Low-temperature sintering of Z-type hexagonal ferrite by addition of fluorine containing glass powder

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In order to reduce the sintering temperature of $Ba_3Co_2Fe_{24}O_{41}$ (Co_2Z), fluorine containing glass powder was added as a sintering aid to ferrite powder with a Co_2Z stoichiometric composition prepared by a solid-state reaction, and dense sintered specimens could be obtained at 1000°C in air. The densification was achieved by liquid-phase sintering which was induced by the melting of the additive glass at ~800°C. The main crystalline phase was Co_2Z, and spinel ferrite appeared as the impurity phase. By sintering in a sealed container, the densification was accelerated still more, and in addition to spinel ferrite, Ba-M also appeared as the impurity phase. The Ba-M contained some Co instead of Fe, and grew to discontinuously large hexagonal plate-like grains. In a fluorine and/or fluorides rich atmosphere, Co_2Z was discomposed to Ba-M and spinel ferrite, and large hexagonal plate-like grains appeared. These results suggest that fluorine and/or fluorides evaporated from the additive glass decomposed Co_2Z to Ba-M and spinel ferrite, and induced the discontinuously grain growth of Ba-M. The initial permeability was lower than that of the specimen with no additive glass but remained almost constant in the frequency regions up to 1 GHz. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The hexagonal ferrites are the groups of ferromagnetic compounds discovered by Philips at 1952–1956. As the typical hexagonal ferrites, there are M type ($BaFe_{12}O_{19}$; Ba-M), Y type ($Ba_2Co_2Fe_{12}O_{22}$; Co_2Y), W type ($BaCo_2Fe_{16}O_{27}$; Co_2W) and Z type ($Ba_3Co_2Fe_{24}O_{41}$; Co_2Z) [1, 2]. Among these ferrites, Co_2Z has a high initial permeability in frequency regions higher than 300 MHz [2]. On the other hand, NiCuZn spinel ferrites are now commercially used for multi-layer chip inductors (MLCI), but cannot be used in such high frequency regions. Therefore, it is expected that Co_2Z can be used in high frequency regions of electronic devices such as MLCI. MLCI is produced by co-firing multi-layered NiZnCu spinel ferrites with an internal electrode such as copper or silver which are relatively cheap and good electrical conductors. If Co_2Z is applied to MLCI with a copper internal electrode, it must be sintered at ≤1000°C. However, presently, this is difficult [3, 4], so Z type hexagonal ferrites with Sr, Cu or Pb substituted for Ba and Co in Co_2Z are synthesized [3, 5–7]. Though their sintering temperatures are lower than that of stoichiometric Co_2Z, they must be sintered at >1100°C to be densified [3, 5–7].

In this work, we proposed a densification technique of Co_2Z at lower sintering temperatures. As a sintering

aid, a fluorine containing glass powder, of which the chemical composition is shown in Table I, was added to Co_2Z powder prepared by the solid-state reaction. The powder mixture was sintered in air or in a sealed platinum container. The influences of the glass addition and the sintering condition on the densification, phase change and microstructure development were investigated. Furthermore, Co_2Z powder, to which the additive glass powder was not added, was sintered together with the additive glass or fluoride (MgF_2 or LiF) powder pellet in the sealed platinum container. Also, the influence of fluorine and/or fluoride evaporated from such powder pellets on the crystalline phases and microstructure development was investigated.

2. Experimental procedure
2.1. Preparation of additive glass and ferrite powders

The reagents of Li_2CO_3, K_2CO_3, $SrCO_3$, $CaCO_3$, MgO, SiO_2, CaF_2 and Al_2O_3 were used as starting materials of the additive glass with the chemical composition shown in Table I, mixed and calcined at 900°C for 1 h. The mixture was then melted in a sealed platinum container at 1450°C for 2 h and cooled rapidly in cold water. The resulting glass was ground using an alumina mortar,

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TABLE I Chemical composition of the additive glass used in this study (mass%)

	Li_2O	K_2O	MgO	SrO	Al_2O_3	SiO_2	CaF_2
Additive glass	10	10	7	7	1	46	19

Figure 1 DTA curve of the additive glass.

passed through a 100-mesh sieve and subsequently, pulverized by ball-milling in ethanol using a zirconia jar and balls. The average particle size of the resulting additive glass powder was ∼0.52 μm.

