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Transmission Electron Microscopic Study of Ba-Doped Ni–Zn–Co Ferrites

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Ba-doped Ni–Zn–Co ferrites were studied using transmission electron microscopy. Randomly distributed rectangular platelets of hexagonal ferrite W-phase were found to join the spinel grains along the $(111)_S \| (0001)_W$ faces forming a topotactic grain boundary.

Introduction

Several attempts have been made to improve the linearity of the permeability–temperature curves of cobalt containing ferrites by introducing a small amount of barium ions. It has been suggested that during sintering of such ferrites Ba^{2+} ions cause a distortion of the spinel structure and influence the grain morphology and size (*1, 2*). In particular, it was found that the final grains were hardly larger than the average grain size of the powdered starting material (*1, 2*).

To further elucidate the influence of barium on the growth process of these ferrites a transmission electron microscopic study was undertaken, and some microstructural features observed are discussed in the present work.

Experimental

The specimens were prepared by conventional high-temperature solid-state reaction from 57% Fe_2O_3, 28% NiO, 13% ZnO, 1% CoO, and 0.075–3% BaO (all in mole%), where the oxides were 99.5% pure with the main impurity being SiO_2 (<0.2 wt%).

The oxides were wet mixed, dried, and prefired at 1420K for several hours and subsequently wet-milled until the average particle size was less than 1.5 μm. The mixture was dried, mixed with organic binder, pressed into pellets, sintered in air at 1520K for 3 hr, and furnace cooled to room temperature.

The samples for transmission electron microscopy were prepared by mechanical grinding to thicknesses of approximately 40 μm, followed by ion-erosion with Ar until a hole appeared in the middle of the specimen. The examinations were carried out in a Philips EM 301 electron microscope equipped with a high-resolution goniometer stage.

Results and Discussion

Figure 1 shows a typical region of close-packed spinel grains, where the average grain size was not essentially larger than the particles of the starting material. Occasionally, some pores filled by an amorphous second phase between three or more grains were found.

Another microstructural feature consisted of randomly distributed rectangular

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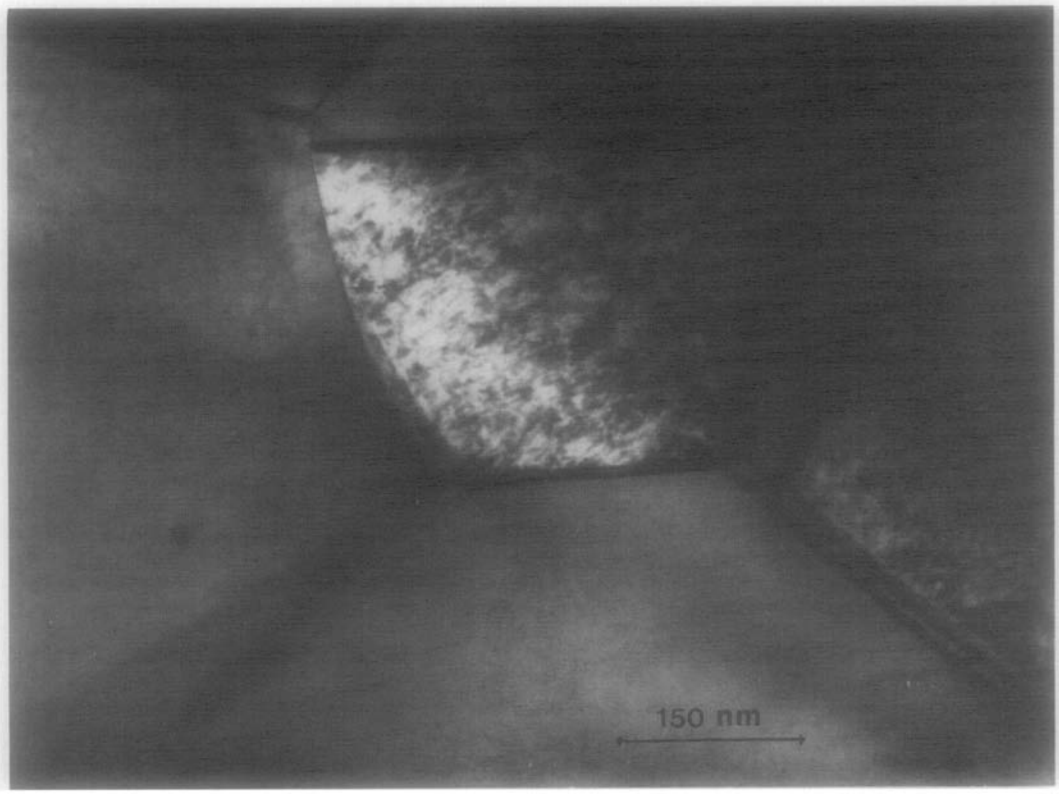

