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Directional solidification and interface structure of $BaTiO_3$-$CoFe_2O_4$ eutectic

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The directional solidification and the interface structure of $BaTiO_3$-$CoFe_2O_4$ eutectic grown by the floating zone melting method were investigated. The microstructure of the eutectic were found to consist grains of lamellar or fibrous morphology. Two types of crystal structures of $BaTiO_3$ were observed for different growth conditions. The orientation relationships between $BaTiO_3$ and $CoFe_2O_4$ (the spinel-type crystal structure) are a) hcp $BaTiO_3$: (111) $CoFe_2O_4$ // (001) $BaTiO_3$ and (110) $CoFe_2O_4$ // (110) $BaTiO_3$, and b) tetra/cubic $BaTiO_3$: (001) $CoFe_2O_4$ // (001) $BaTiO_3$ and (100) $CoFe_2O_4$ // (100) $BaTiO_3$. The interface has misfit dislocations due to the accommodation of lattice mismatch.

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1. Introduction

The directional solidification of eutectics is a method used to produce an anisotropic composite directly from the melt [1, 2]. Production of composite materials having designed physical properties has been attempted with this method [3, 4].

The $BaTiO_3$-$CoFe_2O_4$ eutectic system is an interesting system because $BaTiO_3$ and $CoFe_2O_4$ are materials with large electric striction and magneto striction, respectively. Van den Boomgaard *et al*. have investigated the directional solidification of this system and shown that it is possibilly applicable for new devices [5]. Application of this system will be achieved by the combination of magnetic and electric properties (magneto electric effect) through strain, a common property of the two oxides. The interface between the two oxides is important for the production of the magneto electric effect, because strain propagates through the interface and the bonding at the interface affects the efficiency of this effect. Though the directional solidification of the $BaTiO_3$-$CoFe_2O_4$ eutectic system has been studied, little information on the microstructure, including the interface, has been reported. The aim of this study was to investigate the growth morphology, orientation relationship, and interface structure of directionally solidified $BaTiO_3$-$CoFe_2O_4$ eutectics.

2. Experimental procedure

The eutectic composition was determined from the phase diagram of the $BaTiO_3$-$CoFe_2O_4$ system proposed by Van den Boomgaard, the given eutectic composition being 38 mol% $CoFe_2O_4$ for the $BaTiO_3$-$CoFe_2O_4$ eutectic [5]. Two kinds of blended raw powders, namely, (1) $BaTiO_3$ and $CoFe_2O_4$, and (2) Fe_2O_3, TiO_2, CoO (99.99% purity) and BaO (99.8% purity), were used in the present experiment. Powders were weighed, blended, and pressed into a rod with a diameter of 5 mm and a length of 80 mm. This rod was sintered at 1470 K for 3.6 ks. Directional solidification was conducted by the floating zone melting method using a single ellipsoid image furnace [6, 7]. Starting with the powders of (1), samples were grown in air at a growth rate of 10 to 90 mm/h. When powders of (2) were used as starting materials, directional solidification was performed by the same procedure as mentioned above, except that an atmosphere of 2.5% O_2 in N_2 was employed during solidification.

Directionally solidified eutectics were cut and polished perpendicular to the direction of growth. Qualitative chemical analysis of the phases was performed using EPMA (Electron Probe Micro Analyzer) on a polished surface of directionally solidified eutectics. Thin foil was prepared by sectioning the directionally solidified eutectics. The sections were ion-beam thinned in argon at 5 kV at an angle of 30 degrees. The resulting foil was examined by H-800 and JEOL-1250 transmission electron microscopy.

3. Results and discussion

Fig. 1 shows optical photographs of the directionally solidified $BaTiO_3$-$CoFe_2O_4$ eutectic grown in air

