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Abstract

In this paper, the X-ray powder diffraction and Raman scattering measurements for cannonite crystal structure $[(\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4)]$ are presented. Cannonite was obtained as a by-product of tests for the chemical durability of glass in the system $\text{Bi}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-ZnO}$. The assignment of the vibrational bands of the crystal growth on the glass-corroded surface was done by comparison with Raman spectrum of a cannonite mineral sample. Both crystals showed the same spectral pattern making possible to determine the crystalline phase deposited on the glass surface. Contrary to report in the literature, our samples did not transform in oxo-carbonated bismuth salt when exposed to air, being chemically stable.

1 Introduction

Cannonite ($\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$) is a relatively new mineral species which appears to have formed as an alteration product in a Cu-Bi-S deposit, found in a specimen collected from the Tunnel Extension mine of the Ohio Mining District, Marysvale, Utah, USA (STANLEY et al., 1992). Repichet et al. (2002) studied the preparation of bismuth (III) trifluoromethanesulfonate and found cannonite as a by product in one of the methods used. However, they reported that cannonite transformed spontaneously to an oxo-carbonated bismuth salt, $(\text{BiO})_4(\text{OH})_2\text{CO}_3$, when it was exposed to air.

To our best knowledge, from 1993 to 2015, no works were published with emphasis on any application related to this compound. Zhang et al. (2015) published an interesting paper about large-scale synthesis of a self-assisted ultralong cannonite nanobelt. These authors reported that bismuth-containing nanomaterials with a layered structure presents fairly high photocatalytic activities. Since then, this kind of material has been receiving much attention.

In a study of chemical durability of glass in the system Bi_2O_3 - SiO_2 - B_2O_3 in 0.5 mol/L H_2SO_4 at 80 °C for 5 h, Fredericci et al. (2008) found some crystal morphology at the glass surface after a chemical-attack test. The crystalline phase was identified as cannonite by X-ray diffraction. However, for this kind of identification, it was necessary to use many samples, in order to remove the corroded glass surface and have enough material for X-ray diffraction characterization. To facilitate the identification of the crystalline phase on material surfaces, micro-Raman spectroscopy can be a much more interesting technique because it is non-destructive and requires little material.

The aim of this paper is to present Raman spectrum of cannonite which, for our best knowledge, is published here for the first time. The use of Raman spectroscopy to identify and to verify the composition of materials is widely increasing and data about them are important for this area of analyses. Not even in one of the world's largest mineral database (RRUFFTM, 2018), the Raman spectrum of cannonite was found.

2 Experimental procedure

Glass, with the composition 72.5 Bi_2O_3 -13.0 SiO_2 -3.0 Al_2O_3 - 3.5 B_2O_3 - 8.0 ZnO (wt %), was prepared in platinum crucible in an electric furnace at 1200 °C for 1 h. The viscous liquid was quenched by pouring it onto a steel plate and then pressing it quickly with another stainless-steel plate to suppress crystallization. Glass samples with dimensions of about (1 x 1) cm² and 0.1 cm thick were ground with SiC water slurries on plane brass tools and polished with a diamond paste. The chemical resistance of the glass samples was carried out in a 5 mL of 0.5 mol/L H_2SO_4 solution inside a hermetically closed glass flask at 80 °C ± 2 °C for 5 h. After the tests, the glass samples were removed from the acid solution and then, dried in an oven at about 80 °C for 1 h. The corroded surface of the glass samples was analyzed by scanning electron microscopy (SEM, JEOL JSM 6300) and X-ray diffraction (XRD, Shimadzu, 6000) analysis, using Cu K α radiation. These analyses were carried out at least 24 h after the chemical durability tests. All the experiments were carried out in the Center for Metallurgical and Materials Technology (CTMM) - Laboratory of Metallurgical Processes (LPM) of the Institute for Technological Research of São Paulo State - IPT.

Raman spectra were recorded on a T64000 Horiba Jobin-Yvon spectrometer with a microprobe under a 50X objective using the 514.5 nm line of an Ar⁺ ion laser, installed in the Department of Physics at Federal University of São Carlos (UFSCar). The resolution in the spectra is about 1 cm⁻¹. A natural mineral sample of bismuthinite (Bi_2S_3) with white, microscopic globular aggregates of cannonite (up to 0.5 mm in diameter) from Nagyborzsony, Borzsony Mountains, Hungary, gently donated by Bela Feher from Herman Otto Museum, was analyzed by micro-Raman and the its spectrum was compared with the Raman spectrum of the crystals developed over the corroded glass surface. These experiments complement the training and knowledge in Raman spectroscopy of one of the authors of this paper (Fredericci C.).

