

Room temperature solid-state transformation from $\text{Ag}_2\text{Cu}_2\text{O}_3$ to $\text{Ag}_2\text{Cu}_2\text{O}_4$ by ozone oxidation

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Abstract

The mixed silver–copper oxide, $\text{Ag}_2\text{Cu}_2\text{O}_4$ has been previously synthesized by electrochemical oxidation of suspensions of the precursor $\text{Ag}_2\text{Cu}_2\text{O}_3$ and also by direct oxidation/coprecipitation of soluble salts. This work shows how the transformation from $\text{Ag}_2\text{Cu}_2\text{O}_3$ to $\text{Ag}_2\text{Cu}_2\text{O}_4$ can take place in solid state at room temperature by ozonization of the precursor. The final phase is overstoichiometric in oxygen but shows the same structural features of the firstly described phase $\text{Ag}_2\text{Cu}_2\text{O}_4$. The maximum content of oxygen achieved is 4.34 per unit formula.

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1. Introduction

The synthesis of the ternary compound $\text{Ag}_2\text{Cu}_2\text{O}_3$ in 1999 marked the birth of a new family of oxides containing silver and copper, a combination previously unknown among natural or synthetic systems. The relative instability of silver oxides toward reduction at high temperature may be at the heart of this surprising lack of precedents. The approach followed was a soft chemistry method involving a coprecipitation reaction and aging at room temperature [1]. Only later, when the stoichiometry was known, high temperature and pressure conditions were found to prepare the same phase [2].

In order to isolate and study new members of the new family, we considered and followed several strategies using a variety of synthetic methods. First, the number of metals present in the oxide can be increased. In this sense, novel mixed oxides containing silver, copper and lead have been already reported [3]. Their synthesis was also achieved by coprecipitation. Another interesting

strategy for the isolation of new oxides is to vary the oxygen content and/or metals oxidation states in $\text{Ag}_2\text{Cu}_2\text{O}_3$, which would formally imply changing the oxidation state of the metals. This later alternative has also been very recently achieved in our laboratory by using a novel method. Thus, $\text{Ag}_2\text{Cu}_2\text{O}_4$ was obtained oxidizing electrochemically an alkaline aqueous suspension of $\text{Ag}_2\text{Cu}_2\text{O}_3$ [4]. Contrary to topotactic reactions, in which smooth structural changes take place, in this case the introduction of a whole atom of oxygen per unit formula takes place with a radical change in the structure that goes from three-dimensional in $\text{Ag}_2\text{Cu}_2\text{O}_3$ to bidimensional in $\text{Ag}_2\text{Cu}_2\text{O}_4$ (see Fig. 1). Surprisingly, oxidation of Ag and Cu metals or oxidation of binary oxides in suspension also yields the final oxide $\text{Ag}_2\text{Cu}_2\text{O}_4$.

However, far from providing a straightforward new structure, the new phase presents interesting and intriguing new features. XPS studies of $\text{Ag}_2\text{Cu}_2\text{O}_4$ indicate an electronic structure with oxidized silver more complex than anticipated, which in addition is also affected by irradiation with X-rays through an inner charge re-distribution [4–6]. Evidence of ionic mobility and disorder favors a view of

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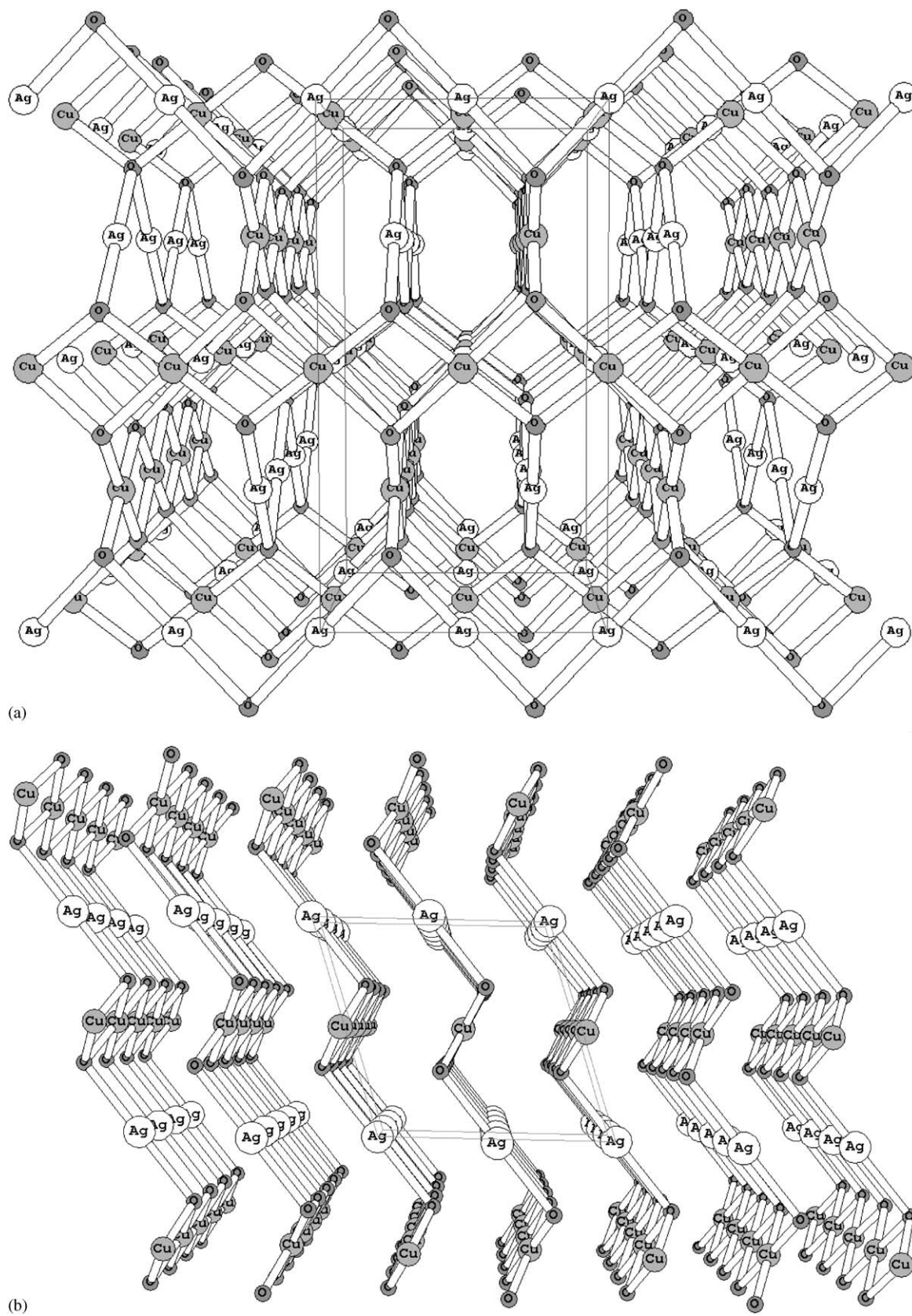