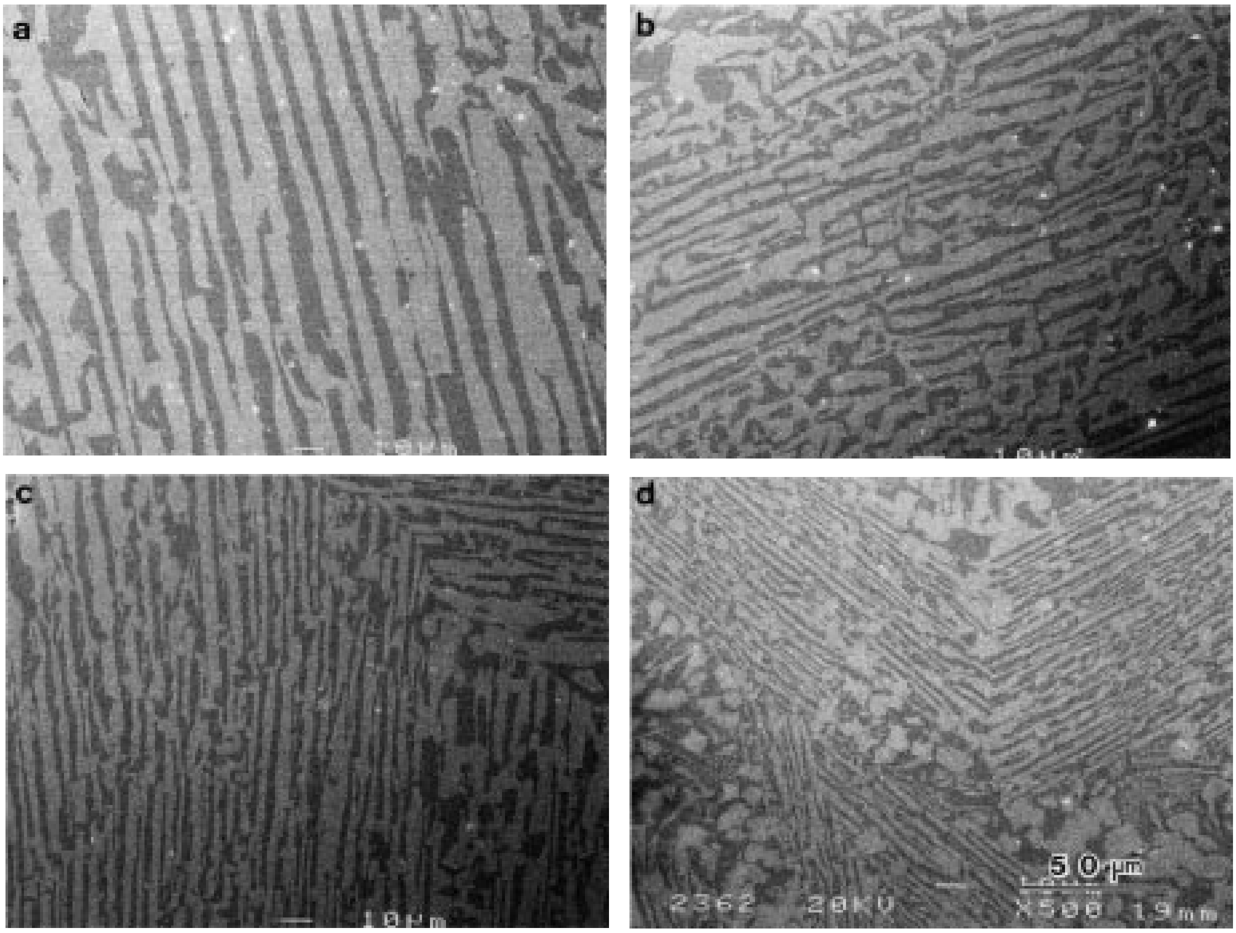

Figure 1 Optical photographs of samples of the directionally solidified $BaTiO_3$-$CoFe_2O_4$ eutectic grown in air. The growth rate: 10 mm/h (a), 20 mm/h (b), 40 mm/h (c) and 90 mm/h (d).

using the starting materials (1) of mixed $BaTiO_3$ and $CoFe_2O_4$ powders. The surface observed was that perpendicular to the direction of growth. The growth morphology of this system is a plate structure, i.e., a structure with lamellae. The structure of directional solidification was retained up to a growth rate of 90 mm/h without any cell structure. The relationship between the spacing of lamellae and the growth rate is shown in Fig. 2. The smaller the spacing of the lamellae is, the larger the growth rate is. In directionally solidified eutectics, the spacing between the two phases is plotted with the inverse of the square root of the growth rate, revealing the existence of a linear relationship between the two phases, which means that the relation $\lambda^2 R$ = constant holds in this system as shown in Fig. 2, where λ and R indicate the spacing between the two phases and the growth rate, respectively.

