Crystallography

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On the symmetry of $(Sr,Nd)_{11}Ru_4O_{24}$

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Introduction

Ruthenium belongs to the 4*d* transition metal group and allows a wide range of oxidation states from +2 to +8. Therefore, the effect of oxidation states on the charge density distribution is an interesting topic. Recently, we have first grown a series of $M_{11}Ru_4O_{24}$ crystals by the flux method, where M denotes alkaline earth (AE) metals and lanthanide (Ln) [1,2]. The crystal structure was composed of two crystallographically independent RuO_6 octahedra; one is populated with Ru^{4+} and Ru^{5+} almost evenly, whereas the other with Ru^{5+} almost exclusively. Since they are isolated with each other and embedded in a matrix composed of M, the structure can be classified as a sort of zero dimensional RuO_6 network. Isostructural crystals are reported for $M_{11}Re_4O_{24}$ [3,4] and $M_{11}Os_4O_{24}$ [5,6] with various space groups, $I4_1/a$, $I4_1$, and $I2/a$, etc. Careful analyses on highly accurate diffraction data sets are necessary for further examination. This paper is an interim report on the symmetry of $(Sr,Nd)_{11}Ru_4O_{24}$ based on the single-crystal X-ray diffraction experiments performed at BL14A.

Experimental

Vertically polarized white X-rays from a vertical wiggler were diffracted twice by two pieces of Si 111 single crystals and monochromatized to 0.7528 Å. The incident beam was then focused by curved fused quartz mirror and collimated using 0.4 millimeter incident pinhole, and led to 0.1 millimeter pinhole placed at the sample position. The half-slit box in front of the detector was adjusted mechanically so that the direct beam intensity was halved when all angles are set to zero.

Single crystals of $(Sr,Nd)_{11}Ru_4O_{24}$ were grown by the flux method using alkaline earth chlorides. The crystal was ground into a sphere of 80 micrometer in diameter and mounted on the glass capillary and used for diffraction experiments. Data were collected in a whole reciprocal space up to $2\theta<45^\circ$ and standard reflections were monitored after every 200 reflections.

Results and Discussions

Values of R_{int}, a measure of agreement in intensities between crystallographically equivalent reflections, are tabulated in Table 1. The reflection statistics are compared in Figure 1, assuming 2 and 4/m point groups for the crystal. Both R_{int} and the reflection statistics were significantly improved by assuming 2 or 2/m rather than 4 or 4/m, suggesting an absence of the 4-fold rota. Whereas the *a*-glide planes perpendicular to *c* were rejected for their presence in $(Ca,Nd)_{11}Ru_4O_{24}$ [1], it was difficult in the present study to assert the same in $(Sr,Nd)_{11}Ru_4O_{24}$, because the difference in R_{int} between 4 and 4/m was less significant (see Table 1).

Table 1: R_{int} ($F^2>1.5\sigma F^2$) assuming different point groups

2	2/m	4	4/m
0.027	0.030	0.042	0.044

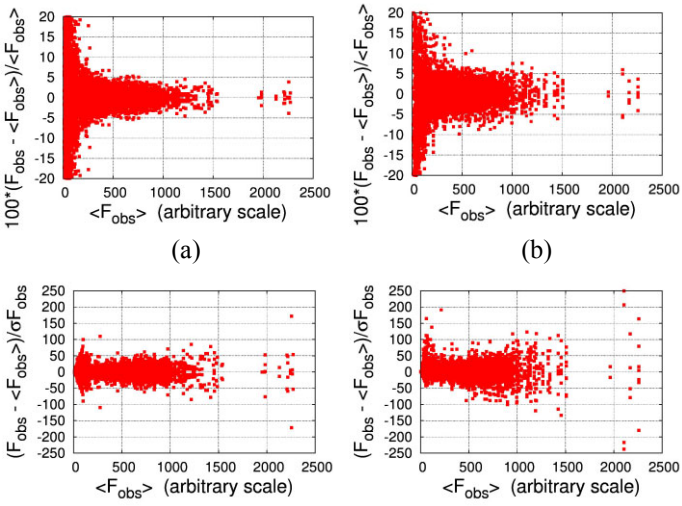

Figure 1: Reflection statistics assuming 2 and 4/m point groups for $(Sr,Nd)_{11}Ru_4O_{24}$; (a) and (c) for 2. (b) and (d) for 4/m. (a) and (b) plot $100\cdot(|F_{obs}|-\langle|F_{obs}|\rangle)/\langle|F_{obs}|\rangle$ against $\langle|F_{obs}|\rangle$, and (c) and (d) plot $(|F_{obs}|-\langle|F_{obs}|\rangle)/\sigma|F_{obs}|$ against $\langle|F_{obs}|\rangle$.

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