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SYNTHESIS AND PHYSICO-CHEMICAL STUDY OF Co, Ni, Cu, AND Sn NANOPARTICLES

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ABSTRACT

Cobalt, nickel, copper, and tin nanosized particles were synthesized through a borohydride reduction method with a reducing agent of $NaBH_4$. *The reductive precipitation was carried out at room temperature and atmospheric pressure. The nanoparticle powders were synthesized from water solutions of sulfate salts. The obtained nanosized particles were investigated by scanning electron microscopy (SEM) and XRD analyses. The SEM micrographs showed the nanoparticles' morphology and structure. The chemical elements' distribution was determined by energy dispersive spectroscopy (EDS) analysis. The X-ray diffraction (XRD) analysis determined the phase composition and state (amorphous or crystalline).*

Keywords: nanoparticles, nanosized particles, borohydride reduction, Co, Ni, Cu, Sn, SEM analyses, XRD analyses, EDS analysis.

INTRODUCTION

In recent years, the synthesis of metal nanoparticles has become an important area of science research. Nanoparticles with a size of 1 to 100 nanometers are distinguished by properties significantly different from those of bulk materials with the same chemical composition [1]. Due to their nanoscale dimensions, the properties of the particles become similar to "quantum dots," according to quantum mechanical rules. Nanoparticles have a large surface-to-volume ratio, which makes them exceptionally catalytically active. Metallic cobalt, nickel, copper, and tin nanoparticles are particularly attractive as they are important materials in modern technology. They are interested in their unconventional optical, catalytic, mechanical, and electrical properties [2]. There are various methods for obtaining such nanoparticles, including thermal decomposition, metal salt reduction, microwave heating, microemulsion technique, radiation methods, laser evaporation, arc sputtering, etc. [3]. Chemical reduction is a commonly used method for synthesizing monodisperse metal nanoparticles that can self-assemble when metal salts are added to a reducing solution [4, 5].

The present study aimed to synthesize metal (Co, Ni, Cu, and Sn) nanoparticles by borohydride reduction using $NaBH_4$ in aqueous solutions of the corresponding sulfide salts. Furthermore, SEM-EDS was used to investigate the morphology of the nanoparticles. XRD analysis studied the synthesized particles' phase composition.

EXPERIMENTAL

Preparation of Co, Ni, Cu, and Sn nanosized particles by borohydride reduction method

The borohydride reduction method in aqueous solutions of the corresponding copper, cobalt, nickel, and tin sulfate salts with $NaBH_4$ was used to synthesize the nanosized particles. The synthesis was carried out in a cell providing a sequential introduction of the starting solutions and continuous mechanical stirring.

To prepare Co, Ni, Cu, and Sn particles, 0.2 mol dm^{-3} aqueous solutions of the corresponding chloride, sulfide, and nitrate salts and 0.2 mol dm^{-3} $NaBH_4$ solution of the reducer were used. The reducer was added during continuous stirring with a mechanical stirrer. The mixing time was 2 minutes. The obtained fine particles were filtered, washed with distilled water, and dried in a vacuum dryer at 80°C for 24 hours.

Research technics

The morphology and elemental composition of the synthesized nano-sized particles were studied using a scanning electron microscope SEM/FIB LYRA I XMU, TESCAN company, at an accelerating voltage from 200 V to 30 kV. The SEM apparatus has the following characteristics: electron source - tungsten heated filament, resolution - 3.5 nm at 30 kV, spectroscopic resolution at Mn-Ka, and 1 kcps 126 eV.

Elemental distribution analysis on the surface of the obtained nanosized particles was performed by a BRUKER Quantax 200 EDX detector. X-ray diffraction patterns of all samples were collected within the 2θ range from 5° to 90° with a constant step of 0.053° and counting time 53.8050 s/step on Philips PW 1050 diffractometer using CuKα radiation.

RESULTS AND DISCUSSION

SEM analysis

Co nanosized particles

Fig. 1 presents the SEM images of Co nanosized particles at 20000x magnification. Fine nano-sized spherical-shaped agglomerated particles were observed, but the agglomerates were not tightly adhered, forming a porous structure.

