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Effects of non-stoichiometry and chemical inhomogeneity on the order–disorder phase formation in the complex perovskite compounds, $Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$

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The order–disorder phase formation of the complex perovskite compounds, $Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, was investigated by various heat treatments. Heat-treated samples were characterized using X-ray diffraction, SEM, and EDS, interactively. On the basis of lattice parameter measurements, the defect concentration in the complex perovskite compounds was thought to control ordered or disordered phase formation. The chemical inhomogeneity in the calcined powder was responsible for the formation of a liquid phase in the non-equilibrium state. These compounds are postulated to melt incongruently above temperature at which the ordered phase forms. Irrespective of extended heat treatments, second phases were observed but could not be identified by XRD due to lack of information. The second phase in BNN was unreacted NiO with a small amount of barium and niobium, and the second phase in BZN was a pyrochlore-like compound of which the composition was Ba:Nb = 1:1 with a small amount of zinc.

1. Introduction

Of interest is the order–disorder phase formation in the complex perovskite compounds of $A(B'B'')O_3$ structure, which is evidenced in the physical properties associated with dielectric, piezoelectric, and electro-optic properties. Ordering is, in general, believed to be attributed to the difference in ionic charge and ionic radius of cations occupying the octahedral B-position. It is still unclear why some of them, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ [1], have a disordered structure but others, e.g. $Ba(Mg_{1/3}Nb_{2/3})O_3$ [2], have 1:2 ordering. Although $Pb(Mg_{1/3}Nb_{2/3})O_3$ has a short-range ordering, the configuration of ordering is not 1:2 but 1:1.

In our previous work [3], 1:2 ordered phases of $Ba(Ni_{1/3}Nb_{2/3})O_3$ (BNN) and $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) were obtained by sintering in the temperature range 1200–1350 °C for BNN, and 1200–1300 °C for BZN. When BNN and BZN were sintered above the temperature for forming the ordered phase, disordered phases of BNN and BZN were formed along with niobium-rich liquid phases in the grain boundaries. It has been proposed that non-stoichiometry brought about by the formation of liquid phase, resulted in disordering.

The order–disorder phase formation in complex perovskite compounds, $A(B'B'')O_3$, is suggested to be controlled by the inter-diffusion of B-site cations [3]. If defects concentration is high, the inter-diffusion of B cations, i.e. diffusion of B′ cation to B″-site and B″ cation to B′-site, will be enhanced, and subsequently favours disordering.

From the view point of phase transition, a stoichiometric compound undergoes a structural change when the composition deviates from the stoichiometric with increasing temperature. In multi-component oxides, a compound is frequently encountered to melt incongruently, which leads to the formation of a compound with a different structure and/or composition. In the case of BNN and BZN, however, the perovskite structure has been maintained, regardless of the formation of liquid phase. The compositional deviation gives rise to a change in the arrangement of cations, leading to a disordered configuration. The phase transition of BNN and BZN is considered to be quite different from the order–disorder phase transition of Cu_3Au alloy [4], which arises primarily from an increase in entropy instead of the compositional change.

In this study, the formation of ordered and disordered phases in BNN and BZN was investigated, by varying the heat treatments. The defects concentration is estimated from a change in lattice parameters measured by X-ray diffraction (XRD). The order, disorder phase formation may be interpreted on the basis of chemical inhomogeneity, resulting from powder processing. Also, the equilibrium state is determined from the coexistence of the liquid and disordered phase by a prolonged sintering.

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2. Experimental procedure

2.1. Sample preparation and heat treatments

The samples of BNN and BZN were prepared by the conventional mixed oxide method starting from high-purity powders. Details of the preparation procedure are outlined in our previous work [1].

Powders calcined twice at 1100 °C were pressed into the shape of disc. The two kinds of schedule for heat treating pellets were annealing and prolonged sintering. In the case of annealing, pellets were sintered at a desired temperature for 2 h with a heating rate of 5 °C min^{-1} and then furnace cooled to 1350 °C for BNN and to 1300 °C for BZN, respectively. Samples were annealed at each temperature for 2 h, followed by furnace cooling to room temperature. In the prolonged sintering, pellets were sintered for 30 h at a desired temperature with a heating rate of 5 °C min^{-1} and then furnace cooled.

2.2. XRD analysis

In order to investigate order–disorder phase formation, powder diffraction patterns were taken for $15° < 2\theta < 40°$. XRD (Model PW 1800, Philips, Eindhoven, The Netherlands) data were collected on a back-loaded specimen ([5] p. 365) using ground powders (average particle size less than 20 μm) with $\text{Cu}K_\alpha$ radiation and a graphite monochromator. A step scanning with step size 0.02° and counting time 10 s/step were used.

Powder diffraction patterns were taken for $60° < 2\theta < 140°$ with 0.01° step scanning for precise lattice parameter measurements. Silicon powders (SRM, Standard Reference Material, 640b, National Bureau of Standards, Gaithersburg, USA) were mixed in as an internal standard. Extrapolation against $\cos^2\theta/\sin\theta + \cos^2\theta/\theta$ ([5] p. 464) was used to calculate a of silicon and cubic perovskites.