FIG. 1. A typical arrangement of the spinel grains; note the absence of pores at triple junctions of grain boundaries.

platelets, which were identified as the W-phase of hexagonal ferrites (*3*), with the composition $BaCo_2^{2+}Fe_{16}O_{27}$, $a = 0.588$, $c = 3.284$ nm. These were usually joined to spinel grains along a planar interface, as shown in Fig. 2. The region in uniform contrast is a part of the spinel grain in the $[\bar{1}12]$ orientation, as evident from the corresponding diffraction pattern in Fig. 2. The hexagonal ferrite is in the $[01\bar{1}0]$ zone and the mutual relationship is

$$[\bar{1}12]_{spinel} \parallel [01\bar{1}0]_{hex.}$$
$$(111)_{spinel} \parallel (0001)_{hex.}$$

Hence the fringes in the micrograph, parallel to the boundary, represent the basal hexagonal planes with $d_{00.1} = 3.284$ nm.

There are a few hexagonal ferrites (*3*) which are closely related and derived from the spinel structure, and the Ba-rich ones were already studied by high-resolution TEM (*4*). The one found in this investigation is the W-phase having the lowest concentration of Ba of all the members of this family of ferrites. Its structure and relationship with the spinel structure is schematically shown in Fig. 3, in the same orientation as in Fig. 2. The ferrite consists of spinel layers S, intergrown by layers R, where all the Ba^{2+} ions are concentrated. These layers, in fact, twin the spinel structure along the (111) plane, forming an S* layer. Consequently a W-ferrite structure can be written as SSRS*S*R*. . . .

It is obvious that the ferrite grains are formed because the large Ba^{2+} ions cannot be accommodated in the original spinel

