Materials Letters 234 (2019) 233–236

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Preparation of high purity compact galena bulk by hot pressed sintering

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ARTICLE INFO

Article history:
Received 6 July 2018
Received in revised form 18 September 2018
Accepted 20 September 2018
Available online 21 September 2018

Keywords:
Semiconductors
Sintering
High purity
Compact
Galena bulk
XRD

ABSTRACT

By using PbS powder as raw materials, high-purity compact and machinable galena bulk was successfully prepared by sintering method under high pressure and temperature for the first time. The hot pressed sintering was performed at 0.9 GPa and 550 °C for 1 h. The as-prepared products were characterized by powder X-ray diffraction (XRD), Electron Probe Microanalysis (EPMA), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Carbon and Sulfur Analyzer, and optical microscopy, respectively. XRD results show that the as-prepared samples have a cubic structure and were identified as galena without any impurity. Based on microscopic observations and element analyses, only galena was identified, and it is consistent with the results of XRD analysis. The density of galena bulk was measured and it is equal to the theoretical value. It is machinable and can be processed into fixed shape.

1. Introduction

Galena (PbS) is an important semiconductor mineral with special electrochemical, electrical, optical, thermoelectric properties [1–3]. Galena is of great value to application and scientific research. It can be used as Pb^{2+} ion-selective sensors [4], infrared detectors [5], and photoelectric conversion materials [6]. The study of the electrochemical corrosion behavior of galena in the high pressure hydrothermal system is helpful to understand the genesis, composition and change process of hydrothermal deposits, and to provide a theoretical basis for high temperature wet metallurgy and mineral processing, also closely related to understanding of the earth about lead and sulfur element cycling.

However, it is very difficult to find high purity natural block galena as the research object that can up to the research standard. Natural galena is often associated with sulfide minerals such as sphalerite, pyrite, and chalcopyrite. The galvanic interaction between symbiosis minerals will cause interference to the electrochemical corrosion process of galena. Besides, the presence of impurity in the galena crystal would change the structure energy band and semiconductor type of galena [7,8]. On the other hand, galena is a brittle mineral; it is difficult to be processed into regular geometry and therefore cannot meet the requirements of many scientific researches about its properties, for instance, the electrode needed for high temperature and pressure electrochemical research.

Though various methods have been employed to produce galena pellets, films, or nanoparticles [3,9,10], there has been almost no ready-made galena bulk for geoscience experimental research to ensure high quality and high purity. In this paper, a novel and simple route for the preparation of high purity, compact, and machinable galena bulk based on high pressure and temperature sintering method have been studied for the first time. Mineralogy, phase structure, element content, element distribution, density, compactness, and wear resistibility about as-prepared samples are analyzed and measured.

2. Materials and methods

The sample assembly is shown in Fig. 1. The raw material was high-purity (99.99%) PbS powder. The PbS powder after grinding was pressed into a cylinder by a powder tablet followed by sealing into a sample capsule made from high-purity silver foil. Sodium chloride and cube massive pyrophyllite are the pressure transmitting medium. Besides, the dehydrated pyrophyllite also plays the role of seal, heat preservation and thermal insulation. A k-type thermocouple used to measure and monitor temperature was placed just close to the sample, and stainless steel sheet as the heater. The hot pressure sintering experimental was performed at 0.9 GPa and 550 °C in a large volume press apparatus (LVP (DS6×1400 t, ZZSM and GYIG, China)).

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https://doi.org/10.1016/j.matlet.2018.09.113
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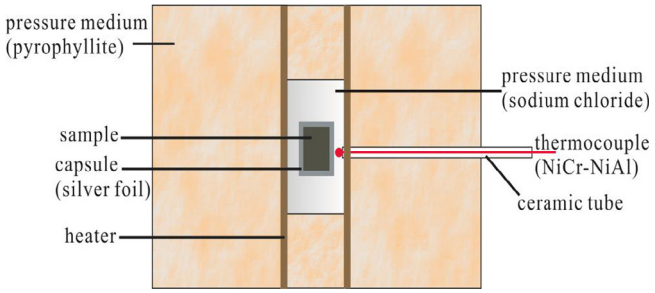

Fig. 1. Typical sample assembly.

XRD (Empyrean, PANalytical, Holland) was used to measure the crystal structure and identify phase of as-sintering galena precisely. The mineralogy of the post-sinter sample was observed by reflected-light optical microscopy. Chemical composition, element content and distribution of the sintered galena were studied by EPMA (JXA8230, JEOL, Japan), ICP-AES (ARCOS II, SPECTRO, Germany), and Carbon and Sulfur Analyzer (CS-206, BAOYING TECHNOLOGY, China). The density of the prepared galena bulk was measured by an Electronic Densimeter (DH-1200, DAHON, Japan). The wear resistibility of as-sintered sample was tested by a grinding machine. A multifunctional autoclave was used to test the compactness of the samples after grinding and polishing.

