Post-spinel transformations and equation of state in $ZnGa_2O_4$: Determination at high-pressure by in situ x-ray diffraction

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Abstract: Room temperature angle-dispersive x-ray diffraction measurements on spinel $ZnGa_2O_4$ up to 56 GPa show evidence of two structural phase transformations. At 31.2 GPa, $ZnGa_2O_4$ undergoes a transition from the cubic spinel structure to a tetragonal spinel structure similar to that of $ZnMn_2O_4$. At 55 GPa, a second transition to the orthorhombic marokite structure ($CaMn_2O_4$-type) takes place. The equation of state of cubic spinel $ZnGa_2O_4$ is determined: V_0 = 580.1(9) Å^3, B_0 = 233(8) GPa, B_0'= 8.3(4), and B_0''= -0.1145 GPa^{-1} (implied value); showing that $ZnGa_2O_4$ is one of the less compressible spinels studied to date. For the tetragonal structure an equation of state is also determined: V_0 = 257.8(9) Å^3, B_0 = 257(11) GPa, B_0´= 7.5(6), and B_0''= -0.0764 GPa^{-1} (implied value). The reported structural sequence coincides with that found in $NiMn_2O_4$ and $MgMn_2O_4$.

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I. Introduction

Cubic oxide spinel AM_2O_4 compounds (A: bivalent cation and M: trivalent cation) occur in many geological settings of the Earth's crust and mantle, as well as in lunar rocks and meteorites. The study of their high-pressure structural properties is important for improving the understanding of the constituents of the Earth. High-pressure studies have been performed in MgM_2O_4 spinels (e.g. $MgAl_2O_4$) revealing that upon compression they may adopt orthorhombic $CaFe_2O_4$-, $CaMn_2O_4$-, or $CaTi_2O_4$-type structures [1]. However, the structure and properties of post-spinel phases is presently still under debate. On top of MgM_2O_4 spinels, the high-pressure properties of ZnM_2O_4 cubic spinels (e.g. $ZnAl_2O_4$) have been studied too. Among them, $ZnAl_2O_4$ [2] and $ZnFe_2O_4$ [3] have been experimentally investigated. The first one remains stable up to 43 GPa in the cubic spinel structure but the second one transforms to either a $CaFe_2O_4$- or a $CaTi_2O_4$-type structure beyond 24 GPa. In addition to these facts, in other compounds like AMn_2O_4 spinels, cubic-to-tetragonal transitions have been reported to occur at pressures as low as 12 GPa [4]. In contrast with the materials above mentioned, the high-pressure structural stability of AGa_2O_4 spinels has not been studied yet. In order to shed more light on the understanding of the high-pressure properties of AM_2O_4 cubic spinels, we report a study of the high-pressure structural properties of zinc gallate ($ZnGa_2O_4$) up to 56 GPa. The present research work contributes to achieve a fuller understanding of how cation replacement affects the high-pressure behavior of oxide spinels.

II. Experimental details

$ZnGa_2O_4$ powders were synthesized by a solid state reaction at high temperature by mixing appropriate quantities of ZnO and Ga_2O_3 precursors and firing at 1100ºC for 24 h [5]. Chemical and structural analyses have shown the stoichiometric composition