Ni nanosized particles

Fig. 2 presents the SEM images of Ni nanosized particles at 20000x magnification. Ni particles' morphology was similar to that of Co. It also showed fine aggregated spherical particles, but the agglomerates are not tightly adhered, forming a porous structure. Even the images were unclear; it can be determined that the particles were in the nanoscale region.

Cu nanosized particles

The SEM images presented in Fig. 3 demonstrate the morphology of Cu particles, which were characterized by particles of different sizes and shapes. Cu particles' morphology differs from Co nanosized particles' morphology. Agglomerated irregularly shaped particles were observed, forming network-like structures. The agglomeration of the particles was probably due to the active unsaturated surface and existing attractive forces.

Sn nanosized particles

In Fig. 4, Sn particles of different sizes and shapes in the nanoscale region were observed; clearly defined particles with spherical, cubic, and irregular shapes were noticed. This suggested that Sn nanoparticles were in a crystalline state, which should be proven by X-ray phase analysis. Aggregation of the particles was less pronounced than with Cu, Co, and Ni nanosized particles.

EDS analysis

Figs. 5 - 8 represent an EDS spectrum for the distribution of elements in an arbitrary area on the surface of Co, Ni, Cu, and Sn particles, respectively. The content of the elements in three different regions is given in Table 1.

Co nanosized particles

From the results presented in Table 1, the presence of the element Co (up to 75.22 mass %), O (up to 32.27 mass %), and small amounts of Na, probably a residue of the reductant $NaBH_4$, were found.

Ni nanosized particles

From the results presented in Table 1, the presence of the elements Ni (up to 66.58 mass%), O (up to 37.38 mass %), Na (up to 2.96 mass %), S (up to 0.94 mass%) and Fe (up to 22.56) was found. The small amounts of Na and S were probably a residue of the reagents $NaBH_4$ and $NiSO_4$, respectively, used as starting components. The small percentage of iron reported was likely due to the technical grade $NiSO_4$ used while the high amount of Fe could be the reading error due to the proximity of the Ni and Fe peaks.

Cu nanosized particles

The elements Cu (up to 87.43 mass %) and O (up to 22 mass %) were found to be present in Table 1. The most likely reason for the presence of O was oxidation processes during the drying or analysis.

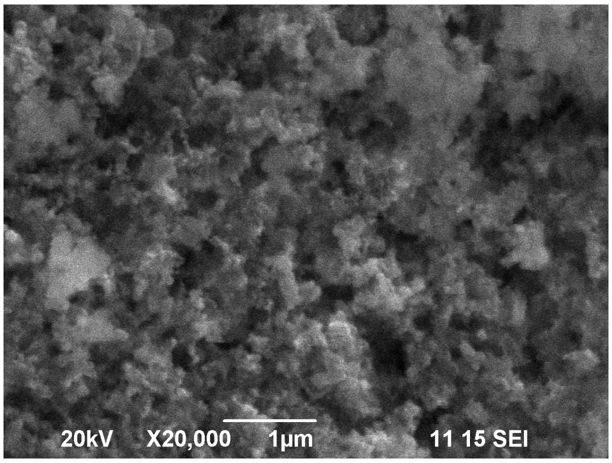

Fig. 1. SEM images of Co nanosized particles at 20000x magnification.

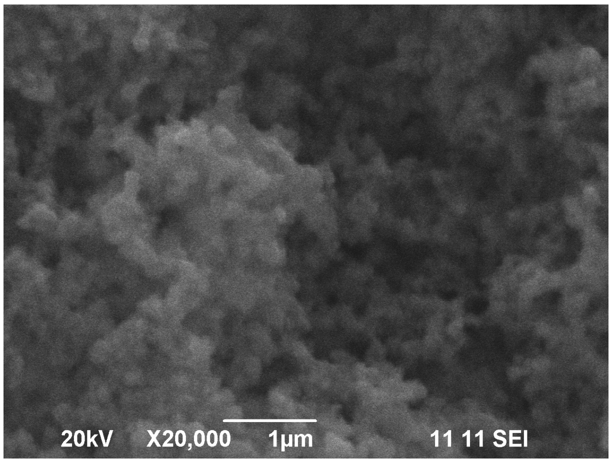

Fig. 2. SEM images of Ni nanosized particles at 20000x magnification.

