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X-Ray Diffraction, Spectroscopic study and Thermogravimetric analysis of natural galena (PbS) from Agadez

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Abstract

The results of an experimental investigation on the study of natural galena from Agadez/Niger were discussed. The collected galena sample was analyzed by X-ray diffraction, Infrared, Raman and Thermogravimetric analysis. The XRD analysis indicated galena as the main mineral phase. The sample crystallizes in the cubic crystal with space group $Fm\bar{3}m$ with unit cell parameter $a = 5{,}931$ Å. The vibration of the S-S bond is observed at 618 cm^{-1} and the peaks at 1111 cm^{-1} and 1634 cm^{-1} indicate the Pb-S bond. The Raman spectrum exhibits absorption bands at 142 cm^{-1}, 195 cm^{-1}, 448 cm^{-1} and 973 cm^{-1}. The band centered at 142 cm^{-1} corresponds to the Pb-S bonds. The peak at 448 cm^{-1} can be attributed to the presence of elemental sulphur. It comes from the first and second harmonics of the fundamental longitudinal phonons 2LO and 3LO. The peak at 973 cm^{-1} is characteristic of the presence of sulfates. The TGA curve indicates an initial mass loss of about 5% and the second mass loss from 600 to 900°C attributed to evaporation of sulphur.

Keywords: Agadez, Galena, Infrared, Raman, X-rays and TGA.

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1. Introduction

Galena (PbS) is the natural mineral form of lead (II) sulphide and is the most important ore of lead. Galena exists in terrestrial deposits and seafloor massive sulfide (SMS) deposits. It is composed of lead as a dominant metal followed by sulphur. The composition varies from one location to another due to the variation in geochemical and environmental effects [1,2]. Galena exists in two crystallographic forms, octahedrons and cubes [3]. Galena is commonly associated with other sulphide minerals, such as sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS) [4]. Thus, the oxidation and dissolution of galena, under the influence of mining activities or specific geochemical processes, are accompanied by the release of lead and other toxic heavy metal ions (such as zinc, arsenic and cadmium), which threatens human health and affects the ecosystems [5,6]. Others minerals formed by the oxidation of galena are anglesite ($PbSO_4$) and cerussite ($PbCO_3$) [7].

Several studies on the characterization of galena ore from different localities around the world have been carried out. Some of the reported results show that the composition different from one locality to another. For example, the galena found in Japan, Nigeria and the USA is the richest as reported respectively by Awakura et al. [8], Olanipekun [9] and Feurstenau et al. [10]. While the poorest galena was found in Mexico and China as reported respectively by Makita [11] and Wang et al. [12]. The Republic of Niger is very rich in minerals and a large number of sulphide and other types of ore deposits are present particularly in the region of Agadez. Therefore, there are tittle literature data about minerals from Agadez. Our aim is to collect, identify as well as spectroscopic and structural characterization of minerals originating from this locality. In the present work, the results of the study of the collected galena (PbS), using FTIR and Raman spectroscopies as well as powder X-ray diffraction methods are presented. Identification was based on the comparison of the results of our study with the literature data for the corresponding mineral originating from other localities over the world.

2. Materials and methods

2.1. Study area

The galena ore used for this study was collected from the massif of Aïr in the northern of Niger. The galena ore was finely pulverized and sieved into two fractions 75 and 100 µm. All experiments were performed with 100 µm fraction **(Photo 1)**.

Photo 1: Galena Samples from Agadez.

2.2. Experimental methods

The XRD analysis was performed by a diffractometer model Siemens D5000 type, equipped with a copper anticathode (Cu Kα radiation, λ = 1.5406 Å), operating at 40 kV and 30 mA, on uncompressed powders in order to collect the maximum of the diffraction lines and better identification of the phases. The diffractogram was recorded at room temperature in 2θ mode by scanning from 5° to 120° in steps of 0.02°/s.

Thermogravimetric analysis (TGA) was carried out using an A 5c 1000c apparatus in an inert atmosphere.

Infrared analysis was performed in the range 400 to 4000 cm^{-1} on a Nicolet 20 SX Fourier transform spectrometer. Samples were prepared by the potassium bromide pressed-pellet technique at a concentration of 1%.

