

Precise structure analyses of boron spinel synthesized under high-pressure and high-temperature

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Introduction

Many spinel type compounds exhibit complex disordering phenomena involving the mixing of cation on two sites, which have important consequences for both thermodynamic and physical properties. It is important to know pressure effect on solubility of boron in materials as solid solutions and crystal chemical behavior in the Earth's interior. Boron is the same group element as Al and Ga and its ionic radius is considerably small. Crystal chemical behavior of boron has not been known in detail in spinel phase under pressure. We report the refined structure of synthetic B-bearing MgAl₂O₄ spinel and describe its peculiar structural [1].

Experimental

Single crystals of MgAl_{2-x}B_xO₄ (x = 0.0, 0.11 and 0.13) spinel were synthesized under high pressure and high temperature using a 1000ton "6-8" type uniaxial split-sphere apparatus (USSA-1000) installed at the ISEI of Okayama University. Compositions of the single crystals were determined using EPMA and LAM-ICP-MS installed at University of Tsukuba [1].

Single-crystal X-ray diffraction measurements for the smaller size crystals were carried out with a four-circle diffractometer at the BL-10A beam line of the Photon Factory, Tsukuba, Japan, using monochromatized synchrotron X-ray ($\lambda = 0.70006 \text{ \AA}$) radiation. After the convergences of refinements difference Fourier synthesis was computed to check the boron ions positions [1].

Results and Discussion

Based on the X-ray diffraction analyses, the maximum content of boron was about x=0.13 at 1273K and 11GPa. The small size B³⁺ ions occupy the larger octahedral site completely instead of the smaller tetrahedral site. The smallest B ion occupies the octahedral site in top priority in the spinel solid solution of the Mg-Al-B systems. It is different from the empirical laws of the ionic radius. The Mg ion with a larger ionic radius occupies the smaller tetrahedral site and smaller Al ion takes the larger octahedral site in pure MgAl₂O₄ spinel. Moreover, the most important result in this study is that B³⁺ ions can

occupy the octahedral site and replace considerably bigger Al³⁺ ion under pressure. Boron can dissolve to spinel, though the site preference depends greatly on the coexistence elements (chemical composition), structure of host crystal (high symmetry spinel) and physical conditions (high pressure). It is presumable that natural spinel type minerals such as cromite and magnetite may contain a large amount of boron under the Earth's mantle conditions.

We have estimated the cation distribution of each site from the reproduction of the observed average distance using the observed local bond distances for Mg-O and Al-O and the expected distance for B-O. The chemical formula of B-bearing spinel are estimated as:



The Debye-Waller factor, equivalent isotropic temperature factor B_{eq} (\AA^2), includes the effects of static and dynamic disorders. The values of B_{eq} for both the octahedral tetrahedral cation sites are normal comparing with pure MgAl₂O₄ spinel (Table 2), though the cation sites are occupied with several kinds of ions with different sizes. This shows that all cation are located at the center of crystallographic sites. A larger static disorder appears only at the position of oxygen site in the structure of boron-bearing spinel. Only the positional shifts of oxygen ions have, therefore, been relaxing the disorder in structure. The value of 0.02 \AA has increased as for the root-mean-square displacement at the oxygen position.

Reference

[1] Akira Yoshiasa, Tomokazu Ito, Kazumasa Sugiyama, Akihiko Nakatsuka, Maki Okube, Masanori Kurosawa, Tomoo Katsura, *Z. Anorg. Allg. Chem.* (2010) 636, 472-475

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