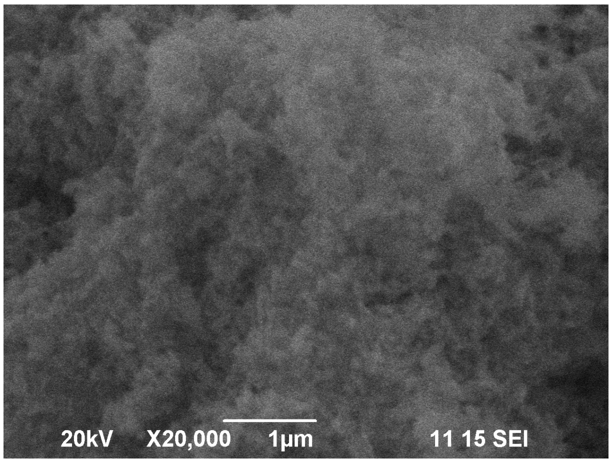

Fig. 3. SEM images of Cu nanosized particles at 20000x magnification.

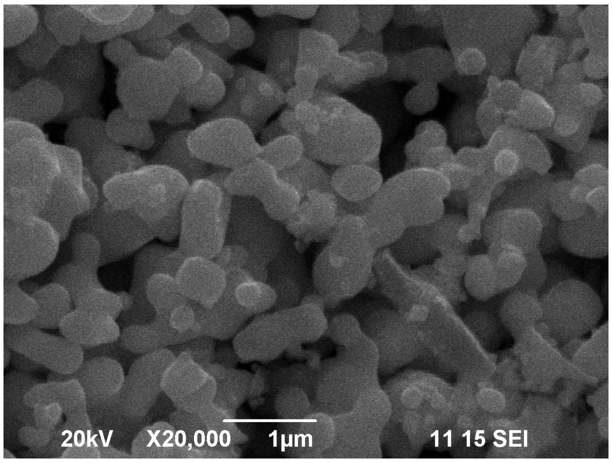

Fig. 4. SEM images of Sn nanosized particles at 20000x magnification.

Sn nanosized particles

Fig. 8 represents an EDS spectrum for the distribution of elements in an arbitrary area on the surface of Sn particles. From the results in Table 1, the element Sn (up to 92.5 mass %) and O (up to 21.67 mass %) were present. The oxygen is most likely due to oxidation during the drying, and the tests carried out.

XRD analysis

Figs. 9 - 12 present XRD spectra of Co, Ni, Cu, and Sn nanosized particles.

Co nanosized particles

In Fig. 9, representing the XRD diffractogram of Co particles, the typical peaks characterizing the crystalline state were not observed. An amorphous halo was observed, which proves that the Co nanosized particles were amorphous.

Ni nanosized particles

In Fig. 10, peaks characteristic of the mineral Jamborite $(Ni_{0.5}Ni_{0.4}Fe^{2+}_{0.1}(OH)_{2.8}S_{0.1}(H_2O)_{0.1})$ [6] and $NiSO_4$ [7] were observed. The presence of these phases suggests that the reaction did not proceed completely, and most of the particles were not metallic Ni, which was the target.

Cu nanosized particles

Fig. 11 shows peaks corresponding to Cu [8], Cu_2O [9], and CuO [10] phases. The presence of CuO and Cu_2O phases confirmed the EDS analysis data that Cu nanosized particles were easily oxidized during synthesis and drying.