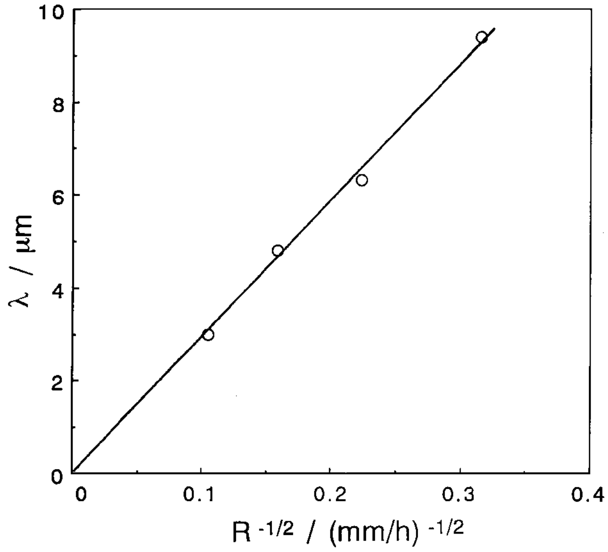

Figure 2 Relationship of spacing between the two phases shown by the inverse of the square root of the growth rate.

Chemical analysis of both phases in the $BaTiO_3$-$CoFe_2O_4$ eutectic was carried out by employing an EPMA as shown in Fig. 3. The bright area in Fig. 1 was identified as the $BaTiO_3$ phase consisting almost entirely of $BaTiO_3$, though a small amount of Fe was detected. On the other hand, the dark area in Fig. 1 was coincident with the $CoFe_2O_4$ phase and a small amount of Ti was detected in it.

Fig. 4 is an electron diffraction pattern taken from the interface of a directionally solidified eutectic grown at a rate of 20 mm/h in air. The two phases of the eutectic were confirmed as being $BaTiO_3$ with a hcp structure and $CoFe_2O_4$ with the spinel-type structure, respectively. If we use $CoFe_2O_4$ as a standard material for estimation of lattice parameters, the lattice parameters of the hcp $BaTiO_3$ can be determined from the electron diffraction pattern shown in Fig. 4. From this procedure, the lattice parameters of the hcp $BaTiO_3$ were $a = 0.575$ nm and $c = 1.406$ nm. These values, which are very close to those given in the references

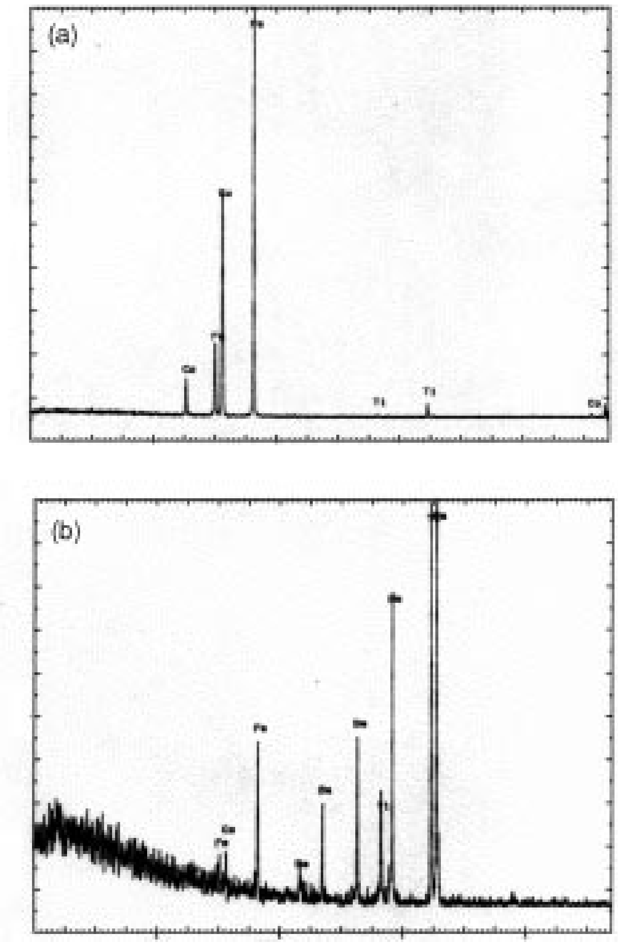

Figure 3 Chemical analysis of both phases in the $BaTiO_3$-$CoFe_2O_4$ eutectic by employing an EPMA. The dark and bright area in Fig. 1 was given by (a) and (b), respectively.

