Structure Analysis of Sodium Paradodecatungstate on BL02B1 of SPring-8

Tomoji Ozeki* (User No. 3530) and Setsuko Nakamura (User No. 3880)

Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2–12–1 O-okayama, Meguro-ku, Tokyo 152

Introduction

One of the serious difficulties encountered in a precise X-ray structure analysis is the absorption effect, especially when crystals containing heavy elements, such as W, are analyzed. High energy X-rays from SPring-8 suffer much less absorption effect and are expected to provide data of high quality. In the structure determination of molecules in their excited or metastable states, resolution of disorder with very small occupancies are inevitable. Thus a very precise structure determination is required. As a first attempt at such an project, structure analysis of sodium paradodecatungstate, $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$, was employed using high-energy X-rays from the BL02B1 beamline of SPring-8.

Experimental

The X-rays from the bending magnet beamline BL02B1 were monochromatized using Si 311 double monochromator and focused using the mirror optics. The wavelength was set at 30.748 keV (0.3937Å). During the experiment, the SR ring current ranged from 18.74 mA to 17.22 mA. A single crystal with the approximate size of 0.2×0.1×0.1 mm was sealed in a glass capillary and mounted on the ϕ axis of a Huber off-center 7-axis goniometer. Diffraction data, up to $(\sin\theta/\lambda)_{max}$=0.90, were collected with imaging plates equipped in a cylindrical vacuum camera fixed on the ω axis of the goniometer. 23 images were collected with the ϕ oscillation of 6° with the overlap of 1°. The *DENZO* program suit was used for the indexing and the integration of the diffraction intensities.

Results and Discussion

For the 30.748 keV X-rays, the absorption coefficient of the target compound was 5.25 mm^{-1}, which is less than a quarter of the value of 23.2 mm^{-1} expected for the MoK_α radiation. Currently no correction is applied for the absorption effect, as the absorption correction program is still under development. However, the structure was successfully refined using the *SHELXL97* program, giving the $R(F)$ factor of 0.042 for 14592 reflections with $Fo>4\sigma(Fo)$ and the wR factor of 0.1186 for all the independent 19610 reflections. The e. s. d.'s for the W–O distances are in the range of 0.004–0.007 Å. The residual electron density deviated from -2.64 to +2.57 eÅ^{-3}. These results are significantly better than those obtained by the conventional diffractometers with the MoK_α radiation. With appropriate absorption correction applied, even better results are expected. High energy X-rays from SPring-8 were proved to be very useful for the precise structure determination of the crystals containing heavy elements.