Fig. 1. $\text{Ag}_2\text{Cu}_2\text{O}_3$ (a) and $\text{Ag}_2\text{Cu}_2\text{O}_4$ (b) structures, showing several unit cells, from Refs. [1,4,5].

a rather flexible structure that can lead to a variety of intercalation reactions.

In addition to electrochemical methods, chemical oxidation represents an alternative for the isolation of oxides such as $\text{Ag}_2\text{Cu}_2\text{O}_4$. Indeed, a silver copper oxide obtained by coprecipitation in presence of persulfate, reported as AgCuO_2 [7], corresponds to the same phase as the one we have described as $\text{Ag}_2\text{Cu}_2\text{O}_4$, after the precursor $\text{Ag}_2\text{Cu}_2\text{O}_3$.

Among chemical oxidation procedures, ozonization is an important alternative method. Without leaving impurities after the chemical process, it could extend the oxidation extent beyond the one found previously. Also, it could involve a different oxidation mechanism and therefore allow the synthesis of new phases or even favor a different particle size. It can also prove if the previously observed transformation between $\text{Ag}_2\text{Cu}_2\text{O}_3$ and $\text{Ag}_2\text{Cu}_2\text{O}_4$ can occur by solid-state reaction at room temperature.

The method of oxidation by ozone has indeed presented important advantages in other cases. Oxidation with ozone allows simpler reactions, as in the case of the tubular phase $\alpha\text{-MnO}_2$ which can be obtained in absence of stabilizing cations [8] in a clean oxidation method since the only byproduct is oxygen. Nickel oxides with higher oxidation states constitute another example of the efficiency of ozone as oxidizing agent [9]. Furthermore, ozone and electrochemical oxidation follow different mechanisms even in presence of the same solvent and pH. The reaction between ozone gas and the solid phase, in addition, would overcome the chemical potential limitations imposed by the solvent needed on the electrochemical reactions. All those

factors may indeed contribute to yield new phases or different oxidation states in the same phase, and therefore the experiments described are designed in an attempt to evaluate the effect of ozone itself and the absence of water as a solvent.

In this work, we show the results of using ozone as oxidizing agent of several silver and/or copper precursors under different conditions. We also present the synthesis of $\text{Ag}_2\text{Cu}_2\text{O}_4$ with ozone, and compare it with the product obtained using electrochemical methods.

2. Experimental

All the experiments have been performed using the setup shown in Fig. 2. A flow of oxygen gas pass through an ozonizer A.C.W. BMT 803. The generated ozone is transported by the oxygen flow through three different reaction chambers. Reaction chamber A is placed over a magnetic stirrer, and is used for the oxidation of suspensions and for the experiments performed with wet ozone. Chamber B is used when oxidizing dry solid materials. Finally, reaction chamber C contains a chemical trap consisting of a solution of KI and $\text{Na}_2\text{S}_2\text{O}_3$ to ensure that no remaining unreacted ozone escapes into the atmosphere. The whole setup is placed inside a hood.

The exact flow of ozone used was constant and the actual value was evaluated semi-quantitatively. To do so, a solution of an excess of KI was treated with ozone. The resultant I_2 was then titrated with a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution (Aldrich, 0.1016 N). An approximate effective flow of 3.5×10^{-3} mol O_3/h was obtained.

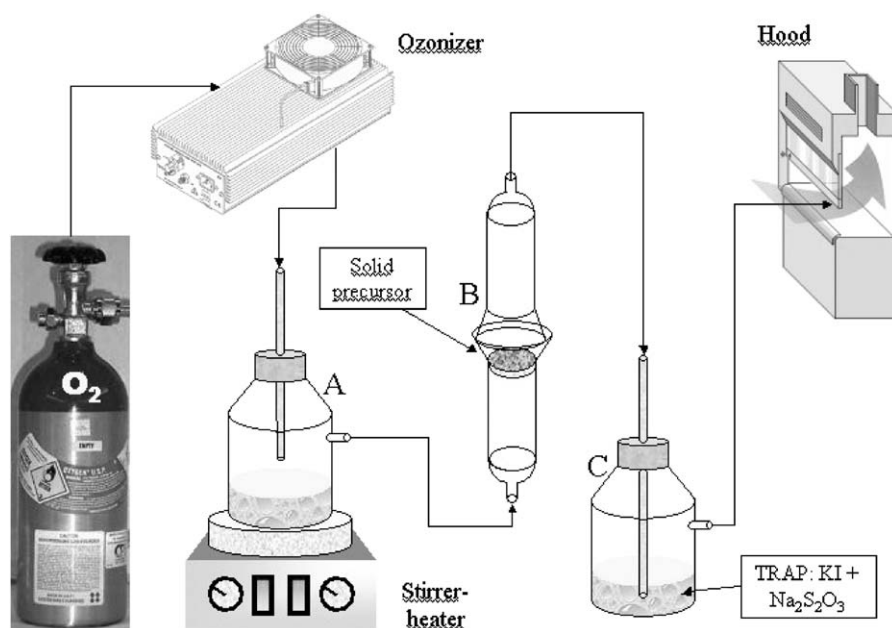


Fig. 2. Experimental ozonization setup.

