Phonons and oxygen diffusion in Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$

Prabhatasree Goel$^1$, M K Gupta$^1$, R Mittal$^{1,2,*}$, S J Skinner$^3$, S Mukhopadhyay$^{4,6,*}$, S Rols$^5$ and S L Chaplot$^{1,2}$

$^1$ Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
$^2$ Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India
$^3$ Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom
$^4$ ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot, Oxon OX11 0QX, United Kingdom
$^5$ Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

E-mail: rmittal@barc.gov.in and sanghamitra.mukhopadhyay@stfc.ac.uk

Received 13 February 2020, revised 7 April 2020
Accepted for publication 14 April 2020
Published 20 May 2020

Abstract

We report investigation of phonons and oxygen diffusion in Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$. The phonon spectra have been measured in Bi$_2$O$_3$ at high temperatures up to 1083 K using inelastic neutron scattering. Ab initio calculations have been used to compute the individual contributions of the constituent atoms in Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ to the total phonon density of states. Our computed results indicate that as temperature is increased, there is a complete loss of sharp peak structure in the vibrational density of states. Ab initio molecular dynamics simulations show that even at 1000 K in δ-phase Bi$_2$O$_3$, Bi–Bi correlations remain ordered in the crystalline lattice while the correlations between O–O show liquid like disordered behavior. In the case of (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$, the O–O correlations broadened at around 500 K indicating that oxygen conductivity is possible at such low temperatures in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ although the conductivity is much less than that observed in the undoped high temperature δ-phase of Bi$_2$O$_3$. This result is consistent with the calculated diffusion coefficients of oxygen and observation by quasielastic neutron scattering experiments. Our ab initio molecular dynamics calculations predict that macroscopic diffusion is attainable in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ at much lower temperatures, which is more suited for technological applications. Our studies elucidate the easy directions of diffusion in δ-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$.

Keywords: phase transition, order disorder, phonon, ab initio, molecular dynamics, diffusion

(Some figures may appear in colour only in the online journal)

1. Introduction

Solids exhibiting high levels of oxygen-ion conduction have always been of considerable interest to researchers all over the world [1–7]. These solids find potential technological applications in fuel cells, gas sensors, ceramic oxygen generators and are the backbone for light photo-catalysts and redox catalysts for several chemical processes [3, 4, 7–11]. High ionic conductivity in these compounds is attributed to the migration of oxygen-ion vacancies at high temperature. Yttria-stabilized zirconia (YSZ), a widely used oxygen-ion conductor, is a typical example. In this category, bismuth sesquioxide (Bi$_2$O$_3$) is a frontrunner, which has a conductivity two orders of magnitude greater [12, 13] than YSZ at temperatures above 1000 K. Bi$_2$O$_3$ occurs in the monoclinic α-phase at ambient conditions [3, 4, 14], whilst the high temperature δ-phase above 1003 K exhibits defective fluorite structure including a large amount of vacant sites in the oxide ion sublattice [14, 15]. Also, Bi$_2$O$_3$ is polymorphic, depending upon temperature and thermal history; several phases like β, γ, δ, ε and ω phases are formed. The defect fluorite type structure [16] (δ-phase) of Bi$_2$O$_3$ has six anions (O$^{2–}$) and they are randomly distributed over the

---

* The authors to whom any correspondence should be addressed.
eight tetrahedral holes of the fcc lattice formed by Bi\(^{3+}\) ions. The \(\delta\)-phase is known \([2, 13]\) to have high solid-state oxide ionic conductivity \((1–2 \text{ S cm}^{-1})\) over its narrow stability range of 1003–1090 \(\text{K}\). The fast high oxygen-ion conduction behavior of \(\delta\)-Bi\(_2\)O\(_3\) in general is linked \([17]\) to the intrinsic oxygen ion vacancies and asymmetric arrangements of anions due to the lone pair \((6s^{2})\) of Bi\(^{3+}\) ions.

There have been several theoretical and experimental studies to understand the origin of diffusion in this oxide. Several structural models have been formulated to understand the high temperature defective cubic phase of Bi\(_2\)O\(_3\). Gattow and Schroder suggested \([3, 4, 16, 18, 19]\) a random distribution of oxygen ions over the tetrahedral positions, so there is an equal probability of oxygen occupying any of the Wyckoff sites. Battle \textit{et al}\([20]\) proposed that 32f interstitial sites are occupied, Sillen \textit{et al}\([3, 4, 18, 21]\) surmised that three-quarters of regular tetrahedral sites are occupied while one-quarters are vacant, leaving a lattice with 25% oxygen vacant contents. Willis \textit{et al}\([3, 4, 18]\) suggested that the oxygen ions are displaced along \((111)\) directions from their regular sites towards the octahedral vacancies. Several other authors suggest a preference along \((111)\) directions of the oxygen atoms, while there are preferences of a preference for \((110)\) as it is energetically more favourable. Studies using density functional theory (DFT) have shown that \((100)\) oxygen vacancy alignment has the lowest energy while along \((110)\) configuration it is marginally higher. Mohn \textit{et al}\([3]\) reported that the irregular local structure of \(\delta\)-Bi\(_2\)O\(_3\) is closely connected to increased electron density around Bi, thus facilitating the presence of a stereo chemically active lone-pair. This observation of higher cation polarizability associated with the lone pair of electrons in Bi, is understood to be a key factor in achieving sustained oxygen diffusion. Neutron scattering studies \([15]\) reveal presence of micro-domains where there is short-range ordering. These various studies have tried to understand the role of local structure disorder and its electronic properties in diffusion. With aging, oxygen ions slowly undergo some ordering processes of the unoccupied sites leading to reduction in the conductivity of Bi\(_2\)O\(_3\). Long-term changes in the structure and oxygen ordering have been reported in the literature \([22]\). In these oxides the ionic conductivity is attributed to disorder in the oxygen sublattice and the loss in long-term conductivity is believed due to oxygen ordering. It is reported \([22]\) that after 300 h aging in Nb, Y doped Bi\(_2\)O\(_3\) long term conductivity is reduced by 40%. There have been diffuse elastic neutron scattering studies \([23]\) on doped Bi\(_2\)O\(_3\) to understand the effect of different cation doping on the structure of the cubic phase.