3 Results and discussion

The SEM analysis of the corroded glass surface revealed the presence of a significant fraction of radially distributed needle-like crystals forming spherulites (**Figure 1**).

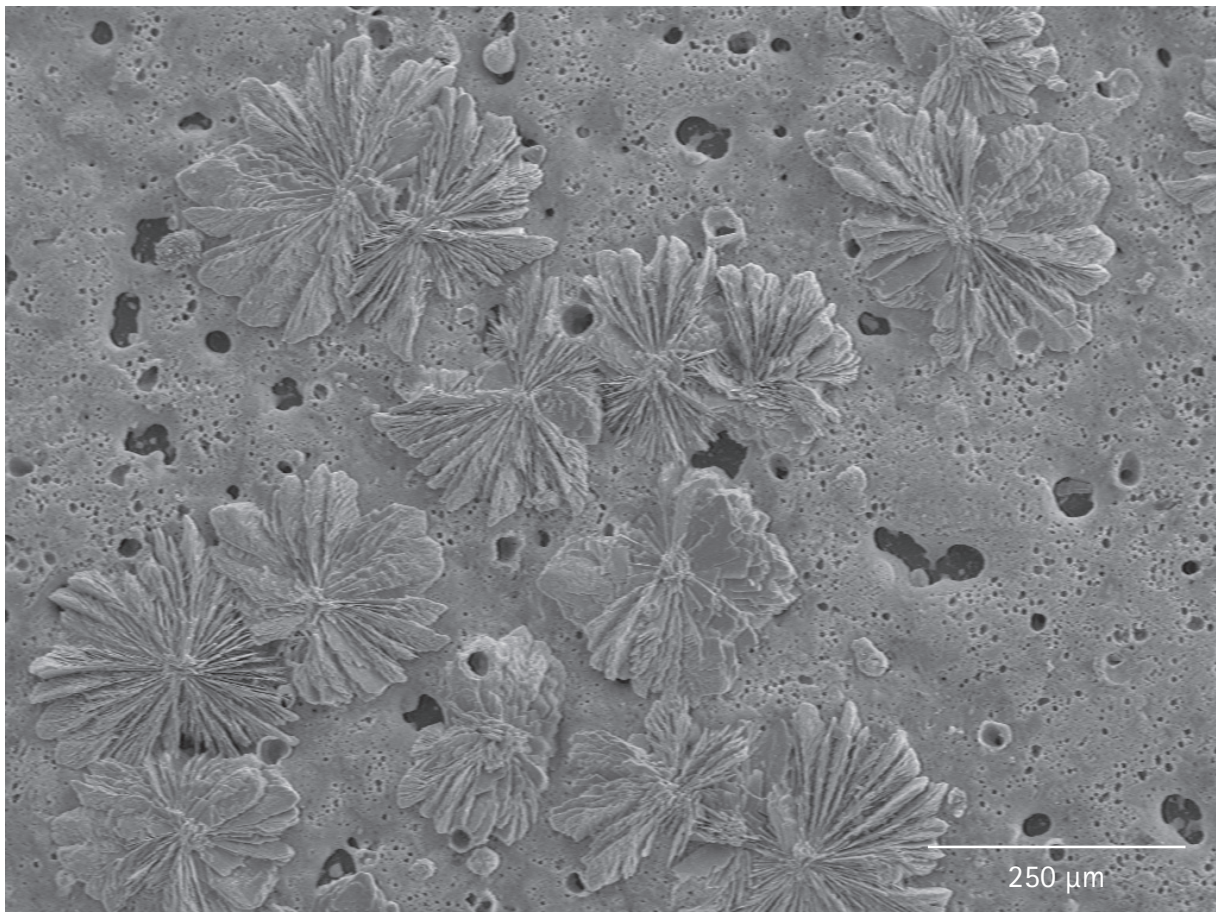


Figure 1 – SEM micrograph of the corroded glass surface after chemical durability test in 0.5 mol/L H_2SO_4 at 80 °C for 5 h.

The X-ray diffraction analysis (**Figure 2**) indicated that these crystals were $(Bi_2O(OH)_2SO_4)$ as indicated by the JCPDS file 73-1598. Although the analyses were carried out at least 24 h after the chemical durability tests, no oxo-carbonated bismuth was observed as reported previously, by Repichet et al. (2002).

