08-Inorganic and Mineralogical Crystallography

PS-08.04.27 CRYSTAL STRUCTURES OF BORON NITRIDES DETERMINED FROM X-RAY POWDER DATA. By H. Hira- guchi, N. Soda, H. Hashizume, S. Nishino (1) and O. Fukunaga (1). Res. Lab. of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama 227, Japan. (1) Dept of Inorganic Materials, TIT.

The crystal structures of magnesium boron nitride $\text{Mg}_3\text{BN}_4$ in the low- and high-pressure forms have been determined ab initio from X-ray powder data. The powder patterns were decomposed to estimate individual reflection intensities, which were used to calculate Patterson functions and build try-and-error structure models. The obtained structure parameters were refined by the Rietveld method. 94 and 21 reflections were used to solve the structures of $\text{Mg}_3\text{BN}_4(\text{L})$ and $\text{Mg}_3\text{BN}_4(\text{H})$ respectively. Low-pressure $\text{Mg}_3\text{BN}_4(\text{L})$ has a hexagonal cell (space group $\text{P}6_3/mmc$, $Z = 2$) with $a = 3.5443(4)$ and $c = 16.0353(3)$ Å. While the high-pressure $\text{Mg}_3\text{BN}_4(\text{H})$ cell is orthorhombic ($\text{Pnma}$, $Z = 1$) with $a = 3.0933(1)$, $b = 3.1336(2)$ and $c = 7.7005(5)$ Å. The two structures commonly include linear N-\(\equiv\)N molecular ions, considered to play a role in the catalytic property of the material in the reaction converting hexagonal boron nitride into a cubic form at high pressure-temperatures. A 2 % shorter B-N interatomic distance was observed for $\text{Mg}_3\text{BN}_4(\text{H})$. Applications of standard direct methods to the $\text{Mg}_3\text{BN}_4(\text{L})$ intensity data resulted in a very similar structure. High-quality electron density maps have been calculated for this form using the maximum-entropy method with phased structure factors. A separate application of maximum-entropy multisolution program (C. Gilmore et al.: Acta Cryst. A47, 830 (1991)) to the unphased structure factors yielded quite a similar map in support of the determined structure of $\text{Mg}_3\text{BN}_4(\text{L})$.

A structure solution from $\text{Sr}\text{Mg}_3\text{BN}_4$ X-ray powder data will also be reported.

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PS-08.04.30 DETERMINATION OF IRON VALENCE IN NATURAL MAGNETITES AND GARNETS BY EPMA. By I. P. Lapatin*, O. V. Polozova, Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) Russian Academy of Sciences, Moscow, Russia.

The influence of various valence states of transition elements in chemical compounds on the L-emission spectra is well known. We have shown in earlier papers that the structural-chemical state of iron atoms in natural oxides, silicates and sulfides is exhibited in x-ray emission spectra of FeKα by distinct shifts of the wavelengths and of the band profiles as well as in changes of peak/intensity intensity ratio [1].

In this study we attempted to determine the Fe valencies in natural Fe-spinels and garnets by EPMA. Crystal-chemical feature of Fe-O system, possibility of wide exchange between octahedral and tetrahedral sites for Fe$^{2+}$ and Fe$^{3+}$ in different physico-chemical environments make this system very important in the investigations of natural processes, because magnetic and Fe-spinels are often throughgoing minerals formed during several stages of mineralization.

Optimum conditions of investigations have been defined. The measurements were performed at high voltage $E = 10$ kV, $i = 100$ nA, $i = 30^\circ$, using crystal monochromator KAP and anti-contamination.

By measuring x-ray intensity FeKα in standard natural ferrous oxides with known Fe$^{2+}$/Fe$^{3+}$ ratios, three characteristic trends with corresponding crystal-chemistry feature were established: 1. for hematite-magnetite-wustite, 2. for hematite-ilmenite, 3. for magnetite- Ti-magnetite-ulvospinel-ilmenite and 4. for natural garnets of the series almandine-andradite. Based on these results, the equations for quantitative determination of Fe$^{2+}$ and Fe$^{3+}$ were found. Aware of the results, the intensities of FeKα and FeKβ total concentration of iron by EPMA, we de signate