Synthetic MgAl$_2$O$_4$ (spinel) at high-pressure conditions (0.0001–30 GPa): A synchrotron X-ray powder diffraction study

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ABSTRACT

The equation of state and the structural behavior of synthetic MgAl$_2$O$_4$ have been investigated using synchrotron X-ray powder diffraction data collected to 30 GPa at room temperature. The Birch-Murnaghan, Vinet, and Poirier-Tarantola models have been fitted to the observed P-V data. The Birch-Murnaghan equation of state, with $V_e$ fixed at its experimental value, yields $K' = 190.8(±1.2)$ GPa, $K'' = 6.77(±0.15)$ and $K'' = −0.075$ GPa$^{-1}$ (implied value). The compression of spinel occurs with a negligible change of the fractional coordinate of oxygen. Therefore the structural shrinking is a function of cell edge shortening alone. The results presented here are compared with those from the literature.

INTRODUCTION

Spinels (AB$_2$O$_4$, where A and B are, in most cases, divalent and trivalent cations, respectively; space group Fd$\bar{3}$m) have structures described by three symmetry-independent sites: a tetrahedral site (T), an octahedral site (M), and an O atom-bearing site [u,u,u]. The A and B cations are distributed over the T and M sites and undergo order-disorder reactions triggered by temperature (T) which have been extensively investigated [see, for example, Andreozzi et al. (2000), Redfern et al. (1999), and the references reported therein]. The cation partitioning in spinels allows one to speculate on the thermal path experienced by the samples, and hence spinels can be exploited as geo-thermometers and petrogenetic indicators (Sack 1982).

The study of spinels at high pressure (P) is relevant for planetary interiors, given that the structure of these minerals is a model for phases which are stable under Earth mantle conditions; for this reason the behavior of spinels as a function of P has been the subject of several studies (Levy et al. 2001, 2000; Haavik et al. 2000; Fei et al. 1999; Funamori et al. 1998; Yutani et al. 1997).

Among spinels, MgAl$_2$O$_4$, i.e., spinel in sensu stricto (hereafter called simply spinel), is one of the most significant minerals of this group for geophysical purposes, as it is a constituent of the upper mantle of the Earth (Navrotsky 1994) and is believed to occur in subducted oceanic crust with the CaFe$_2$O$_4$-type structure (Kesson et al. 1994).

The study of the structural behavior of spinel at high pressure (HP) was first carried out by Finger et al. (1986), up to about 5 GPa. Subsequently Pavese et al. (1999) investigated spinel by neutron powder diffraction up to 4 GPa, paying particular attention to the cation partitioning.

Liu (1978), Irfune et al. (1991), and Funamori et al. (1998) pointed out that spinel undergoes transformations under pressure, though ambiguities persist about their nature.

O’Connell and Graham (1971), Chang and Barsch (1973), Liu et al. (1975), Yoneda (1990), Cynn (1992), and Askarpour et al. (1993) studied the elastic properties of MgAl$_2$O$_4$ by measuring the elastic constants.

The present study is devoted to investigating the equation of state and the structural behavior of spinel from ambient conditions to about 30 GPa by in situ high-pressure powder diffraction using X-rays from a synchrotron source, at room temperature. This investigation complements the previous studies by significantly extending the P interval explored such that the equation of state of this material can be properly stated, and so that an account of the structural response of spinel in the high-pressure regime can be given.

EXPERIMENTAL METHODS

Sample

The sample used in the present experiment was synthesized by heating a quasi-stoichiometric mixture of reagent grade MgO and Al$_2$O$_3$ (supplied by Carlo Erba SpA), with a slight excess of the former, for 18 hours at 1600 °C. The product of the reaction was first cooled to room temperature at a rate of ≈30 °C/hour, which took approximately three days, and then treated with dilute nitric acid to eliminate the residual MgO. A powder diffraction pattern collected with a laboratory diffractometer (X’PERT Philips) confirmed the spinel structure and did not reveal any occurrence of the parent phases. The chemical composition of the synthesized spinel was determined by averaging 24 analyses performed with an ARLSEMQ electron microprobe, which yielded Mg$_{0.95}(±0.04)$Al$_{2.03}(±0.01)$O$_4$. The uncertainties reported take into account the propagation of errors in averaging.

The cation partitioning of the synthesized sample was determined using the approach of Lavina et al. (2002). This method is based on minimization of the differences between...