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Supercritical hydrothermal synthesis of Cu₂O(SeO₃): Structural characterization,

thermal, spectroscopic and magnetic studies

Aitor Larrañaga^a, José L. Mesa^{b,*}, Luis Lezama^b, José L. Pizarro^a, María I. Arriortua^a, Teófilo Rojo^b

^a Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco/EHU, Apdo. 644, E-48080 Bilbao, Spain ^b Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco/EHU, Apdo. 644, E-48080 Bilbao, Spain

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ABSTRACT

Cu₂O(SeO₃) has been synthesized in supercritical hydrothermal conditions, using an externally heated steel reactor with coupled hydraulic pump for the application of high pressure. The compound crystallizes in the $P_{2,3}$ cubic space group. The unit cell parameter is a = 9.930(1) Å with Z = 12. The crystal structure has been refined by the Rietveld method. The limit of thermal stability is, approximately, 490 °C. Above this temperature the compound decomposes to SeO₂(g) and CuO(s). The IR spectrum shows the characteristic bands of the (SeO₃)²⁻ oxoanion. In the diffuse reflectance spectrum two intense absorptions characteristic of the Cu(II) cations in five-coordination are observed. The ESR spectra are isotropic from room temperature to 5 K, with g = 2.11(2). The thermal evolution of the intensity and line width of the signals suggest a ferromagnetic transition in the 50–45 K range. Magnetic measurements, at low temperatures, confirm the existence of a ferromagnetic transition with a critical temperature of 55 K.

1. Introduction

An important area in materials science is the design of compounds with condensed frameworks, which can give rise to original physical properties with potential practical applications such as ion exchange, surface absorption chemistry, conductivity, etc., due to the great number of different cations and arrangements that they can exhibit [1,2]. In this way, the crystal chemistry of selenium(IV) oxo compounds shows abundant structural versatility expressed by the significant number of different compounds [3]. The transition metal-selenium-oxygen system has been the subject of many previous investigations. Several phases have been reported in which selenium is found in an oxidation state IV. Depending on the conditions in solution [4] transition-metal compounds with $(HSeO_3)^-$, $(SeO_3)^2^-$ or $(Se_2O_5)^2^-$ oxoanions are known [5–7]. The electronic configuration of the selenium(IV) oxoanion promotes the formation of three bonding electron pairs with the oxygen atoms. Furthermore, the presence of an active lone-pair of electron on the Se(IV) centers can play an important role in the crystalline architectures of this family of compounds [3], affected by the requirement for empty space to accommodate the

selenium lone-pair electrons. Thus, it can be predicted that the combination of the inherent asymmetry of $(SeO_3)^{2-}$ with various transition metals will result in a rich structural chemistry in transition metal selenites. In this way, in the $Mn_4(H_2O)_3(SeO_4)_3$ and Mn₃(H₂O)(SeO₃) phases [8] which exhibit a three-dimensional crystal structure constructed by chains, there exist cavities delimited by the MnO₆ octahedra, and SeO₃ trigonal pyramids, with the lone-pair, in an sp³ hybrid orbital, pointing towards the center of the cavities. Similarly, the two Mn(SeO₃) polymorps [9] also exhibit a three-dimensional crystal structure formed by chains that give rise to hexagonal channels with the lone electronic pair directed towards the center of these channels. Recently, a few amine-templated metal selenites have also been synthesized under hydrothermal/solvothermal conditions in presence of organic amines as templates. These systems have open-framework structures [10].

Effenberger and Pertlik synthesized the $Cu_2O(SeO_3)$ compound, whose crystal structure was solved from single-crystal X-ray diffraction [11]. The crystal structure of $Cu_2O(SeO_3)$ consists of a very compact three-dimensional framework constructed by two CuO_5 square pyramids and two SeO₃ trigonal pyramids (Fig. 1). Two kinds of structural units are observed in the structure, with the square pyramid geometry habitually found in the copper(II) compounds. The unit with greater connectivity is formed by link of four square pyramids, one $Cu(1)O_5$ and three $Cu(2)O_5$, sharing the





^{*} Corresponding author. Tel.: +34 946015523; fax: +34 946013500. *E-mail address:* joseluis.mesa@ehu.es (J.L. Mesa).

