Inelastic neutron scattering and lattice dynamics of $GaPO_4$

R MITTAL, S L CHAPLOT, A I KOLESNIKOV[2], C-K LOONG[2],
O D JAYAKUMAR[1] and S K KULSHRESHTHA[1]

Solid State Physics Division; [1]Novel Materials and Structural Chemistry Division,
Bhabha Atomic Research Centre, Mumbai 400 085, India
[2]Intense Pulsed Neutron Source Division, Argonne National Laboratory, Illinois 60439,
USA
E-mail: rmittal@apsara.barc.ernet.in

Abstract. We report here measurements of phonon spectrum and lattice dynamical calculations for $GaPO_4$. The measurements in low-cristobalite phase of $GaPO_4$ are carried out using high-resolution medium-energy chopper spectrometer at ANL, USA in the energy transfer range 0–160 meV. Semiempirical interatomic potential in $GaPO_4$, previously determined using ab-initio calculations have been widely used in studying the phase transitions among various polymorphs. The calculated phonon spectrum using the available potential show fair agreement with the experimental data. However, the agreement between the two is improved by including the polarisability of the oxygen atoms in the framework of the shell model. The lattice dynamical models are also exploited for calculations of various thermodynamic properties of $GaPO_4$.

1. Introduction

The MPO_4 (M=Al, Ga, Fe) consist of MO_4 and PO_4 tetrahedral units and are found in various polymorphic forms. They display phase transitions at high pressure depending on the compressibility of the constituent tetrahedra. High pressure experiments on these compounds have been reported [1–4]. The high pressure experiments on quartz structured $AlPO_4$ indicate a crystal-to-crystal reversible transition at a pressure around 15 GPa. In case of $GaPO_4$ the quartz phase transforms irreversibly to an amorphous phase. High pressure X-ray diffraction and Raman studies for quartz $FePO_4$ show an irreversible transformation to a coexisting crystalline and amorphous phase at a pressure of around 2.5 GPa, which is in contrast to the behavior of $AlPO_4$ and $GaPO_4$. The orthorhombic low-cristobalite form of $GaPO_4$ shows a transformation at 16 GPa to another orthorhombic phase (Cmcm phase). The low-cristobalite phase transforms [5] to a cubic phase at 200°C and

$600°C$ for $AlPO_4$ and $GaPO_4$ respectively. Measurements of the phonon disper-
sion relation and lattice dynamics calculations for quartz $AlPO_4$ have also been
reported [6].

Semiempirical interatomic potentials [7] are available for $AlPO_4$ and $GaPO_4$.
Molecular dynamics simulations have been reported [8,9] using these potentials to
understand the nature of phase transitions in different polymorphs of $AlPO_4$ and
$GaPO_4$. The results of simulations, however, depend on the interatomic potentials.

In order to assess and improve the available interatomic potential models [7], we
have measured the phonon spectrum in low-cristobalite phase of $GaPO_4$ by neutron
inelastic scattering experiments. The lattice dynamical calculations are carried out
in both the rigid ion and shell model. Similar experiments and calculations were
earlier reported for quartz phase of $FePO_4$ [10].

2. Experimental

The inelastic neutron scattering experiments are carried out using the high-
resolution medium-energy chopper spectrometer at the intense pulsed neutron
source of Argonne National Laboratory. A polycrystalline sample of 35 g was placed
inside a sealed aluminum container. The data have been collected with three dif-
ferent incident neutron energies of 200 meV, 120 meV and 60 meV in order to get
a good resolution over a wide range of the phonon energies. The spectrometer has
a large number of detectors covering a range of momentum transfers $Q = 4$ to 19
Å^{-1}. In order to reduce the multiphonon scattering the measurements are carried
out at 7 K.

3. Lattice dynamical calculations

Transferable interatomic potentials [7] have been used for the calculations of phonon
spectrum of $GaPO_4$. The same potentials have been transferred to $FePO_4$ with
suitable modification for the Fe–O terms [10]. The parameters of the potentials
satisfy the conditions of static and dynamic equilibrium. The current version of
the program DISPR [11] has been used for the lattice dynamical calculations. The
procedure for the calculations of specific heat and thermal expansion is given in
ref. [12].