Ionic conductivity of Bi\(_2\)O\(_3\) drops at room temperature. The problem of stabilizing the high conducting phase at room temperature can be eliminated by suitable cation doping, such as rare-earth ions, \(\text{Y}^{3+}\), \(\text{Sc}^{3+}\), etc. The high ionic conducting \(\delta\)-phase can be stabilized \([6, 24]\) at ambient temperature in a range of compositions, viz., \((\text{Bi}_{1-x}\text{Y}_x)\)\(_2\)O\(_3\) \((x = 0.1–0.5)\). Doping with suitable cations stabilizes the superionic conducting phase of Bi\(_2\)O\(_3\) at lower temperature, but the flip side is that it also reduces the ionic conductivity as the activation energy observed in the Arrhenius plot for oxygen migration is raised. The ionic conductivities of these non-stoichiometric compounds are found to be higher than that of yttria-stabilized zirconia at similar temperature. The studies on diffusion \([19, 25]\) and transport properties of yttria-doped bismuth oxide shows that it can be a potential material for low or intermediate temperature applications based on oxygen-ion diffusion.

Progress is being made to achieve solid electrolytes with ionic conductivity of the order of 0.0001 to 0.1 \text{Ohm}^{-1}\text{ cm}^{-1}\) and activation energy of about 0.1 \text{eV}. Accurate measurement and calculation of phonon frequencies are needed to evaluate the jump frequency and hence the diffusion coefficient. Quasielastic neutron scattering (QENS) is a very good technique to study \([26–28]\) oxygen-ion transport in such oxides. The diffusion of oxygen atoms can be investigated using this technique to understand the microscopic nature of diffusion, such as, the jump length, jump path and the residence time, etc. Recently we have employed \textit{ab initio} DFT and molecular dynamics (MD) simulations in the analysis of inelastic neutron scattering (INS) measurements \([29–32]\) \textit{ab initio} MD (AIMD) also been used to analyse QENS experiments to understand diffusions microscopically \([33, 34]\).

The high ionic conducting \(\delta\)-phase can be stabilized \([6, 24]\) at ambient temperature in a range of compositions, viz., \((\text{Bi}_{1-x}\text{Y}_x)\)\(_2\)O\(_3\) \((x = 0.1–0.5)\). So, for our study we have used the composition of \(x = 0.3\). Here we report detailed vibrational study on the different phases of the Bi\(_2\)O\(_3\) and \((\text{Bi}_{0.7}\text{Y}_{0.3})\)\(_2\)O\(_3\). Further, we have performed extensive \textit{ab initio} molecular dynamics simulations to study the phonons and diffusion of oxygen in \(\delta\)-Bi\(_2\)O\(_3\) and in \(30\%\ \text{Y}_2\)O\(_3\) doped in Bi\(_2\)O\(_3\), i.e., \((\text{Bi}_{0.7}\text{Y}_{0.3})\)\(_2\)O\(_3\). We also report neutron inelastic measurements of the phonon density of states in Bi\(_2\)O\(_3\) at different temperatures, from 300 \(\text{K}\) to 1048 \(\text{K}\). Subsequently QENS measurements are done in the temperature range 353 \(\text{K}–1083 \text{K}\). Possible preferred direction of oxygen-ion movement has always been of intrigue and several studies have been devoted to understand the same. Our aim is to understand the difference in oxygen-ion diffusion in the \(\delta\)-Bi\(_2\)O\(_3\) and \((\text{Bi}_{0.7}\text{Y}_{0.3})\)\(_2\)O\(_3\) by employing integrated study using neutron scattering experimental along with theoretical \textit{ab initio} lattice dynamics and molecular dynamics simulations.

2. Experimental

Samples of Bi\(_2\)O\(_3\) were obtained from Sigma Aldrich, UK \((99.999\%)\) and used without further processing. The inelastic neutron scattering experiment on Bi\(_2\)O\(_3\) was carried out using the IN4C spectrometer at the Institut Laue Langevin (ILL), France. The spectrometer was based on the time-of-flight (TOF) technique and was equipped with a large detector bank covering a wide range of about 10° to 110° of scattering angle. The INS measurements were performed at several temperatures from 300 \(\text{K}\) to 1048 \(\text{K}\). About 2 \(\text{cm}^2\) of polycrystalline sample of Bi\(_2\)O\(_3\) has been used for the measurements. For these measurements we have used an incident neutron wavelength of 2.4 \(\text{Å} (14.2 \text{meV})\) in neutron energy gain setup. In the incoherent one-phonon approximation, the measured scattering function \(S(Q, E)\), where \(E\) and \(Q\) were the
energy transfer and momentum transfer vector, respectively, was related [35–37] to the phonon density of states $g^{(n)}(E)$ as follows:

$$\langle \rangle$$

$$g^{(n)}(E) = A \left( \frac{e^{2W(Q)}}{Q^2} \frac{E}{n(E, T) + \frac{1}{2} \pm \frac{1}{2}} S(Q, E) \right) \tag{1}$$

$$g^{(n)}(E) = B \sum_k \left( \frac{4\pi b_k^2}{m_k} \right) g_k(E) \tag{2}$$

where the $+$ or $-$ signs correspond to energy loss or gain of the neutrons, respectively, $n(E, T) = [\exp(E/k_B T) - 1]^{-1}$. $T$ was temperature and $k_B$ Boltzmann’s constant. $A$ and $B$ were normalization constants and $b_k$, $m_k$, and $g_k(E)$ were, respectively, the neutron scattering length, mass, and partial density of states of the $k$th atom in the unit cell. The quantity between $\langle \rangle$ represented suitable average over all $Q$ values at a given energy. $2W(Q)$ was the Debye–Waller factor averaged over all the atoms. The weighting factors $\frac{4\pi b_k^2}{m_k}$ for various atoms in the units of barns/amu were: 0.0438 and 0.2645 for Bi and O respectively.