2.3. Microstructural observation

Polished and thermally etched surfaces of samples were observed using SEM (Model DS 130, Akasi, Japan). Samples of BNN and BZN were thermally etched at 1300 and 1250 °C for 1 h, respectively.

3. Results and discussion

3.1. Order–disorder behaviour

In 1944, Wilchinsky [6] observed the order–disorder phase transition in Cu_3Au alloy. The alloy has a disordered structure of face-centred cubic above 394 °C and an ordered structure of simple cubic below 394 °C. The phase transition of this alloy is very sharp and reversible at the critical temperature. Increase in entropy with temperature is responsible for this order–disorder phase transition [4]. The order–disorder behaviour of the complex perovskite compounds such as BNN and BZN may be interpreted in comparison with that of Cu_3Au alloy.

In our previous work [3], the order–disorder phase formation in BNN and BZN was confirmed by observing the existence of the (1 0 0) superlattice reflection in XRD patterns. The ordered phases were found in BNN samples sintered in the temperature range 1200–1350 °C for 2 h and in BZN samples sintered in the temperature range 1200–1350 °C for 2 h. The disordered phases were formed in BNN and BZN sintered above 1400 and 1350 °C, respectively. In this work, the disordered phase formed at higher temperature was investigated to undergo a phase transition by annealing in the temperature range of the formation of ordered phase. Fig. 1 shows XRD patterns of BNN samples annealed at 1350 °C for 2 h after sintering for 2 h at 1400, 1450, and 1500 °C. The BNN sample annealed after sintering at 1400 °C shows 1:2 ordering but the others do not. Fig. 2 shows XRD patterns of BZN samples annealed at 1300 °C for 2 h

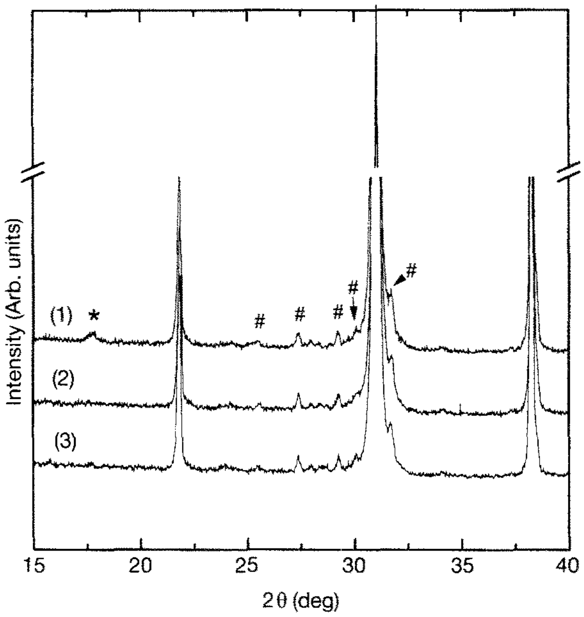

Figure 1 XRD patterns of BNN samples annealed at 1350 °C for 2 h after sintering at (1) 1400 °C, (2) 1450 °C and (3) 1500 °C for 2 h; (∗) superlattice reflection, (#) reflection from second phases.

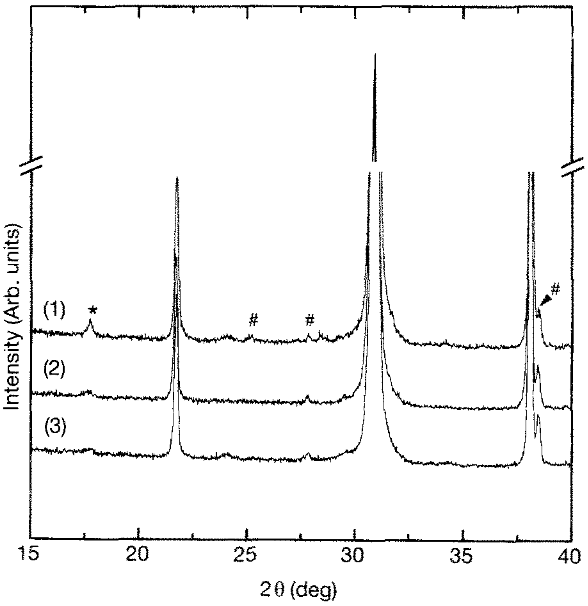

Figure 2 XRD patterns of BZN samples annealed at 1300 °C for 2 h after sintering at (1) 1350 °C, (2) 1400 °C and (3) 1500 °C for 2 h; (∗) superlattice reflection, (#) reflection from second phases.

after sintering for 2 h at 1350, 1400, and 1450 °C. Similarly, only BZN sample sintered at 1350 °C shows 1:2 ordering. Although the samples sintered at a lower temperature have been transformed to an ordered state by annealing them in the ordered phase region, it is difficult to say that it is a reversible transition. In our previous work [3], it has been proposed that the non-stoichiometry brought by the formation of niobium-rich liquid phase was responsible for the disordered phase formation in BNN and BZN above a certain temperature. On the basis of this suggestion, the irreversibility of transition observed in this study can be explained as follows. The higher the sintering temperature is, the more the liquid phase will be formed. In other words, the non-stoichiometry increases with temperature. Because the diffusion of B-site cations to a wrong site, i.e. $B''_{B'}$ and $B'_{B''}$, depends on the non-stoichiometry, it is hardly expected to have ordering if there is more defects in the B-site. The increase in defects concentration with increasing sintering temperature will be discussed in the next section.

