Ann. Phys. (Berlin) **523**, No. 1 – 2, 157 – 167 (2011) / **DOI** 10.1002/andp.201000096

Lattice dynamics of $ZnAl_2O_4$ and $ZnGa_2O_4$ under high pressure

S. López-Moreno[1,*], **P. Rodríguez-Hernández**[1], **A. Muñoz**[1], **A. H. Romero**[2], **F. J. Manjón**[3], **D. Errandonea**[4], **E. Rusu**[5], and **V. V. Ursaki**[5]

[1] Departamento de Física Fundamental II, MALTA Consolider Team, Instituto de Materiales y Nanotecnología Universidad de La Laguna, La Laguna 38205, Tenerife, Spain
[2] CINVESTAV-Queretaro Libramiento Norponiente No 2000 Real de Juriquilla 76230 Queretaro, Qro, México
[3] Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 Valencia, Spain
[4] Fundación General de la Universidad de Valencia ICMUV, MALTA Consolider Team, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, 46100 Valencia, Spain
[5] Institute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova

Received 31 July 2010, revised 18 September 2010, accepted 27 September 2010
Published online 2 November 2010

Key words Lattice dynamics, phonon, *ab initio*, spinel structure, high pressure.

This article is dedicated to Manuel Cardona.

In this work we present a first-principles density functional study of the vibrational properties of $ZnAl_2O_4$ and $ZnGa_2O_4$ as function of hydrostatic pressure. Based on our previous structural characterization of these two compounds under pressure, herewith, we report the pressure dependence on both systems of the vibrational modes for the cubic spinel structure, for the $CaFe_2O_4$-type structure (*Pnma*) in $ZnAl_2O_4$ and for marokite (*Pbcm*) $ZnGa_2O_4$. Additionally we report a second order phase transition in $ZnGa_2O_4$ from the marokite towards the $CaTi_2O_4$-type structure (*Cmcm*), for which we also calculate the pressure dependence of the vibrational modes at the Γ point. Our calculations are complemented with Raman scattering measurements up to 12 GPa that show a good overall agreement between our calculated and measured mode frequencies.

1 Introduction

AB_2O_4 compounds are ceramics with many interesting mechanic, electric, magnetic and optical properties. Many of these oxides crystallize in the cubic spinel structure ($Fd\bar{3}m$) exemplified by $MgAl_2O_4$. In particular, $ZnAl_2O_4$ and $ZnGa_2O_4$ have gained recent interest for their applications as phosphors because they combine a wide direct band-gap above 3.5 eV, transparent and electroconductive properties, high thermal stability, low acidity, and hydrophobic behavior to be used in many different new dispositives [1–3].

Little is known about the pressure dependence of the mechanical, electrical, and optical properties of $ZnAl_2O_4$ and $ZnGa_2O_4$ spinels. High pressure X-ray diffraction studies of these two compounds have shown that while $ZnAl_2O_4$ does not undergo any phase transition till 43 GPa [4], $ZnGa_2O_4$ undergoes two phase transitions towards the tetragonal spinel ($I4_1/amd$) and marokite (*Pbcm*) structures around 34 and 55 GPa, respectively [5]. Recently, S. López et al. have performed first principles calculations to study the stability of the spinel structures of $ZnAl_2O_4$ and $ZnGa_2O_4$ under high pressure and phonon frequencies in the Γ point at zero pressure [6, 7]. It has been predicted that $ZnAl_2O_4$ should undergo a pressure-induced

* Corresponding author E-mail: lsinhue@yahoo.com.mx