The ferrite was prepared by the traditional solid-state reaction method. The reagents of $BaCO_3$, CoO, and Fe_2O_3 were mixed in the ratio corresponding to the stoichiometric Co_2Z ($Ba_3Co_2Fe_{24}O_{41}$) by ball-milling for 8 h. The mixture was calcined in air at 1300°C for 10 h, ground using an alumina mortar, and passed through a 100-mesh sieve.

2.2. Preparation and characterization of sintered specimens

The obtained ferrite and additive glass powders were mixed by ball milling for 48 h in ethanol using a zirconia jar and balls. The content of the additive glass powder was 5 mass%. The powder mixture was passed through a 100-mesh sieve, and compacted to 9 mm diameter and 2 mm thickness by cold isostatic pressing at 98 MPa. Toroidal powder compacts of 9 mm outer diameter, 4.5 mm inner diameter, and 2.5 mm in thickness were also prepared in the same way, and were used for the evaluation of initial permeability. The powder compacts were sintered in air or in a sealed platinum container. To compare the 0% glass added-specimen with the 5% glass added-specimen, the 0% glass added-specimen was prepared in the same way, and was sintered together with the additive glass, MgF_2 or LiF powder pellet in the sealed platinum container. When fluoride such as MgF_2 and LiF was heated in such a manner, a fluorine and/or fluoride rich atmosphere was intentionally achieved.

Thermal properties of the additive glass were analyzed using a differential thermal analyzer (DTA: DTG-50, Shimadzu, Japan) with a heating rate of 10°C/min. Crystalline phases of the as-calcined ferrite powder and the sintered specimens were identified using an X-ray diffractometer (XRD: XRD-6000, Shimadzu, Japan). Relative densities of the sintered specimens were calculated from the bulk and true densities. The bulk densities were measured by the Archimedes method. The true densities were calculated from the true density of the additive glass measured by the pycnometer method and the theoretical density of Co_2Z. Fractured surfaces of the sintered specimens were observed using a field-emission scanning electron microscope (SEM: S-4100, Hitachi, Japan). A quantitative analysis of the elements in the sintered specimens was made using an electron probe micro analyzer (EPMA: JXA-8100, Jeol, Japan). The initial permeability of the sintered specimens was measured at room temperatures using an impedance analyzer (HP4291B, Hewlett Packard).
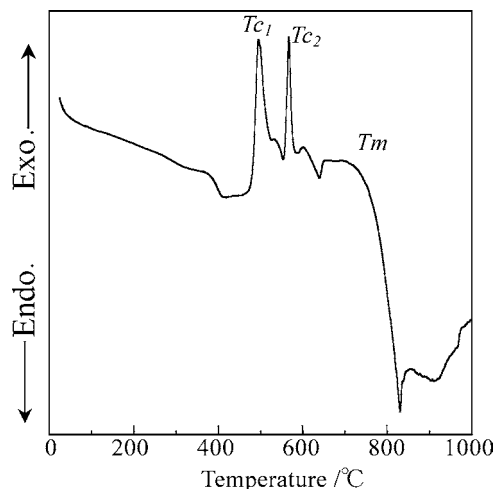
3. Results and discussion
3.1. Densification behavior
DTA curve of the additive glass is shown in Fig. 1. Two strong exothermic peaks at 494°C (Tc_1) and 567°C (Tc_2), and an endothermic peak at about 800°C (Tm) were observed. Tm was attributed to the melting of the glass, so the additive glass powder was heated at 1000°C for 1 h and cooled rapidly. As a result, a clear bulk glass was obtained, and crystal peaks were not observed in its XRD pattern. Even if crystalline phases were separated from the additive glass at 494°C (Tc_1) and 567°C (Tc_2), they would all have turn to liquid phase at 1000°C. These results suggest that this additive glass was suitable as a sintering aid for Co_2Z ferrite production at ≤1000°C.