In the case of ozonization of solid materials, those were placed in reaction chamber B under ozone flow. In these experiments both dry and wet ozone was used. The wet ozone was obtained by passing it through distilled water on reaction chamber A so that a water vapor pressure is generated and carried along with the ozone/oxygen flow.

In the case of suspensions, they were placed in reaction chamber A and ozone was bubbled through the suspension. The solid material was dispersed in water by stirring with a magnetic bar shaped with an angular edge that plows up sediment and provides strong mixing action and hence, an optimum contact of the material with ozone.

Finally, several solutions were also treated with ozone. In each case, the solution was placed in reaction chamber A and the ozone/oxygen flow was bubbled in. Both acidic and neutral solutions were tested.

The materials used were the following: Ag (Aldrich, 99.9%, 2–3.5 μm), Cu (Baker 99%), Ag_2O (Prolabo), CuO (Prolabo, p.a.), Ag/Cu (72/28) alloy (Goodfellow, 0.05 mm thick plates), AgNO_3 (Prolabo, 99.5%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Prolabo), AgClO_4 (Aldrich 99.9%) and finally, $\text{Ag}_2\text{Cu}_2\text{O}_3$, synthesized as in Ref. [1], and $\text{Ag}_2\text{Cu}_2\text{O}_4$, electrochemically synthesized as in Ref. [4].

Scanning electron microscopy studies were also performed in order to characterize the final morphology of the different oxidized products as well as that of some precursors using a field emission scanning microscope Philips XL series XL30 Feg TMP was used. For some samples, EDX analyses were also performed with the same microscope using an OXFORD 6650 analyzer.

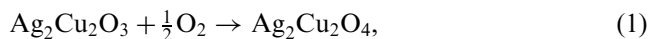
All products obtained were analyzed by powder X-ray diffraction. The measurements were performed on an automatic diffractometer Philips PW1720.

Oxygen contents were determined by thermogravimetry using a Perkin–Elmer thermal balance TGA 7, in Ar/H_2 (5%) (Ag and Cu as final products of reduction in all cases). XPS measurements were performed at room temperature with a SPECS EA10P hemispherical analyzer using both non-monochromatic Mg $K\alpha$ (1253.6 eV) and Al $K\alpha$ (1486.6 eV) radiation (300 W) as excitation source in a base pressure of $\approx 10^{-9}$ mbar.

3. Results and discussion

3.1. Ozonization of $\text{Ag}_2\text{Cu}_2\text{O}_3$ and electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$

As it has been said in the introduction, one of our objectives was to try to reproduce the already reported reaction [4]



using ozone oxidation instead of electrochemical methods. The oxide $\text{Ag}_2\text{Cu}_2\text{O}_3$ was treated in solid state, using either *dry* or *wet* ozone, and also in neutral aqueous suspension.

The X-ray diffractograms corresponding to the treatment of $\text{Ag}_2\text{Cu}_2\text{O}_3$ with *wet* ozone for different times are shown in Fig. 3A and B. As it can be observed, after 13 h the reflections observed can be attributed to the oxidation product $\text{Ag}_2\text{Cu}_2\text{O}_4$. The crystallinity, notwithstanding, is poor as indicated by the large width of the peaks. When ozonization is carried out during longer times than 78 h (not shown), the diffraction pattern shows a further decrease in crystallinity of the product.

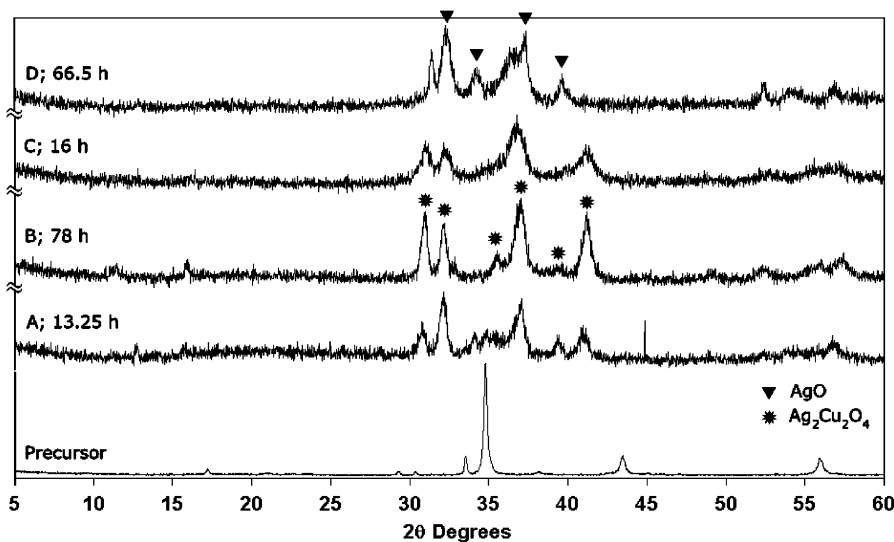


Fig. 3. Bottom: XRD pattern of pure $\text{Ag}_2\text{Cu}_2\text{O}_3$. A and B: solid $\text{Ag}_2\text{Cu}_2\text{O}_3$ treated with *wet* ozone; C and D: solid $\text{Ag}_2\text{Cu}_2\text{O}_3$ treated with *dry* ozone.

On the other hand, the diffraction patterns of the products obtained when $\text{Ag}_2\text{Cu}_2\text{O}_3$ was treated with *dry* ozone are shown in Fig. 3C and D. The behavior of $\text{Ag}_2\text{Cu}_2\text{O}_3$ in this case is similar to that treated with *wet* ozone. After 16 h the peaks that appear correspond to $\text{Ag}_2\text{Cu}_2\text{O}_4$, but in this case the crystallinity of the product is even worse than before, and when the treatment is kept for longer times, $\text{Ag}_2\text{Cu}_2\text{O}_4$ tends to decompose and become amorphous even faster than when *wet* ozone is used. Peaks corresponding to AgO can also be identified after 66.5 h of treatment. In all cases the presence of $\text{Ag}_2\text{Cu}_2\text{O}_4$ can be considered a proof that the transformation of $\text{Ag}_2\text{Cu}_2\text{O}_3$ to $\text{Ag}_2\text{Cu}_2\text{O}_4$ occurs in solid state as a rather special “corrosion reaction”.

