

Low temperature synthesis of cobalt clays

J. THEO KLOPROGGE

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology. GPO Box 2434, Brisbane, Q 4001, Australia

E-mail: t.kloprogge@qut.edu.au

MAYRA HAMMOND, LEISEL HICKEY, RAY L. FROST

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology. GPO Box 2434, Brisbane, Q 4001, Australia

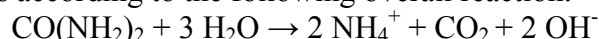
Published as:

Kloprogge, J.T., Hammond, M., Hickey, L. and Frost, R.L. (2002) Low temperature synthesis of Cobalt clays. *Journal of Materials Science Letters*, 21(12), 931-933.

Copyright 2002 Springer

Clay minerals are an important group of naturally occurring minerals found in soils and sediments. They have a sheet-like structure and the order of the sheets as well as the sheet composition contributes to the properties of the clay mineral. The tetrahedral sheets contain continuous T-O linkages with tetrahedral geometry, where T is normally Si or Al [1]. The apical oxygen of each tetrahedron forms part of the adjacent octahedral sheet, with six coordinated cations surrounded by oxygens and hydroxyls. If the cation is trivalent (eg. Al³⁺, Fe³⁺) then two out of three octahedral positions are occupied and the sheet is classified as dioctahedral. If the cation is divalent (eg. Mg²⁺, Fe²⁺, Ni²⁺, Co²⁺) then all three octahedral positions are occupied and the sheet is classified as trioctahedral. The sheets can stack with one tetrahedral sheet to one octahedral sheet giving 1:1 layers, or with two tetrahedral sheets on both sides of an octahedral sheet giving 2:1 layers. An overall negative charge on the 2:1 layers may arise if there is a cation substitution in either the tetrahedral or octahedral position (e.g. substitution of Li⁺ or cation vacancies for Mg²⁺ in the octahedral position or of Al³⁺ for Si⁴⁺ in the tetrahedral position). Hydrated interlayer cations are incorporated between the layers to balance the charge.

The Co-clays were synthesised according to the homogeneous hydrolysis method [2]. Recently the synthesis of pecoraite, a nickel containing clay mineral, was reported using this method [3]. The appropriate amount of amorphous silica was added to deionised water and heated to 90°C. Subsequently cobalt nitrate was added to this suspension, then urea was added and the temperature was held at 90°C for 20 hours. At this temperature the urea slowly decomposed resulting in the homogeneous generation of hydroxyls according to the following overall reaction:



The resulting solids were separated from the suspension by filtration and washed until free of soluble ions. Half of the solid material was dried in an oven at 120°C overnight while the second half was resuspended in water in a Parr hydrothermal vessel for hydrothermal treatment at 190°C and autogenous water vapour pressure for 7 days. After the hydrothermal treatment the solids were washed again and dried at 120°C overnight. Table I gives an overview of the synthesis conditions applied and the resulting products.

The crystalline materials were characterised by X-ray powder diffraction (XRD). The XRD analyses were carried out on a Philips wide-angle PW 1050/25

vertical goniometer applying $\text{CoK}\alpha$ radiation. The samples were measured at 50 % RH in stepscan mode with steps of $0.02^\circ 2\theta$ and a scan speed of 1.00° per minute from 2 to $75^\circ 2\theta$. Oriented samples were prepared by dispersion in water, ultrasonic treatment for 20 seconds, and dropping onto a glass slide. Glycolation was achieved by dropping ethylene glycol (8% in ethanol) onto the oriented sample. Each sample (1mg) was finely mixed with oven dried spectroscopic grade KBr (250mg) and pressed into a disc under vacuum. The infrared absorption (IR) spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector. Baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, U.S.A.). Band component analysis was carried out using the peakfit software package by Jandel Scientific. Lorentz-Gauss cross product functions were used throughout and peakfitting was carried out until squared correlation coefficients with $r^2 > 0.995$ were obtained. The morphology and particle sizes of the samples were investigated with a JEOL 1200EX transmission electron microscope (TEM) operating at 80 kV. Samples were prepared by suspending a small amount of the clay in alcohol followed by 5 minutes sonification. One drop of this suspension was put on a carbon-coated copper grit and allowed to dry prior to use in the TEM.

