

Microstructural study of BaFe₁₂O₁₉ fine particles obtained from a milled precursor

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Abstract

BaFe₁₂O₁₉ fine particles were synthesized after milling an intermediate step precursor in the sol-gel method. The milling process results in a better transformation of the initial mixture into BaM ferrite compared to the non-milled precursor heat treated at the same temperature. Microstructural study by SEM of the modification of the intermediate step precursor upon milling is carried out. The observed structural modifications are discussed with regards to its influence in the final obtained BaM hexaferrite.

keywords: BaM, milling, solid state phase transformation, sol-gel method, γ -Fe₂O₃, α -Fe₂O₃

1. Introduction

The hexagonal M-phase ferrite BaFe₁₂O₁₉ has been studied intensively for many years due to their importance as permanent magnets, potential high-density magnetic recording and other application [1]. Some of these applications require a strict control of homogeneity, particle size and shape and crystalline perfection, which governs their magnetic behavior.

The sol-gel route has emerged as a new method for synthesizing barium ferrite [2]. By this route the final BaM powder exhibits a fine grain size with a narrow grain size. Recently, R. Martinez et al. reported a modification of the sol-gel technique [3]. They introduced ball milling in a intermediate step of the processing route. After eliminating the organic precursors at 450°C, the resulting mixture is milled for several hours. The milled precursor was then heat treated at different temperatures. As a result of milling the resulting sample showed improved magnetic properties compared to the non-milled sample heat treated at the same temperature.

The milling stage seemed to favor the synthesis of the BaM hexaferrite at lower temperature resulting in a better specific magnetization. The possibility of lowering the synthesis temperature and still get a pure BaM powder allows the reduction of the grain size in the final product.

In this paper we study the microstructure modifications of the intermediate precursor upon milling and in the final products in order to explain the observed effect on the final BaM powder.

2. Materials and Methods

A precursor of barium hexaferrite was prepared by the sol-gel method using ethylenglycol as coordinating agent and atomic Fe:Ba ratio of 12. Details of this method are given in [2]. Briefly, iron and barium nitrates in a Fe:Ba ratio of 12:1, were dissolved in ethylene glycol at 40°C. After heating the sol of the dissolved metal compounds to around 100°C, a wet gel derives during an exothermal reaction with increase of temperature up to 130°C. The obtained gel is dried at 250°C and then warm up to 450°C, which eliminates the organic precursors. The mixture was then divided into several samples and milled in a ball mill for 2h, 6h and 10h.

The intermediate precursors of the non-milled and 10h-milled samples were heat treated at 800 °C in order to obtain BaM hexaferrite.

Samples of the intermediate precursor were studied by scanning electron microscopy (SEM) in a Jeol JSM-6300 equipped with a energy dispersive Si-detector.

3. Results

X-ray powder diffraction patterns of the precursors are shown in figure 1. The non-milled precursor is formed by BaCO₃ and α -Fe₂O₃ (maghemite), upon milling the maghemite

starts transforming into $\alpha\text{-Fe}_2\text{O}_3$ (hematite) which is completed after 10h milling. The solid state transformation can be followed by the splitting of the disappearance of (311) reflection of $\gamma\text{-Fe}_2\text{O}_3$ and the appearance of the (012), the (104) and the (110) reflection of the hematite. After 6h milling $\alpha\text{-Fe}_2\text{O}_3$ can be seen already emerging as a new phase.

The non-milled precursor when observed by SEM shows large faceted grains as shown in figure 2 (sei). Some lighter regions are observed in the backscattered micrograph of figure 2 (bei). Microanalysis of both regions showed a difference in composition. While the vast majority of the grains exhibited a atomic Fe:Ba ratio of 24 the lighter regions had a much larger content of Ba with a atomic Fe:Ba ratio of just 1.6. Both composition out of the range of the nominal atomic Fe:Ba ratio of 12. The platelet grains are seen at a larger magnification in figure 3. Some of the grains exhibit an octagonal habit. We believe that the faceted grains belong to the $\gamma\text{-Fe}_2\text{O}_3$.