The QENS experiments were performed on the OSIRIS spectrometer [38] of the ISIS Neutron and Muon source, UK. This instrument was a high-resolution indirect geometry time-of-flight backscattering spectrometer with final energy of $E_t = 1.845$ meV at the analyser setting PG002. In this setting pyrolitic graphite analysers used reflection at its 002 plane to determine the final neutron energy given above and energy resolution 27 µeV. A quartz sample cell was filled with Bi$_2$O$_3$ powder and attached with a gas handling rig supplying pure oxygen. Over the high temperature measurements, the O$_2$ pressure was maintained at 240 mbar and data collected for 5 h at each temperature. Prior to data collection a series of measurements were taken on the empty quartz ampoule. Initial data from the empty quartz were obtained at 353 K, before gathering data every 20 K from 1023 K–1083 K. In this article the analysis of the result obtained at 1083 K has been presented.

The data analysis was undertaken using the QENS data analysis interface as implemented in the Mantid software [39]. One delta function and one Lorentzian together were convoluted with instrument resolution determined from the Vanadium standard cell at room temperature. The background data of the quartz cell has been subtracted from all data analysis mentioned below.

3. Computational details

The lattice and molecular dynamics simulations were performed in the ordered [40] monoclinic $\alpha$-phase and disordered $\delta$-phase [16] of Bi$_2$O$_3$ (cubic phase, space group $Fm-3m$) and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ (cubic phase, space group $Fm-3m$) using $ab$ initio DFT as implemented in the VASP simulation package [41, 42]. We note that the fcc unit cell of the defect fluorite type structure [16] ($\delta$-phase) has six anions (O$^{2-}$) that are randomly distributed over the eight tetrahedral holes of the fcc lattice formed by Bi/Y$^{3+}$ ions. A supercell of $(2 \times 2 \times 2)$ dimension, which consists of 160 atoms, has been used in the computations of the ordered [40] monoclinic $\alpha$-phase. In the lattice dynamics calculations, the required force constants were computed within the Hellman–Feynman framework, on various atoms in different configurations of a supercell with $(\pm x, \pm y, \pm z)$ atomic displacement patterns. The generalized gradient approximation (GGA) exchange-correlation following the parameterization by Perdew, Burke and Ernzerhof [43, 44] has been used for the computation of total energy and forces using the projected augmented wave (PAW) formalism of the Kohn–Sham density functional theory. An energy cut-off of 900 eV was used for plane wave expansion. The Monkhorst Pack method [45] was used for $k$-point generation with a $4 \times 4 \times 4$ $k$-point mesh. The convergence breakdown criteria for the total energy and ionic force loops were set to $10^{-8}$ eV and $10^{-4}$ eV Å$^{-1}$, respectively. We have used PHONON software [46] to obtain the phonon frequencies in the entire Brillouin zone, as a subsequent step to density functional theory total energy calculations.

The $ab$-initio molecular dynamics (AIMD) simulations were performed in the NVE ensemble with a time step of 2 femtosecond. With the time-step of 2 fs in our production runs of 60 ps in the NVE ensemble, the total energy remained stable within $10^{-5}$ eV, which is quite satisfactory. The long-time simulations are necessary since the jump times in the oxygen-ion diffusion are quite long. Due to computational limitations even on a supercomputer, detailed AIMD simulations have been performed on a $2 \times 2 \times 2$ supercell of the monoclinic $\alpha$-phase (consisting of 160 atoms) and also a $2 \times 2 \times 2$ supercell of the disordered cubic $\delta$-phase of Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ (with 80 atoms), and using only a single $k$-point in the Brillouin zone and an energy cut-off of 900 eV for plane-wave expansion. However, for comparison, we have also performed additional simulations at 1000 K on a larger supercell of the $\delta$-phase (with 160 atoms) and with $2 \times 2 \times 2$ mesh $k$-points. The energy convergence criteria of $10^{-5}$ eV has been chosen for self-consistence electron energy convergence. Initially, the structure was equilibrated for 10 picoseconds to attain the required temperature in NVT simulations. The temperature in the NVT simulations was attained through a Nose thermostat [47]. Then the production run was performed for up to 60 picoseconds within NVE ensemble. Simulations were performed for a series of temperatures from 300 K to 1100 K. At each temperature, a well-equilibrated configuration was obtained during the whole simulation. At 1100 K, the simulations were extended up to 200 picoseconds.

The vibrational density of states from $ab$ initio molecular dynamics has been calculated [48] using Fourier transform of the velocity auto-correlation function. The phonon density of states is calculated on the $2 \times 2 \times 2$ supercell of the monoclinic $\alpha$-phase and $2 \times 2 \times 2$ supercell of the cubic unit cell in the disordered $\delta$-phase. For better averaging over the Brillouin zone, one may do the $ab$ initio computations with a larger supercell but this would be computationally expensive. However, we are able to reproduce the experimental spectrum fairly well. The simulations performed up to 60 pico-seconds are sufficient to give an energy resolution of $\sim 0.1$ meV in the calculated density of states.
As noted above, for comparison we have performed additional \textit{ab initio} simulations at 1000 K in the disordered \(\delta\)-phase of Bi\(_2\)O\(_3\) and (Bi\(_{0.7}\)Y\(_{0.3}\))\(_2\)O\(_3\) (cubic phase, space group \textit{Fm-3m}) on the \(2 \times 2 \times 2\) supercell of the cubic unit cell (with 80 atoms) as well as on the \(4 \times 4 \times 4\) supercell of the primitive unit cell (with 160 atoms). In these calculations with 160 atoms supercell we have taken a single \(k\)-point in the Brillouin zone. For additional simulations with 80 atoms supercell, the \(k\)-point generation is with a \(2 \times 2 \times 2\) mesh.