Finally, when an aqueous $\text{Ag}_2\text{Cu}_2\text{O}_3$ suspension is bubbled with ozone, the result is quite different (Fig. 4). Again the peaks that appear correspond to $\text{Ag}_2\text{Cu}_2\text{O}_4$, but in this case, the oxidation product is better crystallized, and as opposed to what happens in the previous two cases, the longer the treatment with ozone the better the crystallinity of the oxidation product. After 60 h of ozonization, only the peaks corresponding to $\text{Ag}_2\text{Cu}_2\text{O}_4$ can be seen and there are no sign of loss of crystallinity or decomposition. Nevertheless, in all cases, even this last one, the crystallinity obtained for $\text{Ag}_2\text{Cu}_2\text{O}_4$ is far less than that of the electrochemically synthesized one (Ref. in Fig. 4) [4,5].

The fact that better crystallinity, and no decomposition/amorphization, is achieved when there is a large amount of water present during the reaction, would imply that the oxidation of $\text{Ag}_2\text{Cu}_2\text{O}_3$ to form $\text{Ag}_2\text{Cu}_2\text{O}_4$ may be proceeding through the formation of an oxygen oxidizing aqueous species, like an oxy- or hydroxyl radical, less reactive than the species found in

gaseous ozone. Such radical may not be able to decompose the $\text{Ag}_2\text{Cu}_2\text{O}_4$ formed, while the active species present in gaseous ozone could be responsible for the $\text{Ag}_2\text{Cu}_2\text{O}_4$ decomposition/amorphization observed with no solvent present. On the other hand, kinetic factors could also affect the reaction outcome when comparing dry and wet ozone. Thus, it could be induced that the oxidation may proceed by different mechanisms in ozone oxidation or by traditional electrochemical methods in aqueous solutions, and also when oxidation is performed in water or in solid state.

In order to see whether the ozone treatment would affect the electrochemically synthesized phase $\text{Ag}_2\text{Cu}_2\text{O}_4$, a sample of it was also treated with *dry* and *wet* ozone. In this case, electrochemical $\text{Ag}_2\text{Cu}_2\text{O}_4$ shows no signs of amorphization/decomposition after long exposures to ozone (31 h). It seems then that well crystallized $\text{Ag}_2\text{Cu}_2\text{O}_4$ is not affected by the higher ozone potential, proving a larger stability vs. ozone than its precursor $\text{Ag}_2\text{Cu}_2\text{O}_3$.

Both electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$ and the product resulting of ozonization of $\text{Ag}_2\text{Cu}_2\text{O}_3$ in suspension were analyzed by SEM, to compare their morphology (see Fig. 5). Fig. 5A corresponds to the electrochemical route phase, while Fig. 5B corresponds to the sample ozonized in suspension for 4.5 h (pattern A in Fig. 4). As in the diffractogram, unreacted needle-like crystals of $\text{Ag}_2\text{Cu}_2\text{O}_3$ are detected in the last, along with much smaller plate-like crystals which would correspond to the $\text{Ag}_2\text{Cu}_2\text{O}_4$ being formed. Fig. 5C corresponds to a sample treated longer time (powder diffraction pattern is shown in Fig. 4B, when all $\text{Ag}_2\text{Cu}_2\text{O}_3$ has already reacted and formed $\text{Ag}_2\text{Cu}_2\text{O}_4$). The particle size obtained in this case shows a higher dispersion and is smaller on average

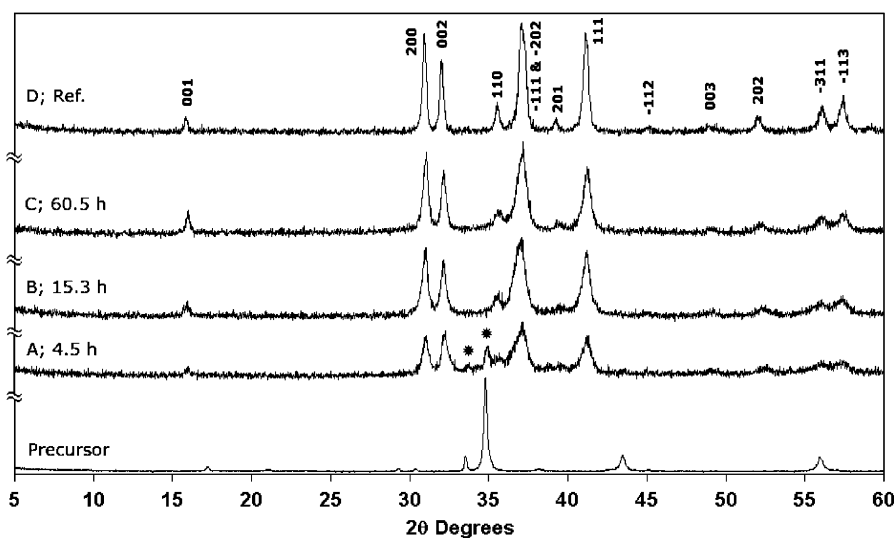


Fig. 4. $\text{Ag}_2\text{Cu}_2\text{O}_3$ suspension treated with ozone for different times. Bottom: XRD pattern of pure $\text{Ag}_2\text{Cu}_2\text{O}_3$ (*). Top: electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$ as Refs. [4,5].