Raman spectroscopy was conducted employing a Renishaw inVia Raman microscope with a 633 nm laser. The spectrum was performed in the range 100 to 1400 cm^{-1}

3. Results and Discussion

3.1. Phase Studies by XRD

The analysis by X-ray diffraction gives better description of the mineral phases present in the ore. The XRD spectrum of galena ore is shown in **Figure 1** and their data presented in **Table 1** are consistent with those given in the American Mineralogist Crystal Structure Database (AMCSD). The X-ray spectrum of the sample shows the characteristic peaks of galena. The peaks are narrow and well-defined, suggesting good crystallinity of the sample.

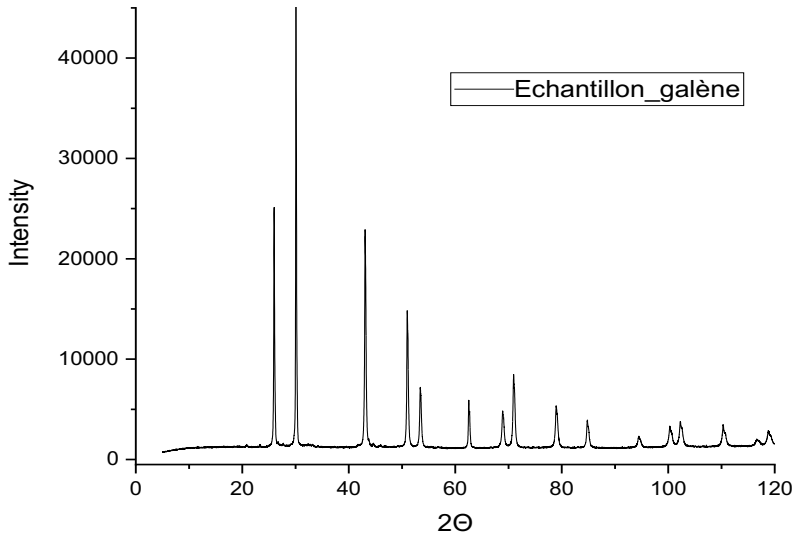

Figure 1: XRD spectrum of galena from Agadez.

The identity of the sample is proved by the comparison of the *d* values of the most intense maxima in the diagrams of the studied sample, with the corresponding maxima for the galena mineral sample taken from the AMCSD [13-14]. The great similarity between the peaks of the studied galena and those in the literature could be taken as evidence that the studied sample belongs to the same mineral. Sample crystallizes in the cubic crystal with space group $Fm\bar{3}m$. Unit cell parameter is: $a = 5{,}931\ Å$. These results indicate that the sample consists exclusively of galena because no trace of another phase was highlighted.

Table 1: Comparison of the inter-reticular distance *(d)* with the data of the literature.

This work			**AMCSD 0010042[13]**			**AMCSD 0011372[14]**		
2θ	d(Å)	Intensity (%)	2θ	d(Å)	Intensity (%)	2θ	d(Å)	Intensity (%)
25,99	3.42	54,31	26.10	3.4146	97.59	26	3.4273	97.93
30,09	2.96	100	30.2	2.9571	100	30.11	2.9681	100
43,07	2.09	49,50	43.27	2.0910	73.12	43.10	2.0988	69.61
50,97	1.79	32,05	51.23	1.7832	48.35	51.03	1.7898	43.19
53,4	1.71	14,74	53.69	1.7072	25.24	53.47	1.7136	22.86
62,52	1.48	12,78	62.85	1.4786	11.50	62.59	1.4841	9.91
68,86	1.36	9,93	69.25	1.3568	19.12	68.95	1.3619	15.17
70,93	1.32	17,52	71.31	1.3225	31.06	71.01	1.3274	25.43
78,93	1.21	11	79.37	1.2073	22.81	79.02	1.2117	17.75
84,76	1.14	8,11	85.27	1.1382	10.74	84.88	1.1424	7.54
94,32	1.05	4,21	85.27	1.1382	3.58	84.88	1.1424	2.51

3.2. FTIR Analysis

The FTIR spectrum of galena ore is shown in Figure 2. The spectrum exhibits absorption bands at 3444 cm^{-1}, 1634 cm^{-1}, 1111 cm^{-1} and 618 cm^{-1}. According to the literature, the peaks at 3444 cm^{-1}correspond to the free O-H group [15]. The peak at 618 cm^{-1} is due to the S-S bond and the peaks at 1111 cm^{-1} and 1634 cm^{-1} indicate the Pb-S bond [16-17].