The dynamical structure factors \(S(Q, E)\) were calculated from the trajectory obtained from AIMD simulations using nMoldyn software following the procedure reported previously \cite{34, 49}. The pair-correlation function for various atomic pairs has been calculated using the following relation \cite{50}:

\[
g_{IJ}(r) = \frac{n_{IJ}(r)}{\rho_{I} \rho_{J} 4\pi r^2 dr} \tag{3}
\]

where \(n_{IJ}(r)\) is the average number of atoms of species \(J\) in a shell of width \(dr\) at distance \(r\) from an atom of species \(I\) and \(\rho_{I}\) and \(\rho_{J}\) is the average number density of the species \(J\). The time-averaged pair-correlation function from AIMD simulation is obtained by averaging over the simulation run. As evident from equation (3), the correlations have been calculated isotropically and not in any specific direction.

4. Results and discussion

4.1. Temperature dependence of phonon density of states

We have performed INS measurements of Bi\(_2\)O\(_3\) at several temperatures (figure 1(a)) from 300 K to 1048 K beyond the superionic transition at about 1003 K. The room temperature measurements show well defined peak structure in the phonon density of states which disappears at above 973 K below the superionic transition temperature. We have compared the measured phonon density of states at 300 K with the lattice dynamics calculated phonon spectrum in the ambient \(\alpha\)-phase (figure 1(b)). The neutron-weighted phonon density of states shows peaks at about 7, 15, 25, 40, 50 and 61 meV. The calculated total neutron-weighted phonon density of states is in good agreement with measurements (figure 1(b)). The calculated partial contributions from Bi and O atoms to the total phonon density of states are also shown. It can be seen that due to its heavier mass Bi contributes mainly at low energy up to 20 meV, while the contribution from O is in the entire spectrum. All the peaks in the experimental phonon spectra agree well with our calculations. As temperature increases to 773 K, peaks at about 25, 40, 43, 51, and 60 meV all are reduced in intensity. At 973 K, peak at 25 meV almost disappears leaving a broad peak centered around 48 meV. Beyond 973 K, the spectrum lost all the sharp peak structure in the phonon density of states (see figure 1(a)). To understand the atomistic contributions in the vibrational densities of states (VDOS), the neutron-weighted partial VDOS of Bi and O are given in figure 1(b). Further, we have calculated the phonon dispersion relation (figure 2) along the high symmetry directions of the monoclinic space group for ordered \(\alpha\)-Bi\(_2\)O\(_3\), and compared it with the phonon density of states. The latter, as shown in figure 2, is obtained by integrating the contribution of phonons in a mesh of \(10 \times 10 \times 10\) wave-vectors in the monoclinic Brillouin zone.

To include anharmonic contributions in the VDOS, which may be relevant at high temperature, we have performed AIMD simulation to evaluate the phonon spectrum. This has been calculated \cite{51, 52} using the Fourier transform of the velocity auto-correlation function obtained from the AIMD simulations. In figure 3 we have compared the calculated partial VDOS of Bi, O in the \(\alpha\)- and the \(\delta\)-phase of Bi\(_2\)O\(_3\) as well as in (Bi\(_{0.7}\)Y\(_{0.3}\))\(_2\)O\(_3\) at different temperatures using AIMD simulations. In the ambient \(\alpha\)-phase, Bi has contributions up to 25 meV at 300 K; with increase in temperature to 800 K, the Bi contribution remains unchanged, however, the oxygen contribution in the entire Brillouin zone shifts towards lower energies. This shift can be seen from the total VDOS (figure 3).

In the highly conducting \(\delta\)-phase, the partial contribution of Bi does not show any significant change and here again oxygen
Figure 2. Computed phonon dispersion relation and total and partial density of states of in ordered monoclinic phase of Bi$_2$O$_3$ from ab initio lattice dynamics calculations.

Figure 3. Computed partial and total phonon density of states of different phases of Bi$_2$O$_3$ and Y-doped Bi$_2$O$_3$ at different temperature from ab-initio MD calculations.

contributes in the entire Brillouin zone. The partial and total density of states at 1000 K and 1100 K for the δ phase do not show much change. In case of (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$, the computed spectra have been plotted for 300 K, 1000 K and 1100 K. Bi contribution is found to be same as that in Bi$_2$O$_3$, i.e up to 25 meV, while Y contributes up to 40 meV. This is in accordance to their masses; Y’s mass is 88.9 amu while Bi’s is 208.9 amu. Oxygen (16 amu) contributes in the entire range. With increase in temperature, the spectra move down (figure 3) in the energy as expected. The data at 1000 K and 1100 K do not show much change.

The comparison between the molecular dynamics results with the measured phonon density of states is given in figure 4. The ambient phase experimental data have been compared with the computed results and it is found that although the calculations of the α-phase at 300 K do not show distinct peak structure, but peaks at 5, 25, 48, 54 and 60 meV compare well with the experimental data. Similarly, the data at 1100 K of the δ-phase is in qualitative agreement with the experimental data at 1048 K. Due to the small size of the simulation cell in the AIMD simulations, the computed phonon spectra have limitations and may be regarded as in
fair agreement with experiments. The phonon density of states calculations performed using both lattice dynamics (figure 1(b)) and molecular dynamics simulations (figure 4) show a satisfactory agreement indicating a good degree of convergence. The fair agreement between the calculation and measurements validates the employment of the AIMD method for further microscopic analysis of the transport properties of the pure and doped oxide of Bi.

4.2. Pair correlation function

In order to understand the microscopic picture of the lattice at ambient and at higher temperature in ordered Bi$_2$O$_3$, disordered $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$, we have plotted pair correlations of different pair of atoms in figure 5. In the ambient temperature of $\alpha$-phase at 300 K, the minimum Bi–Bi distance is 3.5 Å, while the nearest neighbor Bi–O distance is approximately 2.5 Å, and the closest O–O distance is 3.2 Å. With increase in temperature, at 800 K there are no discernible changes in the pair correlations in $\alpha$-Bi$_2$O$_3$. On further increase in temperature to 1000 K, in the cubic $\delta$-Bi$_2$O$_3$ phase, there is long-range correlation between Bi–Bi pairs. However, the correlation between Bi–O pairs appears to decay gradually beyond the third neighbour at 1000 K and above, while for O–O it decays significantly beyond the first neighbour itself indicating only a short-range order. At these temperatures, the nearest neighbor distance for Bi–Bi is 4 Å. In the case of Bi–O it is 2.4 Å while for O–O it is about 3 Å. This shows the increased disturbances occurring in the oxygen sub-lattice at this temperature range.