In general, the degree of ordering in complex perovskite compounds increases with time of sintering [7–12] thus the effect of a prolonged sintering has been investigated. Fig. 3 shows XRD patterns of BNN samples sintered for 30 h at 1400, 1450 and 1500 °C. Also, Fig. 4 shows XRD patterns of BZN samples sintered for 30 h at 1350, 1400 and 1450 °C. The order–disorder phase formation shown in Figs 3 and 4, is quite different from our previous work [3]. In the previous work, BNN and BZN samples sintered for 2 h at 1400 and 1350 °C, respectively, had disordering. On the contrary, BNN sample sintered at 1400 °C and BZN sample sintered at 1350 °C for 30 h show 1:2 ordering. At these temperatures, the time of sintering is the main factor controlling the order–disorder phase formation. This is contrary to the assumption that prolonged sintering will increase the defects concentration by facilitating the formation of liquid phase.

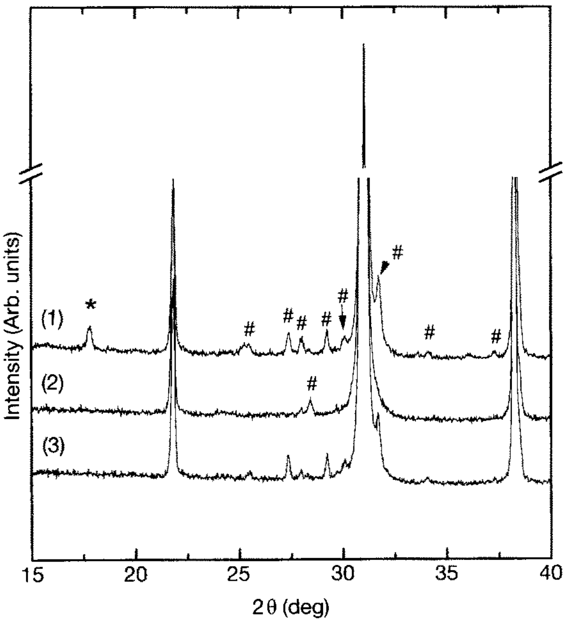

Figure 3 XRD patterns of BNN samples sintered at (1) 1400 °C, (2) 1450 °C and (3) 1500 °C for 30 h; (*) superlattice reflection, (#) reflection from second phases.

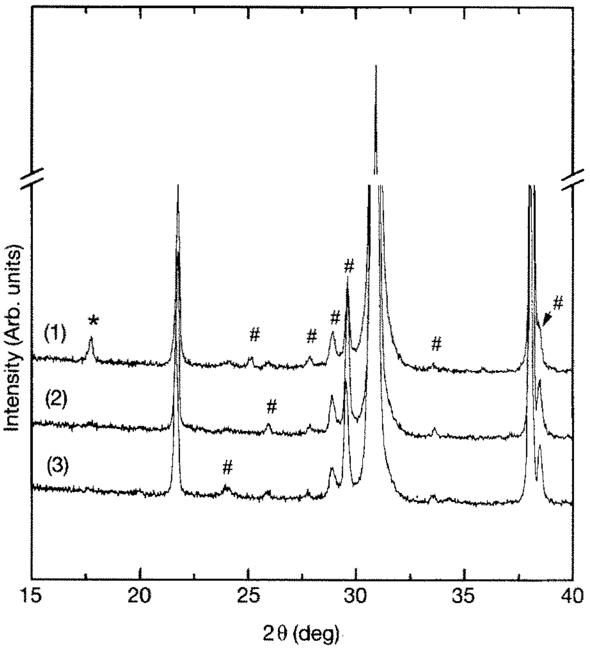

Figure 4 XRD patterns of BZN samples sintered at (1) 1350 °C, (2) 1400 °C and (3) 1450 °C for 30 h; (*) superlattice reflection, (#) reflection from second phases.

As shown in Figs 1–4, all of the heat-treated samples have second phases. The second phases could not be identified due to the lack of information about the diffraction patterns of compounds having barium, nickel (or zinc) and niobium. But the second phases were the crystallized compounds during cooling, the composition of which was about Ba:Nb = 1:1 with a small amount of B′ cation [3].