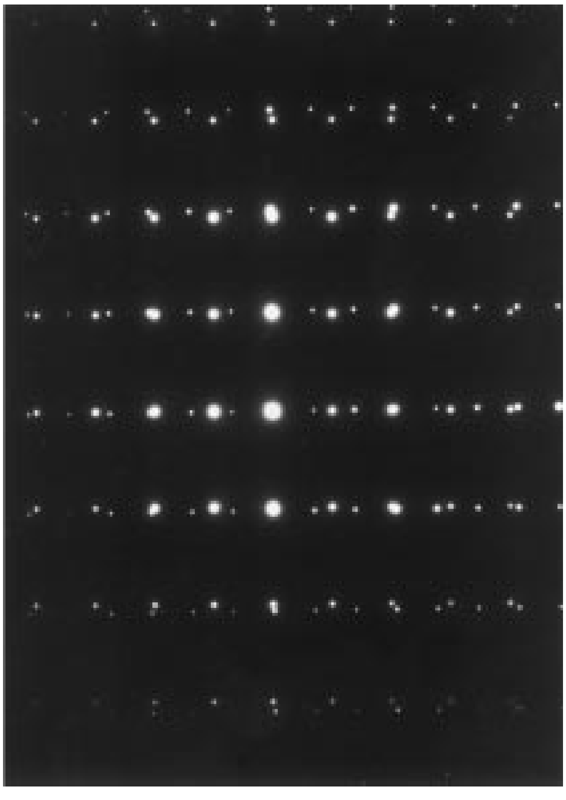

Figure 4 Electron diffraction pattern taken from the interface of a directionally solidified eutectic grown at a rate of 20 mm/h in air.

[8–10], suggest that the hcp $BaTiO_3$ obtained by the present experiment has the same structure as that previously reported. It should be noted that the hcp phase of $BaTiO_3$ is stabilized when Fe is a solute in $BaTiO_3$. In the present experiment, Fe was detected by EPMA analysis as shown in Fig. 3.

The orientation relationship between spinel-type $CoFe_2O_4$ and hcp $BaTiO_3$ can be represented as follows:

$$(111)\ \mathrm{CoFe_2O_4}\ //\ (00.1)\ \mathrm{BaTiO_3}$$

$$(110)\ \mathrm{CoFe_2O_4}\ //\ (11.0)\ \mathrm{BaTiO_3}.$$

The interface plane, which has a lamellar structure, was formed by (111) $CoFe_2O_4$ // (00.1) $BaTiO_3$.

The high resolution lattice image of the interface between $CoFe_2O_4$ and $BaTiO_3$ is shown in Fig. 5, in which the orientation relationship is given as above, and the observed direction, i.e., the direction of the beam, is [112]$CoFe_2O_4$ // $[10\bar{1}0]$hcp $BaTiO_3$. The interface was relatively flat and formed by (111) $CoFe_2O_4$ // (00.1) $BaTiO_3$ microscopically. The continuity of the lattice planes across the interface, in this case the (110) of $CoFe_2O_4$ and (11.0) hcp $BaTiO_3$, was extremely good, the misfit between them being only 3.6%. The misfit of 3.6% introduced misfit dislocations every 28 layers of the $BaTiO_3$, because the spacing of the lattice plane of $CoFe_2O_4$ is a little smaller than that of the hcp $BaTiO_3$.

Fig. 6 shows an optical photograph of a sample perpendicular to the growth direction of the directionally solidified $BaTiO_3$-$CoFe_2O_4$ eutectic. The starting materials of (b), in which the concentration of TiO_2 was a little greater than that of (a), were used to obtain tetragonal $BaTiO_3$. The growth condition was a growth rate of 20 mm/h in 2.5% O_2 in N_2. The growth morphology after directional solidification was a fibrous structure with dendrites.