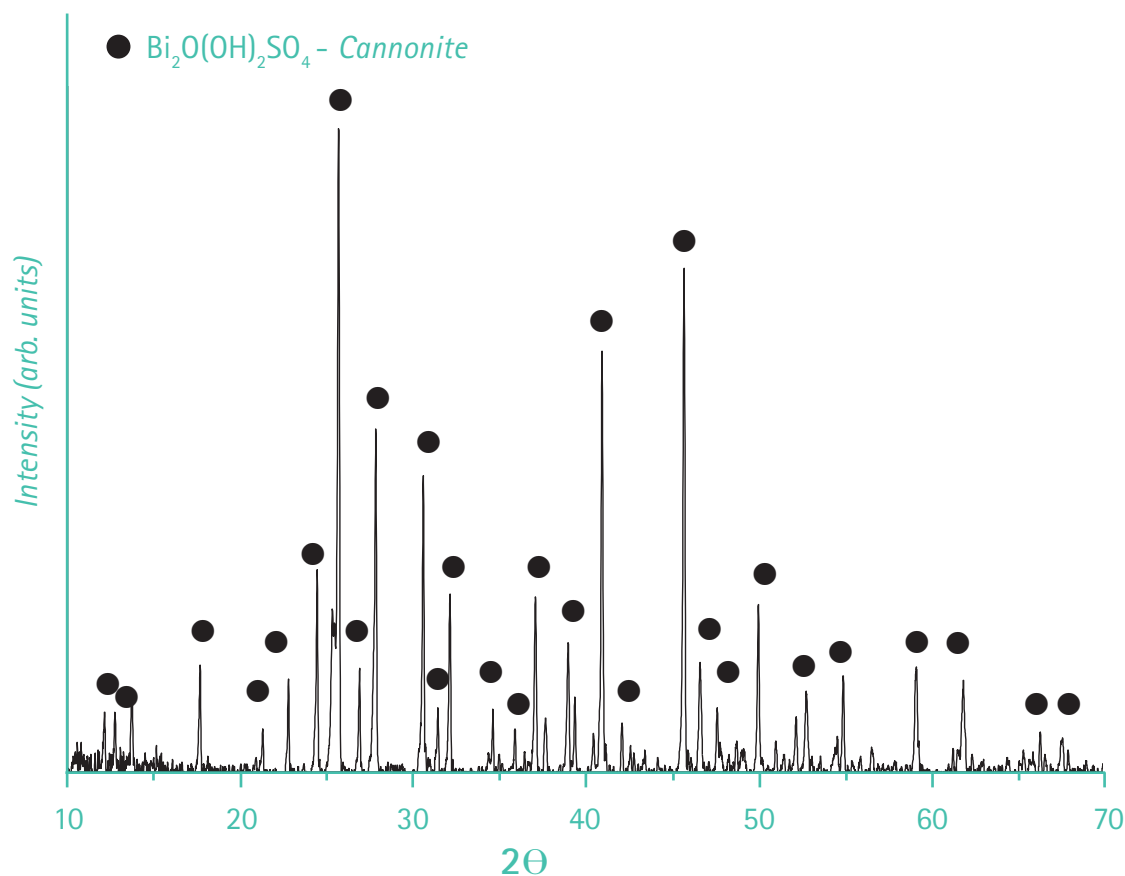


Figure 2 – X-ray pattern of the corroded glass surface after chemical durability test in 0.5 mol/L H_2SO_4 at 80 °C for 5 h.

SEM micrographs of the natural mineral sample are shown in **Figure 3**. It can be observed through EDS analyses that point 1 presents Bi and S and point 2 presents Bi, S and O indicating Bi_2S_3 and $Bi_2O(OH)_2SO_4$, respectively. Raman spectra of this sample were obtained from the region identified by SEM as bismuthinite (point 1 in **Figure 3**) and cannonite (point 2 in **Figure 3**).