3.2. Defects concentration versus order–disorder behaviour

The order–disorder phase formation in BNN and BZN is ascribed to the increase of defects concentration in perovskite grains, resulting from the formation of niobium-rich liquid phase. In general, the variation of linear expansion coefficient ($\Delta L/L$) and the variation of lattice parameter ($\Delta a/a$) of a material with temperature should be determined to identify the type and concentration of point defects (interstitial or vacancy) [13]. When a liquid-phase sintering is involved, the measurements of $\Delta L/L$ are meaningless. Here the defect concentration in sintered samples was deduced from the relative change in lattice parameters.

The lattice parameters of BNN and BZN were corrected using an internal standard (silicon) whose lattice parameter has been known with 1/100 000 accuracy. The reflections of silicon used for BNN were different from those for BZN because some of the reflections were overlapped by reflections from perovskite compounds. In order to enhance the precision of 2θ measurements, XRD patterns of high-angle reflections were collected with a longer counting time. The sets of reflections and counting time for each reflection are listed in Table I.

TABLE I Reflection sets used in lattice parameter measurements

Si				Perovskite compounds	
BNN		BZN		$(h\,k\,l)$	s/step
$(h\,k\,l)$	s/step	$(h\,k\,l)$	s/step		
(4 0 0)	4	(4 0 0)	4	(2 2 0)	2
(3 3 1)	6	(3 3 1)	6	(3 1 0)	2
(4 2 2)	6	(4 2 2)	6	(2 2 2)	2
(3 3 3)	6	(3 3 3)	6	(3 2 1)	2
(5 3 1)	8	(6 2 0)	10	(4 0 0)	2
(6 2 0)	10	(5 3 3)	15	(3 3 0)	2
				(4 2 0)	2
				(3 3 2)	4
				(4 2 2)	4

Each data point in Figs 5–7 are the average of three independent measurements. The standard deviation of lattice parameters of BNN was less than 1/10 000 and that of BZN was less than 1/12 000. A comparatively higher precision of lattice parameters of BZN is attributed to the decrease in the uncertainty of 2θ by employing a higher angle reflection, i.e. (5 3 3) reflection of silicon.

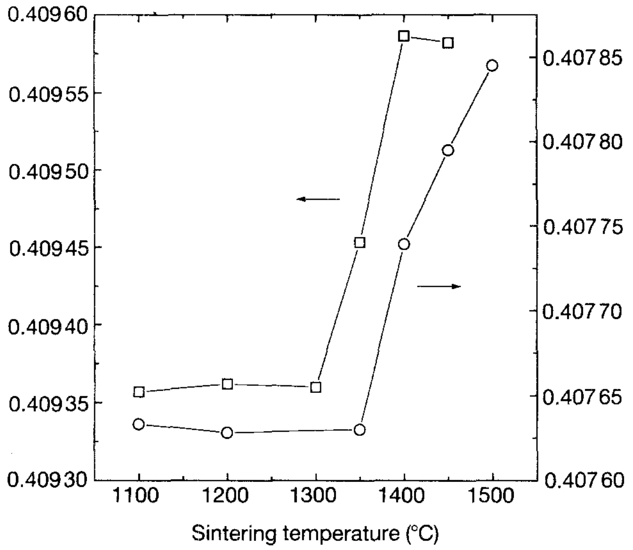

Figure 5 Lattice parameters of samples as a function of sintering temperature. Samples were sintered at a desired temperature for 2 h: (□) BZN, (○) BNN.

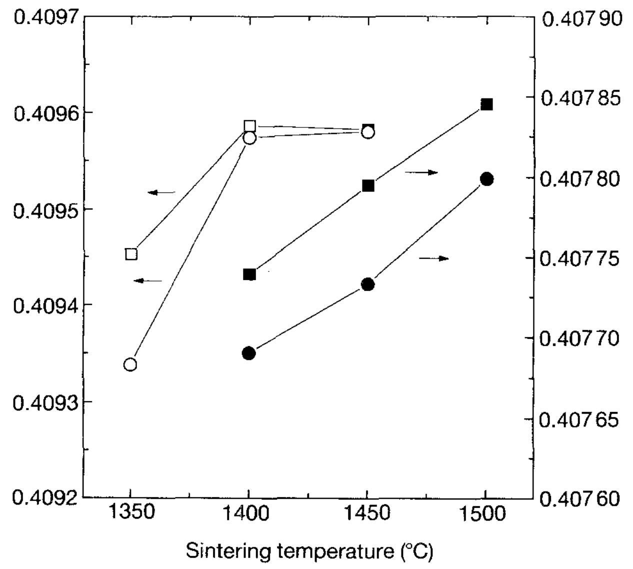

Figure 6 Variation in lattice parameters of samples with annealing. (□) sintered BZN, (○) annealed BZN; (■) sintered BNN, (●) annealed BNN.