Fig. 7 is an electron diffraction pattern from the interface of the directionally solidified eutectic grown at a rate of 20 mm/h in an atmosphere of 2.5%O_2-N_2. The growth direction in both the $CoFe_2O_4$ and $BaTiO_3$ phases is [001]. It is difficult to confirm a phase as being $BaTiO_3$ with a tetragonal or cubic structure, because the tetragonality of $BaTiO_3$ is too small to detect from the electron diffraction pattern ($c/a = 1.01$). Nevertheless, observation of the cubic $BaTiO_3$ suggests that a tetragonal $BaTiO_3$ phase may exist below 380 K. The orientation relationship between spinel $CoFe_2O_4$ and cubic/tetragonal $BaTiO_3$ was

$$(100)\ \mathrm{CoFe_2O_4}\ //\ (100)\ \mathrm{BaTiO_3}$$

$$(001)\ \mathrm{CoFe_2O_4}\ //\ (001)\ \mathrm{BaTiO_3}.$$

The interface planes consisting of a fiber, were almost all (100) $CoFe_2O_4$ planes, which were parallel to (100) $BaTiO_3$ planes. These results suggest that the crystal structure of $BaTiO_3$ is determined by three factors, i.e., oxygen partial pressure during solidification, the addition of a small amount of TiO_2, and the growth direction of the eutectics.

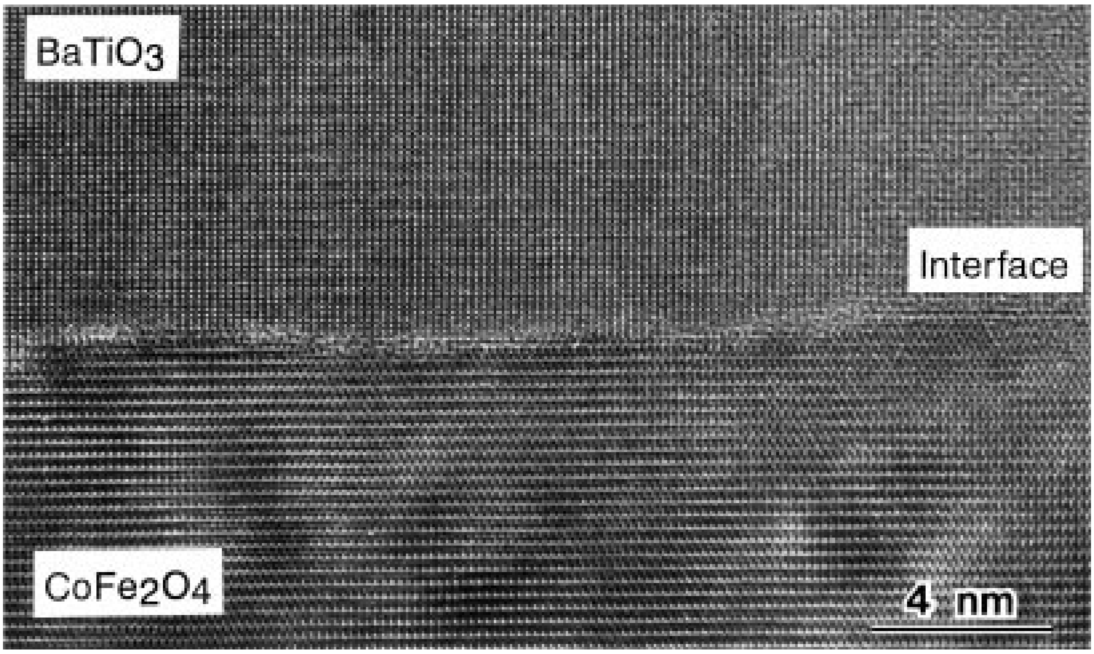

Figure 5 High resolution lattice image of the interface between $CoFe_2O_4$ and $BaTiO_3$. Sample was the same as that in Fig. 4.