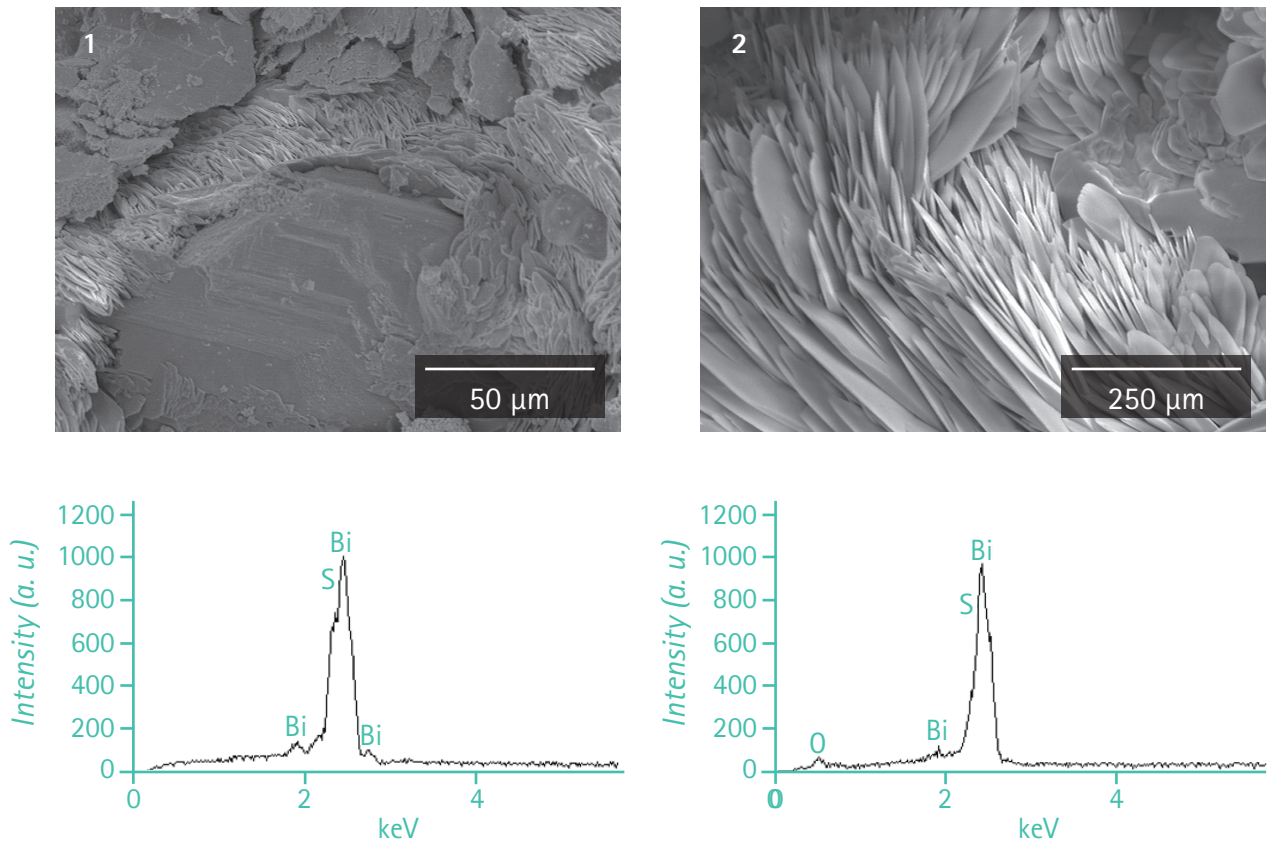


Figure 3 – SEM micrograph of the mineral sample and EDS spectra of point 1 (bismuthinite) and point 2 (cannonite).

Figure 4 shows the Raman spectrum of the mineral sample performed on the region where cannonite can be found and also on the glass surface after chemical durability test. The Raman bands at 64 cm^{-1} , 84 cm^{-1} , 100 cm^{-1} , 128 cm^{-1} , 150 cm^{-1} , 225 cm^{-1} , 320 cm^{-1} , 440 cm^{-1} , 454 cm^{-1} , 562 cm^{-1} , 618 cm^{-1} , 988 cm^{-1} , 1055 cm^{-1} and 1114 cm^{-1} are assigned to cannonite. The bands corresponding to bismuthinite (Bi_2S_3) are at 187 cm^{-1} , 239 cm^{-1} and 258 cm^{-1} , as reported by Shen et al. (2006) and showed in **Figure 5** which are not found in the spectrum of cannonite.