The XRD pattern of 3CoT (Fig. 1) shows a phyllosilicate with poor crystallinity, with no clear basal reflection. There are very broad peaks around 1.56 \AA and 2.69 \AA . When the sample is hydrothermally treated (3CoTb) the crystallinity increases significantly. The XRD pattern shows a broad but intense basal reflection around 12.1 \AA , and much more defined peaks corresponding to 4.42 , 3.24 , 2.55 , and 1.54 \AA . Treatment with ethylene glycol causes the basal reflection to move from 12.1 to 17.7 \AA , indicating that it is a swellable 2:1 clay. Hydrothermal treatment did not change the structure of the material, but increased the crystallinity and the layer-stacking as indicated by the appearance of a basal reflection, and sharpening of peaks (Fig. 1). This supports the crystallisation model for saponites developed by Kloprogge *et al* [4], which suggested that after the nucleation individual layers start to grow (in the direction of the a and b-axes) and later stack together [5-12].

The IR spectrum of 3CoT (Fig. 2) shows very strong and relatively sharp peaks at 451 , 666 , and 1013 cm^{-1} , corresponding to Si-O and Co-O vibrations. The cluster of three small, broad peaks at 1384 , 1402 , and 1449 cm^{-1} are most likely from a carbonate reaction product of urea and undissolved nitrate. The IR spectrum of 3CoTb is identical to that of 3CoT, except that the peaks around 1400 cm^{-1} have disappeared. Table II gives a comparison between 3CoT, 3CoTb and stevensite. The stevensite from N. Tyne (Great Britain) [13] has peaks in very similar positions to 3CoT, and 3CoTb. The appearance of Co-O and Si-O-Co vibrations at lower frequency in 3CoT and 3CoTb is expected because the divalent metal in natural stevensite is mainly magnesium. Since cobalt is heavier than magnesium the energy of the vibrations will be less, and thus the IR frequencies will be lower. Based on the starting composition the charge must arise from cation vacancies in the octahedral sheet as no substitution in the tetrahedral sheet can take place. Thus, the material formed is the cobalt equivalent of stevensite. The product will have a low layer charge since it only arises from cation vacancies, and the charge is balanced by Co^{2+} cations in the interlayer.

The XRD pattern of 3CoC shows multiple crystalline phases and, based on XRD alone, the phases are unidentifiable. There is a broad peak at 9.8 \AA which

indicates the sample may contain a smectite, as well as a sharper peak at 9.01 Å. Treatment with ethylene glycol however did not shift either of these peaks indicating that they are non-swelling phyllosilicates. There is a peak at 1.56 Å that suggests that the nature of the clay is trioctahedral. A broad band at 30° 2θ suggests that there is amorphous material containing mainly silica. There are other sharp peaks that may be from salts, supported by the IR spectrum exhibiting a number of peaks corresponding to carbonates and nitrates, (1350, 1405, 1531 cm⁻¹). Other peaks are observed in the typical Si-O/metal-O regions around 1000, 600 and 450 cm⁻¹. The peaks in the OH-stretching region are at slightly lower frequency (3393, 3501 cm⁻¹) than is typical for most clay materials, which can indicate strong coordination to a metal ion [14]. TEM analysis confirms that several crystalline phases are present with different morphologies including grains, fibres and flakes. X-ray microanalysis (EDX) shows that there are a limited number of particles containing Si, O, and Co together, and that the sample contains mainly a mixture of silica, and metal oxides or hydroxides and salts. This supports the presence of the low frequency OH-stretching vibrations in the IR spectrum. There were a small number of particles that contained Si, Co, and O together in a ratio of 3:3:9, which is close to the ratio of 4:3:10 expected for a Co-stevensite with Co²⁺ as the interlayer cation.