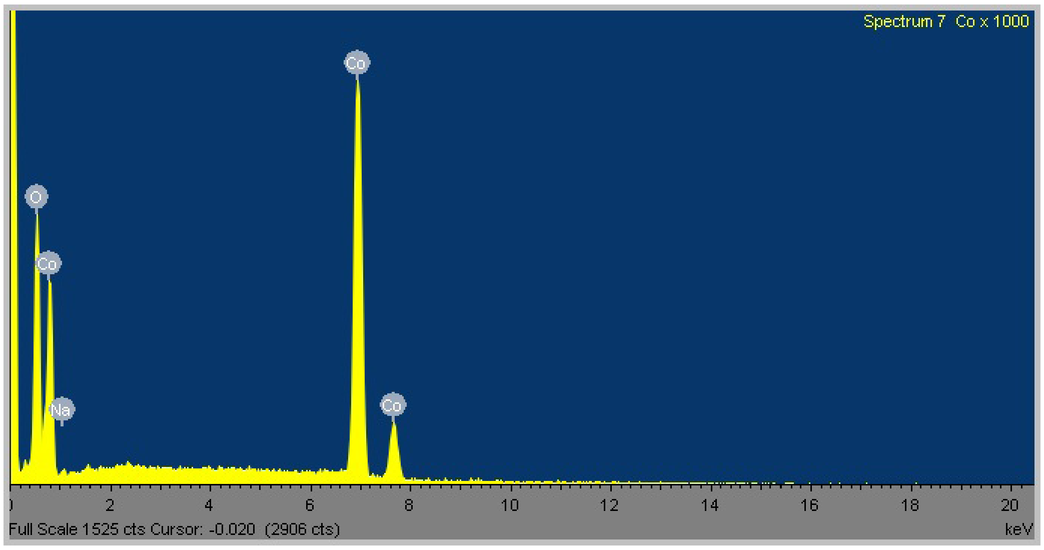

Fig. 5. EDS spectrum for elemental distribution of Co nanoparticles.

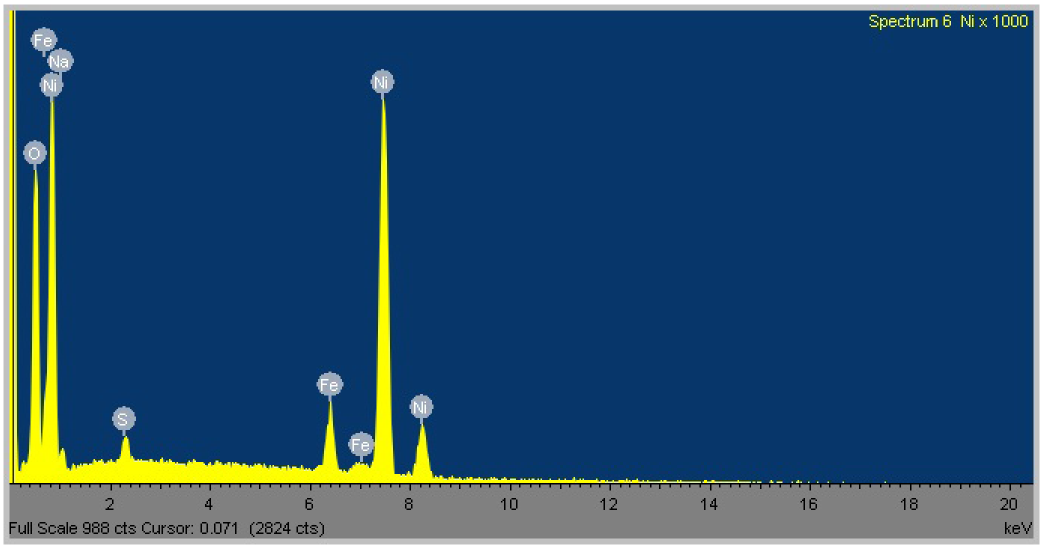

Fig. 6. EDS spectrum for elemental distribution of Ni nanoparticles.