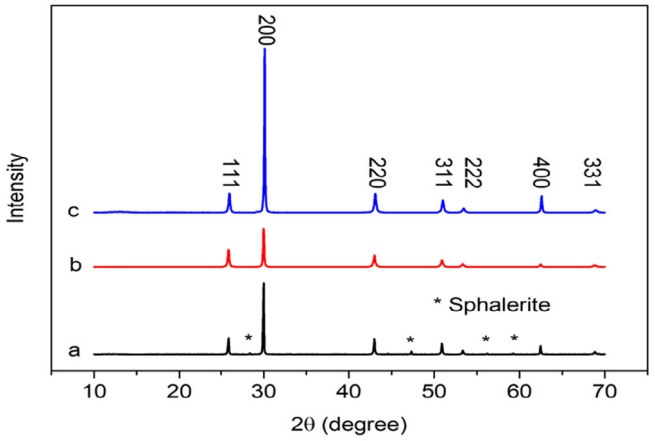

Fig. 2. XRD patterns of (a) natural galena, (b) raw PbS powder, (c) as-prepared galena bulk.

3. Results and discussion

The XRD patterns are shown in Fig. 2. All diffraction peaks are well accord with the pure cubic phase of PbS (PDF card NO. 05-0592). The peak intensity of the sintered samples becomes stronger, especially the peak of (2 0 0) crystal plane, and the full width at half maximum (FWHM) becomes smaller, which is attributed to the better crystallinity and the larger grain size. It also indicates the grains have priority to oriented along (2 0 0) direction. The estimated cell constant a is 5.925 (±0.001) Å, which match perfectly with the standard value, 5.940 Å. No impurity peaks are detected, indicating that no independent impurity phase formed during the sintering process. As shown in Fig. 2 the natural galena is mainly composed of galena and the impurity identified as sphalerite (ZnS). The characteristic peaks of sintered galena are well accord with that of the natural galena, which indicates the same crystal structure between the sintered galena and the natural galena.

Fig. 3a exhibits the reflected light photograph of the as-sintered galena bulk. It is obvious that the sintered sample is compact, uniform, and homogeneous with a single galena phase. The same phenomenon was found in the EMPA element distributed maps of S and Pb element for the sample obtained by plane scanning, as shown in Fig. 3(b, d). Elemental maps revealed that the S and Pb elements are distributed uniformly, indicating that the as-sintered galena bulk is homogeneous. Fig. 3c presents the BSE image of the sintered sample. The brightness of the whole image is homogeneous and consistent, suggesting that is pure phase of galena. Based on EMPA data (Table 1), the chemical composition of the PbS bulk has averages of: Pb (86.494%), S (13.331%). The bulk

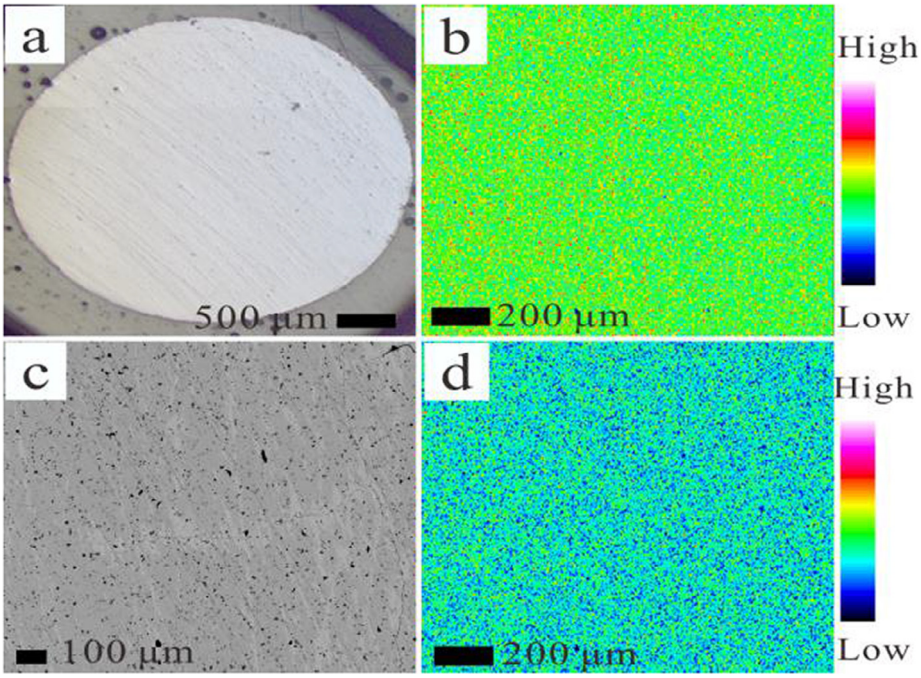

Fig. 3. (a) Reflected light photomicrograph, (b, d) element maps, and (c) back scattered electron (BSE) image of the as-prepared galena bulk.