In the case of (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$; however, there is short-range correlation between Bi–O and Bi–Y pairs up to the second neighbor at different temperatures. Bi–Bi correlations start at 4 Å, which is the same for Y–Y. The first nearest distance for Bi–O and Y–O is the same at 2.2 Å. Bi–Y correlations start at 4 Å, while for O–O the first neighbor distance is about 3 Å at 300 K. Moreover, in the case of O–O correlation, it is very poor even at 300 K. There are no changes in the Bi–Bi, Bi–Y, Bi–O correlations as temperature is increased from 300 K to 1100 K. Our results predict that the first peak in the correlation functions, corresponding to Bi–O nearest neighbor distance, in the disordered phase is around 2.2 Å which is in very good agreement with Mohn et al’s ab initio MD results [3]. Both in cubic disordered Bi$_2$O$_3$ and doped Bi$_2$O$_3$ the correlations are broad after this first peak while in the case of the $\alpha$-phase there is definite peak structure beyond the first neighbor distance. The Bi–Bi first neighbor distance in the $\alpha$ phase is 3.5 Å while that in the case of both doped and disordered $\delta$-phase is about 4 Å.

4.3. Mean squared displacement and diffusion

The mean square displacement (MSD) of various atoms at time $\tau$ is calculated using the following relation [48, 53]
Figure 6. Mean square displacement ($\langle u^2 \rangle$) of various atoms in $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$. Green line is a linear fit to the computed data at different temperatures.

$$u^2(\tau) = \frac{1}{N_{\text{ion}}(N_{\text{step}} - N_{\tau})} \sum_{i=1}^{N_{\text{ion}}} \sum_{j=1}^{N_{\text{step}} - N_{\tau}} |r_i(t_j + \tau) - r_i(t_j)|^2.$$  \hfill (4)

Here $r_i(t_j)$ is the position of $i$th atom at $j$th time step. $N_{\text{step}}$ is the total number of simulation steps and $N_{\text{ion}}$ is the total number of atoms of a particular type in the simulation cell. $N_{\tau} = \tau/\delta t$, where $\delta t$ is the size of the time step used in the MD simulations. The calculated MSD ($u^2$) of various atoms in $\delta$-Bi$_2$O$_3$ and in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ at various temperatures is plotted in figure 6. The MSD of Bi atoms is small and does not increase with time, which implies that Bi atoms do not diffuse and form a rigid framework, while oxygen atoms show extensive diffusion. The calculated value of the MSD for $\delta$-Bi$_2$O$_3$ at 1100 K at 20 ps is obtained to be about 13 Å$^2$ which is in agreement with reported results [1]. It has been found that at 1100 K, the value of MSD for $\delta$-Bi$_2$O$_3$ is almost five times that of (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$.

We have performed additional ab initio simulations at 1000 K in the disordered $\delta$-phase of Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ with 80 atoms and 160 atoms supercells. As mentioned above, for calculations with 160 atoms cell we have taken a single $k$-point in the Brillouin zone, while with the 80 atoms supercell the $k$-point generation is with a $2 \times 2 \times 2$ $k$-point mesh. In case of the disordered Bi$_2$O$_3$, the results of the additional calculations are found to show larger $u^2$ values (figure 7) of up to about 20%. For (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$, figure 7 shows that the $u^2$ values are almost double with the additional calculations performed on the larger supercell. We find that, although quantitatively the diffusion coefficient is underestimated (figure 7) with the smaller supercell and a single $k$-point, the results are fairly convergent in terms of the nature of the jump-diffusion
Figure 7. Mean square displacement ($\langle u^2 \rangle$) of various atoms in $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$. The calculations at 1000 K are performed with combinations of different number of atoms in the super cell and the $k$-points mesh in AIMD.

Figure 8. The calculated mean squared displacements ($\langle u^2 \rangle$) of individual oxygen atoms in the $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$. The $\langle u^2 \rangle$ of selected oxygen atoms at 1000 K is shown with thick solid lines. The trajectories of these oxygen atoms are shown in figures.

Figure 9. Diffusion coefficient and activation energy barriers of oxygen in $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ from ab initio MD simulations.

Since the ab initio molecular dynamics simulations are computationally expensive even with a super computer, we have performed detailed temperature-dependent simulations only using the 80 atoms supercell and a single $k$-point as given in figures 3–6 and 8–11.

The displacement pattern of oxygen atoms in $\delta$-Bi$_2$O$_3$ and (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ is shown in figure 8. We find that at 1000 K in $\delta$-Bi$_2$O$_3$, oxygen ions have a distribution of jump lengths from 2 to 5 Å, while in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ the maximum jump length is smaller and is about 4 Å. In (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ at a lower temperature of 700 K, oxygen ions have shorter jumps distances, as expected, ranging from 2 to 3 Å. The distribution of jump lengths is consistent with the distribution of first-neighbor oxygen–oxygen distances (figure 5) between 2.5 to 3.5 Å and the second neighbor distance at about 5 Å. The pattern of the MSD shows that oxygen atoms diffuse by jumping from one site to another. There is no specific pattern of displacement or any preference of direction as seen from the displacement pattern of a few selected oxygen ions in the disordered and in the doped phase. Further increase in temperature to 1100 K, increases the average MSD of oxygen’s in $\delta$-Bi$_2$O$_3$ and in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ by about almost 130%. This MSD in $\delta$-Bi$_2$O$_3$ is more distributed than in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$, predicting a range of possible jump distances in undoped $\delta$-Bi$_2$O$_3$. This result is consistent with the sudden increase in diffusion coefficient of oxygen in $\delta$-Bi$_2$O$_3$ beyond 1000 K (figure 9).
From the linear fit of the slope of the mean square displacements (figure 6) of oxygen ions at different temperatures, diffusion coefficient of the two compounds have been computed as given in figure 9. The calculated self-diffusion coefficient of oxygen in cubic δ-Bi₂O₃ is about $10 \times 10^{-11}$ m² s⁻¹ at 1100 K, which is similar to the liquid like conductivity (~$10^{-9}$ m² s⁻¹) reported previously [7] and is of the same order as reported ($17 \times 10^{-10}$ m² s⁻¹ at 1100 K) by Wind et al [1]. The doping of yttrium in the lattice hinders the movement of oxygen atoms, leading to reduced diffusion coefficients. The diffusion coefficient of oxygen in (Bi₁₀.₇Y₀.₃)₂O₃ at 1100 K is almost five times smaller ($2 \times 10^{-10}$ m² s⁻¹) than that in δ-Bi₂O₃.