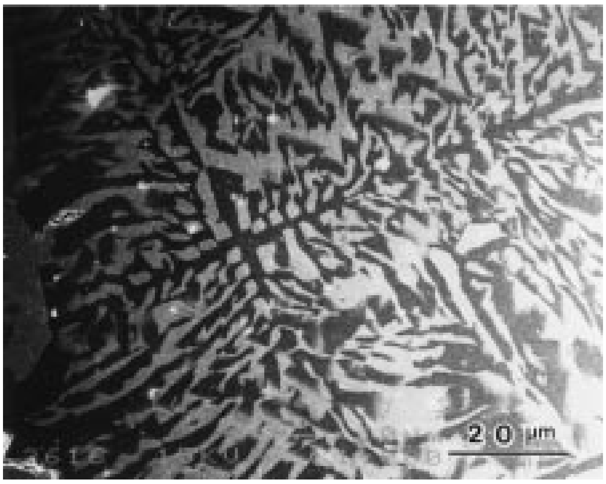

Figure 6 Optical photograph of the directionally solidified $BaTiO_3$-$CoFe_2O_4$ eutectic grown under conditions of a growth rate of 20 mm/h in 2.5% O_2 in N_2.

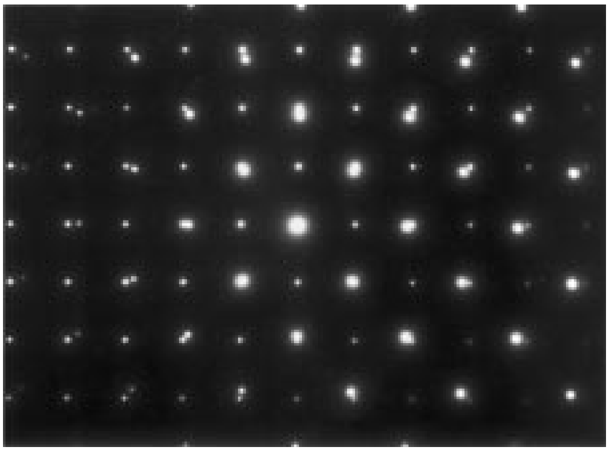

Figure 7 Electron diffraction pattern of the interface in the directionally solidified eutectic grown at a rate of 20 mm/h in a 2.5%O_2-N_2 atmosphere.

The high resolution lattice image of the interface between $CoFe_2O_4$ and cubic/tetra $BaTiO_3$ is shown in Fig. 8, in which the growth direction, i.e., the beam direction, was [001]$CoFe_2O_4$ // [001] cubic/tetra $BaTiO_3$. The interface was relatively flat and formed by (100) $CoFe_2O_4$ // (100) $BaTiO_3$ microscopically. The continuity of lattice planes across the interface, in this case of (010) of $CoFe_2O_4$ and (010) cubic/tetra $BaTiO_3$, was good, the misfit between them being only 4.9%. It should be noted that the misfit of the spinel-type $CoFe_2O_4$/hcp $BaTiO_3$ interface is smaller than that of the spinel-type $CoFe_2O_4$/cubic $BaTiO_3$ interface. The misfit of 4.9% introduces misfit dislocations every 20 layers of the $BaTiO_3$. The contrast at the interface shown in Fig. 8 seems to suggest that the some kinds of solutes were segregated at the interface.

The electrical resistance measured along the direction of growth of the cubic/tetra $BaTiO_3$-$CoFe_2O_4$ eutectic was high at 5×10^8 ohm, i.e., it was an insulator. It was almost constant with the increase of temperature. Fig. 9 shows the temperature dependence of the electric resistance of the hcp $BaTiO_3$-$CoFe_2O_4$ eutectic measured along the direction of growth. As can be seen from this figure, the resistance decreased with the increase of temperature, i.e., the eutectic is a semiconductor. Jonker has investigated the electrical resistivities of $Co_{3-x}Fe_xO_4$ near the composition of $CoFe_2O_4$ [11]. When the composition, x, is less than 1.99 (in Co rich samples), the resistivities are on the order of 10^6–10^8 ohm cm. In the present case, the $CoFe_2O_4$ phase becomes a Co-rich phase, resulting from the dissolution of Fe in the $BaTiO_3$ phase, and then shows a high resistance of 10^8 ohm. Thus it may be concluded that the semiconducting behavior of the hcp $BaTiO_3$-$CoFe_2O_4$ eutectic is due to the semiconductor hcp $BaTiO_3$.

