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Abstract. We present details of the microstructural properties of Y- (Ba2Mg2Fe12O22, Ba0.5Sr1.5Zn2Fe12O22, Ba0.5Sr1.5Zn2Al0.08Fe11.92O22) and Z-type (Sr3Co2Fe24O41) hexaferrite thick films deposited by screen printing and drop casting on unpolished polycrystalline Al2O3 substrates. The hexaferrites thick films obtained by drop casting exhibited considerable roughness and porosity compared with those obtained by screen printing. We found that the powders’ morphology significantly affects the microstructure of the thick films formed by screen printing. The microstructural analysis of the thick films shows that their microstructure differs from that of the powders. Further, during the annealing process the grains in the thick films grow and form hexagonal particles, the latter having the largest size, best shape and being best observed in the case of the Ba2Mg2Fe12O22 film.

1. Introduction
The magneto-electric coupling in hexaferrites has provoked strong interest due to the opportunities this effect offers in finding novel functional applications. Thus, extensive studies have been launched on finding materials – single-phase, composites, thick or thin films – in which both orderings are simultaneously present. The magneto-electric effect in hexaferrites was found for the first time by T. Kimura and co-authors [1] for a single crystal of Ba0.5Sr1.5Zn2Fe12O22 (Y-type hexaferrite) in a magnetic field of about 1 T and at a temperature close to room temperature, with the effect being significant at T < 130 K [2]. The Ba2Mg2Fe12O22 has a relatively high spiral-magnetic transition temperature (~200 K), shows multiferroic properties at zero magnetic field, and the direction of the ferroelectric polarization can be controlled by a small magnetic field (< 0.02 T) [3]. For the first time, the existence of a significant magneto-electric effect in hexaferrites at room temperature was reported by Kitagawa et al. [4], namely, the Z-type hexaferrite Sr3Co2Fe24O41 exhibited a low-field (~ 10 mT) magneto-electric effect at room temperature.

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The Y- and Z-types hexaferrites have a complicated crystal structures in comparison with the M-type. The unit cell of Y-type hexaferrite contains three formula units (Z=3). The structure can be considered as consisting of two types of crystal S- (Me₂Fe₂O₈, spinel block) and T- (Ba₂Fe₉O₁₄) blocks consecutively stacked along the hexagonal c axis in the sequence (TST’S’T’S’T”), with the primes indicating rotation about the c-axis by 120 degrees [5]. The Z-type hexaferrites have a very complex crystal structure, being a combination of M-type and Y-type hexaferrites [6]. The unit cell consists of 140 atoms, distributed in S-, R- and T-blocks, which results in a crystal cell with an especially long c-axis length.

Most of the studies having to do with clarifying the causes of the magneto-electric effect existence in hexaferrites have been conducted on single-crystal samples, while from the viewpoint of future applications it is important to obtain new data on this effect in polycrystalline materials, or in thick and thin film structures. The reason why one predominantly finds in the literature data on the magneto-electric effect in single crystals is the difficulty in preparing single-phase specimens of Y- and Z-type hexaferrites. It is known that the temperature intervals for synthesizing different phases of hexaferrites of M-, Y-, Z-, W-, and U-types overlap [5]. Thus, the complex crystal structure and the difficulties in synthesizing Y- and Z-type hexaferrites combine to drive researchers’ interest in techniques of forming thick films of already synthesized single-phase powders. From practical application point of view, it is very important to obtain a film with good adhesion and microstructural quality as the microstructure affects to a large extent the film’s properties, including the magneto-electric effect. We describe below our studies on the microstructural properties of Ba₂Mg₂Fe₁₂O₃₂, Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂, Ba₀.₅Sr₁.₅Zn₂Al₀.₀₈Fe₁₁.₉₂O₂₂ (Y-type) and Sr₃Co₂Fe₂₄O₄₁ (Z-type) thick films deposited by two different techniques – drop casting and screen printing. An advantage of these two methods is their suitability to producing films with thicknesses from few tens to few hundred microns, thus overcoming the limitation to growing thick films by other deposition techniques; also, no expensive equipment is needed.

2. Experimental
To obtain high-quality thick or thin films, one has to first prepare powders with high homogeneity of the particles’ shape and size. The Ba₂Mg₂Fe₁₂O₃₂, Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂, Ba₀.₅Sr₁.₅Zn₂Al₀.₀₈Fe₁₁.₉₂O₂₂ and Sr₃Co₂Fe₂₄O₄₁ samples were synthesized by citric acid sol-gel auto-combustion, as described in our previous publications [7, 8]. The corresponding metal nitrates were used as starting materials and the citric acid was used as a chelator. The solution was slowly evaporated to form a gel, turned into a fluffy mass and burned in a self-propagating combustion manner. The auto-combusted powder was annealed at 600 °C. The precursor powders produced were synthesized at 1170 °C for Ba₂Mg₂Fe₁₂O₃₂, Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂, Ba₀.₅Sr₁.₅Zn₂Al₀.₀₈Fe₁₁.₉₂O₂₂. To prepare Sr₃Co₂Fe₂₄O₄₁, the precursor powder was synthesized at 1200 °C for seven hours and then quenched rapidly to room temperature to form a single-phase material.