Bulk and relative densities of the sintered specimens are shown in Table II. It is clear that by the 5 mass% addition of the glass powder, the densification of the specimen was promoted. This was achieved by liquid-phase sintering which was induced by the melting of the additive glass at ∼800°C. The relative density of the 5% glass added-specimen reached ∼93% at 1000°C for 1 h. When the sintering time was extended to 10 h at 1000°C, the bulk density stayed almost constant. Consequently, the densification was terminated at 1000°C for 1 h. Also, by sintering in the sealed platinum container, the densification was accelerated still more.

TABLE II Bulk and relative densities of the 5% glass added-specimen and the 0% glass added-specimen

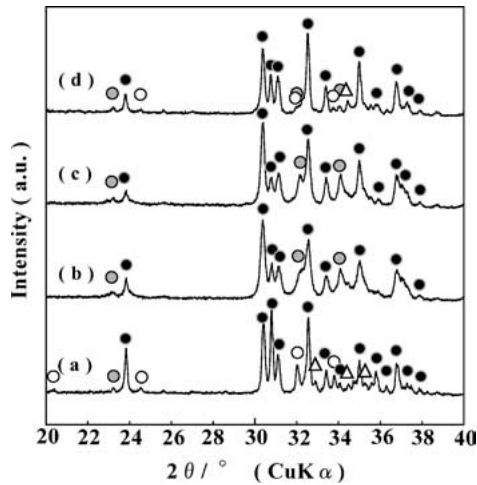| Specimen	Sintering condition		Bulk density (g/cm^3)	Relative density (%)
	Temp. (°C)	Time (h)		
5% glass added-specimen	975	1	4.76	91.2
	1000	1	4.86	93.1
	1000	10	4.88	93.5
	1000	10*	5.01	96.0
0% glass added-specimen	1050	1	4.59	85.7
	1075	1	4.93	92.2
	1100	1	5.08	95.0

Figure 2 XRD patterns of (a) the as-calcined ferrite powder and the 0% glass added-specimen sintered at (b) 1000°C for 1 h in air, (c) 1000°C for 10 h in the sealed platinum container and (d) 1300°C for 1 h in air. (●): Co_2Z, (◑): Ba-M, (○): Co_2Y, (△): Co_2W.

3.2. Crystalline phase

XRD patterns of the as-calcined ferrite powder and the 0% glass added-specimen are shown in Fig. 2. Co_2Z was the main crystalline phase in the as-calcined ferrite powder, and Co_2Y and Co_2W were observed as the impurity phases (Fig. 2a). Though the characteristic peaks of Ba-M, which should appear at 32.1° and 34.0°, could not be confirmed, a small peak of Ba-M was observed near 23.0°. By sintering at 1000°C in air or in the sealed container, the characteristic peaks of Ba-M appeared and the peaks of Co_2Y and Co_2W disappeared (Fig. 2b and c). Furthermore, in the XRD patterns measured at a slow scanning rate (Fig. 3a and b), the peaks of Ba-M were observed near 19.0° and 23.0°. At 1300°C, the peaks of Ba-M became very small and Co_2Y and Co_2W appeared again (Fig. 2d).

