The crystal structure of diopside at pressure to 10 GPa

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ABSTRACT

The crystal structure of diopside has been determined at various pressures to 10.16 GPa. The results to 5 GPa are consistent with Levien and Prewitt (1981). The crystal structures have been analyzed using the geometric pyroxene model of Thompson and Downs (2004), the anion packing algorithm of Thompson and Downs (2001), and a new algorithm that quantifies the distortion of observed pyroxenes from their geometric model equivalents. Diopside is shown to compress via three main mechanisms: isotropic scaling, kinking of the tetrahedral chains, and collapse of the M1 chain toward its axis. The kinking of the chains accounts for most of the anisotropy of compression observed in the a-c plane, and the collapse of the M1 chain explains the anisotropy seen in the b-c plane. Model behavior is shown to reproduce many of the observations of previous workers. Anion-anion interactions are shown to be important in the distortion of observed diopside from its geometric model equivalent.

Keywords: Diopside, crystal structure, high-pressure, model pyroxene

INTRODUCTION

The list of systematic single-crystal studies of the pyroxene structure as a function of pressure to date includes (Ca0.37Fe0.15Mg0.48)(Mg0.82Fe0.18Al0.16Ti0.06)(Si0.72Al0.28)O3 augite (Hazen and Finger 1977), CaMgs2O6 diopside (Levien and Prewitt 1981), Mg2Si2O5 enstatite (Hugh-Jones and Angel 1994), Fe2Si2O5 ferrosilite (Hugh-Jones et al. 1997), CaFeSi2O6 hedenbergite (Zhang et al. 1997), Mg2.14Li0.17Ca0.13SiO4 (Yang et al. 1999), FeGeO3 (Hattori et al. 2000), NaCrSi2O5 kosmochlor (Origlieri et al. 2003), (Mg0.23Ca0.57)MgSi2O6 pigeonite (Nestola et al. 2004), (Mg0.93Ca0.07)MgSi2O6 enstatite (Nestola et al. 2006), (Ca0.88K0.12)(Mg0.18Al0.17)(Si0.19Al0.22)O3 (Bindi et al. 2006), NaAlSi2O6 jadeite (McCarthy et al. 2008), and the jadeite-hedenbergite join (Nestola et al. in prep.). In addition, there are several studies of the structures of pyroxenes at pressure in which the goals were to determine and characterize phase transitions. These studies were mainly concerned with obtaining cell parameters, but a small number of crystal structures at pressure have been reported, and these include the structures of Fe2Si2O5 ferrosilite (Hugh-Jones et al. 1994), MgSi1.6Mgi.1MgO2.5 (Arlt et al. 1998), LiAlSi2O6 spodumene, Li2ScSi2O6, and ZnSi2O5 (Arlt and Angel 2000). A recent summary of the structural behavior of pyroxene at pressure can be found in Yang and Prewitt (2000).

Pyroxenes have also been characterized at high pressure using Raman spectroscopy (cf. Gatta et al. 2005; Pommier et al. 2003, 2005). Recently, Chopelas and Serghiou (2002) presented Raman spectroscopic evidence for pressure-induced phase transitions in diopside. They observed discontinuous changes in the spectra at 10, 15, and 55 GPa. They suggest that (1) at 10 GPa there is a C2/c to C2/c transition related to bonding changes around the Ca atom in the M2 site; (2) at 15 GPa a change in compression mechanism takes place; and (3) at 55 GPa there is a change in the silicon coordination. A high-pressure C2/c phase has been observed in several different pyroxenes, for instance kanoite (Arlt et al. 1998) and ZnSi2O (Arlt and Angel 2000) but in each case the C2/c phase was formed by a transformation from a structure with P21/c symmetry. Based upon crystal chemical systematics of pyroxenes, Downs et al. (1999) and Downs (2003) proposed that a C2/c to C2/c transition in diopside is possible, and Thompson and Downs (2002, 2004) modeled the transition pathway, but no structural study has yet demonstrated it.

This study follows up on the work of Levien and Prewitt (1981) who compressed diopside to the relatively low pressure of 5 GPa. Because of the pioneering nature of the Levien and Prewitt (1981) study some doubt has been expressed at various scientific meetings about the quality of its data. The present paper shows that while the Levien and Prewitt (1981) study has more scatter in its data than today’s standards, the general trends indicated in their paper are valid and are reproduced.

The scientific purpose of this paper is to present experimental data to higher pressures than previously reported and to analyze the compressional systematics of diopside using a recently developed geometric model of the pyroxenes, described below, and to review the analyses of earlier works in the context of this model. Previous attempts to understand the atomic scale mechanism of compression in diopside have focused on the compression of the individual polyhedral units. Levien and Prewitt (1981) reported their surprise that the MgO octahedra were slightly more compressible than the CaO polyhedra. They suggested that the compression of the structure is not sensitive to composition, but is controlled by the directions and compressibilities of the bonds in the M1 and M2 polyhedra because the least compressed M-O bonds can be correlated with the direction of minimum compres-