Hydrothermal reaction of NaBiO$_3$·$n$H$_2$O with transition-metal (Co, Ni, Cu) salts

Yo YAMAMOTO$^1$, Withanage Isuru Udakara WITHANAGE$^1$, Takahiro TAKEI$^1$, Sayaka YANAGIDA$^1$, Nobuhiro KUMADA$^{1,3}$ and Hisanori YAMANE$^2$

$^1$Center for Crystal Science and Technology, University of Yamanashi, 7–32 Miyamae, Kofu 400–8511, Japan

$^2$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2–1–2 Katahira, Sendai 980–8577, Japan

Hydrothermal reactions of a hydrated sodium bismuth oxide, NaBiO$_3$·1.4H$_2$O were performed with transition-metal salts MCl$_2$, M(NO$_3$)$_2$ and MSO$_4$ (M: Co, Ni, Cu). The common identified products from nitrate and chloride solutions were (Bi,M)$_2$O$_2$(OH)NO$_3$ and (Bi,M)OCl, respectively and every product contained a small amount of unknown impurity phases. Various unknown phases also appeared in the products from the sulfate solutions, and no common crystalline phases were observed. During the course of these hydrothermal reactions, a new bismuth sulfate, BiOHSO$_4$ was found by using a H$_2$SO$_4$ solution, and its crystal structure was clarified by using single-crystal X-ray diffraction data. No photocatalytic activity for the phenol degradation of BiOHSO$_4$ was observed under ultraviolet and visible light irradiation.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words : Hydrothermal reaction, Bismuth oxide, Crystal structure, Photocatalysis

[Received March 20, 2018; Accepted September 11, 2018]
ride and nitrate solutions and Co > Ni > Cu for sulfate solution. The molar ratio of M/Bi was 1.0–4.0 and the reaction temperature was 80–240°C. The reaction duration was 1–4 days. After the reaction, the products were filtered and washed several times with distilled water and dried. The X-ray powder diffraction (XRD) patterns of the products were obtained by using a Rigaku diffractometer (RINT200V) with graphite monochromated Cu Kα radiation. The lattice parameters of the products were refined by the least-square method using the XRD data measured with 2θ/scan speed in the 2θ range of 5–70°. The crystal structure was drawn using VESTA.23) The single crystal X-ray diffraction data were collected by using a Bruker D8 goniometer using graphite monochromated Mo Kα radiation. The morphologies of the samples were observed by scanning electron microscopy (SEM) (HITACHI Miniscope TM3030), and the chemical compositions of the samples were checked by the attached energy dispersive X-ray spectrometry (EDX).

Diffuse reflectance spectra of the powder samples were measured with a JASCO V-550 spectrometer. The photocatalytic activities were examined for the decomposition of phenol (20 ppm solution) under ultraviolet (UV) and visible light irradiation. The solution was stirred without light irradiation for 30 min to check the adsorption of phenol. After 30 min, the solution was irradiated by UV and visible lights from a 300 W Xe lamp (PE300BUV, Excellitas Tec. Corp.) under continuous stirring. Time dependence of phenol concentration (2 mL) was checked by high performance liquid chromatography (C0-2065, Jasco) using ODS column.

3. Result and discussion

3.1 Hydrothermal reaction with nitrate solutions

When nitrate solutions were used, similar phases for the three metal nitrates were obtained under the condition with M/Bi = 2.0 at 90°C. Figure 1 shows the XRD patterns of the starting compound and the products at 90°C with M/Bi = 2.0. The major peaks in the XRD patterns of the similar phases can be indexed with the orthorhombic cell of \( a = 5.38, b = 5.39 \) and \( c = 17.10 \) Å, values that are similar to those of \( \text{Bi}_2\text{O}_2(\text{OH})\text{NO}_3.24) \) When the molar ratio of M/Bi was 1.0 for \( M = \text{Ni} \) at 90°C, the XRD pattern of the product showed amorphous phases. The pH value of the Ni nitrate solution was the highest among the metal nitrate solutions. This result suggested that a lower pH value is needed for crystallization of the orthorhombic phase. The orthorhombic phase was obtained when using \( \text{Co(NO}_3)_2 \) solution with the molar ratio of Co/Bi \( \geq 1.0 \). In the case of \( \text{Cu(NO}_3)_2 \) solution, there was a second phase of \( \text{Cu}_2(\text{OH})_3\text{NO}_3 \)25) appeared, as well as the same orthorhombic phase as with the molar ratio of \( \text{Cu/} \text{Bi} = 3.0 \). Unknown secondary phases appeared for \( M = \text{Co, Ni} \) when the reaction temperature was above 120°C. Figure 2 shows the SEM images of the products at 90°C with M/Bi = 2.0 by using nitrate solutions. The products are mixtures of fine powders and plate-like particles approximately 10 μm in size. EDX analysis indicated that the plate-like particles contained a small amount of impurity phase with Cu/Bi = 2.0; moreover, a second phase of \( \text{Cu}_2(\text{OH})_3\text{NO}_3 \)25) appeared, as well as the same orthorhombic phase as with the molar ratio of \( \text{Cu/} \text{Bi} = 3.0 \). Unknown secondary phases appeared for \( M = \text{Co, Ni} \) when the reaction temperature was above 120°C.

