The crystal structure of “Tetragonal Almandine-Pyrope Phase” (TAPP): A reexamination

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ABSTRACT

X-ray intensities for the “tetragonal almandine-pyrope phase” (TAPP), *(FeMg)VIII(AlMgFe)4[IV(SiAl)O4]3, where * refers to a capped tetrahedral site, reported by Harris et al. (1997) were recollected using the identical crystal, and the crystal structure was refined from these new data. The basic structure of the previous report is confirmed; however, some of the details regarding cation occupancies are revised. The chemical composition of this phase corresponds to a high-pressure origin; however, significant questions remain regarding the crystallization pressure of this phase.

INTRODUCTION

Inclusions in diamonds have been used for many years to study the mineralogy and pressure-temperature conditions of the mantle (e.g., Futerengelder 1969; Harris 1969, Meyer and Boyd 1972; Sobolev et al. 1974; Meyer and Tsai 1979; Harte et al. 1980; Hervig et al. 1980; Gurney 1986; Meyer 1987; Kesson and Fitzgerald 1992). The vast majority of inclusions contain phases that have been observed in natural rocks, or have been synthesized in phase-equilibria studies; however, a new phase was found in eight diamonds from Säo Luiz, Brazil (Harte and Harris 1994). This phase, which has a composition close to the pyrope-almandine join, was given the acronym TAPP, for tetragonal almandine-pyrope phase. This material was studied with X-ray diffraction by Harris et al. (1997) and with Mössbauer spectroscopy by McCammon et al. (1997).

Since publication of the original report on the crystal structure, the synthesis of an isosctructural phase *(Mg,Fe)0.85(VIIIMg)4[VIII(Mg,Fe)O4]3, reported by Harris et al. (1997) were recollected using the identical crystal, and the crystal structure was refined from these new data. The basic structure of the previous report is confirmed; however, some of the details regarding cation occupancies are revised. The chemical composition of this phase corresponds to a high-pressure origin; however, significant questions remain regarding the crystallization pressure of this phase.

DATA COLLECTION

We mounted the pale green crystal studied by Harris et al. (1997) on a Bruker P4 four-circle diffractometer with a SMART 1000 CCD detector employing Mo Ka radiation and the generator set at 50 kV, 40 ma. A hemisphere of data to 0.7 Å was collected with 0.3 degree frames. Counting time for each frame was 60 sec. These data were corrected for geometrical distortion, dark current and flood-field deviations using the normal software. After indexing, integrated intensities were extracted using Bruker software. The resulting data were corrected for Lorentz and polarization effects. Merging of the data, both for redundant reflections and the symmetrical equivalents were completed with program XPREP from the Bruker SHELXTL package. No absorption correction was undertaken. Crystal structure refinement was completed with the RFINE90 suite of programs (Finger and Prince 1975).

The very high sensitivity of the CCD detector and the ability to sample background in all three directions in reciprocal space make this instrument very useful for the study of small and/or weakly diffracting crystals (Burns 1998). Although the size of the crystal is generally emphasized, a more important measure is the intrinsic scattering power of the crystal, which is defined as S = (F^000/V_0)^1/2 V_C / λ^3, where F^000 is the number of electrons in the unit cell, V_0 is the volume of the unit cell, V_C is the volume of the crystal, and λ is the wavelength of the experiment. For a typical laboratory single-crystal diffractometer with a point detector, S = 10^17. In the present study, the size of the crystal (Table 1) yields S = 3.9 × 10^16, thus the TAPP study was not particularly difficult for the CCD system. A total of 355 symmetry-independent intensities were measured. Of these, 326 had structure factors that were greater than twice the standard deviation, see Table 1.

REFINEMENT RESULTS

Preliminary refinements of the crystal structure of TAPP indicated that the structure of Harris et al. (1997) is basically correct. The new crystallographic data are in Tables 1 and 2. The computer program SHELXS, which is part of the Bruker program package was used to solve the crystal structure. The topology is as reported by Harris et al. (1997), with five distinct cation positions. Two of these (T1, T2) are tetrahedrally coordinated by oxygen, two (M2, M3) are octahedrally coordinated, and the last (M1) is a site of 4 symmetry, which generates a capped tetrahedron with four shorter and four longer bonds. The general formula for this structure could be written as M*4M2(TO4)3, where M is an octahedral cation site, T is a...