3.3. Raman spectroscopy

Raman spectroscopy is a high-resolution technique that quickly provides information on the chemical and structure of organic and inorganic materials, allowing their identification. In this technique, only a small amount of sample is needed and the sample does not require special preparation. The

characterization of galena (PbS) by Raman spectroscopy is difficult due to its NaCl structure. Indeed, like all crystalline minerals of the space group Fm3m, galena is a weak Raman scatterer, as predicted theoretically [18] and experimentally [19-21] showing the inactivity of the galena in Raman or its single band at 454 cm^{-1}. However, under certain energies of excitation, the galena can exhibit two other Raman bands located at 154 and 204 cm^{-1} [22]. The Raman spectrum of the sample is showed in **Figure 3**.

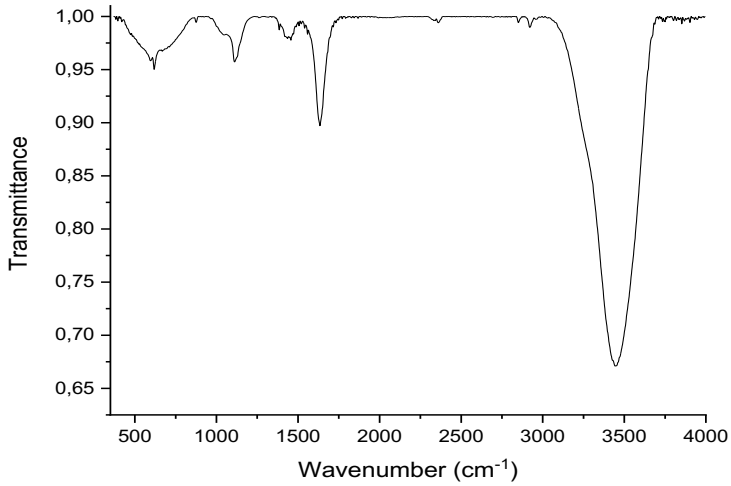

Figure 2: IR spectrum of galena from Agadez.

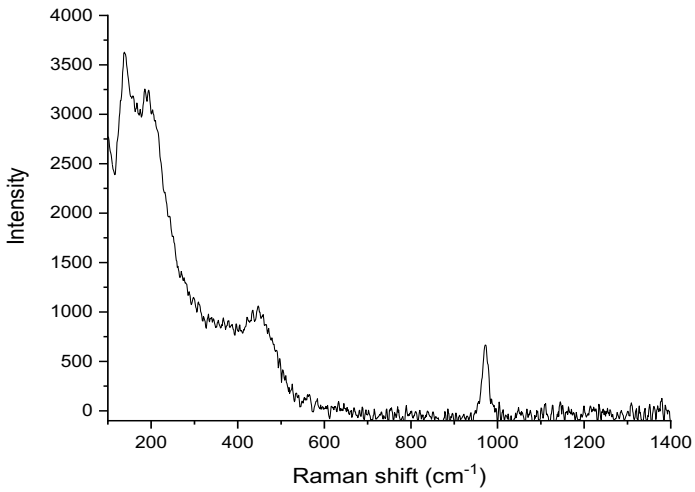

Figure 3: Raman spectrum of galena from Agadez.

The Raman spectrum of the sample is typical of galena as reported [23]. The spectrum exhibit absorption bands at 142 cm^{-1}, 195 cm^{-1}, 448 cm^{-1} and 973 cm^{-1}. The strong band centered at 142 cm^{-1} corresponds to the Pb-S bonds in the mineral crystal structure. It comes from the combination of acoustic phonon modes longitudinal and transverse in PbS crystals according to Tohidi T. et al. [24]. Some researchers associate this band with the oxysulphates formed during oxidation due to laser-induced degradation [25].

The band that appeared around 195 cm^{-1} might be the addition of TO + LA along Σ. The band at 448 cm^{-1} can be attributed to the presence of elemental sulfur [26-27]. It has also been reported that the bands around 430-600 cm^{-1} come from the first and second harmonics of the fundamental longitudinal phonons 2LO and 3LO [28-29]. The band at 973 cm^{-1} is characteristic of the presence of sulfates. According to the bibliography, it results from the rapid oxidation of PbS due to the high temperature induced by laser heating.

