Increasing microwave absorption efficiency in ferrite based materials by doping with lead and forming composites

Ying Liu [a], Xiaojie Li [a,1], Michael G.B. Drew [b], Yue Liu [a,*]

[a] College of Chemistry and Life Science, Shenyang Normal University, Shenyang, 110034, PR China
[b] School of Chemistry, The University of Reading, Whiteknights, Reading RG6 6AD, UK

HIGHLIGHTS

- $Ba_{1-x}Pb_xFe_{12}O_{19}$/polyaniline composites were prepared and characterized.
- Doped lead in ferrite based materials plays a role in microwave absorbance.
- Interface in the composites plays a role in microwave absorbance.
- Retaining waves longer in absorption media can enhance reflection loss.

GRAPHICAL ABSTRACT
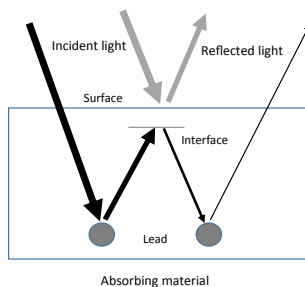
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ABSTRACT

Microwave absorption studies on ferrite based materials have been carried out. Efforts have been made to reduce the reflection and increase the absorption of microwaves by materials thus increasing reflection loss. However, it has been shown previously by this group that reflection from the interface in composites can be used to increase reflection loss if the microwaves penetrate into the absorbing media. This study has been extended to investigate the effect of Pb^{2+} doping and it is found that the dispersion properties of the doped Pb^{2+} can be used to raise microwave absorption efficiency by keeping the waves in the absorbing media for a longer time, thus having a similar effect to the interface in composites. This result will have a considerable effect on the future design and investigation of microwave absorbing materials.

1. Introduction

There is a long history of research on magnetoplumbite barium ferrite materials in a variety of fields. Research is very active [1] and new applications are constantly being discovered. Recent reviews [2,3] show the importance of ferrite materials in modern industry [4,5] and detail aspects of research that can enhance material design. In particular, the microwave adsorption properties of barium hexaferrite and its derivatives have attracted much attention. In order to optimize the properties of barium hexaferrite for its use in various applications, the effect of doping with different cations has been extensively investigated [6]. Pb-doped barium hexaferrites have attracted much attention recently [7—9] and the possibilities of replacing Ba^{2+} and Fe^{3+} by Pb^{2+}/Pb^{3+} have been investigated. In this work, we investigate, for the first time, the effect of lead doping on microwave adsorption. Lead is commonly used as a shielding material to X-ray and gamma radiation. Lead-

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* Corresponding author.
E-mail addresses: yingliusd@163.com (Y. Liu), xiaojie1322@126.com (X. Li), m.g.b.drew@reading.ac.uk (M.G.B. Drew), yueliusd@163.com (Y. Liu).
[1] Present address: Henan Xiangtai Safety Evaluation Co. LTD.

containing compounds can be doped with a variety of materials such as zinc oxide and Ga−Se chalcogenide glass. Lead glasses and lead oxide-epoxy composites are used in the shielding of X-rays and gamma radiation. The shielding property of Pb is attributed to the dispersion properties of Pb. The inner electrons of Pb are primarily responsible for its interaction with X-rays. Shielding from radiation and effects on microwave absorption are likely to be related properties of Pb, thus the latter deserves investigation.

Conductive polymers such as polyaniline are low density adsorption materials [10]. Composites of ferrites with polyaniline have been previously reported [11–13] and enhanced reflection loss has been achieved [14,15]. Imaginary permittivity and permeability of a material are responsible for microwave absorption. Investigations have usually been carried out to enhance the imaginary permittivity and permeability of a material and reduce light reflection. However, in previous work we have shown that microwave reflection from the interface of a ferrite/PANI composite can be used to enhance microwave absorption [16]. The dispersion properties of Pb have a similar effect to that of a composite interface. Thus, our previous work on composites was extended here to study the effect of Pb on microwave absorbance. The implication of this work is that increasing the retention times of microwaves in absorption media by both the dispersion properties of lead and the interface of a composite are important factors to consider in designing microwave absorbing materials.

2. Experimental

Analytical grade chemicals barium nitrate, ferric nitrate, lead nitrate and citric acid were used as raw materials. Molar ratios for $(Ba^{2+} + Pb^{2+})$:Fe^{3+} of 1:11 or 1:11.5 were used. The molar ratio of citric acid to all metal nitrates was 1.2. Deionized water was used as solvent and magnetic stirring was continued until the mixture was completely dissolved. Ammonium hydroxide was then added to adjust the pH to 6.0. The solution was heated to 80 °C. As water evaporated, the solution became viscous and finally formed a brown sol which was dried at 120 °C until it became a dried gel, subsequently calcined at 200 °C in the muffle furnace for 1 h. The residue ash was then milled, and sintered at 1100 °C for 6 h to obtain the black powder of $Ba_{1−x}Pb_xFe_{12}O_{19}$ (x = 0, 0.1, 0.3, 0.5,0.7, 0.9, 1.0).