Upon milling for two hours the microstructure changes drastically and a reduction of grain size is observed (figure 4). Microanalysis studies performed at several regions in the 2h-milled precursor showed lesser variation of composition with an atomic Fe:Ba ratio going from 8 to 12, already in the range of the nominal 12 atomic ratio.

Further milling did not show a significant variation of the microstructure. Figure 5 is a backscattered image of the 6h-milled precursor. Two regions can be observed, microanalysis of both regions shows variation in the atomic Fe:Ba ratio from 19 to 1.3.

The 10h-milled sample is shown in figure 6. The microstructure again shows a small grains forming the powder particles microanalysis in several regions shows almost no fluctuation of composition with an average Fe:Ba ratio of 12:1 which is the same ratio as the nominal one.

Upon heat treatment at 800°C of the non-milled sample the initial precursor transform itself into BaM hexaferrite. The microstructure of the ferrite is shown in figure 7a where the typical hexagonal platelet grains can be seen. Grain size is around 200 nm. The 10h-milled precursor on the other hand shows a smaller grain size (figure 7b) of again BaM hexaferrite. X-ray diffraction of both samples shows that in the non-milled one a small contribution of $\alpha\text{-Fe}_2\text{O}_3$ is observed as the (104) reflection between the (114) and the (107) reflection of BaM (not shown).

4. Discussion

The sample obtained from the 10h- milled precursor shows a specific magnetization of 69 Am²/Kg while the sample from the non-milled one only achieved 26 Am²/Kg. Milling of the intermediate precursor improves the specific magnetization of the specimen. This improvement we be-

lieve is result of the formation of pure BaM hexaferrite from the milled precursor compared to the specimen resulting from the non-milled one, after heat treatment at the same temperature.

X-ray shows that milling induces a solid state phase transformation of the $\gamma\text{-Fe}_2\text{O}_3$ phase, present in the non milled precursor, to $\alpha\text{-Fe}_2\text{O}_3$, this phase transformation is accompanied by a drastic particle size reduction as SEM studies shows. The phase transformation of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ comes as no surprise as both phases are closely structurally related.

The non-milled specimen has well defined $\gamma\text{-Fe}_2\text{O}_3$ grains some of them showing an octagonal habit. The composition of this sample is not completely homogenous, and local variations of Fe:Ba ratio was observed.

On the other hand, the smaller particle size of the milled precursor together with a better homogenization of the composition favors the transformation of the initial constituents to the final BaM. This favoring in the synthesis of BaM from the milled precursor occurs in spite of the fact that $\gamma\text{-Fe}_2\text{O}_3$ is structurally closer to the S block of the BaM hexaferrite than $\alpha\text{-Fe}_2\text{O}_3$.

5. Conclusion

Precursor milling induces a phase transformation of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$. The solid state transformation is accompanied by a reduction of particle size, and a better homogenization of the composition of the specimen. Small particle size together with a more intimate mixture of the Ba and Fe containing phases, are believed to be the cause of the complete transformation to BaM of the milled precursor compared to the non-milled specimen when heat treated below 1000°C.