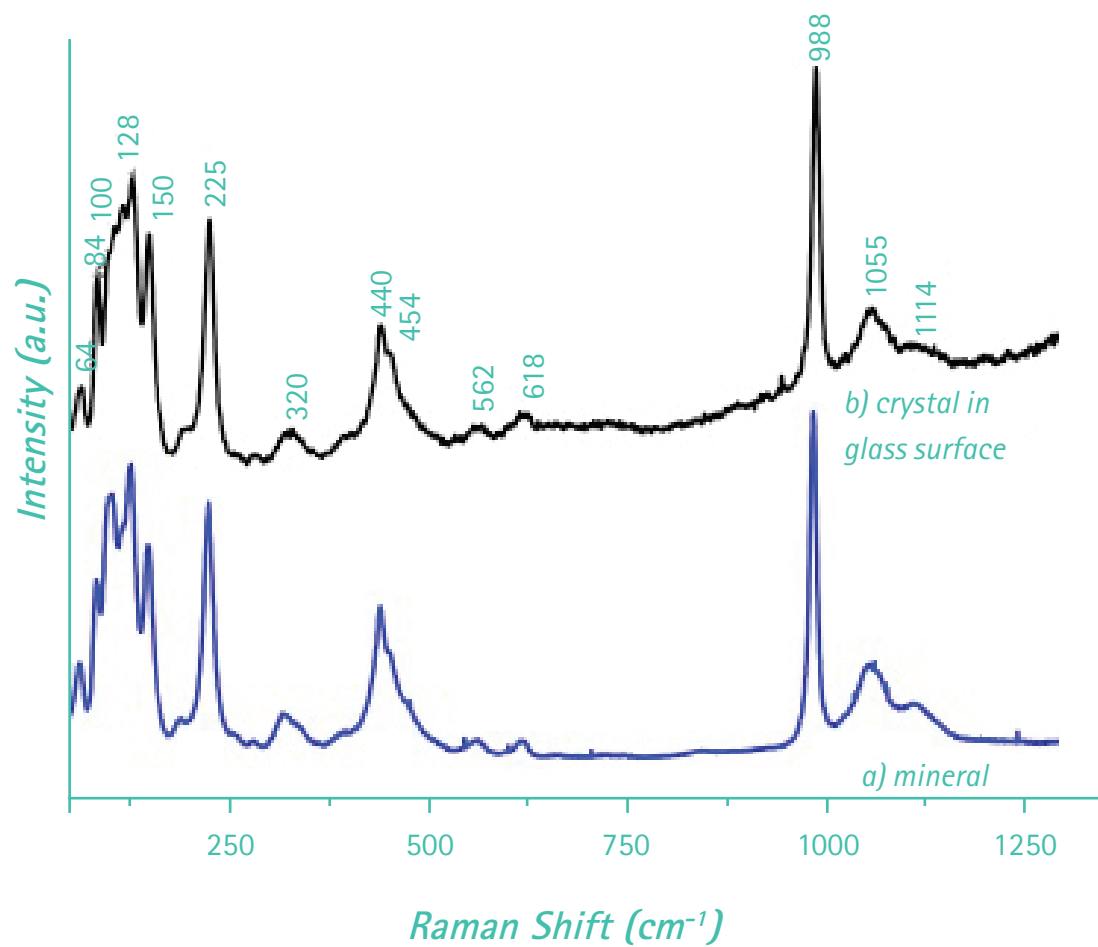


Figure 4 – Raman spectra of the crystals on the mineral sample and on the glass surface after chemical durability test in the region of cannonite. $\lambda = 514.5 \text{ nm}$.