Co_2Z always coexisted with Ba-M in the 0% glass added-specimen in this study and, in an other study [8], coexisted with Y, W and M type ferrites and
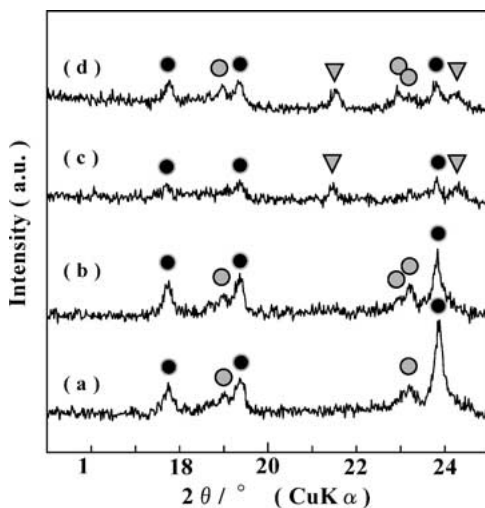

Figure 3 XRD patterns of the 0% glass added-specimen sintered at 1000°C (a) for 1 h in air and (b) for 10 h in the sealed platinum container and the 5% glass added-specimen sintered at 1000°C (c) for 1 h in air and (d) for 10 h in the sealed platinum container. (●): Co_2Z, (◑): Ba-M, (▽): Unknown.
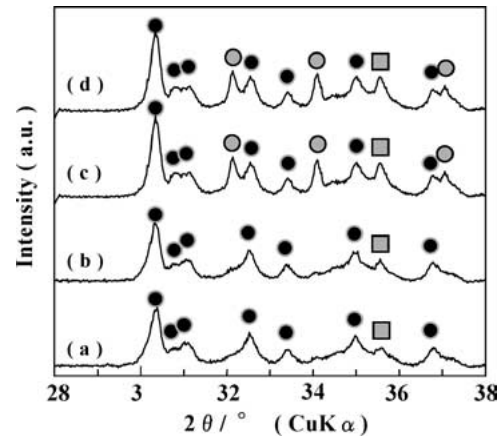

Figure 4 XRD patterns of the 5% glass added-specimen sintered at (a) 975°C for 1 h in air, (b) 1000 °C for 1 h in air, (c) 1000°C for 10 h in the sealed platinum container and (d) at 1050°C for 1 h in air. (●): Co_2Z, (◑): Ba-M, (△): Co_2W, (◼): Spinel ferrite.
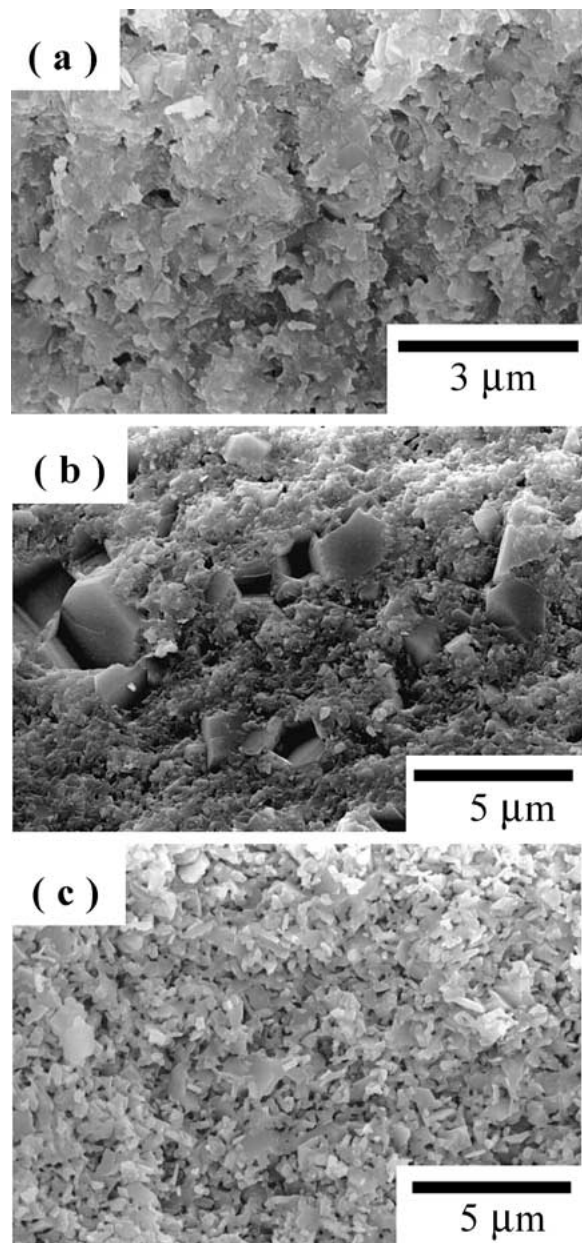