In conclusion it can be said that the use of homogeneous hydrolysis of cation by the decomposition of urea can be used to synthesis 2:1 clay minerals containing cobalt. However, changing the system to a chrysotile (1:1 clay mineral) composition results in the formation of a mixture of phases instead of Co-chrysotile. This in contrast to the nickel system where in both cases (starting from a 1:1 and 2:1 clay composition) pecoraite, a 1:1 clay mineral, was formed [3]. This can be explained by the difference in the chemical behaviour of nickel and cobalt during hydrolysis, where nickel remains in the same valence state, while the valence state of cobalt can change.

Acknowledgments

The financial and infra-structural support of the Queensland University of Technology, Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. Dr. Thor Bostrom of the Analytical Electron Microscopy Facility is thanked for his valuable help with the transmission electron microscopy.

References

- [1] G. W. BRINDLEY and G. BROWN, "Crystal Structures of Clay Minerals and their X-ray Identification", Mineralogical Society, London, 1984.
- [2] R. J. M. VOGELS, PhD Thesis, Utrecht University (The Netherlands), 1996.
- [3] J. T. KLOPROGGE, M. HAMMOND and R. L. FROST, *N. Jb. Miner. Mh.* **5** (2000) 193.
- [4] J. T. KLOPROGGE, S. KOMARNENI and J. E. AMONETTE, *Clays Clay Miner.* **47** (1999) 529.
- [5] J. BREUKELAAR, F. J. A. KELLENDONK and R. A. VAN SANTEN, *European Patent* 317,006, 1989.
- [6] J. BREUKELAAR, R. A. VAN SANTEN and A. W. DE WINTER, *European Patent* 398,429, 1990.
- [7] V. C. FARMER, G. S. R. KRISHNAMURTI and P. M. HUANG, *Clays Clay Miner.* **39** (1991) 561.
- [8] J. T. KLOPROGGE, J. BREUKELAAR, J. B. H. JANSEN and J. W. GEUS, *Clays Clay Miner.* **41** (1993) 103.

- [9] J. T. KLOPROGGE, J. BREUKELAAR, J. W. GEUS and J. B. H. JANSEN, *Clays Clay Miner.* **42** (1994) 18.
- [10] J. T. KLOPROGGE, J. BREUKELAAR, A. E. WILSON, J. W. GEUS and J. B. H. JANSEN, *Clays Clay Miner.* (1994) **42** 416.
- [11] V. C. FARMER, W. J. MICHARDY, F. ELSASS and M. ROBERT, *Clays Clay Miner.* **42** (1994) 180.
- [12] R. J. M. J. VOGELS, J. BREUKELAAR, J. T. KLOPROGGE, J. B. H. JANSEN and J. W. GEUS, *Clays Clay Miner.* **45** (1997) 1.
- [13] H. W. van der MAREL and H. BEUTELSPACHER, "Atlas of infrared spectroscopy of clay minerals and their admixtures", Elsevier, Amsterdam, **1974**.
- [14] V. C. FARMER, "The Infrared Spectra of Minerals", Mineralogical Society, England, **1974**.
- [15] J. A. GADSDEN, "Infrared Spectra of Minerals and Related Inorganic Compounds", Butterworths, England, **1975**.

TABLE I overview of the synthesis conditions applied for the synthesis of the Co-clays and the resulting products.

sample	Starting composition	Synthesis conditions	Results
3CoT	$\text{Co}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$	20 hours 90°C stirred	Very low crystalline Co-stevensite
3CoTb	$\text{Co}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$	3CoT hydrothermally treated 7 days/190°C/autogeneous water vapour pressure	Co-stevensite
3CoC	$\text{Co}_3\text{Si}_2\text{O}_5(\text{OH})_4$	20 hours 90°C stirred	Mixture of silica, 1:1 and 2:1 clays, Co- oxides, hydroxides and salts

TABLE II Infrared absorption band positions and assignment of synthetic Co-stevensite and natural stevensite.

