Structural and magnetic properties of chemically deposited hexaferrites

B.E. Watts[a], D. Regonini[a], F. Leccabue[a], F. Casoli[a], F. Albertini[a] G. Bocelli[a] and D. Schmool[b]

[a]*Istituto IMEM/CNR, Area delle Scienze 37/A, I-43010 Fontanini (Parma), Italy*

[b] *Departamento de Física Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal.*

Abstract

We have prepared M-type lead hexaferrites ($PbFe_{12}O_{19}$) using alternative and inexpensive sol-gel methods. Lead and iron precursors were dissolved in butoxyethanol and stabilised with acetylacetone to produce a sol with good wetting and surface coating characteristics. Powder samples were investigated in order to optimise conditions for the growth of thin films. The «spin on» technique was used to provide nominally homogeneous films. X-ray diffraction and AGFM have been performed to assess sample structure and surface morphology as a function of heat treatment.

Introduction

Magnetic hexaferrites have been applied for many years, however, they are receiving growing interest as candidates in magneto-electronic devices. In thin film form these materials can be integrated with semiconductor substrates or other functional materials such as ferroelectrics[(1,2)]. Lead hexaferrite ($PbFe_{12}O_{19}$) has not been greatly studied but it may be useful for the low temperature synthesis of hard magnetic oxides[(3)].

This paper describes a sol-gel route suitable for the preparation of $PbFe_{12}O_{19}$ at low temperatures in powder or thin film form. The crystallisation has been studied using X ray diffraction (XRD) and thermomagnetic analysis (TMA). In addition the hysteretic properties measured by using an alternating gradient field magnetometer (AGFM).

Experimental

Powders and films were prepared from the same solutions using 2-butoxyethanol as a solvent. 4,04 g of $Fe(NO_3)_3$ $9H_2O$ were dissolved in 10 ml of 2-butoxyethanol. Two lead iron molar ratios were used (Fe:Pb = 12:1 and 12:1,5) 1,67 ml and 2,5 ml of Pb^{2+} 0,5M solution in methoxyethanol, prepared according to reference(4). A white precipitate (determined to be lead nitrate by XRD) appears and was redissolved by adding 2 ml of acetylacetone.

To study the crystallisation process powders were produced by heating 15 ml of solution on a hot plate at 350 °C. The dry powders were heat treated in a muffle furnace at temperatures between 500-1000 °C.

The solution showed good wetting and surface coating characteristics. Films were prepared by spin coating at 3000 rpm for a period of 60s. The substrate used was $MgAl_2O_4$ (111). Each layer was pyrolised on a hot plate at 350°C to removed the solvent and organic ligands. A total of ten layers were deposited. Powder samples were characterised by XRD and Thermomagnetic Analysis (TMA). Magnetic property of film sample was detected using an alternating gradient field magnetometer (MicroMag 2900 AGFM).

Results and discussion

XRD spectra of powders samples are shown in Fig 1: a), b) and c) spectra referred to Fe:Pb ratio of 12:1,5 and all these showed typical peaks of polycristalline $PbFe_{12}O_{19}$ while d) referred to 12:1 ratio treated at 700°C and hematite (α-Fe_2O_3) is the dominant phase. Magnetuplumbite was obtained at low temperature using lead eccess (Fig.1b vs 1d). Probably eccess is needed to compensate lead evaporation during heating treatments.

The Pb-M phase is predominant above 650°C, however some weak peaks of hematite remains even at 800°C.

Thermomagnetic analysis (TMA), Fig.2, revealed the presence of two different magnetic phase: the first one was due to M-type ferrite (Tc= 450-460°C). The second was probably due to magnetite ($FeFe_2O_4$, Tc= 580°C) or maghemite (γ-Fe_2O_3 , Tc= 590-675°C) and appears only in return path. TMA was carried out with the sample under argon. Further analysis (XRD) of the material after TMA heating cycle showed no evidence of structural change.

The film sample grown at 700°C on monocrystalline $MgAl_2O_4$ (111) was characterized using AGFM. Properties were determined by applying the magnetic field parallel to the plane of the film. The hysteresis loop registrered, reported in Fig.3, suggests the existence of two magnetic phases. The thickness of film is unkown; sample showed magnetic moment ~15 μemu and H_c~2500 Oe.

Conclusions

Lead hexaferrite (magnetoplumbite) powder and thin films have been prepared at low temperatures using an inexpensive sol-gel method.

Xray diffraction and TMA studies show that a predominantly magnetoplumbite powder can be crystallised at 650 °C.

Further investigations are in progress to better understand the crystallisation, particularly, regarding the unusual behaviour during thermomagnetic analysis. Very thin films can be deposited and these are being researched to avoid the presence of other magnetic phases and to optimise condition film growth in order to obtain oriented growth or solid phase epitaxy.

Acknowledgements

The Authors would like to thank the European COST Action 528 and the Consiglio Nazionale delle Ricerche and GRICES Bilateral Agreement for their financial support.