Figure 5 SEM photographs of fractured surfaces of the 5% glass added-specimen sintered at 1000°C (a) for 1 h in air, (b) for 10 h in the sealed platinum container and (c) the 0% glass added-specimen sintered at 1000°C for 10 h in the sealed platinum container.

167

Ba$_2$Fe$_2$O$_5$ at 1200–1300°C. Furthermore, there are reports [3, 4] that a single phase of Co$_2$Z is obtained at 1200–1300°C. The difference between this study and the other reports, in which a single phase of Co$_2$Z was obtained, was the purity of Fe$_2$O$_3$ used as reagent [3] and the sintering atmosphere [4]. The purity of Fe$_2$O$_3$ was 98% in this study, which was lower than that of Fe$_2$O$_3$ used in the other reports (99.4% [3] and 99.9% [4]). Also, a single phase of Co$_2$Z was obtained in the O$_2$ atmosphere [4]. Furthermore, it was reported that the formation of the hexagonal ferrites depended on the sintering condition and the additive content [5–7]. These results suggest that the formation of impurity phases such as Y, W and M type ferrites might depend on the purity of starting materials, the kind of the additive, and the sintering condition.

XRD patterns of the 5% glass added-specimen are shown in Fig. 4. Co$_2$Z was the main crystalline phase in the specimens sintered at both 975°C and 1000°C in air, and spinel ferrite was also observed as impurity phase (Fig. 4a and b). Spinel ferrite might be CoFe$_2$O$_4$ or γ-Fe$_2$O$_3$, according to the JCPDS cards. Zhang *et al.* [7] reported that spinel ferrite was observed in the sintered specimens of Z type hexagonal ferrite with Cu, and also with Zn substituted for Co in Co$_2$Z. The characteristic peaks of Ba-M (19.0°, 23.0°, 32.1° and 34.0°) were not observed in the specimens sintered at either 975°C or 1000°C for 1 h in air (Figs 3c, 4a and b). By sintering at 1000°C for 10 h in the sealed container or at 1050°C for 1 h in air, the characteristic peaks of Ba-M appeared (Figs 3d, 4c and d).

The above results show that by 5 mass% addition of the glass powder used in this study, the dense sintered specimens, in which Co$_2$Z was the main crystalline phase, were obtained at 1000°C. However, spinel ferrite was formed as an impurity phase. By sintering at 1000°C for long time in the sealed container or at 1050°C in air, Ba-M was formed and the quantity of spinel ferrite increased. These results indicate that the addition of fluorine containing glass brought about the decomposition of Co$_2$Z. The details of the influence of the glass addition are discussed later.

3.3. Microstructure development

SEM photographs of fractured surfaces of the 0% glass and the 5% glass added-specimens are shown in Fig. 5. The grains of the 5% glass added-specimen sintered at 1000°C for 1 h in air were <0.5 μm (Fig. 5a). By sintering at 1000°C for 10 h in the sealed container, discontinuously grown hexagonal plate-like grains ~3 μm were observed in the matrix of fine sub-micron grains (Fig. 5b). The discontinuous grain growth is felt to have been induced by the addition of the glass powder because it was not observed in the 0% glass added-specimen (Fig. 5c).