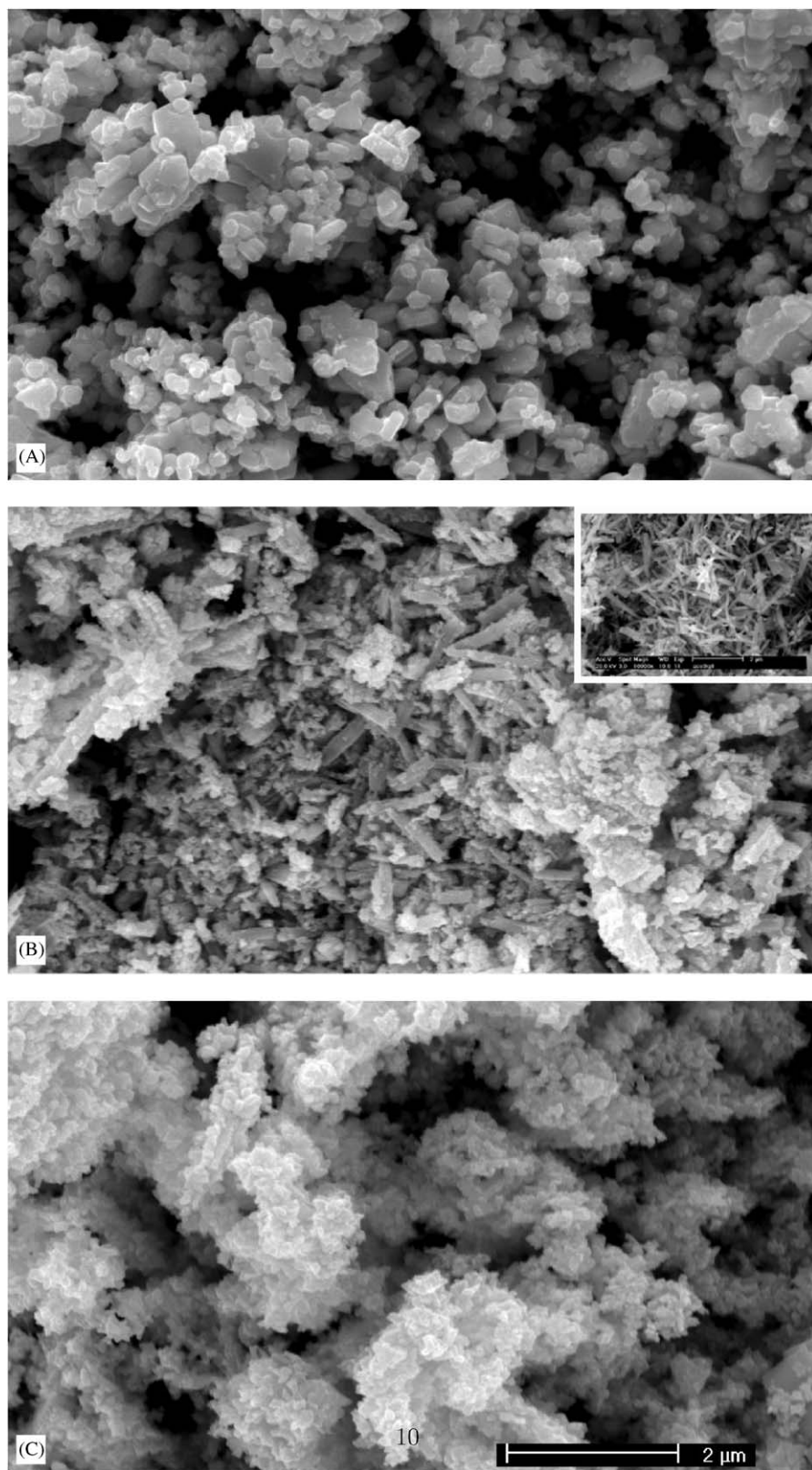


Fig. 5. (A) SEM image of electrochemically synthesized Ag₂Cu₂O₄; (B) Ag₂Cu₂O₃ ozonized in suspension for 4.5 h. Inset: untreated Ag₂Cu₂O₃ and (C) Ag₂Cu₂O₃ ozonized in suspension for 15.5 h.

than for the electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$ (Fig. 5A).

Thermogravimetric analyses were performed for the sample $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesized by ozonization of a $\text{Ag}_2\text{Cu}_2\text{O}_3$ suspension and the results compared with the ones obtained previously for electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$ [4,5]. As it is shown in Table 1, the $\text{Ag}_2\text{Cu}_2\text{O}_4$ obtained by ozonization is considerably richer in oxygen, having 0.34 more oxygens per unit formula. Nevertheless, the reflections that appear in the X-ray patterns are the same in both cases which implies that the main structure remains. This extra oxygen could be occupying interstitial positions, which would not be detectable by X-ray diffraction. Possible interstitial positions could be between Cu or Ag metals from different layers (see Fig. 1b). The amount of over-stoichiometric oxygen is reproducible and it implies a formal change in overall metallic oxidation states, and/or the presence of oxygen in intermediate oxidation state, e.g. as radical ions. Therefore, XPS experiments were performed to get information on that respect. Comparison of the Ag $3d$ XPS spectra for $\text{Ag}_2\text{Cu}_2\text{O}_3$, electrochemical $\text{Ag}_2\text{Cu}_2\text{O}_4$ and $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesized with ozone shows remarkable differences. In the $3d_{5/2}$ region, and for both types of $\text{Ag}_2\text{Cu}_2\text{O}_4$, a new peak at ≈ 367 eV (B) can be detected (Fig. 6) in addition to the peak at ≈ 368 eV (A), typical of compounds with Ag(I)