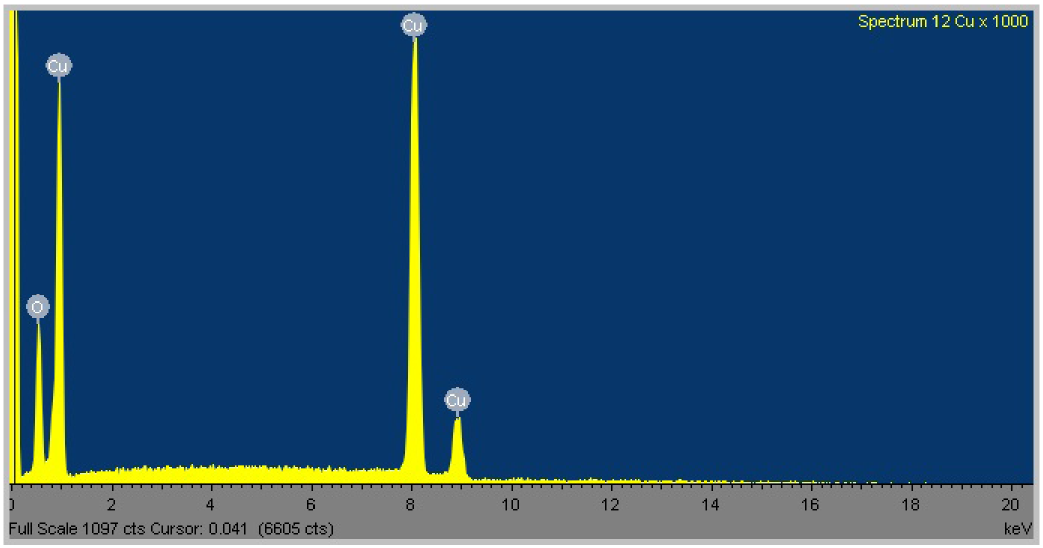

Fig. 7. EDS spectrum for elemental distribution of Cu nanoparticles.

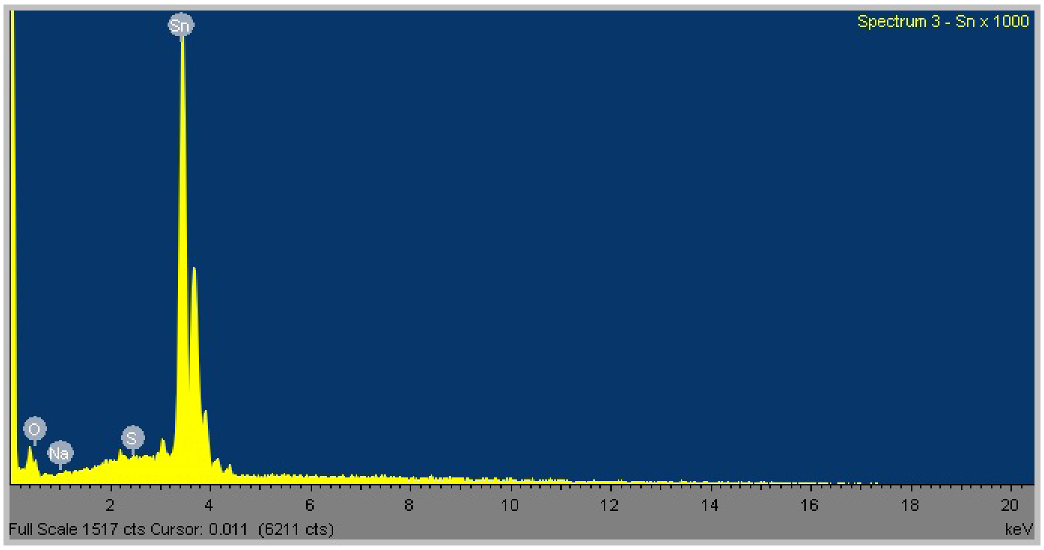

Fig. 8. EDS spectrum for elemental distribution of Sn nanoparticles.

Sn nanosized particles

In Fig. 12, it was observed that peaks correspond to the elemental tin [11]. The peaks were very pronounced, narrow, and high compared to the results for the other metal nanoparticles. This was an indication that the particle size was in the nanoscale range. No different impurity phases were detected, so it could be assumed that the chemical reduction was complete.

Table 1. The content of elements in three different regions of the surface of Co, Ni, Cu, and Sn nanosized particles in mass %, x1000.