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Fig. 1. Polyhedral view of the of the crystal structure of Cu₂O(SeO₃).

O(1)-O(3) edge. The second unit has less connectivity, as it is a trimer formed by three square pyramids, Cu(2)O₅, sharing the O(2) - O(4) edge.

Furthermore, hydrothermal synthesis performed at high temperature and pressure can be used in order to obtain new condensed selenites. Supercritical hydrothermal synthetic techniques can provide an adequate synthetic method to obtain novel and interesting compounds that only exist over narrow stabilization ranges [12] and to obtain mineral or complex selenites with transition metals. In the present work, we report on the supercritical hydrothermal synthesis, structural characterization, thermal, spectroscopic and magnetic properties of the $Cu_2O(SeO_3)$ phase.

2. Experimental

2.1. Synthesis and characterization

Cu₂O(SeO₃) was synthesized in supercritical hydrothermal conditions, using an externally heated steel reactor with coupled hydraulic pump for the application of high pressure. The Cu(SeO₃)·2H₂O phase was used as starting precursor in the synthesis. It was prepared by reaction at room temperature of a mixture containing SeO₂ (9 mmol) and CuCl₂·2H₂O (3.0 mmol), with a the of pH 6. Approximately 0.03 g of Cu(SeO₃)·2H₂O dispersed in 2 ml of water, with a basic $pH \simeq 10$, were sealed in a small gold capsule, 9 mm \times 0.5 mm, which was loaded into a steel autoclave. The reaction vessels were first heated to the final reaction temperature, 300 °C, at 5 °C min $^{-1}$ with a constant pressure of approximately 100 atm. The Cu(SeO₃)·2H₂O stating reagent was maintained under those conditions for 72 h, followed by slow cooling, approximately 50 °C h^{-1} , to room temperature. Temperature and pressure conditions for the synthesis of the compound were 300 °C and 100 atm. Attempts made to carry out the synthesis of the $Cu_2O(SeO_3)$ phase in the absence of high pressure were unsuccessful. The well-formed, blue single-crystals were isolated by filtration, washed with water and acetone and dried over P₂O₅ for 1 h.

The percentage of the elements in the product was determined by inductively coupled atomic emission spectroscopy (ICP-AES). Observed: Cu, 22.2; Se, 28.9. Calculated for Cu₂O(SeO₃): Cu, 23.5; Se, 29.2. The density, measured by picnometry in kerosene, was $5.0(1) \text{ g cm}^{-3}$.

2.2. X-ray powder diffraction characterization

The X-ray powder diffraction characterization of Cu₂O(SeO₃) has been carried out using a PHILIPS X'PERT automatic diffractometer with the Cu-K α radiation. Table 1 gives the experimental conditions in which was recorded the powder diffraction pattern, together with the final values of the residual indices of the refinement.

The FULLPROF program was used to perform the profile refinement of the diffractogram without structural model (pattern matching routine) [13]. The structural refinement was carried out using the refined unit-cell parameters and the atomic coordinates given in the literature for the $Cu_2O(SeO_3)$ phase [11]. The observed, calculated and difference X-ray powder diffraction patterns are shown in Fig. 2. The refined unit cell parameters, the atomic coordinates and the bond distances and angles, obtained from the Rietveld refinement, are very similar to those reported by Effenberger and Pertlik [11] (see Supplementary Material).

2.3. Thermal characterization

Table

The thermal decomposition curve of Cu₂O(SeO₃) shows an experimental mass loss of, approximately, 40.3%, in the 450-500 °C range, which has been assigned to the decomposition of the $(SeO_3)^{2-}$ anion in the form of SeO₂ gas. The X-ray powder diffraction pattern of the inorganic residue obtained at 800 °C shows the presence of CuO(s) [Space group, *Fm*-3*m*;

Table 1			
Summary of crystallographic d	ata and least-squares	s refinement for Cu ₂ O(S	SeO3).