Suggested Assignment	Frequency / cm^{-1}			
	3CoT	3CoTb	Stevensite (N. Tyne, Great Britain) [13]	Stevensite [15]
External OH stretch	3633	3630	3683, 3630	-
OH stretching modes	3030 - 3571	3030 - 3571	3440	3400
H ₂ O (OH bend)	~ 1637	~ 1637	1625	1615
CO ₃ ²⁻ , NO ₃ ⁻ (reaction products of urea and undissolved nitrate)	1384, 1402, 1449	-	-	-
Si-O in plane stretch	1017	1017	1018	1020
	896sh	896 sh		870
Si-O-Co	666	665	671	-
Co-O	451	450	466	-

Figure Captions:

Fig. 1 XRD patterns of the solid products 3CoT and 3CoTb (Co-stevensite) and 3CoC (mixture of unidentified phases).

Fig. 2 Low frequency region between 400 and 1900 cm^{-1} (a) and the OH-stretching region between 2500 and 400 cm^{-1} (b) of the solid products 3CoT and 3CoTb (Co-stevensite) and 3CoC (mixture of unidentified phases).

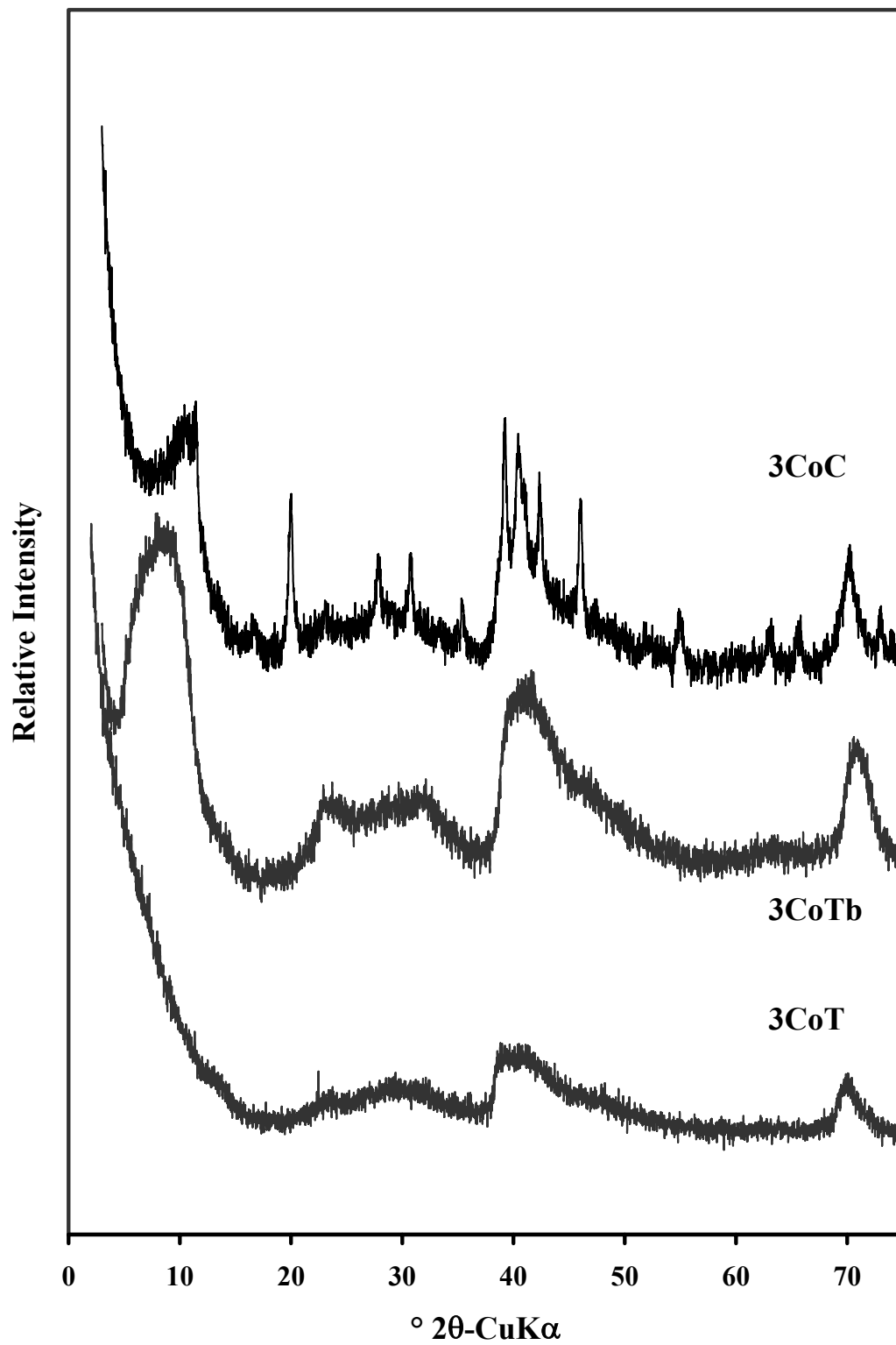


Fig. 1

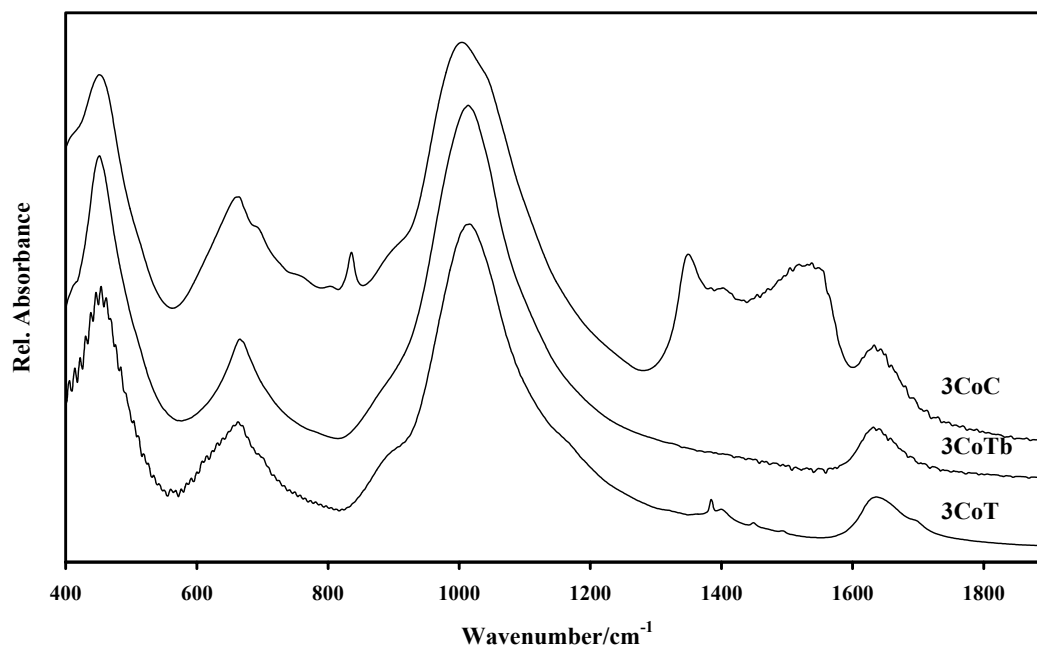


Fig. 2a

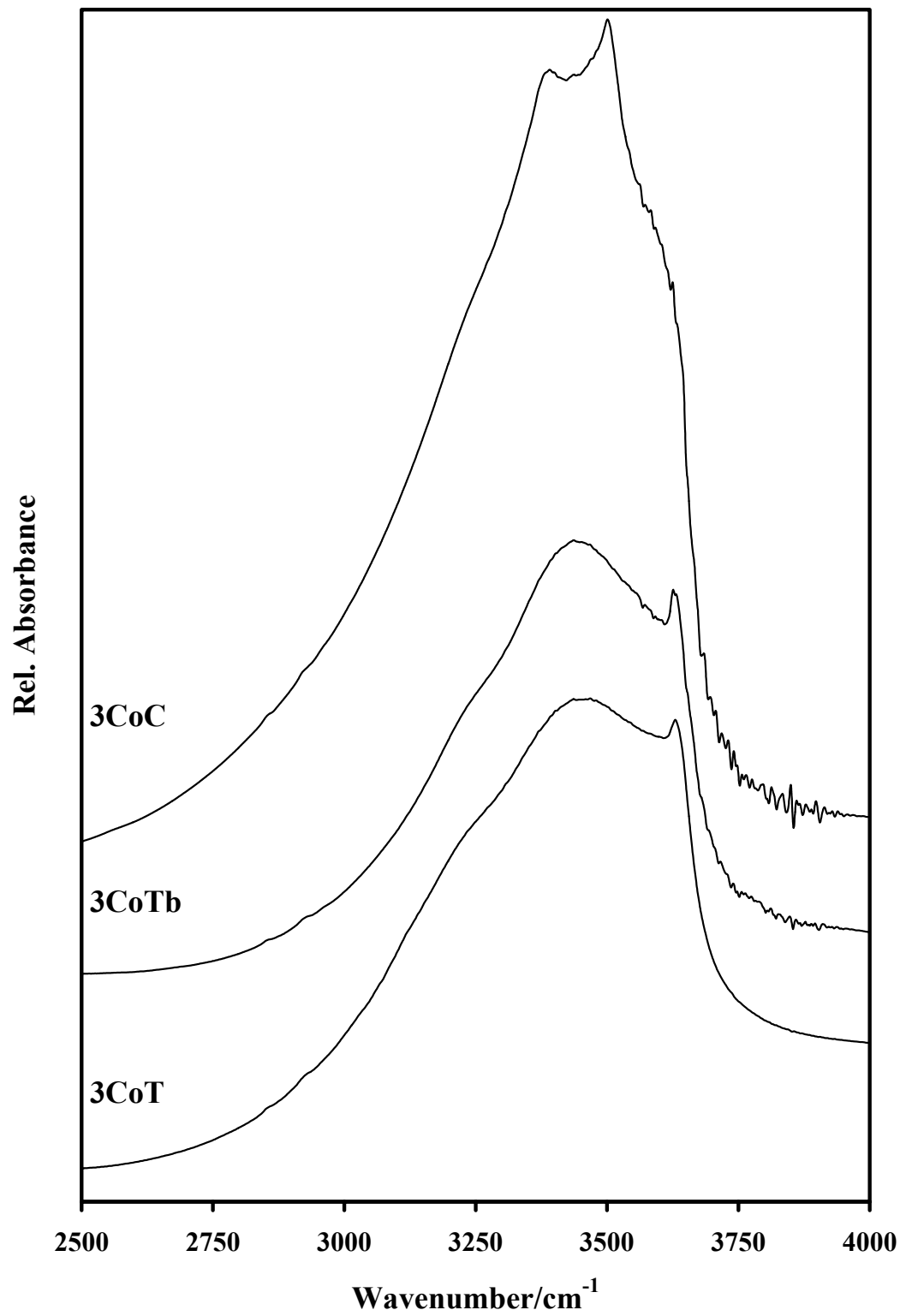


Fig. 2b