![Fig. 1. XRD patterns of the starting compound and the product at 90°C with M/Bi = 2.0, 3.0 by using nitrate solutions; (a) starting compound, (b) Co/Bi = 2.0, (c) Ni/Bi = 2.0, (d) Cu/Bi = 2.0, (e) Cu/Bi = 3.0. Circles and triangles denote an unknown phase and \( \text{Cu}_2(\text{OH})_3\text{NO}_3 \), respectively.](image-url)
from these results, the products are thought to be isostructural with Bi$_2$O$_2$(OH)NO$_3$. The chemical composition of the Co-, Ni- and Cu phases prepared from nitrate solutions is thought to be (Bi,M)$_2$O$_2$(OH)NO$_3$ (M: Co, Ni, Cu). A small amount of transition-metals is incorporated to the only metal site in Bi$_2$O$_2$(OH)NO$_3$ and the O$_2$\(^-\), OH\(^-\) or NO$_3$\(^-\) group is partly removed to achieve charge balance. The crystal structure of Bi$_2$O$_2$(OH)NO$_3$\(^{24)}\) is shown in Fig. 3. This compound is crystalized in the orthorhombic space group, Cmc\(_2\)(\#36) in which (Bi$_2$O$_2$)$^{2+}$ layers form and OH\(^-\) and NO$_3$\(^-\) groups are located in the interlayer. The mean Bi–O distances in the (Bi$_2$O$_2$)$^{2+}$ layers were 2.510 and 2.574\(\text{Å}\), values that are longer than typical atomic distances (~2.0\(\text{Å}\)) between transition-metals and oxygen atoms. These long metal-oxygen distances are considered to be the result of the partial replacement of Bi atoms with transition-metal atoms. It was reported that Bi$_2$O$_2$(OH)NO$_3$ exhibited second harmonic generation (SHG) and photocatalytic activity under UV light irradiation.\(^{26),27)}\) These properties of (Bi,M)$_2$O$_2$(OH)NO$_3$ (M: Co, Ni, Cu) are now under investigation because of non-reproducibility for photocatalytic experiments for (Bi,M)$_2$O$_2$(OH)NO$_3$ (M: Co, Ni, Cu). The non-reproducibility may come from the presence of a small amount of an amorphous impurity phase.