as $\text{Ag}_2\text{Cu}_2\text{O}_3$. The same effect is observed in the $3d_{3/2}$ region. The existence of extra lines involves silver oxidation above Ag(I), with a d^{10} configuration, and the corresponding opening of the d -shell (d^{10-n}) which leads to the appearance of new electronic states and multiple splitting [6] not necessarily related with the existence of localized states. The intensity ratio B/A is larger for $\text{Ag}_2\text{Cu}_2\text{O}_{4.34}$ obtained with ozone than for $\text{Ag}_2\text{Cu}_2\text{O}_4$ obtained electrochemically, evidencing a larger extent in silver oxidation. If this is compared with the oxygen over-stoichiometry derived from TGA analysis, it is evident that the extra amount of oxygen is associated with oxidation of silver. Oxidation of the rest of elements in the structure cannot be discarded. However, both Cu $2p$ and O $1s$ XPS have not shown noticeable changes with respect to electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$ [4–6]. Unfortunately, oxidation of Cu(II) into Cu(III) can hardly be determined by XPS because of the instability of Cu(III) to irradiation in UHV [10]. A very labile oxygen may also be lost in high-vacuum conditions. In any case this oxidation occurs without notable change in the observed X-ray diffraction as it has been reported in other cases of oxygen intercalation in the oxides La_2CuO_4 and Ca_2MnO_4 [11,12]. It is worth remarking that, the inelastic electron mean free path in XPS is approx. 2 nm, corresponding to Ag $3d$ electrons excited with Al $K\alpha$ radiation. This average probing depth represents a significant part of the nanocrystals volume that exhibit a layered morphology with thickness in the order of 10 nm. This fact is even amplified because of the preferential orientation of the nanocrystals in the pressed pellets. Furthermore, the survey XPS spectra (not shown) show the characteristic bulk plasmon loss spectra (plasmon energy around 23 eV) indicative of the above. Also, previous XANES experiments on both $\text{Ag}_2\text{Cu}_2\text{O}_3$ and $\text{Ag}_2\text{Cu}_2\text{O}_4$, stable

Table 1
TGA analyses of $\text{Ag}_2\text{Cu}_2\text{O}_4$ obtained by ozonization and electrochemically

Sample	% weight loss _{anal.1}	% weight loss _{anal.2}	Average O value
$\text{Ag}_2\text{Cu}_2\text{O}_4(\text{elect.})$	15.83	15.96	4.04 ± 0.01
$\text{Ag}_2\text{Cu}_2\text{O}_4(\text{susp.}+\text{O}_3)$	17.00	17.05	4.34 ± 0.01

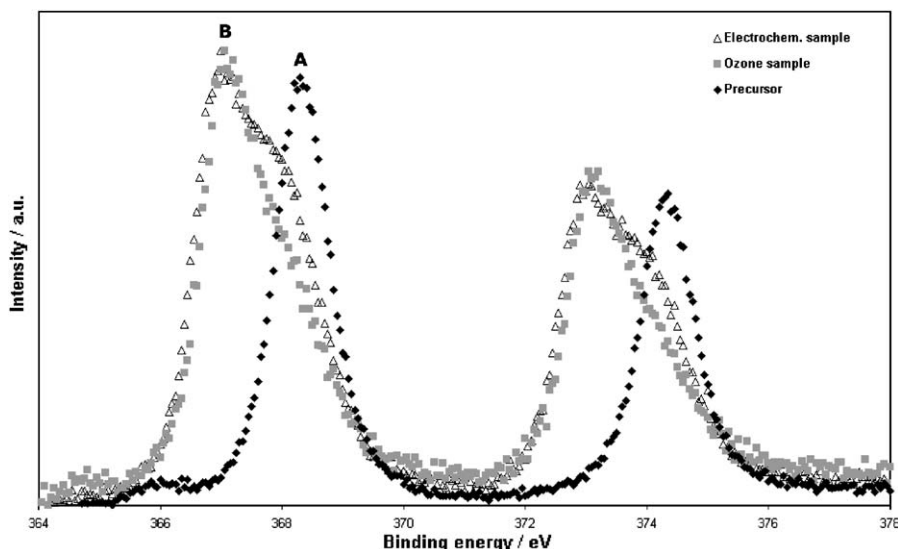


Fig. 6. Ag $3d$ XPS spectra for $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesized with ozone and electrochemically.

under synchrotron radiation, are consistent with XPS measurements [6].

3.2. Ozonization of other silver and copper compounds

3.2.1. Ag and Cu

Metallic silver and copper were treated with ozone to compare their behavior with that of $\text{Ag}_2\text{Cu}_2\text{O}_3$.

First, silver powder was treated with *wet* and *dry* ozone. In both cases, after few hours of treatment we could observe the formation of the oxides Ag_2O and AgO , along with some remaining metallic silver, as expected from previous reports [13]. When the same experiments are performed with copper powder, only a very slight amount of copper gets oxidized to CuO . Fig. 7 shows, as an example, the powder diffraction patterns corresponding to the oxidation of Ag (A) and Cu (B) with *wet* ozone.

A physical mixture in a 1:1 molar ratio of silver and copper powders were also treated with *wet* ozone. The result was again the same, the only oxidation product being a combination of Ag_2O and AgO . But when the same mixture was treated with ozone as an aqueous suspension, we could observe the formation of $\text{Ag}_2\text{Cu}_2\text{O}_4$, although the main products are still Ag_2O and AgO . Again, no peaks corresponding to CuO are observed, and while all Ag has been oxidized, there is still some metallic Cu remaining. (It has to be noted that silver powders dispersed much better than copper powders, which tended to remain in the bottom of the reaction chamber and stuck to its walls, hence the difference in intensities in the diffractogram (Fig. 7C)).

This results are consistent with previous electrochemical observations that show that $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesis is possible by electrochemical oxidation of suspensions containing Ag^0 and Cu^0 powders [4].

3.2.2. Ag_2O and CuO

Again the same three experiments were performed with CuO and Ag_2O (treatment with *wet* and *dry* ozone and as a suspension). While Ag_2O was easily oxidized to AgO in all cases, the only oxidation product observed, CuO remained unchanged regardless of the reaction time (after 17 h under *wet* ozone no oxidation products were observed). While the results for Ag_2O where expected mainly from the experiments above explained and from several References [13], CuO , as Cu, proved to be far more stable to ozone.

3.2.3. Silver copper alloy

A $\frac{72}{28}$ Ag/Cu alloy was also treated with *wet* ozone to see whether $\text{Ag}_2\text{Cu}_2\text{O}_3$ or $\text{Ag}_2\text{Cu}_2\text{O}_4$ could be directly formed. To do so, a 2×1 cm, 0.05 mm thick foil, having the longitudinal ends bent, was directly placed in reaction chamber B. The foil was half covered with tape to compare the non-exposed and exposed parts.