	O	Na	Co	S	Fe	Ni	Cu	Sn	Total
Co	23.59	1.19	75.22						100
Co	27.38	1.60	71.02						100
Co	32.27	1.58	66.15						100
Ni	24.16	2.88		0.94	5.44	66.58			100
Ni	37.38	2.02		0.50	22.56	37.55			100
Ni	30.32	2.96		0.9	3.01	62.80			100
Cu	12.57						87.43		100
Cu	19.97						80.03		100
Cu	21.99						78.01		100
Sn	9.59							90.41	100
Sn	7.50							92.50	100
Sn	21.67	1.74	0.88					75.72	100

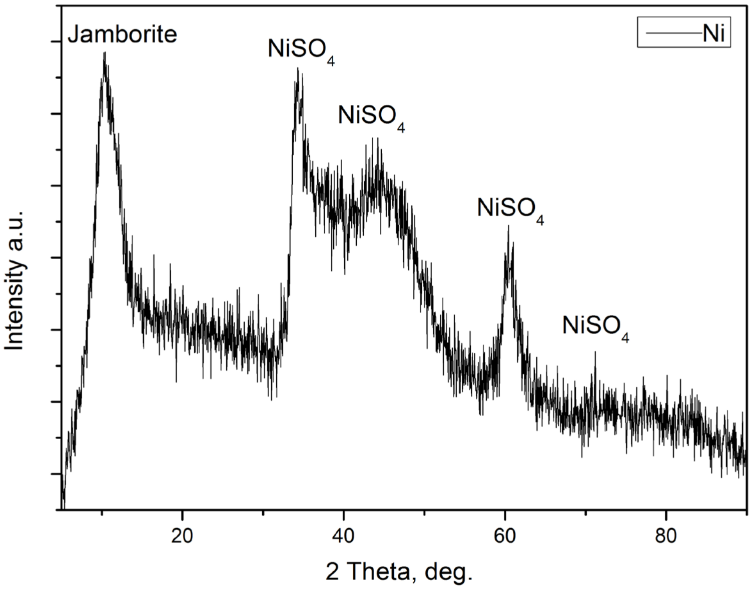

Fig. 9. Co particles’ XRD diffractogram.

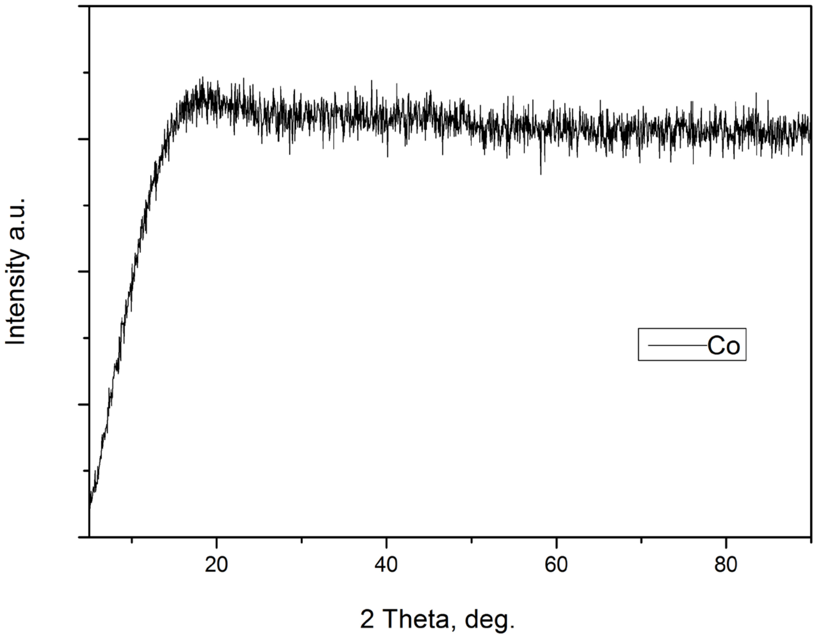

Fig. 10. Ni particles’ XRD diffractogram.