Using drop casting, the thick film was deposited from a suspension containing Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂ or Sr₃Co₂Fe₂₄O₄₁ powder. The suspension was made by dispersing hexaferrite particles into a polyvinyl alcohol solution (PVA) and dropped on the polycrystalline Al₂O₃ substrates. The as-deposited samples were slowly dried and annealed for five hours at 1170 °C in the case of Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂ film and at 1200 °C in the case of Sr₃Co₂Fe₂₄O₄₁ film.

For screen printing, the suspensions were made by homogeneously dispersing the corresponding Y-hexaferrite powders in varnish, and Z-hexaferrite powders in a PVA solution or in varnish. The prepared suspensions were screen printed on unpolished polycrystalline Al₂O₃ substrates. The as-deposited samples were slowly dried and annealed at 1170°C for 30 min.
The powders and the thick films were characterized using X-ray diffraction with Cu-Kα radiation. The microstructure of the samples was observed by scanning electron microscopy (Philips ESEM XL30 FEG and JEOL 6390).

3. Results and discussion

The X-ray phase analysis of the powder samples and the thick films showed the presence of only $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$, $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, $\text{Ba}_0\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ and $\text{Sr}_2\text{Co}_2\text{Fe}_{22}\text{O}_{41}$.

Figure 1 shows SEM images of the $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ powder and the corresponding thick film produced by drop casting. The thick films show considerable roughness and porosity. The shapes and sizes of the grains in the films are different from those in the initial powder used for casting. A melting process was also observed. Figure 2 shows SEM images of a $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ thick film prepared by screen printing deposition of powder admixed in varnish. The roughness and porosity of the film surface are lower than those in the case of drop casting. During the high-temperature annealing, the grains in the thick films grow and form hexagonal particles. Similar results are observed for $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ and $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ thick films formed by screen printing (figure 3). The largest size and best hexagonal shape are seen in the case of the $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ film, where the thickness of the grains is less than 350 nm (figure 3c).

In our previous work [8], we reported the results of microstructural analysis of $\text{Sr}_2\text{Co}_2\text{Fe}_{22}\text{O}_{41}$ thick films prepared by drop casting, which exhibited a considerable roughness similar to that of the $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ thick film. Also, the particles had the perfect hexagonal shape typical for hexaferrites. Figure 4 presents the SEM images of $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ thick films prepared by screen printing deposition from PVA paste resulting in very bad coverage; thus, it is not a technique suitable for forming $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ thick films. However, the grains have grown to a hexagonal shape, in contrast with the grains in the powder used for preparing the suspension. The thickness of the grain is between 200-350 nm. Figure 5 shows SEM images of the $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ powder and the corresponding thick film obtained by screen printing of powder admixed in varnish. The particles’ shapes and size in the films are different than those of the precursor powder. The surface morphology of the thick film is characterized by a lower degree of roughness compared with the ones discussed before, but not a sufficiently well-expressed hexagonal shape of the grains.
Figure 3. SEM images of Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ (a) and Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Al$_{0.08}$Fe$_{11.92}$O$_{22}$ (d) powders, and (b, c) Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ thick film and (e, f) Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Al$_{0.08}$Fe$_{11.92}$O$_{22}$ thick film prepared by screen printing deposition of powder admixed in varnish.

Figure 4. SEM images of Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ (a) powder and (b, c) thick films prepared by screen printing deposition of powder admixed in PVA.

Figure 5. SEM images of Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ thick films prepared by screen printing deposition of powder admixed in varnish.

4. Conclusions
Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$, Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$, Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Al$_{0.08}$Fe$_{11.92}$O$_{22}$ and Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ thick films were prepared by drop casting and screen printing. The hexaferrites thick films produced by drop casting are considerably more rough and porous compared with those formed by screen printing. The screen printing deposition from PVA paste results in a very bad coverage, i.e., using PVA as solvent is not suitable for depositing Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ thick films. The only advantage of using PVA is that it enhances the processes of grain growth to a hexagonal shape, even after a very short high-temperature annealing. The powder’s morphology significantly affects the microstructure of the thick films formed by screen printing. The microstructural analysis of the thick films show that their microstructure
differs from that of the powders and during the annealing process the grains in the thick films grow and form hexagonal particles, the latter having the largest size, best shape and being best observed in the case of the $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ film.

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