3.2 Hydrothermal reaction with chloride solutions

Figure 4 shows the XRD patterns of the starting compound and the product at 240°C with M/Bi = 4.0 by using chloride solutions; and the similar XRD patterns are observed for the products at temperatures above 80°C. The lower reaction temperature and lower M/Bi ratio produced the mixtures of unreacted starting compounds or unknown phases. The major peaks of the XRD patterns of every product can be indexed using the tetragonal cell of \(a = 3.8870(5)\) and \(c = 7.3540(5)\) reported for BiOCl.\(^{28)}\) Weak peaks from an unknown impurity phase were observed for every product, and the impurity phase for Ni product was same as that for the Cu product and both were different from that for the Co product. Figure 5 shows the SEM images of the products at 240°C with M/Bi = 4.0 by using chloride solutions. Every product has a mixture of plate-like particles and fine powders, similar to the products using nitrate solutions. The plate-like particles of the Co and Ni products were approximately 30\(\mu\)m in size, but the Cu particles were smaller than the Co and Ni particles (10\(\mu\)m). EDX analysis indicated that the plate-like particles contained transition-metals; Co:Bi = 0.07:0.93, Ni:Bi = 0.06:0.94 and Cu:Bi = 0.06:0.94. These amounts are larger than those for the products using nitrate solution. The lattice parameters of the Co-, Ni- and Cu phases were \(a = 3.8888(8)\), \(c = 7.357(1)\)\(\text{Å}\), \(a = 3.8876(7)\), \(c = 7.360(1)\)\(\text{Å}\) and \(a = 3.8960(7)\), \(c = 7.368(2)\)\(\text{Å}\), respectively. From these results, the products are thought to be isostructural with BiOCl, with a small amount of transition-metals incorporated to the only metal site in BiOCl. It is also thought that O$_2$\(^-\) or Cl$^-$ ions are partly removed to achieve charge balance. The chemical composition of the Co-, Ni- and Cu phases prepared from chloride solutions is thought to be (Bi,M)OCl (M: Co, Ni, Cu). The crystal structure of BiOCl is shown in Fig. 6. Bismuth oxychloride, BiOCl, has the tetragonal space group, P$\text{4}_1$/nmm (\#129) in which (Bi$_2$O$_2$)$^{2+}$ layers form and OH$^-$ and NO$_3$$^-$ groups are located in the interlayer. The Bi–O distance in (Bi$_2$O$_2$)$^{2+}$ layers was 2.317\(\text{Å}\), and this value is shorter than those of (Bi,M)$_2$O$_2$(OH)NO$_3$. This short Bi–O distance is considered to be the result of the greater number of transition-metal atoms replacing Bi atoms than that of (Bi,M)$_2$O$_2$(OH)NO$_3$. Although BiOCl also exhibited photocatalytic activity under UV light irradiation,\(^{27),29),30)}\) photocatalytic activity of (Bi,M)OCl (M: Co, Ni, Cu) is
now under investigation for the same reason as the products by nitrate solutions.

3.3 Hydrothermal reaction with sulfate solutions

When the products were used in sulfate solutions, various unknown phases were observed and no common crystalline phases were observed, unlike the products from nitrate and chloride solutions. The XRD patterns of the products changed depending on the reaction temperature and the M/Bi molar ratio. There has been no successful indexing of the XRD patterns yet. Figures 7 and 8 show the XRD patterns and SEM images of the product form $\text{M}/\text{Bi}=4.0$ at $180^\circ\text{C}$ by using sulfate solutions. The Co and Ni products were a mixture of fibrous powder and irregular shaped block-like particles, whereas the Cu product had needle-like particles. The identification and crystal structure determination for these phases are under investigation, but a hydrothermal reaction with H$_2$SO$_4$ solution was attempted to help with the identification. The synthesis condition was as follows: NaBiO$_3$$\cdot$1.4H$_2$O (2 g) was put into an autoclave with conc. H$_2$SO$_4$ (5 mL) and H$_2$O (30 mL). The autoclave was heated at $240^\circ\text{C}$ for 2 days. This attempt produced a new compound in the form of single crystals (Fig. 9). The single crystal X-ray diffraction analysis revealed that the crystal structure was composed of a Bi atom coordinated by 8 oxygens and a SO$_4$ tetrahedron (Fig. 10). The chemical composition of this new phase was BiOHSO$_4$. The final R-factors are $R = 0.0093$. 

Fig. 4. XRD patterns of the starting compound and the product at $240^\circ\text{C}$ with $\text{M}/\text{Bi}=4.0$ by using chloride solutions; (a) starting compound, (b) Co/Bi = 4.0, (c) Ni/Bi = 4.0, (d) Cu/Bi = 4.0. Circles denote an unknown phase.

Fig. 5. SEM images of products from (a) Co/Bi = 4.0, (b) Ni/Bi = 4.0 and (c) Cu/Bi = 4.0 at $240^\circ\text{C}$ by using chloride solutions.