References

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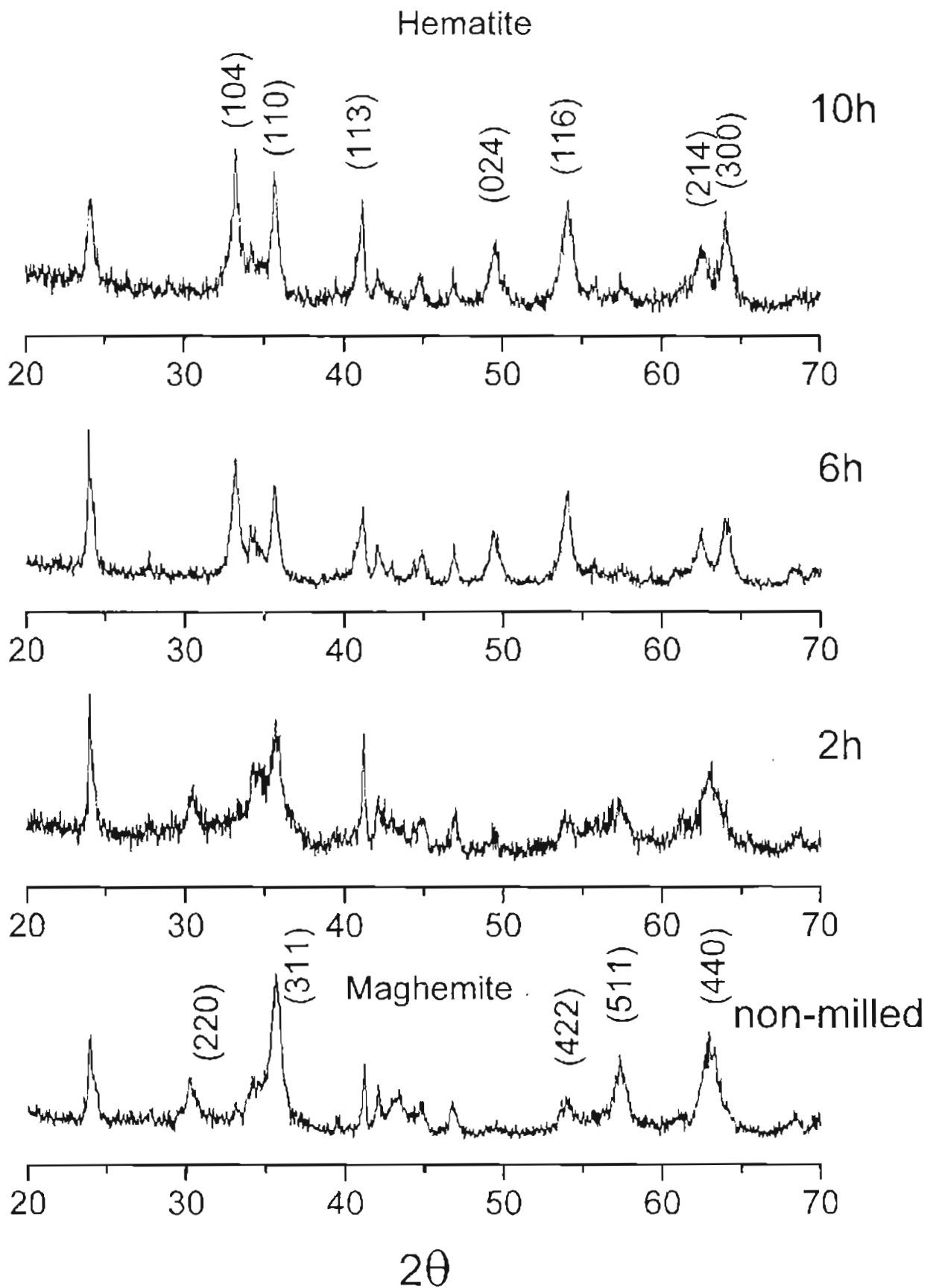


Figure 1 X-ray powder diffraction pattern of the intermediate precursor with different milling times.