4. Results and discussion

Figure 1 shows the experimental phonon spectrum for $GaPO_4$ measured with the
incident neutron energy of 200 meV. The spectrum consists of several peaks centered
at energies of about 20, 50, 60, 80 and 130 meV. There is a gap in the phonon density
of states in the range 100–125 meV. Comparison between the experimental data
and calculated phonon spectrum based on rigid ion model using the semi-empirical
interatomic potentials proposed by Murashov [7] is shown in figure 1. Above 40
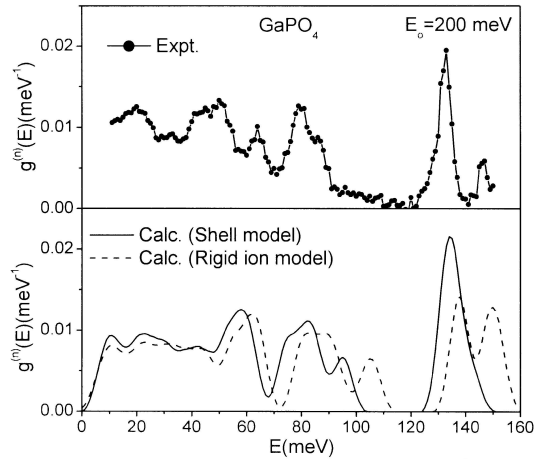meV all the phonon bands in the calculations are shifted by about 10–15 meV.

Figure 1. Comparison between the experimental (filled circles – the line through the filled circles is only a guide to the eye) and calculated (dashed line – rigid ion model; full line – shell model) one phonon neutron-weighted phonon density of states for low-cristobalite phase of GaPO₄. The multi-phonon contribution has been subtracted from the experimental data. The calculated spectra have been convoluted with a Gaussian of FWHM of 7 meV for comparison with the experimental spectra in order to correspond to the energy resolution in the experiment (which varies from 2 to 4% of the incident neutron energy of 200 meV).

The gap in the calculated spectrum is smaller in comparison to the gap in the experimental data in the range 90–120 meV.

The main reason for the above discrepancies may be that the calculations using the Murashov potentials [7] are carried out in the rigid ion model. However, the atoms are not rigid during vibrations. The electric field set up by the displacements of the ions are modified by their electronic polarisability which in turn modifies the force on them and affects the phonon frequencies. So we have carried out another calculation in the framework of the shell model [12]. The polarisability of the oxygen atoms has been introduced with the shell charge $Y(O) = -1.8$ and shell-core force constant $K(O) = 250$ eV Å^{-2}. The calculated phonon spectrum based on the shell model is also shown in figure 1. It can be seen that all the phonon bands above 40 meV are now shifted to lower energies by about 10–15 meV in comparison with the calculations carried out in rigid ion model and the agreement between the calculations and experiments seems to be better.

The thermodynamic properties are calculated using the shell model in the quasi-harmonic approximation. Thermal expansion and specific heat have been calculated (figure 2) over the temperature range of stability of low-cristobalite phase of GaPO₄. The experimental specific heat $C_P(T)$ data for GaPO are not available. The difference $C_P - C_V = \alpha_V^2 BVT$, where α_V is the volume thermal expansion and B the bulk modulus, is significant at high temperatures and is about 14% at about 850 K. A comparison of the calculated thermal expansion of GaPO₄ with available experimental data is shown in figure 2.
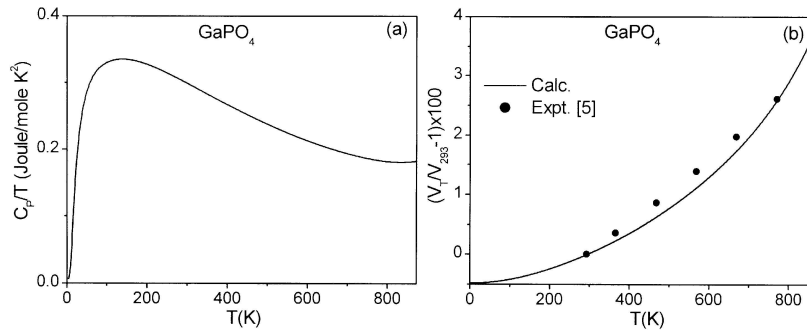
Figure 2. (**a**) Calculated specific heat C_P/T variation with temperature T for low-cristobalite GaPO. (**b**) Comparison between the calculated and experimental data [5] of cell volumes $(V_T/V_{293} - 1) \times 100\%$, at different temperatures (V_T and V_{293} being the cell volumes at temperatures T and 293 K respectively).

5. Conclusions

The measured phonon spectra have been very useful for assessing the quality of the interatomic potentials [7]. The experimental data compare fairly well with calculations carried out in the rigid ion model. However, the agreement between the two is improved by including the polarisabilty of the oxygen atoms in the framework of a shell model. The model has been used for the calculations of various thermodynamic properties of $GaPO_4$.

Acknowledgements

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