After several minutes under the ozone flow, the uncovered part of the foil darkened, and after several hours the XRD pattern of the oxidized part showed mainly the peaks corresponding to AgO , along with a small amount of Ag_2O . This implies that silver has been segregated from the alloy to get oxidized while copper again remains unaffected by ozone treatment. To further confirm this result, SEM/EDX analyses were

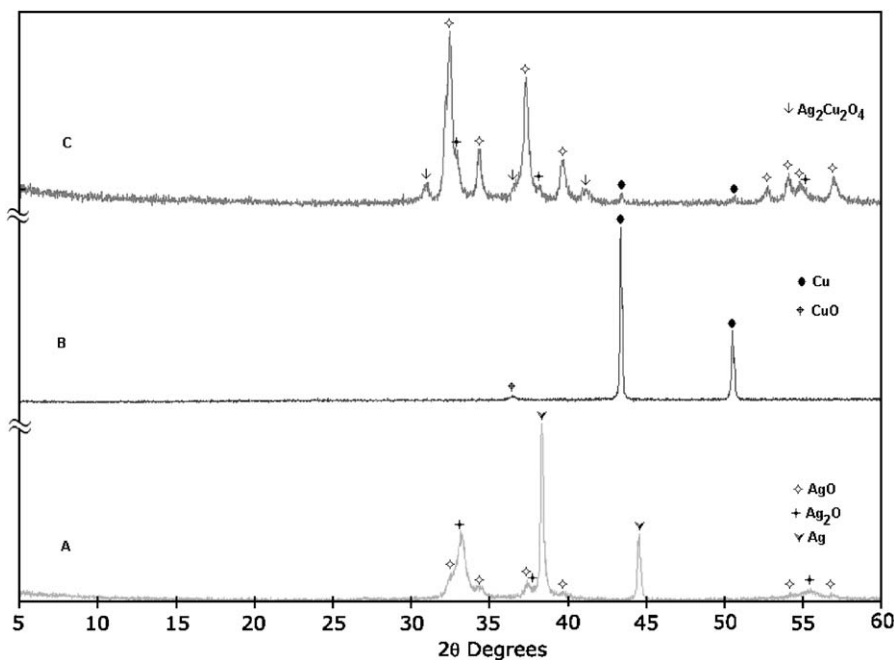


Fig. 7. (A) Metallic silver treated with *wet* ozone; (B) metallic copper treated with *wet* ozone and (C) 1:1 molar Ag/Cu aqueous suspension treated with ozone.

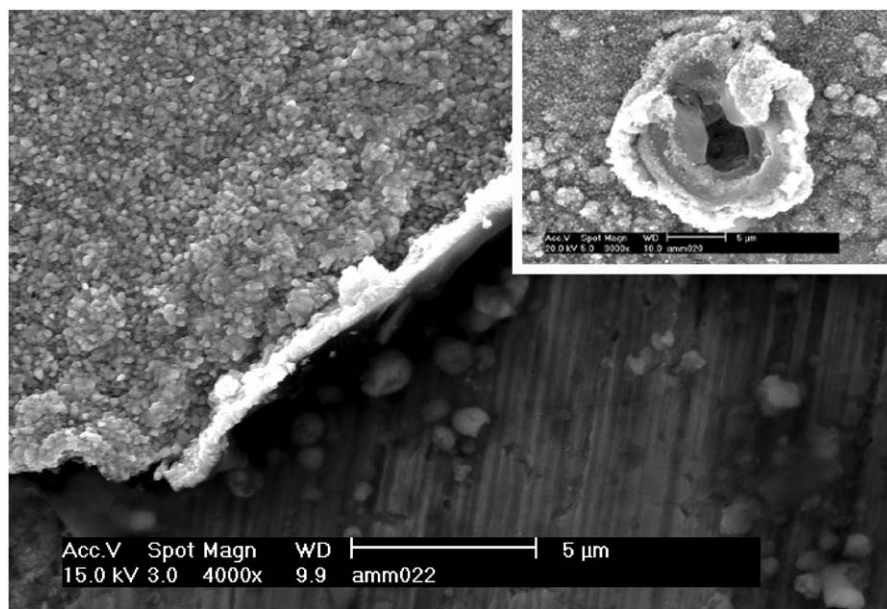


Fig. 8. Compared SEM images of exposed and non-exposed Ag/Cu alloy to ozone. Inset: Irregularities present on the silver oxide layer.

performed. The difference between the exposed and non-exposed part can be seen in Fig. 8. A clear layer of silver oxide small crystals has been formed onto the uncovered area while the smooth alloy surface can be observed where the foil was protected. EDX analyses performed on the unoxidized parts show a Ag/Cu composition ratio of $\frac{70}{30}\%$, as expected from the nominal alloy composition.

When the EDX analyses were performed on the oxidized surface, a higher proportion of Ag was obtained, reaching a 92% when the oxide crystal were examined with a magnification of $160\,000\times$. This silver oxide layer is not uniform presenting irregularities such as those observed in Fig. 8 (inset). Through those holes the underlying alloy can be investigated showing an EDX analysis with a richer composition in copper than that of the starting alloy, up to 45% for a magnification of $160\,000\times$. This result thus confirms that part of the silver present in the original alloy has segregated during the ozonization treatment and has migrated to the surface of the material, so that the underlying alloy is enriched in copper.

The results obtained for the ozonization of Ag/Cu alloy foil are equivalent to those reported in Ref. [14] where a silver foil is treated with ozone and AgO is obtained upon long exposure times. The presence of copper in the alloy composition does not affect the process and no mixed product is obtained.

3.3. Ozonization of different solutions containing Cu^{2+} and Ag^+ ions

Although the reaction of a AgNO_3 solution with ozone has been already reported [15], the experiment

was carried to evaluate whether a Ag/Cu mixed oxidation product could be obtained. In first place, a AgNO_3 and $\text{Cu}(\text{NO}_3)_2$ (both 0.1 M) neutral aqueous solution was bubbled with ozone at room temperature. The solution was stirred during the process to ensure that any solid material formed would remain in contact with the whole solution and gas flow, in homogeneous conditions. After some time of ozonization the solution started to darken and a solid appeared in suspension. The ozone flow was maintained for several hours. The XRD pattern of the generated solid, showed very sharp peaks which correspond to the oxynitrate $\text{Ag}_7\text{O}_8\text{NO}_3$, as in Ref. [15], as the only oxidation product. Again no copper oxidation product was found. The $\text{Ag}_7\text{O}_8\text{NO}_3$ thus obtained was very crystalline, showing a big dispersion in crystal size and a high degree of twinning.