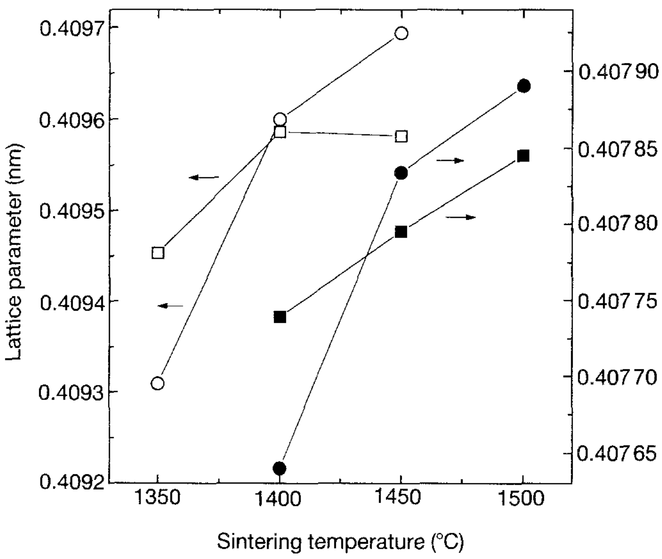

Figure 7 Variation in lattice parameters of samples with prolonged sintering. (□) BZN, 2 h; (○) BZN, 30 h, (■) BNN, 2 h; (●) BNN, 30 h.

Fig. 5 shows the lattice parameters of powder calcined at 1100 °C and samples sintered for 2 h at a temperature higher than 1100 °C. In the case of BNN, an abrupt increase in the lattice parameters is observed apparently in the samples sintered above 1400 °C. In the case of BZN, an abrupt increase is observed in the samples sintered above 1350 °C. These sintering temperatures coincide with the temperatures at which liquid phases have been observed [3]. The abrupt increase in lattice parameters may be attributed to the increase of defects concentration resulting from the formation of niobium-rich liquid phase.

The ordered phase of both BNN and BZN has a hexagonal crystal structure. However, in this study, the crystal structure of the ordered phase has been indexed as a pseudo-cubic unit cell for a direct comparison of lattice parameters. Although this will cause some error in the lattice parameter measurements of the ordered phases, the error can be negligible because of the slight deviation of the crystal structure from an ideal cubic unit cell. For instance, the deviation is less than 4% in the case of $Ba(Zn_{1/3}Ta_{2/3})O_3$ [14].

Fig. 6 shows lattice parameters of samples annealed for 2 h after sintering in comparison with those of sintered samples shown in Fig. 5. All samples sintered for 2 h in this temperature range have the disordered structure. Among the annealed samples, only two samples show 1:2 ordering, which are BNN sintered at 1400 °C and then annealed at 1350 °C, and BZN sintered at 1350 °C and then annealed at 1300 °C. Comparing Fig. 6 with Fig. 5, it is evident that there is a strong correlation between ordering and defects concentration. In Fig. 5, samples having ordering have been solid-state sintered. Although all samples in Fig. 6 were sintered in the presence of a liquid phase, the defects concentration of two ordered samples is postulated to decrease enough to have ordering by annealing. Samples sintered at a higher temperature still have a defects concentration high enough to have disordering irrespective of annealing. This can be ascribed to the increase in the liquid phase with temperature. However, it is unclear why defects concentration of BZN sintered at a temperature higher than 1400 °C is not decreased by annealing.

Fig. 7 shows lattice parameters of samples undergoing a prolonged sintering for 30 h in comparison with those of samples sintered for 2 h (Fig. 5). On the basis of Figs 3, 4, and 7, a higher defects concentration gives rise to the disordered structure. The sharp decrease in defects concentration of BNN sintered for 30 h at 1400 °C, and of BZN sintered for 30 h at 1350 °C, implies that rehomogenization occurs due to a prolonged sintering. The liquid phase formed in the initial stage of sintering at those temperatures is postulated to be not in the equilibrium state. The liquid phase might be developed by the chemical inhomogeneity in the powder due to an inappropriate calcination. Further discussion on this subject will be given in the following section. However, BNN samples sintered at a temperature higher than 1400 °C and BZN samples sintered at a temperature higher than 1350 °C, show an increase in defects concentration with sintering time. One of the possibilities is that these compounds melt incongruently above those temperatures. Thus, liquid phases formed at those temperatures are in the equilibrium state with solid phases of matrix grains. The longer the sintering time is, the more the solid grains undergo a compositional change. The composition of matrix grains is deviated further from the stoichiometric, resulting in the higher defect concentration, which is demonstrated in the measurements of lattice parameters.

3.3. Effect of chemical homogeneity on the 1 : 2 ordering

The conventional mixed oxide method is well known to be inadequate to prepare a chemically homogeneous powder, because the reactions between oxide powders are controlled by the diffusion of ions through solid particles whose dimensions are much bigger than the diffusion length of ions. Furthermore the mixture of raw materials is locally inhomogeneous.

