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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Lattice dynamics of Nd5Mo3O16 and Pr5Mo3O16 oxygen ion conductors	**Experiment number**: **HC-2191**
Beamline: ID18	**Date of experiment**: from: 07/09/2015 to: 13/09/2015	**Date of report**: 22/02/2016
Shifts: 18	**Local contact(s)**: BOSSAK Alexei	*Received at ESRF:*

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Report:

The complex oxides are of interest for development of an adequate anode material for intermediate-temperature solid oxide fuel cells, catalysts and oxygen sensors. High ionic conductivity has been observed in rare-earth molybdenum oxides $Ln_5Mo_3O_{16+x}$ (*Ln* = La, Pr, Nd, Sm, Gd) by Tsai *et al*. [1]. The highest ionic conductivity of $\sim 10^{-2}$ (S/cm) at 670 °C was found in $La_5Mo_3O_{16+x}$ ($x \sim 0.5$), while the electron conductivity predominates in reduced $Ln_5Mo_3O_{16+x}$ (x=0) molybdates. Voronkova *et al.* [2] studied phase relations and electrical properties in the Nd_2O_3–MoO_3 system (25–50 mol. % Nd_2O_3). According to this study, the electrical conductivity of $Nd_{14}Mo_8O_{45}$ is about 10^{-2} S/cm at 800 °C and is predominantly ionic. The electron contribution to conductivity increases with reducing the oxygen pressure, while the oxygen ion contribution remains almost constant. Authors consider that the most part of oxygen ions in $Nd_5Mo_3O_{16+x}$ reside in their regular sites tightly bound in the crystalline lattice and only excess oxygen, x, contribute to ionic transport. Recently another neutron diffraction study of $Ln_5Mo_3O_{16+x}$ (*Ln* = Pr, Nd) powder samples has been performed at 3K – 973K [3]. The temperature dependence of the lattice parameter and width of Bragg peaks indicate that the crystal structure remains cubic in the whole temperature region. The nuclear density distribution of $Nd_5Mo_3O_{16+x}$ calculated by maximum entropy method shows that the excess oxygen atoms of $R_{10}Mo_6O_{33}$ are localized near the O_2 atomic positions and play a critical role in forming the diffusion through the neighboring O_2 atoms.

The ionic conductivity will depend not only on the crystal structure but on the bond strength between oxygen and the neighboring ions, the lattice flexibility and dynamics. The investigation of the lattice dynamics in $Ln_5Mo_3O_{16+x}$ (*Ln* = Pr, Nd) compounds and similar systems is therefore important for the fundamental understanding of the mechanism of ionic transport, in general, and for potential applications as ionic conductors. Because of the small crystal size of these compounds the neutron scattering experiment was not feasible and measurements with $Nd_{10}Mo_6O_{33}$ were done with X-ray inelastic scattering beamline ID28.

The single crystal sample $Nd_{10}Mo_6O_{33}$ was obtained by spontaneous crystallization of the binary Ln2O3–MoO3 melts with excess amount of MoO3 in alumina or platinum crucibles [2]. The inelastic scattering spectra in temperature range from 24° C to 700° C were taken from the sample about 70 μm in size, sealed in a quartz capillary and heated by the nitrogen gas flow. The Si (999) reflection with wavelength 0.6968 Å was used. For this experiment the sample was aligned in the [HKK] scattering plane and the dispersion curves were measured for longitudinal and transverse branches in directions [100], [011] and [111].

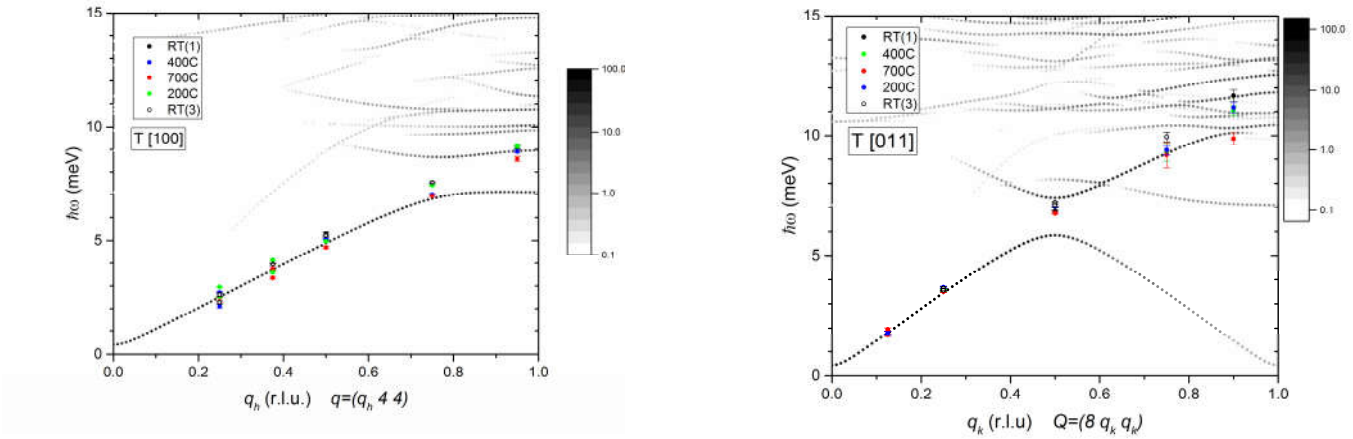

Figure 1. Transverse phonon dispersion in $Nd_{10}Mo_6O_{33}$ for directions [100] and [011].
Experimental data shown for temperatures 24° C (RT1), 400° C, 700° C, 200° C and 24° C after cooling (RT3). Dotted lines present the calculated from first principles phonon dynamical structure factor *S(Q,ω)*.

Experimental results for transverse phonons in [100] and [011] directions are shown in Fig. 1. Acoustic [100] and [011] phonons have rather low frequencies. In direction [011], the calculated scattering function shows the "avoid-crossing" of acoustic and low-energy optic modes in the middle of Brillouin zone, but it was not confirmed in experiment, probably because of insufficient resolution of spectrometer. The TA [111] phonon mode has noticeably higher frequencies at zone boundary. At the same time, this acoustic mode drastically change the slope at q >0.5, shows optic-like behavior and merges into the optic branches. The similar q-dependence was observed for longitudinal [100], [011] and [111] modes. Notice that this behavior of dispersion curves is characteristic for materials with high ionic conductivity, $Cu_{2-x}Se$, as an example [4].
We did not observe noticeable modification in phonon peaks with temperature, both in position and width. The softening of phonon frequencies was less than 5 % at 700° C in average. This shows that interatomic potential in $Nd_{10}Mo_6O_{33}$ is rather harmonic and the ionic transport has little effect on the propagation of acoustic phonons, probably because of low fraction of mobile ions.

References

[1] M. Tsai, M. Greenblatt, W. H McCarroll, Chem. Mater. 1 (1989) 253–259.
[2] V. I. Voronkova, E. P. Kharitonova, D.A. Belov, Solid State Ionics 225 (2012) 654–657.
[3] Y. Ishikawa, S. A. Danilkin, M. Avdeev, V. I. Voronkova, Takashi Sakuma, Solid State Ionics (2015), http://dx.doi.org/10.1016/j.ssi.2015.12.005
[4] S. A. Danilkin, M. Yethiraj, G. J. Kearley, J. Phys. Soc. Jpn. 79 (2010) Suppl. A, 25-28.