Another experience that exemplifies how silver gets oxidized by ozone was the ozonization of a AgClO_4 solution. After several minutes the solution darkened and became a suspension that was bubbled for several hours. The XRD analyses of the oxidation product showed the presence of AgO and the further oxidized Ag_3O_4 and Ag_2O_3 . The latter two are not stable and decomposed to AgO when the powder was treated at 50°C for drying (Fig. 9).

Experiments were also performed with acidic solutions and at different temperatures. Changes in pH and temperature has proven to be key factors in order to obtain different phases by ozonization, as is the case of the tubular MnO_2 , which is obtained by ozonization of a Mn^{2+} solution at pH below 2 and temperatures over 70°C [8]. In our case, a solution containing both copper and silver nitrates and HNO_3 3M was treated with ozone at room temperature and high temperatures. In

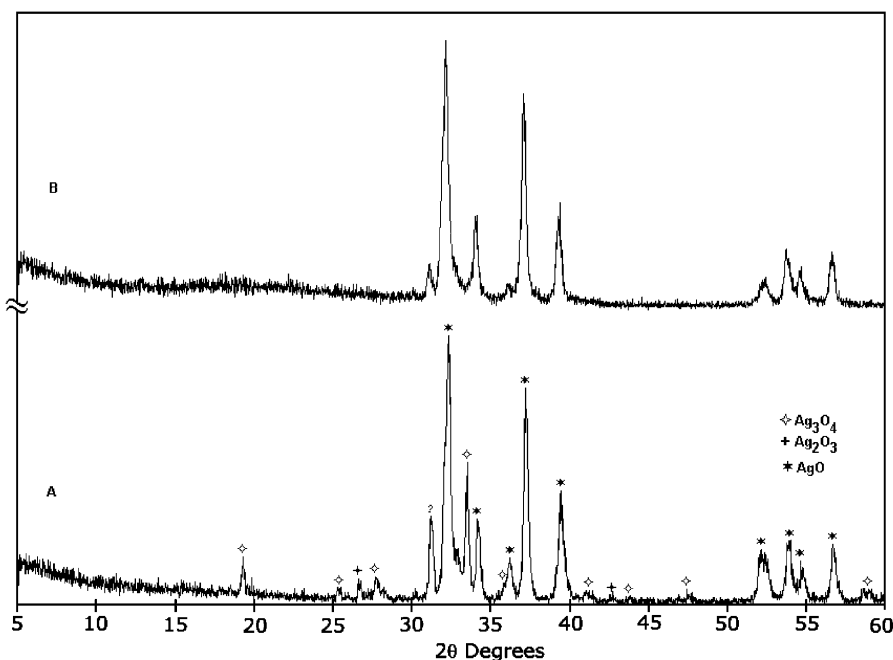


Fig. 9. (A) Mixture of silver oxides obtained after ozonizing a AgClO_4 solution. (B) Mixture shown in A after several hours at 50°C .

both cases, the solution darkened upon ozonization and no precipitated formed. After several hours the solution was even darker. The dark color of this solution is the same that the one obtained when $\text{Ag}_2\text{Cu}_2\text{O}_4$ was dissolved in concentrated nitric acid. In both cases the dark color disappears with time giving rise to the characteristic green color. The color can be attributed to the formation of an unstable soluble oxidized species produced either by ozone or the highly oxidizing oxide $\text{Ag}_2\text{Cu}_2\text{O}_4$. The same results were obtained when H_2SO_4 3M was used instead of HNO_3 . In this case, only experiments at high temperature could be performed due to the slight solubility of Ag_2SO_4 at room temperature.

4. Conclusions

$\text{Ag}_2\text{Cu}_2\text{O}_4$ has been obtained from reaction of $\text{Ag}_2\text{Cu}_2\text{O}_3$ with ozone in what seems to be a reaction between a gas and a solid. It has also been obtained from ozonization of a suspension of $\text{Ag}_2\text{Cu}_2\text{O}_3$. The crystallinity of $\text{Ag}_2\text{Cu}_2\text{O}_4$ increases when the amount of water present during the reaction is larger. Thus, the $\text{Ag}_2\text{Cu}_2\text{O}_4$ obtained with dry ozone showed the worst crystallinity and was the one that became amorphous or decomposed faster when the treatment with ozone was long, whereas the $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesized in suspension was the only product and the best crystallized. It was also stable upon long reaction times. The crystallinity of the $\text{Ag}_2\text{Cu}_2\text{O}_4$ synthesized by ozonization did not reach in any case that of the phase electrochemically synthesized.

The fact that the crystallinity and stability of $\text{Ag}_2\text{Cu}_2\text{O}_4$ improves when water is present, could imply that what is oxidizing $\text{Ag}_2\text{Cu}_2\text{O}_3$ is a product of the reaction of ozone with water, e.g. like a hydroxyl or oxy-radical, and that this reaction between water and ozone is preventing the decomposition of the $\text{Ag}_2\text{Cu}_2\text{O}_4$ upon direct contact with ozone.

Another products containing both silver and copper, together or independently, were also treated with ozone. In all cases it was silver the oxidized element giving different products depending on how the reaction was performed. The presence of copper showed no effect on the silver oxidation products and all copper compounds, except for $\text{Ag}_2\text{Cu}_2\text{O}_3$, showed a high stability against the oxidation with ozone. Oxidation of $\text{Ag}_2\text{Cu}_2\text{O}_3$ with ozone to form $\text{Ag}_2\text{Cu}_2\text{O}_4$ proceeds in larger extent than by electrochemical methods and involves oxidation of silver as shown by XPS.

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