Fig. 6. Crystal structure of BiOCl. The solid line denotes the unit cell.
and $wR = 0.0213$, and details of the data collection, structure parameters, and anisotropic displacement parameters are summarized in Tables 2 and 3, respectively. The selected interatomic distances are summarized in Table 4. The lower value of the bond valance sum for O(4) proved to be hydrogen-bonded oxygen, and this oxygen atom bridged the Bi atoms. According to ICSD (Inorganic Crystal Structure Date Base) two types of compounds, Bi$_2$(OH)$_3$(SO$_4$)$_2$(H$_2$O)$_2$ and Bi$_2$O$_2$SO$_4$(H$_2$O), have been reported in bismuth oxysulfates. Because these two

![Fig. 7](image1.png)

Fig. 7. XRD patterns of the product from (a) Co/Bi = 4.0, (b) Ni/Bi = 4.0, (c) Cu/Bi = 4.0 at 180°C by using sulfate solutions.

![Fig. 8](image2.png)

Fig. 8. SEM images of the product from (a) Co/Bi = 4.0, (b) Ni/Bi = 4.0, (c) Cu/Bi = 4.0 at 180°C by using sulfate solutions.

![Fig. 9](image3.png)

Fig. 9. SEM images of BiOH$_2$SO$_4$.

![Fig. 10](image4.png)

Fig. 10. Crystal structure of BiOH$_2$SO$_4$. Solid lines denote the unit cell.
compounds are different from BiOHSO₄, this compound is a new one in this group.

3.4 Photocatalytic property of Bi₂O₂(OH)-NO₃, BiOCl and BiOHSO₄

As mentioned above, the photocatalytic activity of (Bi,M)₂O₂(OH)NO₃ and (Bi,M)OCl (M: Co, Ni, Cu) is now under investigation. Photocatalytic activity of the new compound, BiOHSO₄ was checked and compared with those of Bi₂O₂(OH)NO₃ and BiOCl. Bi₂O₂(OH)NO₃ was prepared by following the published method²⁷) and BiOCl was used a commercial reagent (Wako Pure Chemical Industry, Ltd.). Figure 11 shows UV–vis spectra and Tauc plot for Bi₂O₂(OH)NO₃, BiOCl, and BiOHSO₄. Both Bi₂O₂(OH)NO₃²⁷) and BiOCl³⁰) were reported to have indirect transition, and because the Tauc plot of BiOHSO₄

Table 2. Crystal data and intensity collection of BiOHSO₄

| Color      | Colorless          |
|------------|--------------------|
| Size (mm)  | 0.02 × 0.05 × 0.1  |
| Crystal System | Monoclinic        |
| Space group | C2/m (No.12), Z = 4|
| Lattice parameters | a = 6.4470(1) Å  |
|             | b = 7.2778(1) Å  |
|             | c = 8.6251(2) Å  |
|             | β = 106.711(1)°  |
| Volume     | 387.598(12) Å³   |
| Formula weight | 322.05          |
| Calculated density (g/cm³) | 5.52          |
| Diffractometer | Bruker D8 goniometer |
| Radiation  | Graphite monochromated MoKα |
| Temperature (°C) | 28                   |
| μ (MoKα) (cm⁻¹) | 463.53              |
| Refinement method | Full-matrix least-squares on F² |
| No. Observations (All reflections) | 786          |
| No. Variables | 40                  |
| Reflection/Parameter Ratio | 19.65             |
| Residuals: R (All reflections) | 0.0093       |
| Residuals: wR (All reflections) | 0.0216      |
| GOF        | 1.188              |

Table 3. Structural parameters, bond valence sum and anisotropic displacement parameters of BiOHSO₄

| Atom | Site | x   | y   | z   | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|-----|-----|-----|------|------|------|------|------|------|
| Bi   | 4i   | 0.54512(2) | 0.0  | 0.22176(2) | 0.00990(5) | 3.07 |
| S    | 4i   | 0.08282(9)  | 0.0  | 0.29813(8)  | 0.00870(10) | 5.94 |
| O(1) | 8j   | 0.4411(2)   | 0.3370(2) | 0.2820(2)   | 0.0168(3)   | 1.89 |
| O(2) | 4i   | 0.1766(3)   | 0.0  | 0.1561(2)   | 0.0123(3)   | 1.95 |
| O(3) | 4i   | 0.2614(4)   | 0.0  | 0.4442(3)   | 0.0206(4)   | 1.79 |
| O(4) | 4g   | 0.0  | 0.3372(3) | 0.0  | 0.0162(4)   | 1.50 |