The hexaferrite/PANI(polyaniline) composites were synthesized by the solvothermal method with in situ polymerization. 4, 8, and 10 g respectively of hexaferrite were placed in a flask with 100 ml of 1 mol/L hydrochloric acid, and then 6 ml aniline was added. The resulting solutions were labeled Cw-x where w is the amount of hexaferrite added in grams and x is the amount of substitution in $Ba_{1−x}Pb_xFe_{12}O_{19}$. The solutions were then dispersed ultrasonically for 30 min. Ammonium peroxydisulfate with a 1:1 mol ratio to aniline was dissolved into 30 ml, 1 mol/L hydrochloric acid and the resulting solution was then added into the flask at a suitable speed. It was stirred at room temperature for 12 h, and then filtered under reduced pressure, washed with distilled water and anhydrous ethanol. The composites so obtained were then dried at 60 °C for 12 h.

Property characterizations were carried out with an X-ray powder diffractometer (XRD) using the D/MAX 2400 (Rigaku) with Cu Kα radiation, a Field Emission Scanning Electron Microscope (FEI): (FEI Sirion, Holland, Philips), a vibrating sample magnetometer (JZ-8MM3, Physcience Opto-electrionic Co. Ltd, Beijing), and an Agilent E5071C ENA Series Network Analyzer with the frequency range: 15−20 GHz, using the 85070E Dielectric Probe Kit with a high-temperature probe (8710−2036). The reflection loss was measured by contacting the powdered product with the plate of the high-temperature probe. Air, a standard short, and water were used

in the calibration. A plastic bag of 4.5 cm wide and 7 cm height was used to hold the powdered sample (ca 20 g). The high-temperature probe was then inserted to contact the powdered sample firmly.

3. Results and discussion

3.1. Characterization of $BaFe_{12}O_{19}$

3.1.1. Results from XRD

When a mole ratio of 1:11.5 was used for Ba^{2+}:Fe^{3+}, a characteristic peak of α-Fe_2O_3 was observed at $2\theta = 33.410°$ in the XRD pattern. This peak disappeared when a mole ratio of 1:11.0 was used (Fig. 1) and thus all samples in the subsequent study were synthesized using this latter ratio.

In barium hexaferrite synthesis, Ba^{2+} is usually used in excess with respect to the ideal mole ratio. While this excess is generally found to be necessary, the reason for it is unclear and several explanations have been put forward including firstly the relatively low solubility of barium hydroxide [17,18], secondly that the excess of Ba^{2+} favors the formation of hexaferrite over that of α-Fe_2O_3 [19], and thirdly that as citric acid combines with Fe^{3+} preferentially compared to Ba^{2+}, a larger amount of Ba^{2+} is required for it to participate effectively in the reaction. Clearly when the reaction mixture contains excess Fe^{3+} with insufficient Ba^{2+}, α-Fe_2O_3 will be precipitated.

3.1.2. Results from SEM

The SEM results (Fig 2) for the ferrite obtained with a mole ratio of 1:11.0 were compared with those obtained from ferrites synthesized with a mole ratio 1:11.5 and it was found that using the former ratio, the results were better as the degree of agglomeration is less, the grain is thinner, and the grain size is dispersed more uniformly. The grains in Fig. 2a are somewhat glued together while in Fig. 2b the grains are piled up and the agglomeration is less severe. The thinner grain is better for preparing nanocrystals. The results from XRD patterns (Fig. 1) and SEM images (Fig. 2) show similar amounts of crystallization. Although the difference in Fig. 2a and b is not large, the characteristics for both samples can be noted especially when they are coupled with the XRD pattern where the α-Fe_2O_3 peak appears in the sample with mole ratio 1:11.5.

3.2. Characterization of $Ba_{1−x}Pb_xFe_{12}O_{19}$

As the doping amount of Pb^{2+} is increased, no trace of $BaFe_2O_4$ or α-Fe_2O_3 phases appeared in the XRD patterns (Fig. 3) which
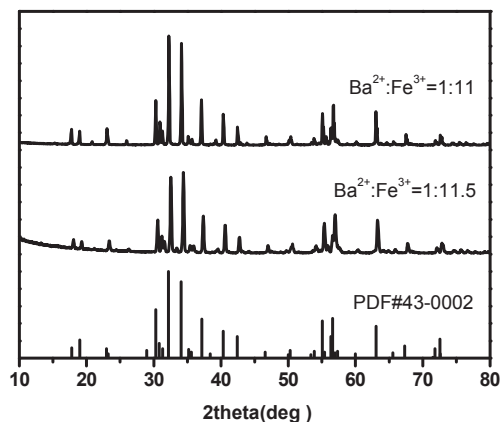

Fig. 1. The XRD patterns of $BaFe_{12}O_{19}$. The mole ratios of Ba^{2+}:Fe^{3+} in the synthesis are 1:11.5 and 1:11.0. The standard pattern of PDF#43-0002 is also included.