	,
Compound	$Cu_2O(SeO_3)$
$M (\text{g mol}^{-1})$	270.04
Crystal system	Cubic
Space group	P2 ₁ 3 (no. 198)
a (Å)	8.930(1)
Volume (Å ³)	712.1(1)
T (K)	273
λ (Cu-Kα)	1.5418
Ζ	12
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	5.04
2 heta range (°)	10-90
2 heta step-scan increment (°)	0.02
Time per step (s)	10
No. of reflections, independent	266, 124
No. of structural parameters	14
No. of profile parameters	12
No. of atoms refined	8
$R_{\mathrm{Bragg}}, R_{\mathrm{f}}$ (%)	3.88, 3.85
$R_{\rm p}, R_{\rm wp}$ (%)	3.12, 4.00
χ^{2} (%)	1.94



Fig. 2. Observed, calculated and difference X-ray powder diffraction patterns of Cu₂O(SeO₃).



Fig. 3. Thermodifractograms of Cu₂O(SeO₃).

a = 4.694 Å] [14]. The proposed decomposition reaction is: Cu₂O(SeO₃) (s) \rightarrow SeO₂ (g) + 2CuO (s).

The thermal behavior of this selenite has also been studied by time-resolved X-ray thermodiffractometry. The pattern were recorded in 2θ steps of 0.02° in the range $5-40^{\circ}$, counting for 2 s per step and increasing the temperature at 5 °C min⁻¹. The results are given in Fig. 3. Cu₂O(SeO₃) is stable up to approximately 490 °C. This step is characterized by small displacements in the diffraction maxima, caused by the thermal expansion. Above approximately 490 °C starts the decomposition of the selenite, and subsequent formation of CuO, whose crystallinity increases with increasing temperature. This oxide is the final inorganic residue obtained at the higher temperature of the experiment, 700 °C. The result is similar to that observed in the thermogravimetric study.

2.4. Physicochemical characterization techniques

The thermogravimetric analysis was carried out under oxygen in a SDC 2960 Simultaneous DSC-TGA TA Instrument, at 5 °C min⁻¹ in the temperature range 30-800 °C. A crucible containing ca. 20 mg of sample was used. The X-ray thermodiffractometry in air was performed on a PHILIPS X'PERT automatic diffractometer (Cu-Ka radiation) equipped with a variable-temperature stage (Paar Physica TCU2000) with a Pt sample holder. The IR spectrum (KBr pellets) was obtained with a Nicolet FT-IR 740 spectrophotometer in the 400-4000 cm⁻¹ range. Diffuse reflectance spectrum was registered at room temperature on a Cary 5000 spectrometer in the 210-2000 nm range. A Bruker ESP 300 spectrometer was used to record the polycrystalline ESR spectra. The temperature was stabilized with an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter and the frequency inside the cavity was determined using a Hewlett-packard 5352B microwave frequency counter. Magnetic measurements on a powdered sample were performed in the temperature range 5-300 K, using a Quantum Desing MPMS-7 SQUID magnetometer. The magnetic fields were 0.1, 0.05 and 0.01 T, values within the range of linear dependence of magnetization vs. magnetic, field even at 5 K.

3. Results and discussion

3.1. Infrared and UV-vis spectroscopies

The infrared spectrum of Cu₂O(SeO₃) shows the bands corresponding to the (SeO₃)^{2–} anion. The symmetric and antisymmetric stretching vibrations, ν_s (SeO₃), ν_{as} (SeO₃) and the deformation mode, δ (SeO₃), appear at 830; 755, 700 and 480, 450 cm⁻¹, respectively. The positions observed for these vibrational modes are in good agreement with those expected for this kind of compounds and are similar to those found in the literature for other selenite phases [15].

In the diffuse reflectance spectrum of $Cu_2O(SeO_3)$ are observed two intense absorption bands at 800 y 1100 nm, which are characteristic of five-coordinated environments with square pyramidal geometry [16].