3.4. Thermal analysis

In the thermal analysis, three kinds of data were obtained: TG gives quantitative information on the change in sample mass as a function of the temperature; the derivative of the TG (DTG) curve allows us to detect changes in the slope of the TG curve, occurring, for example when thermal events overlap, which might otherwise not be detected and DTA gives qualitative information on the endo or exothermicity of transformations occurring during the thermal treatment.

DTA has found valuable application in the study of clay minerals, carbonates, sulfates and zeolites. Sulfides, arsenides and related minerals have until recently received little attention in DTA studies. The investigation of sulfides minerals is much more difficult than that of other minerals, because they are very strongly oxidative and their oxidation behaviour is complicated (complete oxidation of the original compound, incomplete oxidation with the formation of intermediate sulphates and oxysulphates…) [30]. The thermogravimetric analysis (TGA) was performed in controlled environment (inert atmosphere) to observe the mass loss and thermal phase decomposition in the galena ore. The TGA and DTG curves of the sample are showed in the Figure 4.

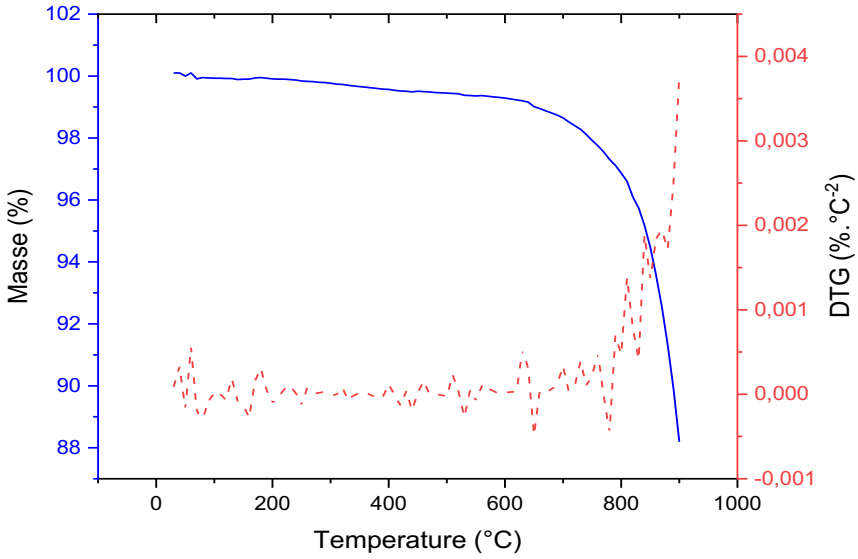

Figure 4: ATG and DTG curves of galena from Agadez.

TGA curve indicates an initial mass loss of about 5% from 50 to 200°C. This is confirmed by DTG curve which reveals peaks corresponding to removal of water of crystallization and liberation of sulfur. The second mass loss from 600 to 900°C is attributed to evaporation of sulfur and production of metallic lead Pb with associated DTG peaks appearing at 815 and 870°C.

The data in Figure 4 show that the sample is stable and it consists exclusively of galena. The result is in agreement with those of the XRD.

4. Conclusion

The objective of this work is a contribution to improving knowledge on the galena from the massif of Aïr in the northern of Niger. This objective is justified by the fact that these accumulations are little known because very little work has been done. On the basis of the results of the characterization, the following conclusions can be drawn:

(i) The XRD analysis confirmed the originality of the galena ore and no trace of another phase was highlighted;

(ii) The FTIR spectrum exhibits bands at 3444 cm^{-1}, 1634 cm^{-1}, 1111 cm^{-1} and 618 cm^{-1}. The peaks at 1111 cm^{-1} and 1634 cm^{-1} indicate the Pb-S bond;

(iii) Resonance Raman spectra of natural galena have been measured in the range 100 to 1400 cm^{-1}. Four bands at 142 cm^{-1}, 195 cm^{-1}, 448 cm^{-1} and 973 cm^{-1}have been identified as belonging to PbS. The band at 195 cm^{-1} might be the addition of TO + LA along Σ and the band at 448 cm^{-1} comes from the first and second harmonics of the fundamental longitudinal phonons 2LO and 3LO;

(iv) The themogravemetric analysis indicates that the sample is stable and it consists exclusively of galena. The result is in agreement with those of the XRD.

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Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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