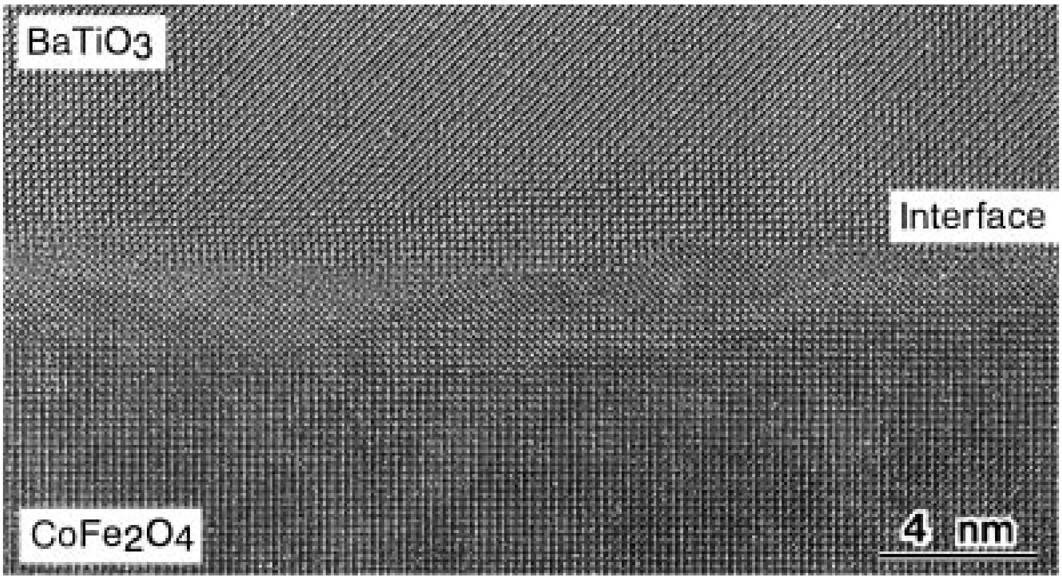

Figure 8 High resolution lattice image of the interface between $CoFe_2O_4$ and cubic/tetra $BaTiO_3$.

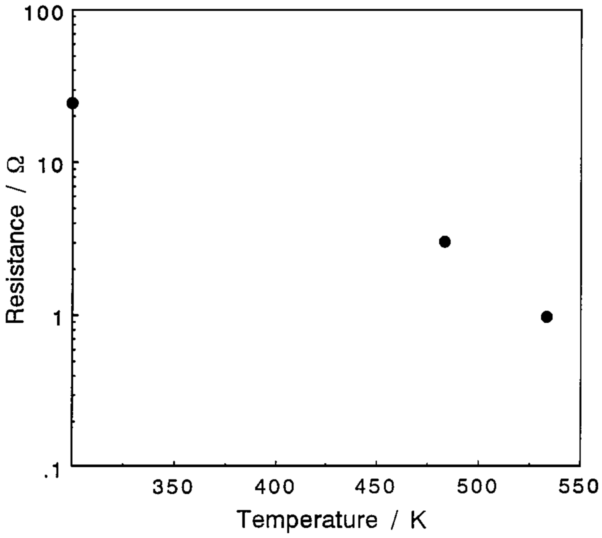

Figure 9 Temperature dependence of the electric resistance of the hcp $BaTiO_3$-$CoFe_2O_4$ eutectic measured along the direction of growth.

4. Conclusions

The directional solidification and the interface structure of $BaTiO_3$-$CoFe_2O_4$ eutectic were investigated by the floating zone melting method and following results were obtained.

(1) The micro structure of the eutectic consisted of grains of lamellar or fibrous morphology.

(2) The orientation relationships between $BaTiO_3$ and $CoFe_2O_4$ (the spinel type crystal structure) are a) hcp $BaTiO_3$: (111) $CoFe_2O_4$ // (00.1) $BaTiO_3$ and (110) $CoFe_2O_4$ // (11.0) $BaTiO_3$, b) tetra/cubic $BaTiO_3$: (001) $CoFe_2O_4$ // (001) $BaTiO_3$ and (100) $CoFe_2O_4$ // (100) $BaTiO_3$.

(3) The interfaces had misfit dislocations due to the accommodation of lattice mismatch.

(4) The semiconducting behavior of the hcp $BaTiO_3$-$CoFe_2O_4$ eutectic may be caused by the existence of the hcp $BaTiO_3$ due to the dissolution of Fe.

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