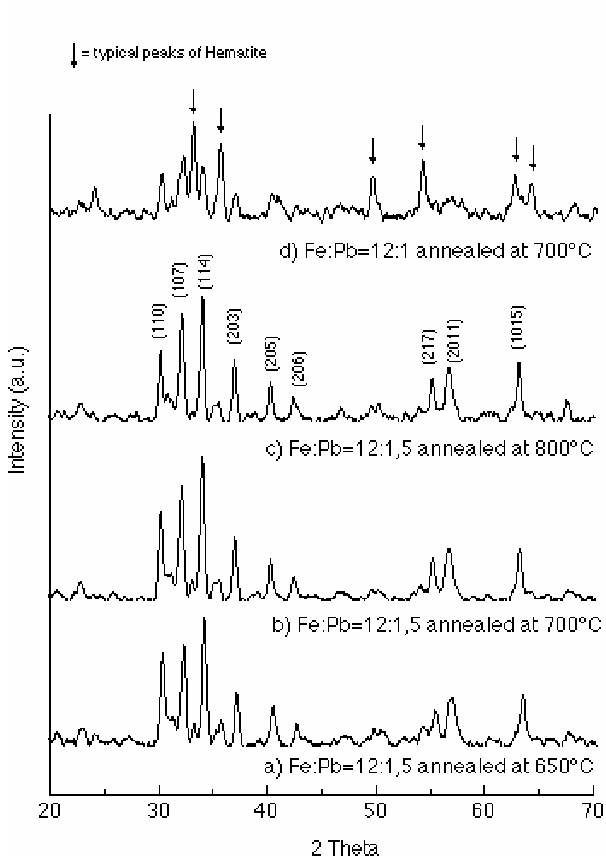

Fig.1

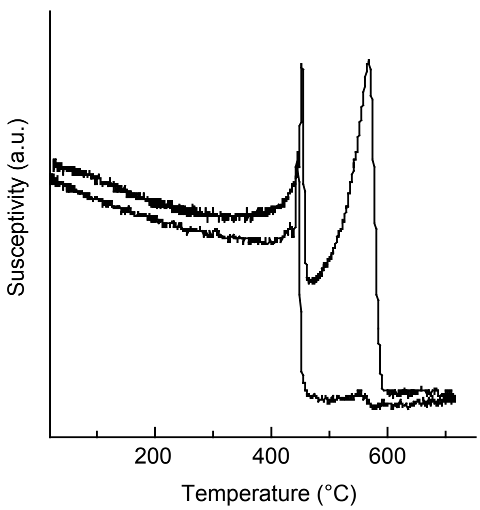

Fig.2

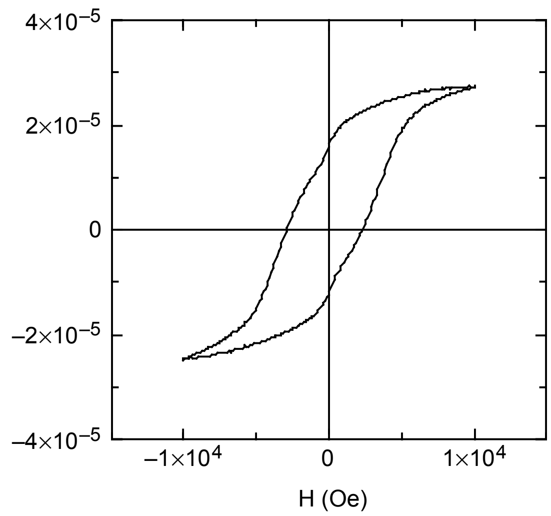

Fig.3

Figure Captions

Fig.1 XRD of powder samples: comparing the effects of different crystallisation temperatures and different Pb:Fe ratios

Fig.2 TMA of magnetoplumbite powder sample.

Fig.3 Hysteresis loop of thin film sample annealed at 700°C.

References

1. Oliver, S. A., Yoon, S. D., Kozulin, I., Chen, M. L. & Vittoria, C., Growth and characterization of thick oriented barium hexaferrite films on MgO (111) substrates, *Appl. Phys. Lett.,* 2000, **76**, 3612-3614.

2. Qi, X. W., Zhou, J., Yue, Z. X., Gui, Z. L. & Li, L. T., Study on magnetic and dielectric properties of ferroelectric/ferromagnetic composites, *Electronic Components & Materials,* 2003, **22**, 3-5.

3. Díaz-Castañón, S., Leccabue, F., Watts, B. E., Yapp, R., Asenjo, A. & Vázquez, M., Oriented $PbFe_{12}O_{19}$ thin films prepared by pulsed laser deposition on sapphire substrate, *Mater. Lett.,* 2001, **47**, 356-361.

4. Chiorboli, G., Leccabue, F., Watts, B. E., Di Cristoforo, A., Mengucci, P. & Majni, G., The crystallisation behaviour of $Pb(ZrTi)O_3$ sol-gel films on platinum electrodes, *Mat. Sci.e and Eng.: B,* 1997, **47**, 263-268.