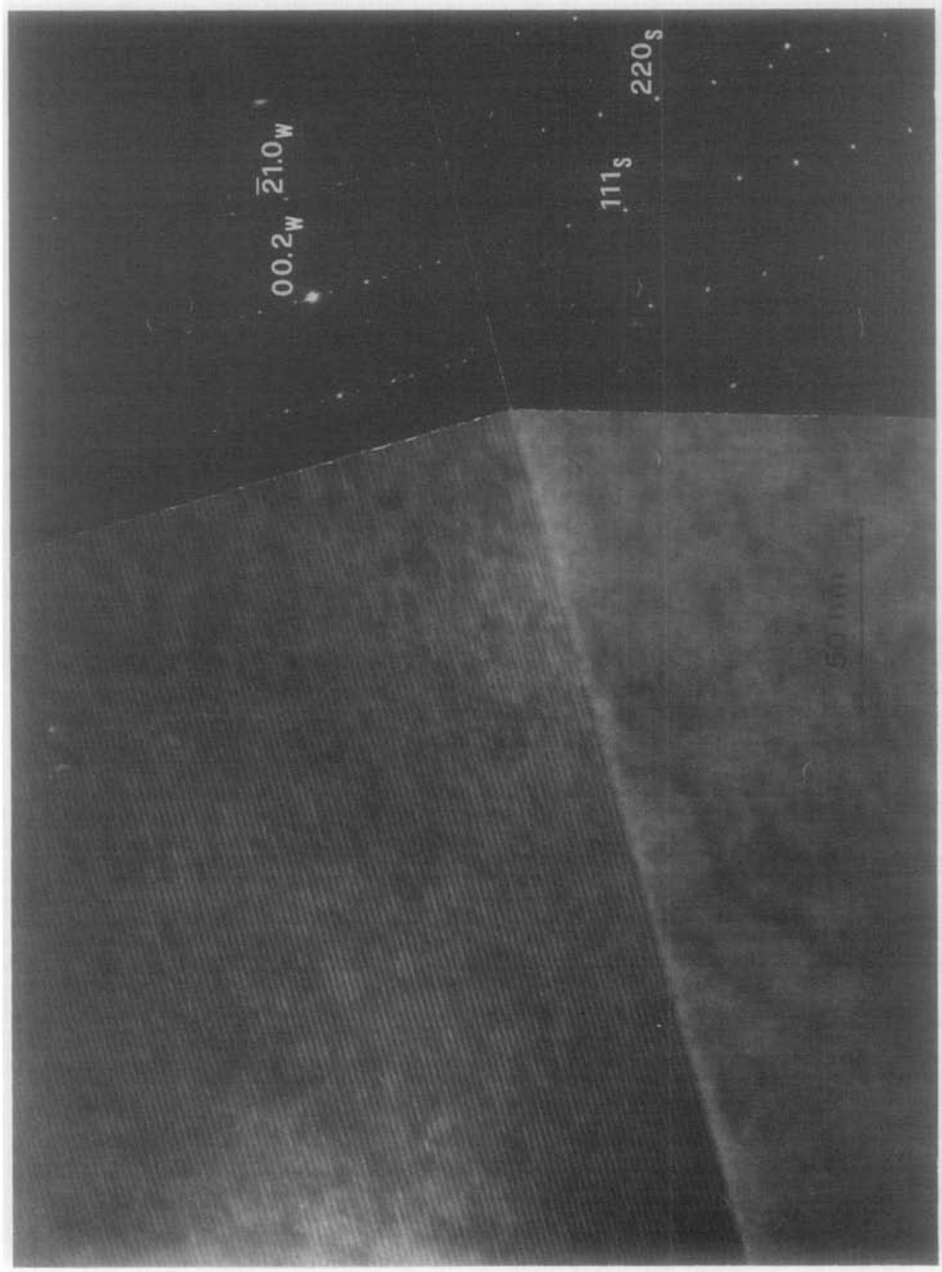

FIG. 2. The interface between the spinel and the W-phase is parallel to the $(111)_S$ and the $(00.1)_W$, respectively; note the lattice image of the basal planes in the W-phase.

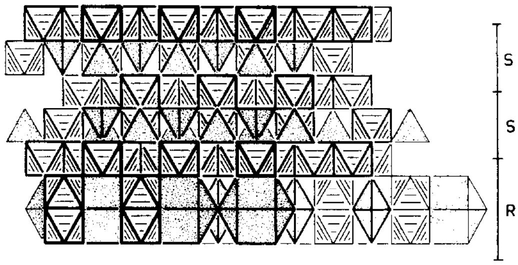

FIG. 3. The structural model of the interface shown in the same orientation as the sample in Fig. 2. Cations are at the centers and anions are at the corners of the polyhedra, respectively. Heavy-lined polyhedra are on top of the light-lined ones.

structure by simply deforming it. In the ferrite, they occupy original anion sites in the twin-plane itself, which results in large 12-coordinated polyhedra. Further, the other polyhedra–octahedra, tetrahedra, and trigonal dipyramids are occupied by Fe^{3+} and Co^{2+} ions, giving the ferrite its magnetic properties. As a result, all the Co^{3+} ions are also concentrated in these W grains and a topotactic grain boundary is formed between the ferrite and the spinel. The spinel structure at the boundary is retained, but the cations in tetrahedral coordination are changed from Co^{2+} in the ferrite to a mixture of Ni^{2+} and Zn^{2+} in the spinel.

On the basis of the results presented above it can be concluded that the addition of BaO influences grain growth during sintering most probably by enhancing the concentration of Ba ions along grain boundaries.

Acknowledgments

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