Table 4. Selected interatomic distances (Å) of BiOHSO₄

| Bi–O(1) | 2.633(2) × 2 |
| Bi–O(1) | 2.727(2) × 2 |
| Bi–O(2) | 2.278(2) |
| Bi–O(3) | 2.791(3) |
| Bi–O(4) | 2.197(1) × 2 |

Fig. 11. (a) UV–vis spectra and (b) Tauc plot for (Bi,M)₂O₂(OH)NO₃, BiOCl and BiOHSO₄.
has a long linear region like the Tauc plots of Bi₂O₂(OH)NO₃ and BiOCl. BiOHSO₄ is also estimated to have indirect transition. The exact transition behavior will be investigated using density-of-state (DOS) calculations by first-principles density functional theory. The optical band gaps of Bi₂O₂(OH)NO₃ and BiOCl were calculated to be the same value (3.25 eV) and this value is close to the published data [3.17 eV for Bi₂O₂(OH)NO₃27] and 3.2 eV for BiOCl30]. However, the optical band gap of BiOHSO₄ was somewhat higher value (3.30 eV) than the other two compounds. The time dependence of phenol degradation under UV and visible light irradiation is shown in Fig. 12. High photocatalytic activity is observed for BiOCl, as previously reported; however, Bi₂O₂(OH)NO₃ exhibited weak photocatalytic activity, unlike the previous data. This difference may be caused by the synthetic condition that is reported to influence photocatalytic activity.22) However, the new compound, BiOHSO₄, exhibits no photocatalytic activity phenol degradation under UV and visible light irradiation.

4. Conclusions

Hydrothermal reactions of a hydrated sodium bismuth oxide, NaBiO₃·nH₂O were performed with transition-metal salts MCl₂, M(NO₃)₂ and MSO₄ (M: Co, Ni, Cu). The common products from nitrate solutions and chloride solutions were (Bi,M)₂O₂(OH)NO₃ and (Bi,M)OCl, respectively, with a small amount of unknown impurity phases. Various unknown phases appeared in the products from sulfate solutions, and no common crystalline phases were observed. During these hydrothermal reactions, a new bismuth sulfate, BiOHSO₄ was found by using H₂SO₄ solution, and its crystal structure was clarified by using single crystal X-ray diffraction data. The new bismuth sulfate, BiOHSO₄ exhibited no photocatalytic activity phenol degradation under UV and visible light irradiation.

Acknowledgements

This research work was partly supported by JSPS KAKENHI Grant 17H03388.