The chemical compositions of both the discontinuously grown grains and the fine grains were analyzed using EPMA. The reflection electron image and distributions of Ba, Co and Fe on a polished surface of the 5% glass added-specimen sintered at 1000°C for 10 h in the sealed container are shown in Fig. 6. The contrast in Fig. 6b, c and d means that the brighter
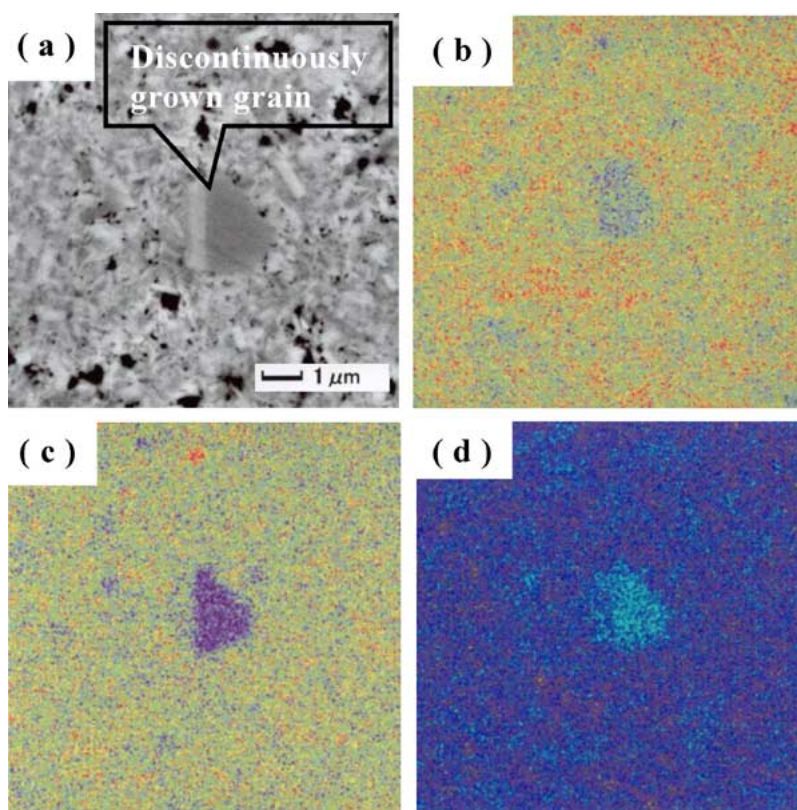

Figure 6 (a) The reflection electron image of the polished surface of the 5% glass added-specimen sintered at 1000°C for 10 h in the sealed platinum container. Distribution of (b) Ba, (c) Co and (d) Fe on the same surface of the sintered specimen. The contrast of (b), (c) and (d) means that the brighter part is richer in the element.

TABLE III Quantitative analysis for both discontinuously grown grain and fine grains of the polished surface shown in Fig. 6 and quantity of elements in the stoichiometric Co$_2$Z and Ba-M

	Ba	Fe	Co	O
	Analysis value of elements (mass%)			
Discontinuously grown grain	12.6	58.7	1.2	27.1
Fine grains	16.3	51.1	4.7	26.3
	Quantity of elements in the stoichiometric composition (mass%)			
Co$_2$Z	16.3	53.0	4.7	26.0
Ba-M	12.4	60.3		27.3

part is richer in the element. In the discontinuously grown grains, the concentrations of Ba and Co were relatively low, and that of Fe was high, compared with that of the corresponding elements in the fine grains. The results of the quantitative analysis for the discontinuously grown grains and the fine grains using EPMA are shown in Table III with the quantity of elements in the stoichiometric Co$_2$Z and Ba-M. The composition of the fine grains almost coincided with that of Co$_2$Z. The concentration of Fe in the discontinuously grown grains was relatively low, compared with Fe content in stoichiometric Ba-M. The detected quantity of Co was close to the quantity of the missing Fe in the discontinuously grown grains, which was assumed to be Ba-M. That is, the discontinuously grown grains were Ba-M (BaFe$_{11.65}$Co$_{0.35}$O$_{19}$) in which Fe was partially replaced with Co.