Although the double calcining technique has been used in this study to prepare a powder of higher chemical homogeneity, several unknown second phases were observed in the calcined powders [3]. These second phases are thought to be inter-compounds between the starting materials with various chemical compositions. It takes time to form the homogeneous compounds through the multiple processes of complex reactions. In the case of BNN and BZN, binary reactions of different oxide powders are expected to occur in the first stage of calcination. Several eutectic compounds such as $BaO:Nb_2O_5 = 3:5$ (m.p. = 1288 °C) and $BaO:Nb_2O_5 = 6:4$ (m.p. = 1320 °C), are found to have a low melting point in the binary phase diagram of BaO and Nb_2O_5 [15]. Therefore it is possible that some of the second phases, of which the compositions are close to the eutectic ones, are responsible for the formation of liquid phases in non-equilibrium state. In this case, a prolonged sintering will result in rehomogenization.

Pellets of BNN and BZN were prefired at 1300 and 1250 °C, respectively, for 10 h, which is thought to be long enough to complete reactions to form a homogeneous compound. These prefired samples of BNN and BZN were sintered for 2 h at 1400 and 1350 °C, respectively. Under these sintering temperatures, a liquid phase in the non-equilibrium state is thought to occur. Fig. 8 shows microstructures of specimens prefired, and sintered after prefiring. The microstructures of BNN and BZN specimens sintered after prefiring are not different from those of specimens prefired. This observation implies that solid-state sintering occurs in the samples sintered after prefiring. The prefiring eliminates second phases responsible for the formation of liquid phase in these sintering temperatures by increasing chemical homogeneity. Thus it can be concluded that the liquid phase formed in the samples without prefiring is in the non-equilibrium state.

Fig. 9 shows XRD patterns of samples sintered after prefiring. Not only do samples of BNN and BZN sintered after prefiring show 1 : 2 ordering, but also the intensities of the (1 0 0) superlattice reflections are higher than those shown in Figs 3 and 4. Therefore, it can be concluded that the chemical homogeneity of BNN and BZN samples is a main factor in controlling order–disorder phase formation in BNN and BZN. Furthermore, the higher the chemical homogeneity, the higher is the degree of ordering.

Suggestions deduced from the results are as follows.

(i) The previous works on the order–disorder behaviour of complex perovskite compounds such as $Pb(Sc_{1/2}Ta_{1/2})O_3$ [7–9], $Ba(Zn_{1/3}Ta_{2/3})O_3$ [10, 11], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [12], etc., are mainly concerned with increasing the degree of ordering by increasing thermal energy. However, the degree of ordering can be enhanced by increasing the chemical homogeneity of the compounds through a chemical powder processing such as coprecipitation, the sol–gel technique, or the Pechini process.

(ii) Our results show that the temperature of disordered phase formation can be lowered by the formation of liquid phase in the non-equilibrium state. Many complex perovskite compounds containing oxides with a low melting point, such as PbO, FeO, CuO, etc., have been known to be in a disordered state. One possibility is that the disordering might be responsible for the non-stoichiometry brought about by the formation of liquid phase or by volatilization.

(iii) The chemical inhomogeneity in a powder mixture is hardly identified. X-ray diffraction thus has an ineffective detection limit when a small amount of various second phases exist. However, inspection of the reaction processes might give an insight into the chemical homogeneity.

3.4. Second phases in BNN and BZN

Although the samples shown in Fig. 9 were extensively heat treated for homogenization, XRD patterns of