In order to estimate the activation energy barriers in both compounds, the temperature dependence of diffusion coefficients is fitted with Arrhenius relation, i.e.

$$D(T) = D_0 \exp(-E_a/k_B T). \quad (5)$$

One can linearize this equation, i.e.,

$$\ln(D(T)) = \ln(D_0) - E_a/k_B T \quad (6)$$

where $D_0$ is a constant factor representing diffusion coefficient at infinite temperature, $k_B$ is the Boltzmann constant and $T$ is temperature in K. The calculated diffusion coefficients as a function of temperature is fitted (figure 9) to equation (6). It can be found (see figure 9) that the slope of δ-Bi₂O₃ is more negative than that of the doped Bi₂O₃, hence activation energy for oxygen diffusion is lower in yttria-doped Bi₂O₃ as compared to disordered δ-Bi₂O₃. Fitting of the data in figure 9 for δ-Bi₂O₃ gives a value of $9.4 \times 10^{-6}$ m² s⁻¹ for $D_0$ and the activation energy ($E_a$) for oxygen diffusion is obtained as $0.87 \pm 0.1$ eV, which is somewhat larger than the value reported by Wind et al [1] ($E_a = 0.4$ eV). In the case of (Bi₁₀.₇Y₀.₃)₂O₃, we find (figure 9) that there are two different activation energies at two different ranges of the temperature. It seems the nature of diffusion changes around 900 K. Below 900 K, the jumps are shorter, and longer jumps set in at higher temperatures (figure 8). The latter longer jumps may encounter a larger activation energy. Below 900 K, the values of $D_0$ and activation energy are $0.81 \times 10^{-10}$ m² s⁻¹ and $0.04 \pm 0.01$ eV respectively, while on increasing temperature beyond 900 K, these values are $7.5 \times 10^{-9}$ m² s⁻¹ and $0.58 \pm 0.23$ eV respectively. The Y-doped compound occurs in the δ-phase over a wide range of temperatures. The δ-phase has large oxygen disorder that may enable diffusion. In the undoped compound the δ-phase exists only at high temperatures above 1003 K and shows large oxygen diffusion. When we compare the diffusion in the doped and undoped compound at high temperatures in the δ-phase, we find that the presence of the large Y atom reduces the diffusion.

Figures 10 and 11 give the pathways in which selected oxygen ions diffuse in both the compounds over several picoseconds. In case of the undoped compound, the two selected oxygen ions appear to diffuse first along the b-direction and then along the c-direction. In case of the doped compound, both the selected oxygens diffuse within a plane and move along an edge. There appears to be no preferred direction for diffusion, both in the pure and doped Bi₂O₃. These observations are in agreement with those of Wind et al [1], namely, that the jumps are essentially isotropic, not dominated by any preferred direction as claimed by some previous reports [3, 4, 14].

From the QENS experiment, broadening of the elastic line is obtained from the diffusion of the oxygen in Bi₂O₃. As oxygen is a coherent scatterer, the microscopic understanding of the diffusive behavior of oxygen atoms in the lattice may be obtained by calculating the dynamical coherent structure factor for δ-Bi₂O₃. The lowest value of $Q$ obtained from calculation is 0.55 Å⁻¹, which is limited by the size of the supercell.

The Lorentz peak functions were fitted to the calculated dynamical incoherent structure factors $S(Q,E)$

$$S(Q,E) = A1 \frac{\Gamma_1}{\Gamma_1^2 + E^2}. \quad (7)$$

The Bi and O both scatter coherently, so the $Q$ dependence of coherent $S(Q,E)$ has also been obtained from ab initio calculation. The coherent $S(Q,E)$ was better described by combination of Lorentz and Gaussian peak functions, which are fitted to the calculated dynamical coherent structure factors $S(Q,E)$

$$S(Q,E) = \frac{2 \pi A1 \Gamma_1}{4\pi E^2 + 4\pi/2} + \frac{A2}{\Gamma_2 \sqrt{\pi/2}} \exp \left( -\frac{Q^2}{\Gamma_2^2} \right). \quad (8)$$

Here $A1$ and $A2$ are the area of Lorentzian and Gaussian respectively, while $\Gamma_1$ and $\Gamma_2$ are the half width at half maximum energy (HWHM) of the Lorentzian and the standard deviation of the Gaussian, respectively. The sum of the area of
Figure 12. (a) The variation of wave vector dependence ($Q$) of half width at half maximum (HWHM) of Lorentzian peak fitted to the experimental dynamical neutron scattering function $S(Q, E)$ obtained from QENS experiment for $\delta$-Bi$_2$O$_3$ at 1083 K. (b) The calculated $Q$ dependence of HWHM of Lorentzian obtained from fitting to coherent (open circles) and incoherent (closed circles) $S(Q, E)$ obtained from $ab$ initio calculation. (c) The area of Gaussian and Lorentzian extracted from fitting to coherent $S(Q, E)$ from $ab$ initio calculation. $S(Q)$ is normalized to 1 at 1.6 Å$^{-1}$ which is below the first Bragg peak. (d) The multiplication of the HWHM of Lorentzian and sum of the area of Gaussian and Lorentzian.

Lorentzian and Gaussian gives the static structure factor, $S(Q)$. In the fitting procedure the value of $\Gamma_2$ is fixed at 0.027 meV. The same value of the resolution was used while calculating the coherent $S(Q, E)$ from AIMD calculations. The extracted $Q$ dependence of HWHM from coherent and incoherent calculations at 1100 K is shown in figure 12(b). The areas of the Lorentzian and Gaussian from coherent calculations at 1100 K are also shown in figure 12(c).