3.4. Influence of fluorine and/or fluorides on crystalline phase formation and microstructure development

In order to clarify the origin of the discontinuous grain growth, we focused on fluorine and fluorides in the additive glass and investigated the influence of fluorine and/or fluorides on the sintering of Co$_2$Z. XRD patterns of the 0% glass added-specimen sintered at 1000°C for 10 h together with the additive glass powder or MgF$_2$ powder pellet in the sealed container are shown in Fig. 7. By sintering in the atmosphere where MgF$_2$ was volatilized and/or decomposed into F$_2$ gas, Co$_2$Z did not exist at all, and Ba-M, BaF$_2$ and spinel ferrite appeared (Fig. 7b). By sintering together with a LiF powder pellet in the sealed container, Ba-M and spinel ferrite were observed in the XRD pattern, and LiF vanished due to decomposition or evaporation during the firing. These results show that fluorine, MgF$_2$ and/or LiF$_2$ decomposed Co$_2$Z into Ba-M and spinel ferrite. By sintering together with the additive glass powder pellet in the sealed container, not only Co$_2$Z but also Ba-M and spinel ferrite were observed (Fig. 7a). The above results suggest that fluorine and/or fluorides such as MgF$_2$ and LiF, which were evaporated from the additive glass, decomposed Co$_2$Z into Ba-M and spinel ferrite. The formation of Ba-M and spinel ferrite was accelerated by the sintering in the sealed container or at a higher temperature because fluorine and/or fluorides existed abundantly on such sintering conditions. Fig. 8 is an SEM photograph of the 0% glass added-specimen
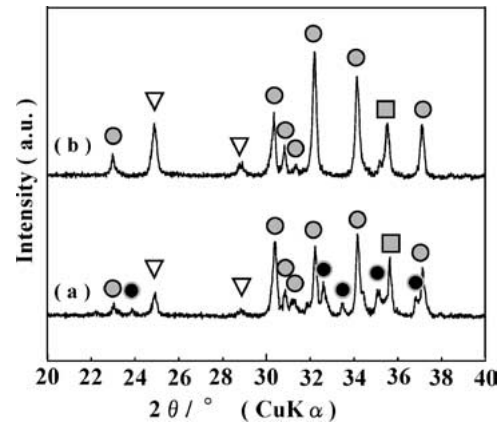

Figure 7 XRD patterns of the 0% glass added-specimen sintered at 1000°C for 10 h together with (a) the additive glass powder pellet and (b) MgF$_2$ powder pellet in the sealed platinum container. (●): Co$_2$Z, (◉): Ba-M, (▽): BaF$_2$ (■): Spinel ferrite.
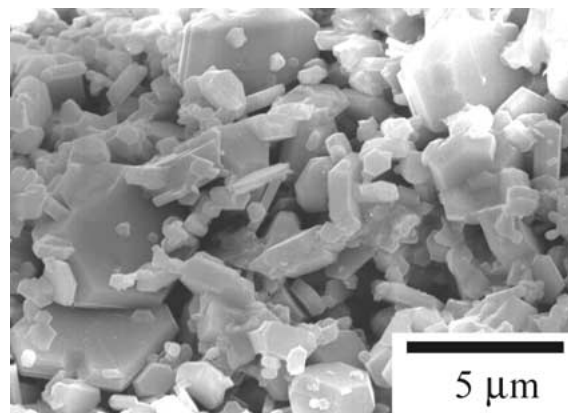

Figure 8 SEM photograph of the fractured surface of the 0% glass added-specimen sintered at 1000°C for 10 h together with MgF$_2$ powder pellet in the sealed platinum container.

sintered at 1000°C for 10 h together with MgF$_2$ powder pellet in the sealed container. While most grains were <1 μm in size, many hexagonal plate-like grains with size of ~5 μm were observed. This indicates that fluorine and/or fluorides induced the discontinuous grain growth of Ba-M.