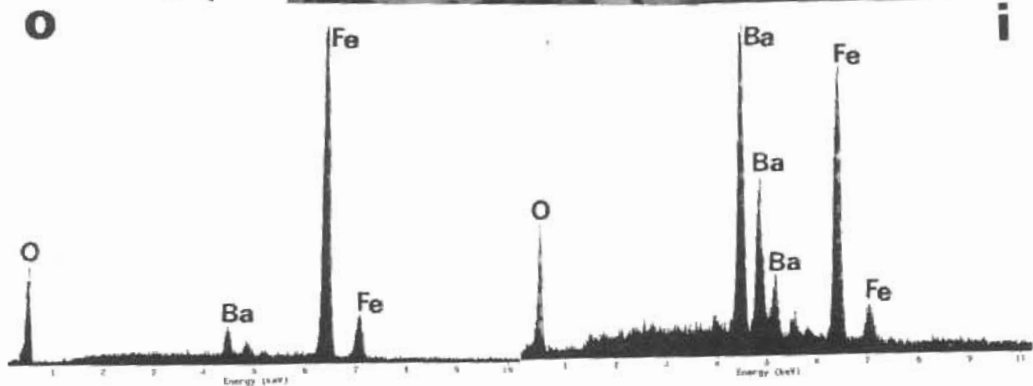
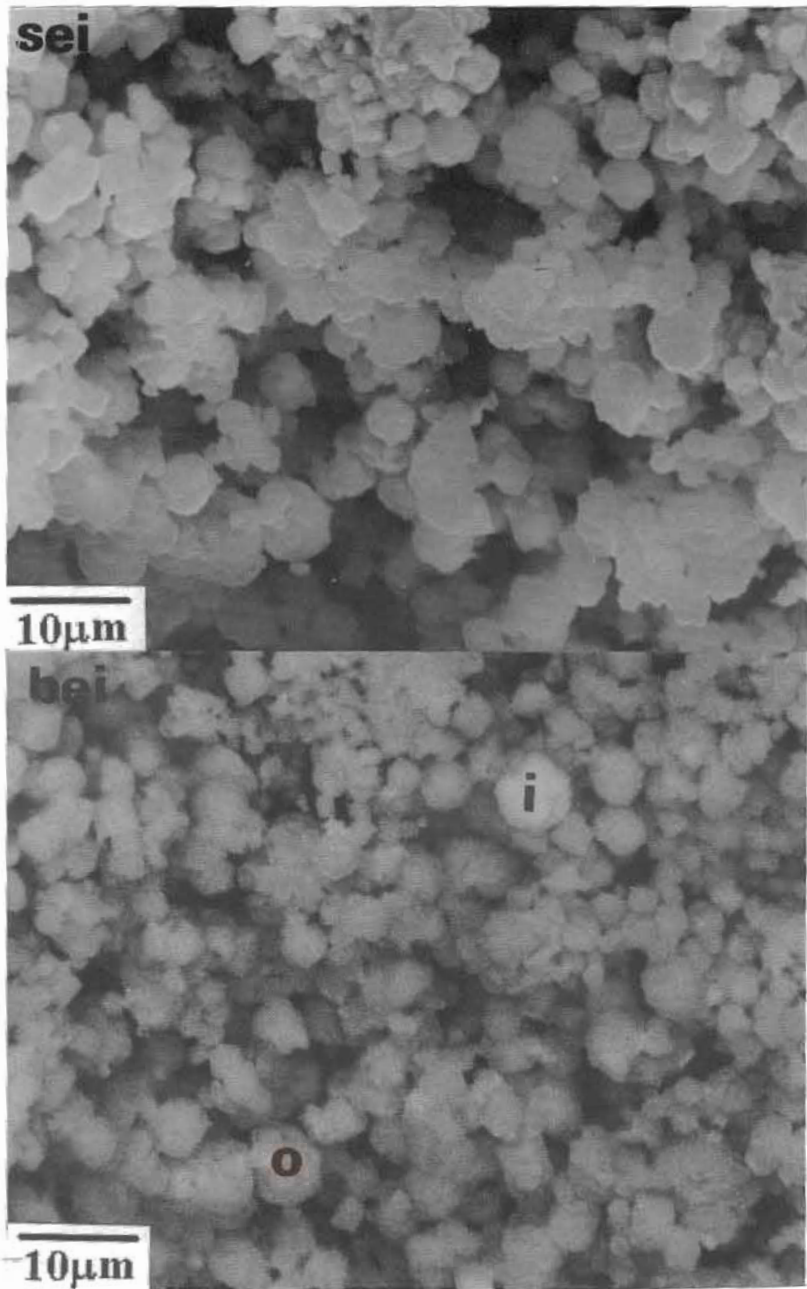


Figure 2. Secondary electron image (sei) and backscattered electron image (bei) of the non-milled sample. Typical spectra of the sample are also shown.

