Exp. Nr: HS 3009, Title: “Infuence of the rare-earth substitution on pressure-dependend structural properties of perovskite-like $LnGaO_3$”

Six samples have been chosen for current studies, four orthogallates $LaGaO_3$, $CeGaO_3$, $PrGaO_3$ and $NdGaO_3$, whose perovskite lattice deformation increases smoothly with increase of periodic number of rare-earth element and two solid solutions $La_{0.50}Pr_{0.50}GaO_3$ and $La_{0.63}Nd_{0.37}GaO_3$ with magnitude of perovskite lattice deformation close to one in cerium gallate. All samples except cerium gallate were grown either by Czhohralski or floating zone technique, while $CeGaO_3$ was synthesized by solid state reaction method with subsequent arc melting. in argon. Crystal structure of chosen materials is well defined in a broad temperature range and their structural studies were already reported in the literature.
More than 140 diffraction patterns have been collected for six samples at plenty of pressures during experiment. The data evaluation has been performed using the Rietveld method and full profile decomposition technique (Le-Bail) implemented into GSAS and FullProf program packages, while single profile decomposition was carried out using WinCSD software.

We have started experiment with lanthanum gallate. Among all rare-earth gallates this material possesses smallest perovskite cell distortion and its thermal and pressure behaviour of crystal structure were studied quite extensively. Thus it is well known from the literature that $LaGaO_3$ undergoes orthorhombic-to-rhombohedral phase transformation which can be either temperature (ca. 420 K) or pressure driven. In our experiment the first diffraction pattern has been collected already at 3.5 GPa and splitting of characteristic Bragg reflections reveals the $LaAlO_3$ type of structure at this pressure unambiguously. Similar behaviour occurs for other rare-earth gallates, where phase transformations have been observed, i.e. $CeGaO_3$ at 10(1) GPa, $PrGaO_3$ at 24(1) GPa, $NdGaO_3$ at 38(1) GPa, $La_{0.50}Pr_{0.50}GaO_3$ at 10.1(2) GPa and $La_{0.63}Nd_{0.37}GaO_3$ at 12.3(6) GPa.

Lattice parameters contract almost linear with temperature, obtained compressibilities $b_L = \partial L/\partial P$ for *a*- and *c*-directions of rhombohedral lattice (b_a and b_c) are listed in Table 1.

Table 1. Parameters of 2nd order Birch-Murnaghan EOS as well as compressibilities in main crysallographic directions of $LaGaO_3$, $CeGaO_3$, $PrGaO_3$ and $NdGaO_3$, $La_{0.50}Pr_{0.50}GaO_3$ and $La_{0.63}Nd_{0.37}GaO_3$.

Compound	Pressure Medium	r_{Ln}, Å	V, Å^3	K, GPa	b_a, GPa^{-1}	b_b, GPa^{-1}	b_c, GPa^{-1}
$LaGaO_3$*	Ethanol-methanol	1.216	353.1(2)	193(2)	-0.0076(2)	-	-0.0198(4)
$La_{0.50}Pr_{0.50}GaO_3$	Ethanol-methanol	1.198	235.2(1)	173(3)	-0.0113(2)	-0.0062(5)	-0.0139(2)
$CeGaO_3$	N_2	1.196	233.61(7)	177(3)	-0.0113(2)	-0.0077(3)	-0.0137(7)
$La_{0.63}Nd_{0.37}GaO_3$	N_2	1.196	234.0(4)	178(6)	-0.0106(3)	-0.0064(9)	-0.0137(9)
$PrGaO_3$	N_2	1.179	231.4(3)	182(5)	-0.0075(5)	-0.0060(4)	-0.0120(9)
$NdGaO_3$	N_2	1.163	231.0(6)	189(8)	-0.0063(3)	-0.0068(2)	-0.0100(2)

* Data for high-pressure (rhombohedral) modification are given

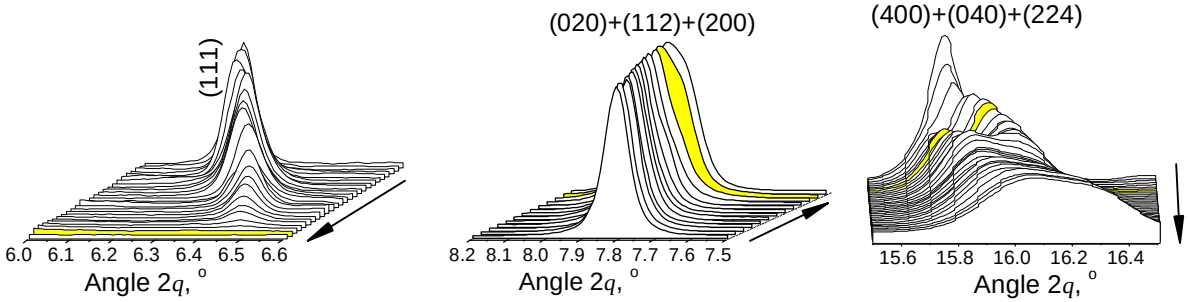

Fig. 1. Pressure evolution of relative intensities for orthorhombic (111) Bragg reflection in $NdGaO_3$ (a), (020)+(112)+(200) triplet in $La_{0.50}Pr_{0.50}GaO_3$ (b) and (400)+(040)+(224) triplet in $CeGaO_3$. Direction of pressure increase is shown by line with arrow, points of pressure instabilities are shown by yellow.