The $Q$-dependence of the HWHM shows an oscillatory behavior due to the combined effect of the jump diffusion and coherent scattering. The analysis of the QENS data of $\delta$-Bi$_2$O$_3$ reported by Wind et al indicated [1] that coherency effects, i.e. the structure factor, must be included to analyze the experimental data of HWHM vs $Q$, using the so-called Skold modification [51] to the Chudley–Elliott model [54]

$$\Gamma(Q) \times S(Q) = \left(1 - \sin(Qd)/Qd\right)/\tau$$  \hspace{1cm} (9)

where $d$ is the jump distance and $\tau$ is the relaxation time. We have also plotted (figure 12(d)) the multiplication of $S(Q)$ and HWHM of the Lorentzian. We find it difficult to fit the above equation (9) to the calculations (figure 12(d)). Although our calculations are in qualitative agreement with our experimental observations as well as that of Wind et al [1], our analysis suggests that diffusion in $\delta$-Bi$_2$O$_3$ cannot be described by a single jump diffusion model.

As shown in figure 12(b), we find that the nature of dependence of HWHM on $Q$ obtained from incoherent $S(Q, E)$ matches well with the experimental data (figure 12(a)), although the values of the calculated HWHM are lower in comparison to those of the experimental data. This result predicts that in the presence of 25% oxygen vacancies in the structure of $\delta$-phase of Bi$_2$O$_3$, oxygen may move rather independently. Therefore, the oxygen dynamics in this material may be described by the incoherent approximation.

A combination of two incoherent jump diffusion lengths ranging from 3.3 Å–10.8 Å and relaxation time 4.1–5.1 ps in the form of the pure incoherent Chudley–Elliott model [54] can be fitted well with experimental HWHM (figure 13). In this fitting two different $Q$ ranges have been fitted with two different set of parameters. For low $Q$, i.e. below 1.3 Å$^{-1}$ about 80% of all O ions have the jump distance of 10.8 Å and relaxation time of 5.1 ps, however, for high $Q$, i.e. above 1.3 Å$^{-1}$, jump distance and relaxation time of all O ions are 3.3 Å and 4.1 ps, respectively. From equation (7) it is clear that for large $Q$, when $S(Q)$ can be normalized to unity, the Skold modification [51] reduces to the incoherent Chudley–Elliott model [54]. This result predicts again that the oxygen vacancies in the $\delta$-Bi$_2$O$_3$ play a crucial role in its diffusion process. In the absence of 25% oxygen in $\delta$-Bi$_2$O$_3$, as explained above, oxygen can diffuse more independently and thus motion can be well described with incoherent approximations. This finding...
Figure 13. The analysis of QENS results using incoherent Chudley–Elliott model. (a) Normalized QENS spectra for $Q = 1.1 \, \text{Å}^{-1}$, (b) fitting of HWHM ($Q$) of QENS spectra at 1083 K using Chudley–Elliott model [54] with two sets of parameters. See text for more details.

agrees well with earlier reports of incoherent diffusion in $\delta$-Bi$_2$O$_3$ [15]. The average diffusion coefficient is thus obtained as $2.14 \times 10^{-8} \, \text{m}^2 \, \text{s}^{-1}$ which compares well with calculated results given above and reported values$^1$.

5. Conclusions

In this article we have reported inelastic neutron scattering data and computational simulations on Bi$_2$O$_3$ in the ambient and high temperature phases, and on Y-stabilized Bi$_2$O$_3$ (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$. Our ab initio lattice dynamics results based on DFT are in very good agreement with the measured data at ambient conditions. High temperature VDOS is measured to understand the increased disorder in the lattice. With increasing temperature, beyond 1000 K, a complete disappearance of sharp vibrational peaks in the measured data indicates the appearance of the highly disordered cubic $\delta$-phase of Bi$_2$O$_3$. Our AIMD calculations of the VDOS indicate that O contributes in the entire frequency spectrum while Bi and Y (in doped Bi$_2$O$_3$) contribute only in the lower energy transfer range. Pair correlations between Bi–O, Bi–Bi, O–O suggest that only the oxygen sub-lattice becomes disordered in the high temperature $\delta$-phase. Calculated MSD of oxygen in $\delta$-phase of Bi$_2$O$_3$ show that oxygen moves randomly and isotropically
from one site to the other and there is no specific preference of direction. Our calculations assume random ordering in the $\delta$-phase which is partially vacant. A combination of different sets of jump distances and relaxation times, obtained from QENS experiments, are determined for different ranges of momentum transfer vectors. Two broad range of parameters are observed for diffusion, for low $Q$, i.e., below 1.3 Å$^{-1}$, the jump distance and relaxation time are of 10.8 Å and 5.1 ps, respectively. However, for high $Q$, i.e., above 1.3 Å$^{-1}$, jump distance and relaxation time are of 3.3 Å and 4.1 ps, respectively.

The pair correlations in $\delta$-phase and in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ are similar emphasizing the fact that high conducting cubic phase can be stabilized at lower temperature by Y doping. Our calculations indicate that diffusion coefficient of oxygen atoms decrease by one-fifth in (Bi$_{0.7}$Y$_{0.3}$)$_2$O$_3$ in comparison to the liquid conduction of the cubic $\delta$-phase, yet increases the conductivity considerably compared to the ambient pure $\alpha$-phase Bi$_2$O$_3$ which does not show any conduction.

Acknowledgments

We thank the ISIS Neutron and Muon Source Facility for the provision of beam time (RB1410490). Institut Laue-Langevin (ILL) facility, Grenoble, France, is acknowledged for providing beam time on the IN4C spectrometer. The use of ANU-PAM super-computing facility at BARC is acknowledged. SLC thanks the Indian National Science Academy for award of an INSA Senior Scientist position.

