-principles potential of the Buckingham type has been used in calculations. The investigation of the lattice dynamics in defective crystal is performed using the phonon local density of states. The calculation of the densities of states is facilitated with Lanczos recursion. Frequencies of localized vibrations induced by oxygen vacancies are determined.

1. Introduction

The progress in development of micro- and optoelectronics demands the investigation of promising materials. Due to unique combination of physical properties, germanium dioxide is compound with a variety of technological applications. However this material has not been the subject of extensive studies unlike silicon dioxide. At ambient pressure there are three solid GeO_2 modifications: a rutile tetragonal structure, an α-quartz trigonal structure and an amorphous glass [1]. The crystal structure and properties of GeO_2 with the α-quartz-type ideal structure have been studied both experimentally [2–8] and theoretically [9–13]. The calculations of the geometric structure and the physical properties are also known for perfect and defective rutile-type GeO_2 phase [14,15]. Many of the peculiar characteristics of GeO_2 are determined by the presence of point defects and are connected with dynamic processes occurring with participation of defects.

The correct description of these processes requires information about localized vibrations induced by defects. In many cases this information can be obtained only from numerical simulations. An important class of intrinsic defects in germanium dioxide is related to oxygen vacancies that may exist in different charged states. One can distinguish several types of such defects. In particular, neutral vacancies V^0 are the variant of so-called oxygen-deficiency centers (ODCs) forming the main luminescent properties of GeO_2 modifications [16,17]. Positively single-charged vacancies V^{+1} correspond to well-known paramagnetic E′-type centers that are the most studied defects [18]. In addition it is assumed that there are doubly positively charged vacancies V^{+2}, although these centers are not found experimentally.

We reported earlier [19] the results of model calculations of the local lattice dynamics of α-quartz SiO_2 containing O-vacancies in different charged states. At the same time the lattice dynamics of α-quartz-like GeO_2 with oxygen vacancies has not been analyzed so far. The effect of O-vacancies on the vibration spectrum is still not well understood.

In the present work we are considering vibrational properties of quartz-like GeO_2 with oxygen vacancies in three states: V^{+2}, V^{+1} and V^0. The influence of these vacancies on the structure and the phonon spectrum of α-GeO_2 is studied using the numerical modeling.

2. Computer simulation

It is known that the α-quartz lattice of GeO_2 is described by the space group $P3_121$ or $P3_221$. A primitive cell includes three formula units and a hexagonal elementary cell consists of three corner-linked GeO_4 tetrahedra that are connected through a common oxygen atom. Each Ge atom sits at the center of GeO_4 tetrahedron and is surrounded by four oxygen atoms. The GeO_4 tetrahedron is distorted: there are two slightly differing Ge–O distances. Each Ge atom has four nearest-neighbor Ge atoms which are at equal distances. The unit cell can be completely defined by the lattice constants *a*, *c* and four internal parameters *u*, *x*, *y*, *z* as in [20].

Germanium dioxides have ionic–covalent chemical bonds. The computer simulation both of atomic configurations and lattice

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dynamics in such crystals containing charged defects encounters considerable difficulties. It is necessary to consider defect-induced relaxation of the surrounding lattice in a large region. Therefore, investigations on static and dynamic behaviors of atoms require the use of a big atomic cluster. The cluster technique allows accurate description of long-range electrostatic interactions. We have already applied it earlier successfully [21,22].

In this approach, the crystal with a defect is divided into several spherical regions: an inner region 1 and an outer region 2 + 3, as shown in Fig. 1. The region 1 is surrounded by the finite region 2. These regions are treated atomistically. The region 3 is represented in the approximation of continuum. Atom displacements in region 1 can be determined by direct minimization of the static lattice energy in the context of the method [23]. Atoms in the region 2 are kept fixed in their ideal positions. Such procedure provides correct calculations of slowly decreasing Coulomb interactions inside the region 1.

The force F_i that acts on the ith atom is obtained using the differentiation of the potential energy $U(r_1, r_2, \ldots, r_N)$ with respect to the relevant coordinates of the atom:

$$F_i = -\frac{\partial U(r_1, r_2, \ldots, r_N)}{\partial r_i}. \tag{1}$$

In our case, the potential energy of the atomic cluster is represented as the sum of pairwise interactions:

$$U(r_1, r_2, \ldots, r_N) = \sum_{k>i}^{N} \sum_{i=1}^{N-1} U_{ik} = \frac{1}{2} \sum_{k \neq i}^{N} \sum_{i=1}^{N} U_{ik}. \tag{2}$$

The interatomic potential U_{ik} is a function of the positions of i and k atoms. It has a specific functional form. We use the ion–ion interaction model [24]

$$U_{ik} = U(r_{ik}) = A_{ik} \exp(-r_{ik}/\rho_{ik}) - \frac{C_{ik}}{r_{ik}^6} + \frac{Z_i Z_k}{r_{ik}}, \tag{3}$$

where the terms describe repulsion, van der Waals and Coulomb interactions, respectively. Here $r_{ik} = |r_k - r_i|$ is the distance between ions i and k; Z_i is the partial charge of the ion i; A_{ik}, ρ_{ik} and C_{ik} are the parameters. The numerical values of parameters appeared in Eq. (3) can be fitted with respect to experimental data [9,10,25] or to the energies obtained from a quantum mechanical calculation [26]. In our calculations, the parameters are used which have been presented in [26]. The choice of these parameters is motivated by the following facts. On one hand, the calculations have reproduced well both the structural and various properties of the perfect crystal including vibrational spectra. On the other hand, parameters of the potential U_{ik} derived from ab initio calculations.