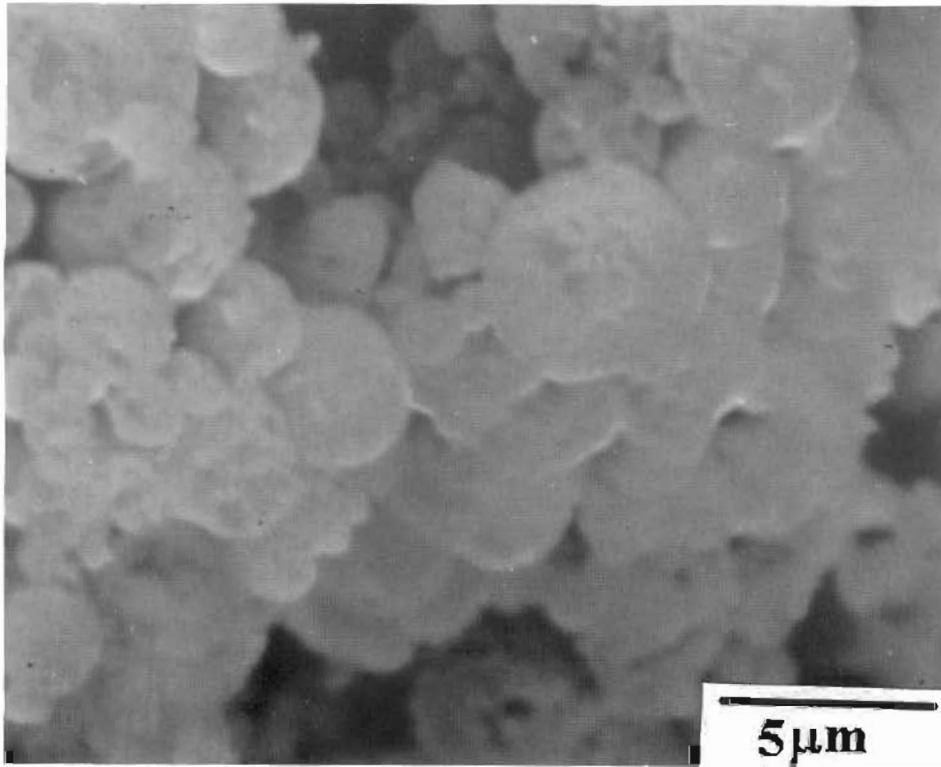


Figure 3. Well defined faceted grains, which we believe, belong to $g\text{-Fe}_2\text{O}_3$.

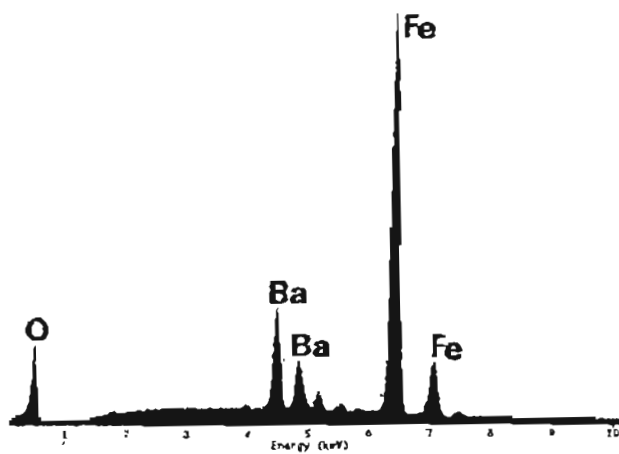
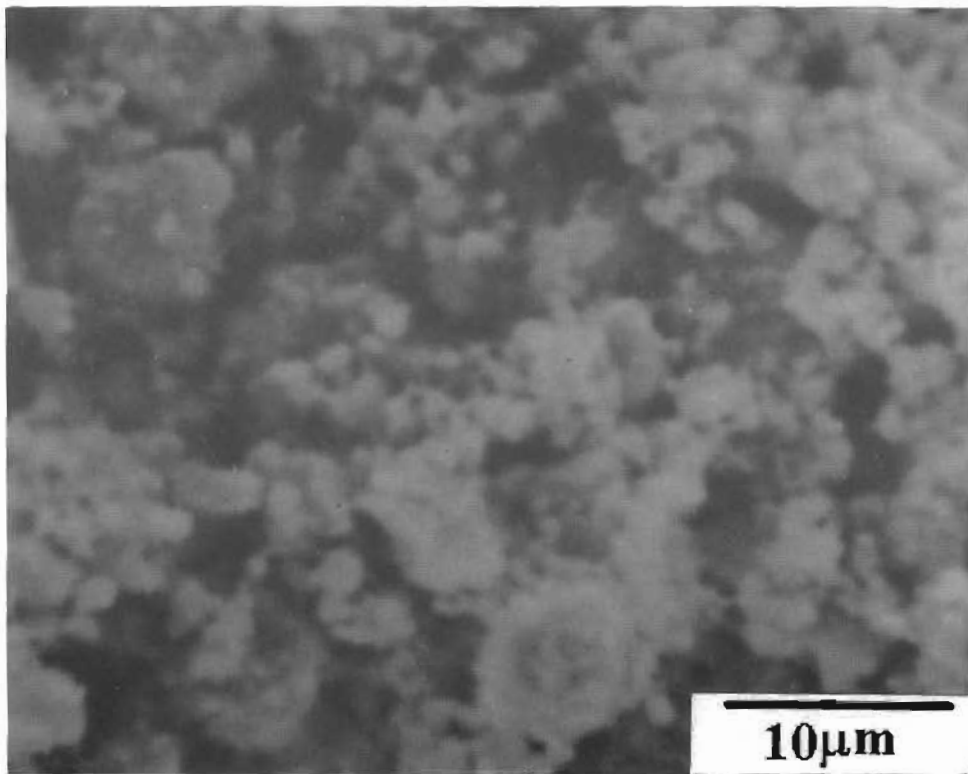