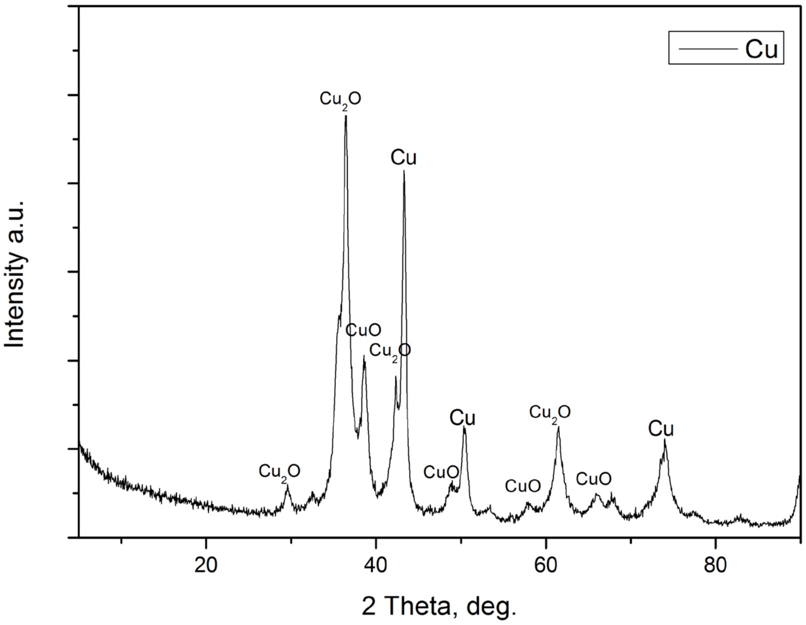

Fig.11. Cu particles' XRD diffractogram.

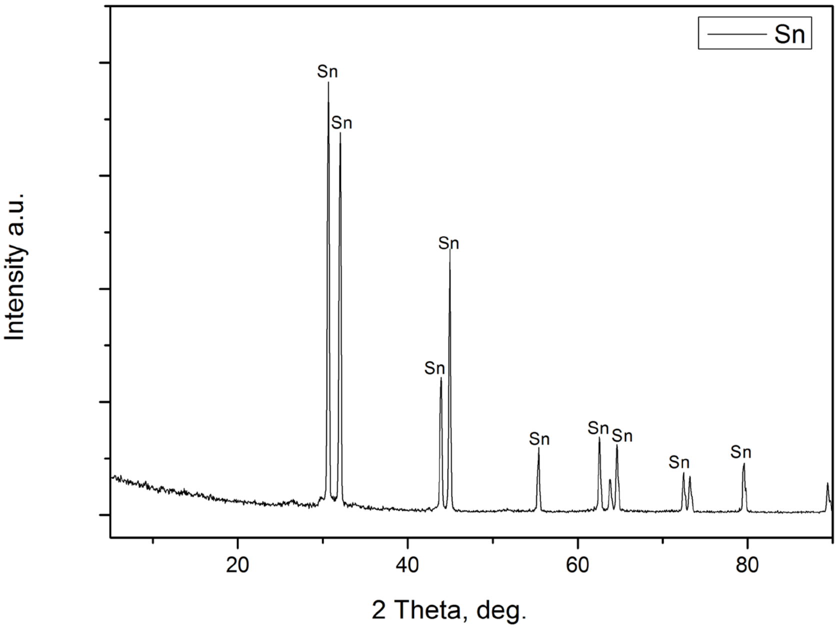

Fig. 12. Sn particles' XRD diffractogram.

CONCLUSIONS

Cobalt, nickel, copper, and tin nanoparticles were synthesized by chemical reduction in an aqueous solution of the corresponding sulfate salts with the reducing agent $NaBH_4$ at room temperature and atmospheric pressure. The morphology examination of the synthesized nano-sized powders found that the particles were of different sizes and shapes and tended to aggregate; the aggregation of Sn nanoparticles was less compared to that of Cu, Co, and Ni. The EDS analysis proved the presence of elements Cu, Co, Ni, and Sn and oxygen due to oxidation processes during the synthesis and drying of the obtained nanopowders. XRD analysis proved the presence of the amorphous Co crystallized phases: and crystals of Jamborite, $NiSO_4$, Cu, Cu_2O, CuO, and Sn. This work is an initial investigation of the resulting particles. Additionally, their electrochemical, electrical and optical properties will be investigated in order to explore their application possibilities.

Acknowledgements

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