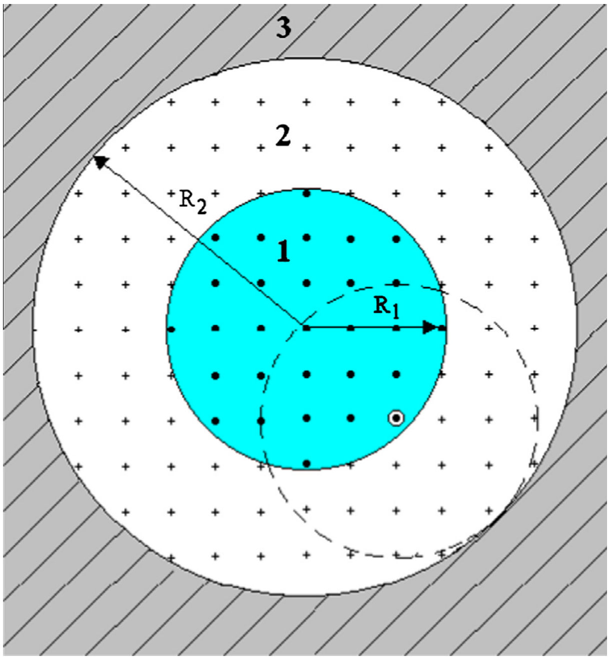

Fig. 1. The structural model of the crystal.

The effect of oxygen vacancies on the vibration spectrum of α-GeO$_2$ was analyzed by calculating the local densities of states (LDOSs) of phonons in ideal and defective crystals using the Lanczos recursion [27,28]. The Lanczos algorithm is a technique to transform a dynamic matrix of the atomic cluster into an equivalent tridiagonal form.

3. Results

Using the ab initio pair interatomic potentials for α-GeO$_2$ mentioned above, we modeled the equilibrium structure of a perfect crystal. The obtained values of the lattice constants a, c and unit cell volume Ω are $a = 5.114$ (4.986) Å, $c = 5.736$ (5.647) Å and $\Omega = 129.96$ (121.57) Å^3, where the numbers in parentheses are the experimental values [5] at 300 K. The experimental values are found to be slightly small, but fairly close to those obtained from our calculations.

The simulated Ge–O bond lengths are 1.743 Å for two oxygen ions (denoted by O(1), see Fig. 2) and 1.751 Å for the other two (denoted by O(2)). Each oxygen ion forms only two O–Ge bonds of different lengths. The Ge ion, which is 1.743 Å away from oxygen that can be removed to form a defect, will be designated Ge(1). The Ge ion is labeled Ge(2) when the O–Ge bond is 1.751 Å long. These results are in qualitative agreement with the experimental findings of the work [5], although the bond lengths are slightly larger than the corresponding experimental values: $d_{\text{Ge–O(1)}} = 1.737$ Å and $d_{\text{Ge–O(2)}} = 1.742$ Å. It should be noted that the authors of work [29] used the same interaction pair potential [26] in molecular dynamics simulations for quartz-like GeO$_2$. They have obtained the Ge–O bond lengths that are almost identical to our results. Thus, calculations [29] and experimental data [5] can be considered as additional arguments in favor of the correctness of the approach used in present paper.

We also calculated the phonon dispersion curves in highly symmetric directions ([100], [010] and [001]) of the Brillouin zone and the one-phonon density of states (DOS) for perfect α-quartz GeO$_2$. The phonon DOS was determined by solving the Fourier transform of the dynamic matrix (dimensionality 27 × 27) for 8500 randomly selected wave vectors of the Brillouin zone. The discrete frequencies were sorted into a histogram of 100 bars. The calculation results are shown in Fig. 3. There are three frequency bands for DOS: an upper limit of the low-frequency band at 10.2 THz, a medium-frequency band between 12.9 and 16.0 THz and a high-frequency band between 26.1 and 28.5 THz. The bands agree very well with the previous computations [26] and with experiments [6]. Experimentally three bands are found: the low-frequency continuum extends to 10.0 THz, the mid-frequency continuum ranges from 12.9 to 17.6 THz, the continuum at high frequency from 25.5 to 28.8 THz.

Then the phonon DOS was calculated using the Lanczos recursion (Fig. 3), in order to test the validity of this method. An analysis of Fig. 3 shows that the $G(\nu)$ curves, which were obtained by different methods, are similar. We have found that a cluster with inner region 1 radius of 19.12 Å containing 2000 ions and with region 2 radius of 25.19 Å containing 4628 ions in which the Lanczos technique is used to 10–12 levels of recursion is sufficient to reproduce phonon LDOS. The upper boundary of the low-frequency band is