Figure 4. 2h-milled precursor, X-ray microanalysis spectrum shows a composition with an atomic Fe:Ba ratio of 12.

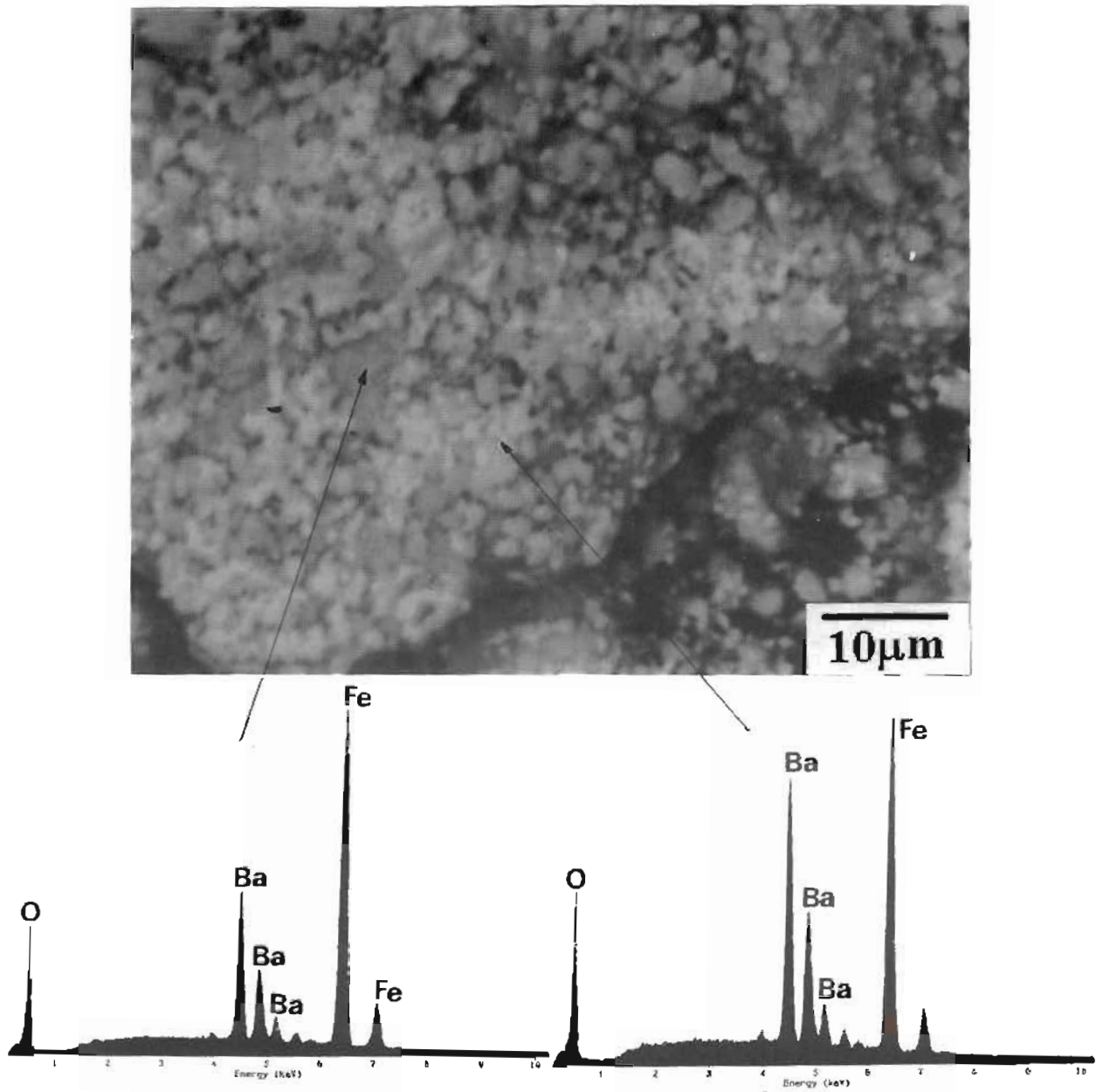


Figure 5. Backscattered electron signal micrograph of 