ORCID iDs

R Mittal https://orcid.org/0000-0003-3729-9352
S Mukhopadhyay https://orcid.org/0000-0002-6501-4089

References

[1] Wind J, Mole R A, Yu D and Ling C D 2017 Chem. Mater. 29 7408
[2] Takahashi T and Iwahara H 1978 Mater. Res. Bull. 13 1447
[3] Mohn C E, Stolen S, Norberg S T and Hull S 2009 Phys. Rev. B 80 024205
[4] Mohn C E, Stolen S, Norberg S T and Hull S 2009 Phys. Rev. Lett. 102 155502
[5] Sannes N, Tompsett G, Nafe H and Aldinger F 1999 J. Eur. Ceram. Soc. 19 1801
[6] Seko A, Koyama Y, Matsumoto A and Tanaka I 2012 J. Phys.: Condens. Matter 24 475402
[7] Bayliss R D, Cook S N, Kotsantonis S, Chater R J and Kilner J A 2014 Adv. Energy Mater. 4 1301575
[8] Packer R and Skinner S 2010 Adv. Mater. 22 1613
[9] Burriel M, Garcia G, Santiso J, Kilner J A, Chater R J and Skinner S J 2008 J. Mater. Chem. 18 416
[10] Packer R, Skinner S, Yaremchenko A, Tsipis E, Kharton V, Patrakeev M and Bakhteeva Y A 2006 J. Mater. Chem. 16 3503
[11] Skinner S J and Kilner J A 2000 Solid State Ion. 135 709
[12] Verkerk M and Burggraaf A 1981 J. Electrochem. Soc. 128 75
[13] Harwig H and Gerards A 1978 J. Solid State Chem. 26 265
[14] Aidhy D S, Nino J C, Sinnott S B, Wachsman E D and Phillpot S R 2008 J. Am. Ceram. Soc. 91 2349
[15] Hull S, Norberg S T, Tucker M G, Eriksson S G, Mohn C E and Stolen S 2009 Dalton Trans. 40 8737
[16] Gattow G and Schröder H 1962 Z. Anorg. Allg. Chem. 318 176
[17] Goméz X, Huang J, Chen Y, Wu M, Liu G, Lei X, Liang J, Cao H, Tang F and Xu B 2013 Int. J. Electrochem. Sci. 8 10549
[18] Shuk P, Wienhöfer H D, Guth U, Göpel W and Greenblatt M 1996 Solid State Ion. 89 179
[19] Mamontov E 2016 Solid State Ion. 296 158
[20] Battle P, Catlow C and Moroney L 1987 J. Solid State Chem. 67 42
[21] Malmaros G 1970 Acta Chem. Scand. 24 384–96
[22] Wei W C J 2012 Adv. Mater. Res. 509 111
[23] Boyapati S, Wachsman E D and Chakoumakos B C 2001 Solid State Ion. 138 293
[24] Sanna S, Esposito V, Andreassen J W, Hjelm J, Zhang W, Kasama T, Simonsen S B, Christensen M, Linderoth S and Pyrd N 2015 Nat. Mater. 14 500
[25] Schröder F, Bagdassarov N, Kitter F and Bayarjargal L 2010 Phase Transit. 83 311
[26] Willis T, Porter D, Voneshen D, Uthayakumar S, Demmel F, Gutmann M, Roger M, Refson K and Goff J 2018 Sci. Rep. 8 1
[27] Funke K 1991 Philos. Mag. A 64 1025
[28] Luceauze G, Gavarrì J and Dianoux A 1987 J. Phys. Chem. Solids 48 57
[29] Gupta M, Singh B, Goel P, Mittal R, Rols S and Chaplot S 2019 Phys. Rev. B 99 224304
[30] Singh B, Gupta M K, Mittal R, Zbiri M, Rols S, Patwe S J, Achary S N, Schober H, Tyagi A K and Chaplot S L 2017 Phys. Chem. Chem. Phys. 19 15512
[31] Singh B, Gupta M K, Mittal R and Chaplot S L 2018 J. Mater. Chem. A 6 5052
[32] Singh B, Gupta M K, Mittal R, Zbiri M, Rols S, Patwe S J, Achary S N, Schober H, Tyagi A K and Chaplot S L 2017 J. Appl. Phys. 121 085106
[33] Mukhopadhyay S and Demmel F 2018 AIP Conf. Proc. 1969 030001
[34] Demmel F and Mukhopadhyay S 2016 J. Chem. Phys. 144 014503
[35] Price K S D L 1986 Neutron Scattering vol A (Orlando: Academic)
[36] Carpenter J M and Price D L 1985 Phys. Rev. Lett. 54 441
[37] Rols S, Jobic H and Schober H 2007 Compt. Rendus Phys. 8 777
[38] Demmel F, McPhail D, Crawford B, Maxwell D, Pokhilchuk K, Garcia-Sakai V, Mukhopadhyay S, Telling M, Bermejo F, Skipper N and Fernandez-Alonso F 2015 EPJ Web Conf. 83 03003
[39] Mukhopadhyay S, Herew B, Howells S and Markwarden A 2019 Physica B 563 41
[40] Harwig H 1978 Z. Anorg. Allg. Chem. 444 151
[41] Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15
[42] Kresse G and Joubert A 1999 Phys. Rev. B 59 1464
[43] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[44] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[45] Parrinello R 2003 PHONON
[46] Nosé S 1984 J. Chem. Phys. 81 511
[47] Allen M P and Tildesley D J 2017 Computer Simulation of Liquids (Oxford: Oxford University Press)
[49] Kneller G R, Keiner V, Kneller M and Schiller M 1995 Comput. Phys. Commun. 91 191

[50] Calandrini V, Pellegrini E, Calligari P, Hinsen K and Kneller G R 2011 École thématique de la Société Française de la Neutronique 12 201

[51] Sköld K 1967 Phys. Rev. Lett. 19 1023

[52] Parker S F, Mukhopadhyay S, Jiménez-Ruiz M and Albers P W 2019 Chem. Eur. J. 25 6496

[53] Sagotra A K, Chu D and Cazorla C 2019 Phys. Rev. Mater. 3 035405

[54] Chudley C T and Elliott R J 1961 Proc. Phys. Soc. 77 353