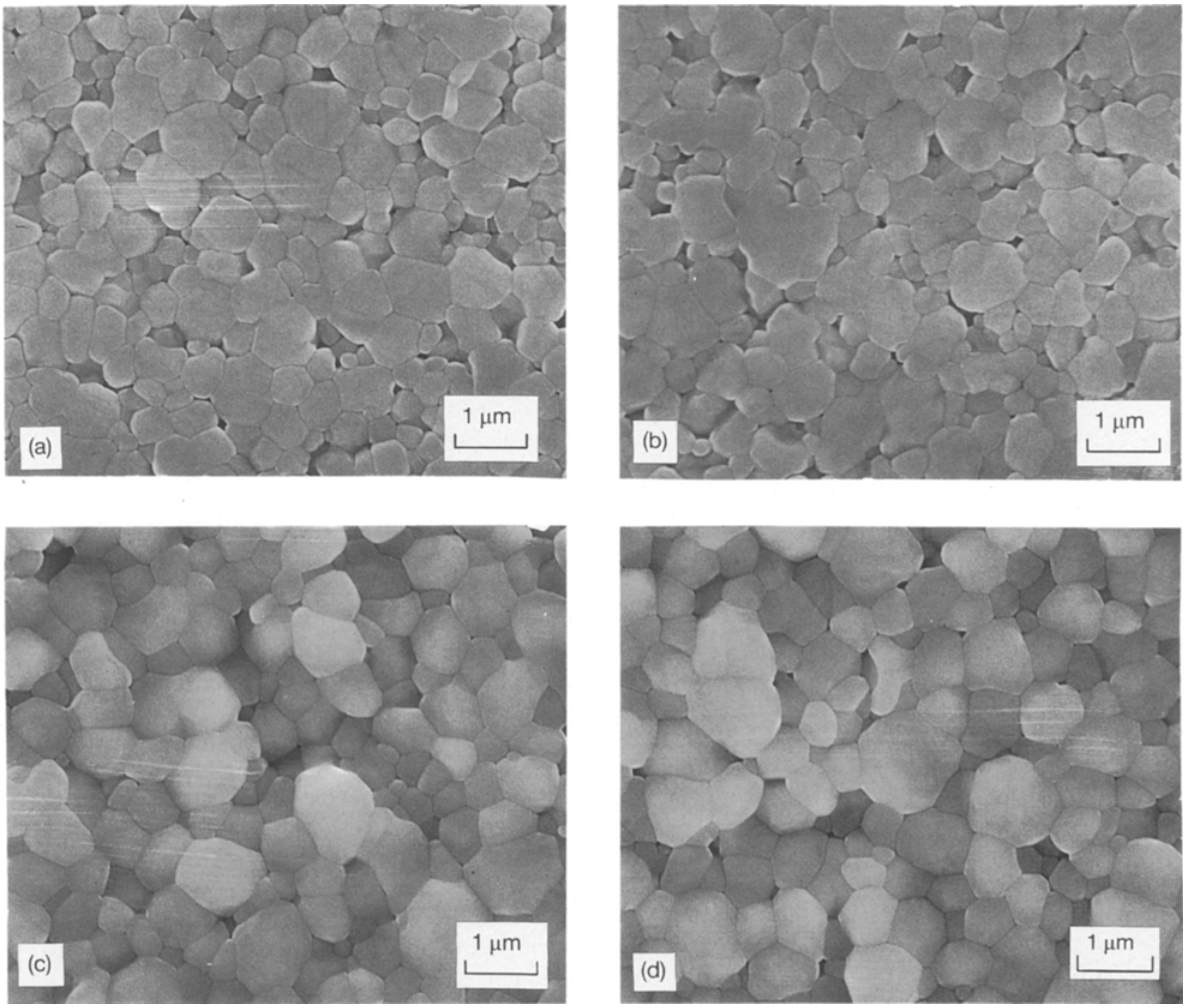

Figure 8 Microstructures of heat-treated samples; (a) BNN sintered at 1300 °C for 10 h, (b) BNN sintered at 1400 °C for 2 h after prefiring at 1300 °C for 10 h, (c) BZN sintered at 1250 °C for 10 h, (d) BZN sintered at 1350 °C for 2 h after prefiring at 1250 °C for 10 h.

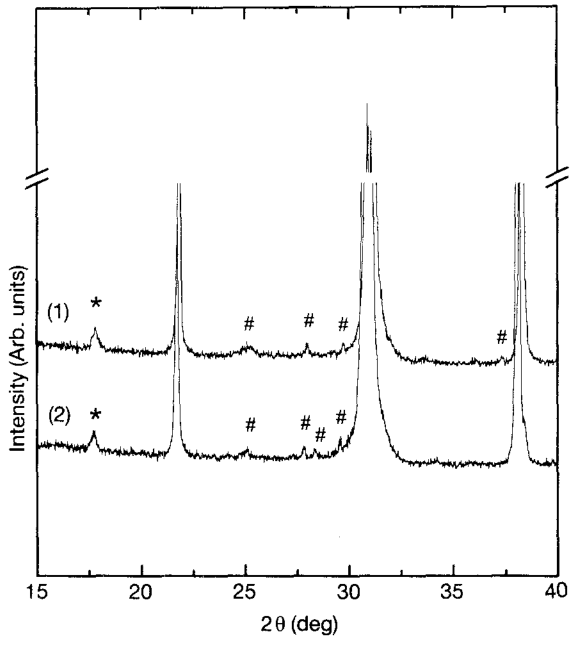

Figure 9 XRD patterns of samples sintered after prefiring; (∗) superlattice reflection, (#) reflection from second phases. (1) BNN, 1300 °C, 10 h/1400 °C, 2 h; (2) BZN, 1250 °C, 10 h/1350 °C, 2 h. Scanning electron.

these samples show the presence of second phases. Because the reflections from second phases in Fig. 9 are too low to be identified, EDS was used to investigate the compositions of second phases. Fig. 10 shows the second phases found in BNN and BZN. The chemical compositions are listed in Table II.

In Fig. 10a the second phase in BNN has a spheroidal shape. Table II shows it is NiO with a small amount of barium and niobium. This implies that NiO has a lower reactivity. The behaviour of NiO in BNN is quite similar to that of MgO in $Pb(Mg_{1/3}Nb_{2/3})O_3$ [16]. In the case of $Pb(Mg_{1/3}Nb_{2/3})O_3$ it has been widely accepted that the inertness of MgO is responsible for the formation of pyrochlore-like second phases. In order to inhibit the formation of second phases in $Pb(Mg_{1/3}Nb_{2/3})O_3$ the columbite precursor method has been used. Thus pre-reaction of NiO and Nb_2O_5 might be effective to eliminate the spheroidal second phase in BNN.