6h-milled precursor. two regions contrast can be seen X-ray microanalysis spectra show a wide variation of atomic Fe:Ba ratio.

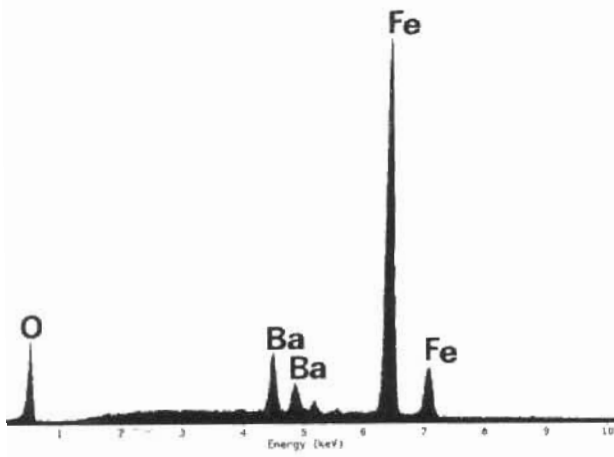
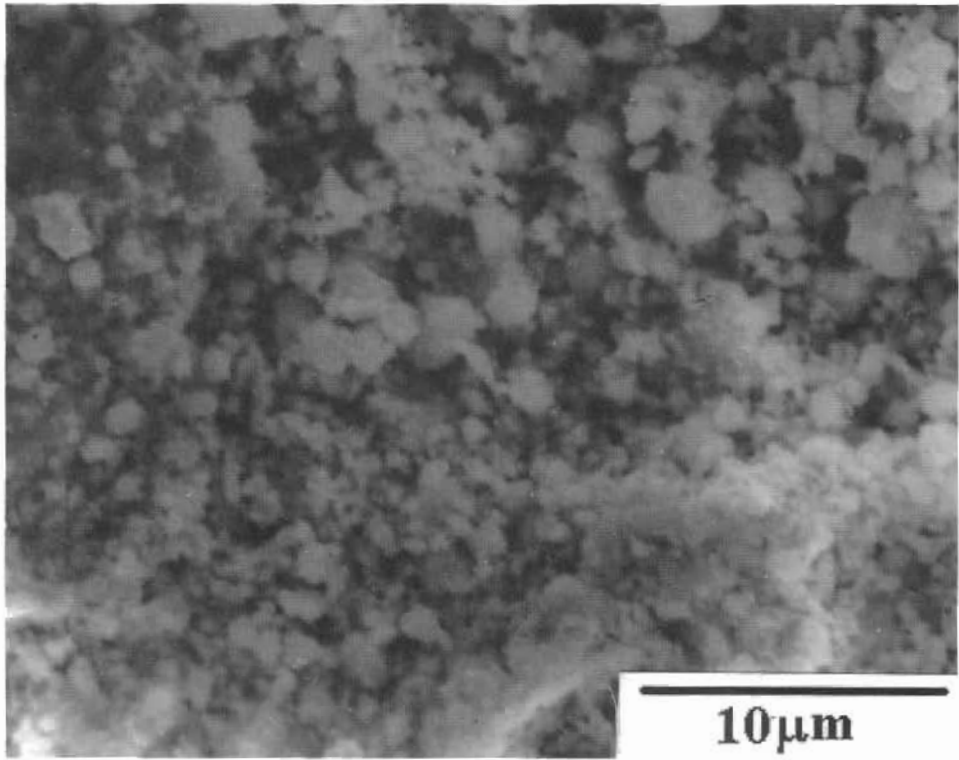