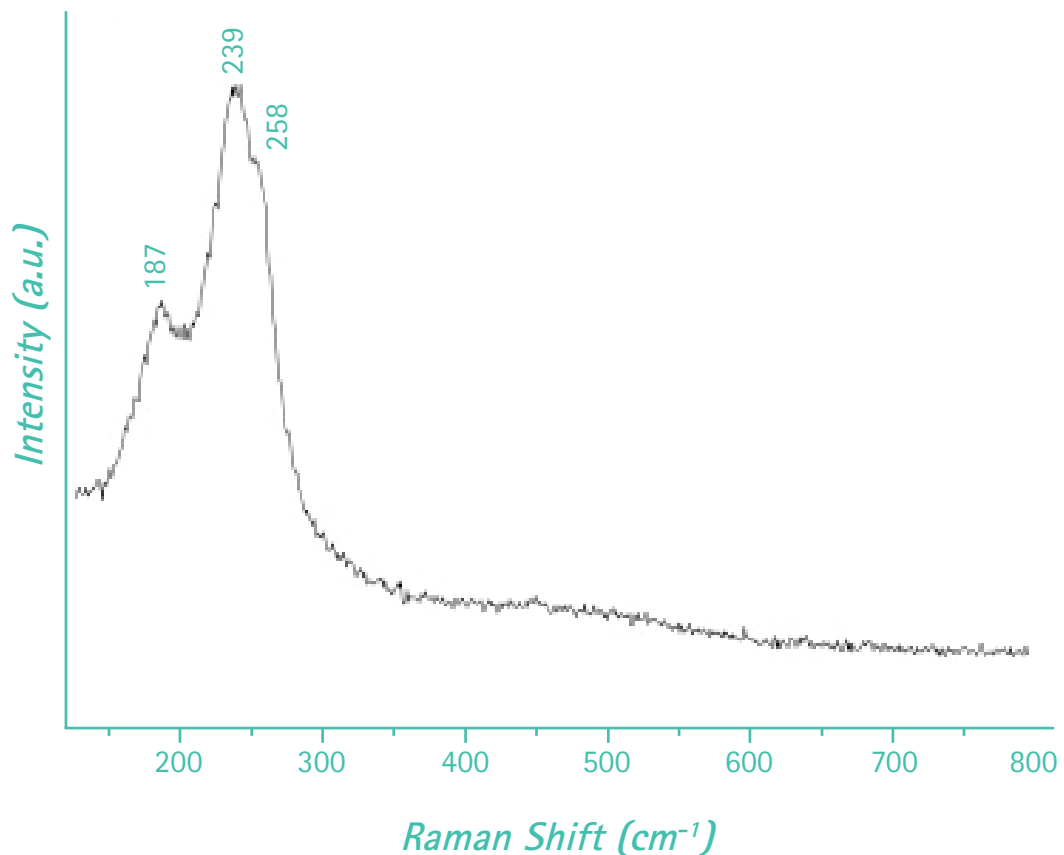


Figure 5 – Raman spectrum of the mineral sample in the region identified as bismuthinite (Figure 3). $\lambda = 514.5 \text{ nm}$.

4 Conclusions

In summary, cannonite $[(\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4)]$, obtained as a by-product of the chemical durability test on glass in the system $\text{Bi}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-ZnO}$, was analyzed by X-ray diffraction and Raman spectroscopy. These results are very important since Raman spectroscopy is a very simple technique which can be used to furnish data and to identify composition about minerals for earth sciences and correlated fields. Furthermore, this is the first time that the Raman spectrum of cannonite is published in the scientific literature, very useful as a reference to identify this mineral species.

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6 References

FREDERICCI, C.; YOSHIMURA, H. N.; MOLISANI, A. L.; FELLEGARA, H. Effect of TiO_2 addition on the chemical durability of $Bi_2O_3-SiO_2-ZnO-B_2O_3$ glass system. *Journal of Non-Crystalline Solids*, v. 354, n. 42-43, p. 4777- 4785, 2008.

REPICHET, S.; ZWICK, A.; VENDIER, L.; LE ROUX, C.; DUBAC, J. A practical, cheap and environmentally friendly preparation of bismuth(III) trifluoromethanesulfonate. *Tetrahedron Letters*, v. 43, n. 6, p. 993-995, 2002.

RRUFFTM. **Search RRUFF Sample Data**. Available in: <<http://rruff.info/>>. Accessed in: Apr. 4 2018.

SHEN, X. P.; YIN, G.; ZHANG, W- L.; XU, Z. Synthesis and characterization of Bi_2S_3 faceted nanotube bundles. *Solid State Communication*, v. 140, n. 3-4, p. 116-119, Oct. 2006.

STANLEY, C. J.; ROBERTS, A. C.; HARRIS, D. C.; CRIDDLE, A. J.; SZYMANSKI, J. T. Cannonite, $Bi_2O(OH)_2SO_4$, a new mineral from Marysvale, Utah, USA. *Mineralogical Magazine*, v. 56, n. 385, p. 605-609, 1992. DOI: 10.1180/minmag.1992.056.385.17.

ZHANG, J.; GU, H.; YANG, X.; CHEN, M.; YANG, Z.; ZHANG, W. Large-scale synthesis of self-assembled ultralong cannonite nanobelt film as a visible-light photocatalyst. *Royal Society of Chemistry (RSC Advances)*, v. 5, n. 12, p. 8537-8543, 2015.