References

1) N. Kumada, N. Kinomura, P. M. Woodward and A. W. Sleight, J. Solid State Chem., 116, 281–285 (1995).
2) N. Kumada, N. Kinomura, N. Takahashi and A. W. Sleight, J. Solid State Chem., 126, 121–126 (1996).
3) N. Kumada, N. Kinomura and A. W. Sleight, Solid State Ionics, 122, 183–189 (1999).
4) N. Kumada, N. Kinomura, N. Takahashi and A. W. Sleight, Mater. Res. Bull., 32, 1003–1008 (1997).
5) N. Kumada, A. Miura, T. Takei and M. Yashima, J. Asian Ceram. Soc., 2, 150–153 (2014).
6) N. Kumada, N. Xu, A. Miura and T. Takei, J. Ceram. Soc. Jpn., 122, 509–512 (2014).
7) M. Saiduzzaman, S. Yanagida, T. Takei, C. Moriyoshi, Y. Kuroiwa and N. Kumada, ChemistrySelect, 2, 4843–4846 (2017).
8) M. H. K. Rubel, R. Takei, N. Kumada, M. M. Ali, A. Miura, K. Tadanaga, K. Oka, M. Azuma, M. Yashima, K. Fujii, E. Magome, C. Moriyoshi, Y. Kuroiwa, J. R. Hester and M. Avdeev, Chem. Mater., 28, 459–465 (2016).
9) N. Kumada, J. Ceram. Soc. Jpn., 121, 135–141 (2013).
10) H. Jiang, N. Kumada, Y. Yonesaki, T. Takei, N. Kinomura, M. Yashima, M. Azuma, K. Oka and Y. Shimakawa, Jpn. J. Appl. Phys., 48, 10216–10218 (2009).
11) M. H. K. Rubel, A. Miura, T. Takei, N. Kumada, M. M. Ali, M. Nagao, S. Watauchi, I. Tanaka, K. Oka, M. Azuma, E. Magome, C. Moriyoshi, Y. Kuroiwa and A. K. M. A. Islam, Angew. Chem. Int. Ed., 147, 3599–3603 (2014).
12) M. H. K. Rubel, A. Miura, T. Takei, N. Kumada, M. M. Ali, K. Oka, M. Azuma, E. Magome, C. Moriyoshi and Y. Kuroiwa, J. Alloy. Compd., 634, 208–213 (2015).
13) M. H. K. Rubel, T. Takei, N. Kumada, M. M. Ali, A. Miura, K. Tadanaga, K. Oka, M. Azuma, E. Magome, C. Moriyoshi and Y. Kuroiwa, Inorg. Chem., 55, 5547–5549 (2016).
14) O. A. Smirnova, M. Azuma, N. Kumada, Y. Kusano, M. Matsuda, Y. Shimakawa, T. Takei, Y. Yonesaki and N. Kinomura, J. Am. Chem. Soc., 131, 8313–8317 (2009).
15) T. Takei, R. Haramoto, Q. Dong, N. Kumada, Y. Yonesaki, N. Kinomura, T. Mano, S. Nishimoto, Y. Kameshima and M. Miyake, J. Solid State Chem., 184, 2017–2022 (2011).
16) N. Kumada, T. Takei, R. Haramoto, Y. Yonesaki, Q. Dong, N. Kinomura, S. Nishimoto, Y. Kameshima and M. Michihiro, Mater. Res. Bull., 46, 962–965 (2011).
17) K. Sardar and R. I. Walton, J. Solid State Chem., 189, 32–37 (2012).
18) K. Sardar, S. C. Ball, J. D. B. Sharmar, D. Thompson, J. M. Fisher, R. A. P. Smith, P. K. Biswas, M. R. Less, R. J. Kashtiban, J. Sloan and R. I. Walton, Chem. Mater., 24, 4192–4200 (2012).
19) P. Kanhere, Y. Tang, J. Zheng and Z. Chen, J. Phys. Chem. Solids, 74, 1708–1713 (2013).
20) M. H. Harunsani, D. I. Woodward, P. A. Thomas and R. I. Walton, Dalton T., 44, 10714–10720 (2015).
21) G. Zhang, G. Li, H. Huang, F. Liao, K. Li, Y. Wang and J. Lin, J. Alloy. Compd., 509, 9804–9808 (2011).
22) N. Kumada, N. Takahashi, N. Kinomura and A. W. Sleight, J. Solid State Chem., 139, 321–325 (1998).
23) K. Momma and F. Izumi, J. Appl. Crystallogr., 41, 653–658 (2008).
24) N. Henry, M. Evain, P. Deniard, S. Jobic, F. Abraham and O. Mentré, Z. Naturforsch. B, 60, 322–327 (2005).
25) H. Effenberger, Z. Krist., 165, 127–135 (1983).
26) R. Cong, T. Yang, F. Liao, Y. Wang, Z. Lin and J. Lin, Mater. Res. Bull., 47, 2573–2578 (2012).
27) H. Huang, Y. He, F. Liao, X. Li, M. Li, C. Zeng, F. Dong, X. Du, T. Zhang and Y. Zhang, J. Mater. Chem. A, 3, 24547–24556 (2015).
28) K. G. Keramidas, G. P. Voutsas and P. I. Rentzeperis, Z. Krist., 205, 35–40 (1993).
29) J. Jiang, K. Zhao, X. Xiao and L. Zhang, J. Am. Chem. Soc., 134, 4473–4476 (2012).
30) Y. Wu, B. Yuan, M. Li, W.-H. Zhang, Y. Liu and C. Li, Chem. Sci., 6, 1873–1878 (2015).
31) B. Aurivillius, Acta Chem. Scand., 18, 2375–2378 (1964).
32) L. Golic, M. Graunar and F. T. Lazarini, Acta Crystallogr. B, 38, 2881–2883 (1982).
33) B. Aurivillius, O. von Heidenstamm and I. Jonsson, Acta Chem. Scand., 14, 944–946 (1960).
34) M. Graunar and F. T. Lazarini, Acta Crystallogr. B, 38, 2879–2881 (1982).