Figure 6. Secondary electron signal micrograph of the 10h-milled precursor. X-ray microanalysis spectrum corresponds to an atomic Fe:Ba ratio near 12.

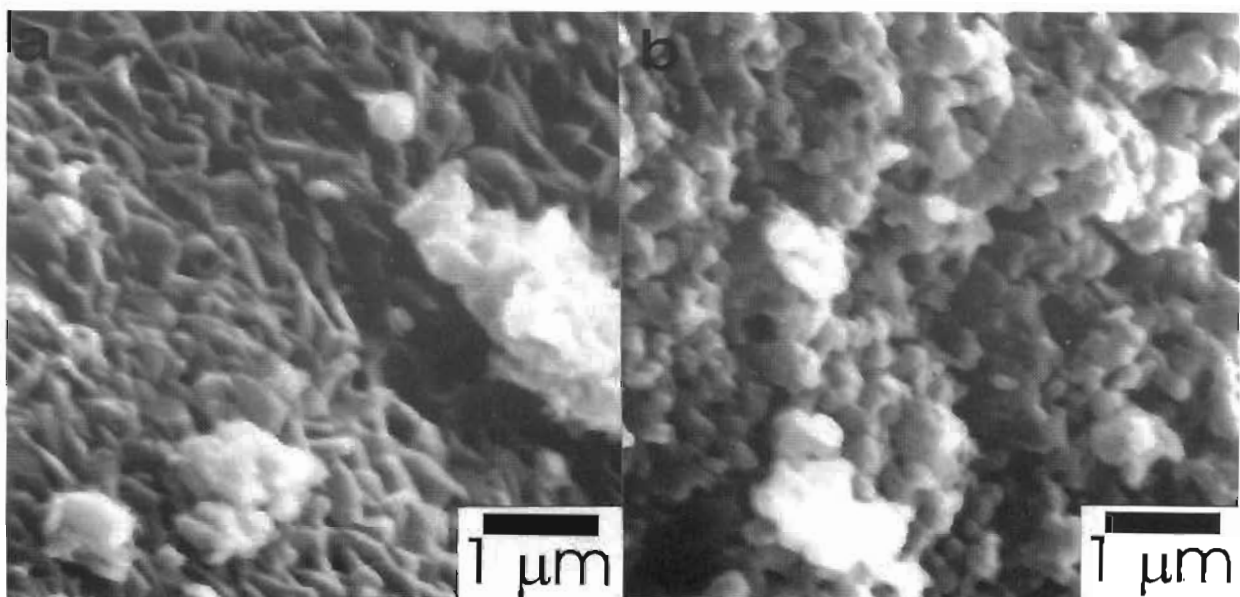


Figure 7. Secondary electron signal micrograph of BaM hexamerite from the non-milled precursor heat-treated at 800°C