Fig. 10b shows that the second phases in BZN have two distinct shapes; one is a triangular board type and the other is a rectangular bar type. However, Table II indicates these have about the same composition, thus the difference in the appearance could be attributed

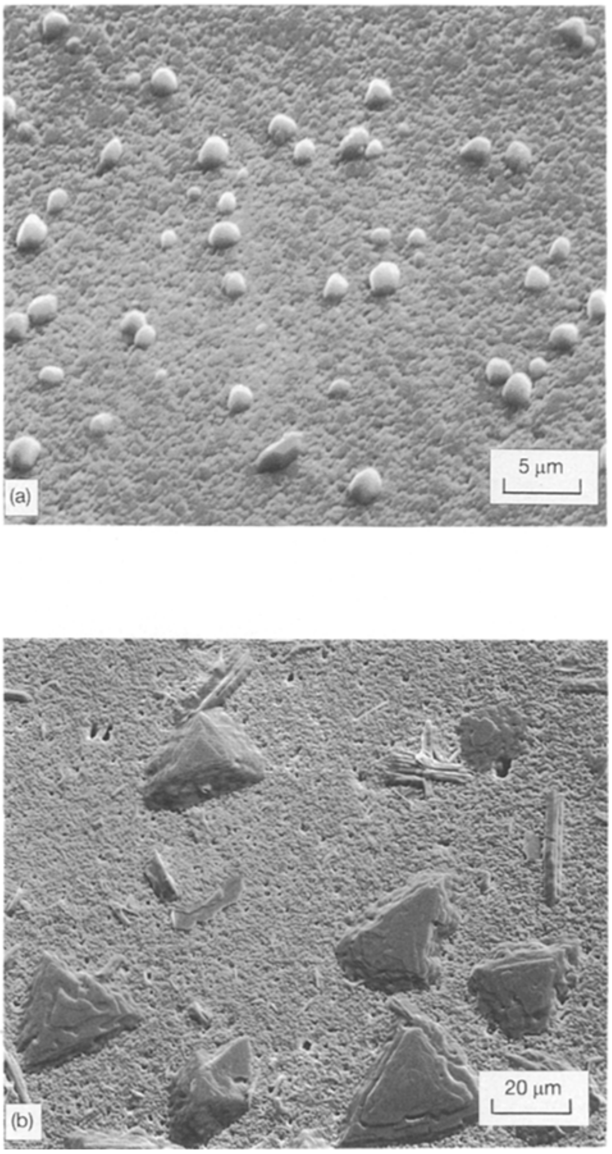

Figure 10 Scanning electron micrographs showing the second phases present in samples sintered after prefiring; (a) BNN sample sintered at 1400 °C for 2 h after prefiring at 1300 °C for 10 h, (b) BZN sample sintered at 1350 °C for 2 h after prefiring at 1250 °C for 10 h.

TABLE II Chemical compositions (at %) of second phases in BNN and BZN

Atom	BNN Spheroidal	BZN	
		Triangular	Rectangular
Ba	5.0	48.8	46.3
Nb	10.0	49.1	49.2
B′	85.0	2.1	4.5

to the sample sectioning. The second phases in BZN have a chemical composition of Ba:Nb = 1:1 with a small amount of zinc. This composition is very close to that of the liquid phase reported in the previous work [3]. BNN and BZN have the same crystal structure but have a different B′-site cation, nickel or zinc. The compositional difference in second phases might be ascribed to the volatility of ZnO [11].

The presence of second phases makes it difficult to investigate the order–disorder phase transition in BNN and BZN. The formation of liquid phase observed in our study implies that BNN and BZN are incongruently melted at higher temperatures. Because the composition of the liquid phase is niobium-rich the incongruent melting would result in an increase in non-stoichiometry and thus favour a disordering. This kind of order–disorder phase transition in complex perovskite compounds has not been reported previously. However, the presence of second phases enables us to identify whether the liquid phase is formed by chemical inhomogeneity (non-equilibrium state) or incongruent melting (equilibrium state). Therefore, a new approach, such as single-crystal growth, will be required to investigate the order–disorder phase transition in BNN and BZN.

4. Conclusions

1. By lattice parameter measurements, defects concentration in BNN and BZN was found to control ordered or disordered phase formation. The increase in non-stoichiometry brought about by the formation of liquid phases resulted in disordering.
2. The liquid phase formed by sintering at 1400 °C for BNN and 1350 °C for BZN was not in an equilibrium state. The defects concentration in samples sintered at these temperatures was decreased by a prolonged sintering, resulting in ordering. This was attributed to the increase in chemical homogeneity by rehomogenization.
3. An extensive heat treatment in the temperature where no liquid phase has been found increased the temperature of liquid-phase formation. The extensive heat treatment is postulated to increase the chemical homogeneity of samples.
4. Irrespective of the extensive heat treatment, second phases were hardly eliminated. The second phase in BNN was NiO aggregates with small amounts of barium and niobium. The second phase in BZN was an inter-compound between BaO and Nb_2O_5 (Ba:Nb = 1:1) with a small amount of zinc.

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