3.5. Permeability of sintered specimens

Real and imaginary parts of initial permeabilities of the 0% glass added-specimen sintered at 1300°C for 1 h in air and the 5% glass added-specimen sintered at 1000°C for 1 h in air are shown in Fig. 9. The real part of the initial permeability of the 0% glass added-specimen decreased, and the imaginary part increased rapidly above 800 MHz. Though the real part of the initial permeability of the 5% glass added-specimen was smaller than that of the 0% glass added-specimen, it remained almost constant in the high frequency regions up to 1 GHz. The initial permeability ($\mu r' = 2.6$) of the 5% glass added-specimen was almost the same as that of the dense Z type hexagonal ferrite (3Ba$_{0.5}$Sr$_{0.5}$O·2CoO·12Fe$_2$O$_3$) with 6 mass% Bi-Zn-B glass sintered at 1050°C for 2 h [9]. The initial permeability of the Z type hexagonal ferrite (3Ba$_{0.5}$Sr$_{0.5}$O·2CoO·12Fe$_2$O$_3$) decreased with an increase in the glass content. This may have resulted
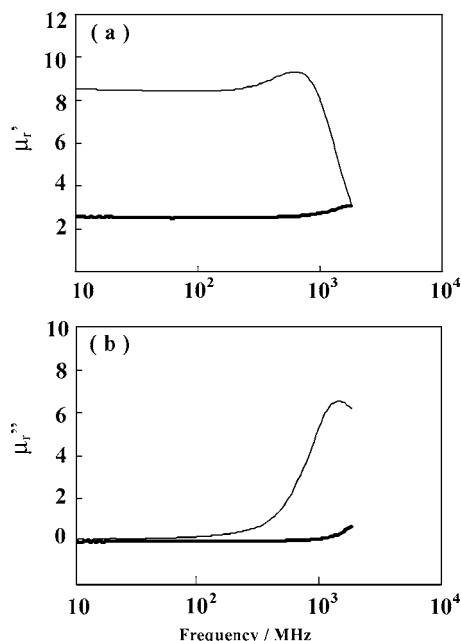
Figure 9 Variations in the (a) real and (b) imaginary parts of the initial permeability of the 0% glass added-specimen sintered at 1300°C for 1 h in air and the 5% glass added-specimen sintered at 1000°C for 1 h in air as the function of frequency. Thick lines are the 5% glass added-specimen and thin lines are the 0% glass added-specimen.

from the nonmagnetic ions by the glass entering the crystal lattice of the ferrite, thus reducing the saturation magnetization, and hence the initial permeability [9]. The same phenomenon might have been induced in this study while the sintering temperature was lower in this study.

4. Conclusion

In order to obtain dense Co_2Z at lower temperatures, the fluorine containing glass powder was added as a sintering aid to the ferrite powder with Co_2Z stoichiometric composition prepared by the traditional solid-state reaction. The dense sintered bodies, in which Co_2Z was the main crystalline phase and spinel ferrite was the impurity phase, could be obtained at 1000°C in air by the 5 mass% addition of the glass powder. The densification was achieved by the liquid sintering which was induced by the melting of the additive glass. By sintering in a sealed container, the densification was accelerated still more, and not only spinel ferrite but also Ba-M appeared as the impurity phase, and grew to discontinuously large hexagonal plate-like grains. In fluorine and/or fluorides rich atmosphere, Co_2Z discomposed to Ba-M and spinel ferrite, and large hexagonal plate-like grains appeared. These results suggest that fluorine and/or fluorides evaporated from the additive glass decomposed Co_2Z to Ba-M and spinel ferrite and induced the discontinuously grain growth of Ba-M. The initial permeability was lower than that of the specimen with no additive glass but remained almost constant in the frequency regions up to 1 GHz.

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