Crystallography

14A/2004G037

Noncentrosymmetric Tb_3RuO_7 with partial structural disorder

Kenji TATEISHI[1], Tsuyoshi SUWA[2], Nobuo ISHIZAWA*[2], and James R. HESTER[3]
[1]Gifu Prefectural Ceramics Research Institute, Tajimi, 507-0811, Japan
[2]Nagoya Institute of Technology, Asahigaoka, Tajimi 507-0071, Japan
[3]Australian National Beamline Facility, KEK, Tsukuba 305-0801, Japan.

Introduction

The series of Ln_3MO_7 crystals composed of trivalent lanthanide (Ln) and pentavalent transition metal (M=Ru, Os) oxides is known to form the *Cmcm* and $P2_1nb$ modifications. The latter is noncentrosymmetric with doubled *b* length compared with the centrosymmetric *Cmcm* structure. The two modifications are related by a phase transition with transition temperatures of 190 K for Sm_3RuO_7, 280 K for Eu_3RuO_7, 235 K for Sm_3OsO_7, 330 K for Eu_3OsO_7, and 430 K for Gd_3OsO_7 (Gemmill et al., 2004, 2005). The $P2_1nb$ modification of Gd_3RuO_7 (Ishizawa et al., 2006) show a curious structural feature: two Gd atom sites out of the six crystallographically independent positions have relatively large atomic displacement ellipsoids prolate along *b*. The present paper focuses on Tb_3RuO_7, which has been identified as a new member of the Ln_3RuO_7 structural family for the first time, and deals with the partial structural disorder found in the $P2_1nb$ modification using single-crystal synchrotron X-ray diffraction data collected with a relatively high resolution of d>0.42 Å.

Experimental

Single-crystal diffraction data were collected using the horizontal-type high-speed four-circle diffractometer at beamline 14A of the Photon Factory, Tsukuba. X-rays of 0.6886 (1) Å were focused through a pinhole of 0.4 mm in diameter on the sample using a Si (111) double crystal monochromator and a Pt-coated toroidal mirror. The wavelength was calibrated by a spherical Si standard crystal of 75 μ in diameter. An eight-channel avalanche photodiode detector was used for photon counting (Kishimoto et al., 1998). Since the detector has a counting linearity above 10^9 cps, neither absorbers nor attenuators were employed. The *Xtal* program package was used for further calculations. The least-squares refinement applying anisotropic atomic displacement parameters for all fully populated atom sites yielded R/R_w factors of 0.027/0.039 for 7559 reflections. However, large residual electron peaks of 33–34 $eÅ^{-3}$ were found about 0.42 Å away from both Tb5 and Tb6 in the difference Fourier map after the refinement. Further refinement to examine the population of Tb and Ru atom sites did not significantly affect the R/R_w factors or the residual electron peaks. The deviation of the populations from 100 % was marginal. A split atom model for Tb5 into Tb5a and Ta5b, and for Tb6 into Tb6a and Tb6b was then undertaken. The refinement decreased R/R_w factors to 0.017/0.027 for 7335 independent reflections and 208 parameters. Thus this model was adopted according to Hamilton's significance test. The residual electron density near Tb5 and Tb6 decreased to less than 3.5 $eÅ^{-3}$. The refined Flack parameter of nearly 50 % suggested the presence of very fine micro-twins related by an inversion operation as is common for most $P2_1nb$ modifications of Ln_3RuO_7 and Ln_3OsO_7.

The structure is composed of infinite $[RuO_5]_\infty$ single chains of corner-linked $[RuO_6]$ octahedra embedded in the matrix of Ln and O atoms. The Ln_3MO_7 structural family is known to possess quasi one-dimensional conduction along the $[RuO5]_\infty$ single chains. The conductivity is believed to increase with decreasing Ru...Ru intermetallic distance. For example, the resistibility at room temperature, the mean Ru–Ru distance and the mean Ru–O-Ru angle for Eu_3RuO_7 are 170 Ωcm (Harada & Hinatsu, 2001), 3.706 Å, 143.9º (Gemmil et al., 2004), while those for Gd_3RuO_7 are 2 Ωcm (Bontchev et al., 2000), 3.692 Å, and 142.2º (Ishizawa et al., 2006). If this is the case in all Ln_3RuO_7, an enhanced conductivity is expected for Tb_3RuO_7 compared with Gd_3RuO_7.

This study was supported by Grant-in-Aid for Scientific Research No. 18206071 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] Gemmill, W. R., Smith, M. D. & zur Loye, H.-C. (2004). Inorg. Chem. **43**, 4254–4261.
[2] Gemmill, W. R., Smith, M. D., Mozharivsky, Y. A., Miller, G. J. & zur Loye H—C (2005). Inorg. Chem. **44**, 7047–7055.
[3] Ishizawa, N., Hiraga, K., du Boulay, D., Hibino, H., Ida, T. & Oishi, S. (2006). Acta Cryst. E**62**, i13-i16.
[4] Kishimoto, S., Ishizawa, N. & Vaalsta, T. P. (1998). Rev. Sci. Instrum. **69**, 384–391.
[5] Harada, D. & Hinatsu, Y. (2001). J. Solid State Chem. **158**, 245–253.
[6] Bontchev, R. P., Jacobson, A. J., Gospodinov, M. M., Skumryev, V., Popov, V. N., Lorenz, B., Meng, R. L., Litvinchuk, A. P. & Iliev, M. N. (2000). Phys. Rev. B, **62**[18], 12235–12240.

* ishizawa@nietch.ac.jp