Table 1
Chemical composition (wt%) of galena bulk determined by EPMA point scanning.

Element	As	Fe	Ni	Cu	Zn	S	Ag	Pb	Cd	Al	Sn	Total
Point-1	0.004	0.022	0	0.028	0.109	13.440	0	86.458	0.084	0	0.025	100.170
Point-2	0	0.015	0	0.016	0.088	13.374	0	86.516	0.195	0	0	100.204
Point-3	0	0.001	0.023	0.018	0.042	13.405	0	86.497	0.209	0.011	0.010	100.216
...	...	...	...	...	...	...	...	...	...	...	...	...
Average	0.001	0.012	0.005	0.029	0.054	13.331	0	86.494	0.151	0.005	0.009	100.091

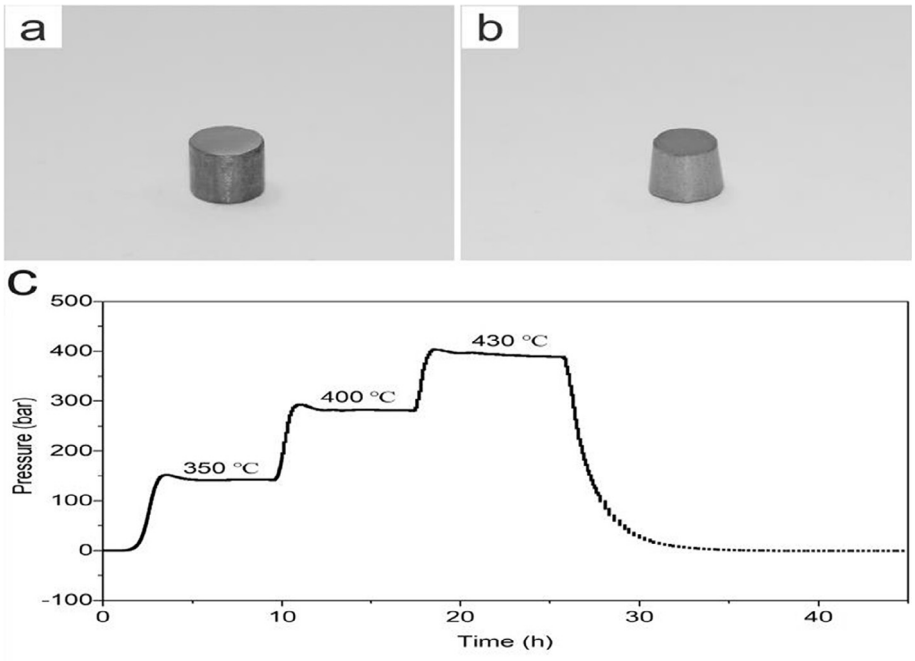

Fig. 4. The pictures of the as-sintered galena bulk (a) before and (b) after grinding, (c) the pressure-time curve when galena bulk acts as seal and electrode.

elemental analyses from ICP-AES for Pb and from Carbon and Sulfur Analyzer for S are 86.3317%, 13.6133%. Thus, the Pb/S ratio is nearly close to the theoretical value, that is, sulfur fugacity has not changed before and after sintering. Based on microscopic observations and element analyses, only galena was identified, and it is consistent with the results of XRD analysis.

According to the calculation of the lattice parameters, the theoretical cell density of galena is 7.580 g/cm^3. The density of the as-sintered pure galena bulk measured by the electronic density analyzer is 7.508 (±0.001) g/cm^3. It is very close to the theoretical density of galena, that is to say, the galena obtained by hot pressed sintering is compact.

Fig. 4(a, b) shows the pictures of the as-sintered galena bulk before and after grinding by a machine. Though the hot pressed sintered sample is columnar, it could be made into circular truncated cone by a grinding machine, which means our sample is capable of being shaped and could be made into fixed shape. When act as seal and electrode, the pressure of the autoclave can keep stable for a long time without decreasing as shown in Fig. 4c, which indicates the sample is compact. In this case, the galena bulk can be the object of electrochemical experiments under high temperature and pressure solutions.

4. Conclusions

In this study, we have described a novel and simple method to obtain high pure compact massive galena bulk. Using the powder PbS as raw material, the galena bulk obtained by high temperature and pressure sintering under 0.9 GPa and 550 °C in a LVP. The products are high purity, and the density is almost equal to the theoretical value. It is machinable and can be processed into fixed shape. Remarkably, the successful preparation of these samples makes it possible to realize the feasibility of studying the corrosion electrochemical corrosion properties of galena in high pressure hydrothermal system.

Acknowledgements

This research was financially supported by the National Key Research and Development Plan (2016YFC0600104) and the "135" Program of the Institute of Geochemistry, Chinese Academy of Sciences (CAS).

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