3.2. Magnetic behavior

3.2.1. ESR and magnetic measurements

The ESR spectra of Cu₂O(SeO₃) were performed at the X-band on a powdered sample from room temperature to 4.2 K (see Fig. 4). The spectra exhibit isotropic signals centred at approximately 3200 G, that were fitted to Lorentzina curves obtaining a value for g = 2.11(1). This value is in the characteristic range of the d^9 –Cu(II) cation [17].



Fig. 4. Thermal evolution of the ESR spectra of Cu₂O(SeO₃).



Fig. 5. Thermal variation of the χ_m and $\chi_m T$ curves and the derivative of χ_m for Cu₂O(SeO₃).

The intensity of the signals is very small from room temperature to approximately 70 K (Fig. 4(a)). Below this temperature, the signals increase vigorously and disappear at approximately 50 K (Fig. 4(a) and (b)). In the 45.0–4.2 K range the intensity of the signals again increases (Fig. 4(b)). These results suggest the possible existence of a ferromagnetic transition in the 50–45 K range.

3.2.2. Magnetic measurements

Magnetic susceptibility measurements were carried out on powdered sample from 5.0 K to room temperature at magnetic fields of 1000, 500 and 100 G in Zero Field Cooling (ZFC) and Field Cooling (FC) modes. The molar magnetic susceptibility measured at 1000 G shows a strong increase from approximately 70 to 5 K, due to a magnetic transition between a paramagnetic state and other ferromagnetic one, showing a ferrimagnetic behavior at low temperature, probably due to a non-collinear ordering of the magnetic moments of the two independent Cu(II) cations with



Fig. 6. Thermal evolution of the χ_m at 1000, 500 and 100 G for Cu₂O(SeO₃).

different multiplicity, present in the crystal structure. The Curie temperature, T_c = 55 K, has been calculated from the derivative of the magnetic susceptibility curve (see inset in Fig. 5). These results are in good agreement with that obtained from the ESR measurements.

From the measurements performed at 500 and 100 G, similar Curie temperatures were obtained. Furthermore, the irreversibility observed between the measurements performed in the ZFC and FC modes is greater when the magnetic field decreases (Fig. 6). These facts corroborate the existence of ferromagnetic couplings at low temperature.

Magnetization measurements at 5, 45 and 80 K, temperatures located below and above of that of the magnetic transition, were also carried out. Below 50 K, the magnetization curve shows saturation at 3000 G, with a value for the imanation of 5500 emu/ mol, equivalent to a value for $M/N_A\beta = 0.90$ electrons (Fig. 7). This value indicates a ferromagnetic contribution of two copper(II) cations [18].



Fig. 7. Hysteresis loops carried out below and above of the magnetic transition for Cu₂O(SeO₃).



Fig. 8. Possible disposition of the crystallographically independent Cu(II) cations in the crystal structure of $Cu_2O(SeO_3)$.

This hypothesis agrees with an antiferromagnetic alignment for the two crystallografically independent copper(II) cations, one of them with a multiplicity three times greater than the other one [Cu(1) multiplicity 4 and Cu(2) multiplicity 12], which allows the ferromagnetic alignment of two copper(II) cations (see Fig. 8), giving rise to a ferrimagnetic behavior.

4. Concluding remarks

The Cu₂O(SeO₃) phase has been synthesized by using supercritical hydrothermal conditions. Its crystal structure has been refined in the $P2_13$ cubic space group. The structure consists of a three-dimensional framework constructed by two CuO₅ square pyramids and two SeO₃ trigonal pyramids. This phase is stable until 400 °C. In the IR spectrum the vibrational bands of the selenite group are observed. The diffuse reflectance spectroscopy is consistent with the existence of copper(II) cations with square pyramidal geometry. The ESR and magnetization measurements confirm the existence of a magnetic transition from a paramagnetic to a ferromagnetic state below 55 K, which gives rise to a ferrimagnetic behaviour, probably due to a non-collinear ordering of the magnetic moments. The global magnetic interactions at the lower temperature measured are antiferromagnetic.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.materresbull.2008.09.023.

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