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Crystallization Behavior of PZN–PFN Powders from Nitrate Solutions

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Abstract

A series of x*Pb*$(Zn_{1/3}Nb_{2/3})O_3\cdot(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3$ *powders were chemically prepared from nitrate solutions by hydrolysis with diethylamine as the precipitation reagent. The as-dried powders were amorphous and consisted of fine particles. The chemical composition of the as-dried powders was homogeneous so that the perovskite and pyrochlore phases were directly crystallized from the amorphous powders at 450~600°C. The amount of the perovskite phase increased with increasing temperature and decreasing* x *value. For the* $x \leqq 0{\cdot}4$ *powders, the perovskite phase was dominant and stable below 600°C, while for the* $x \geqq 0{\cdot}5$ *powders, the pyrochlore phase was dominant and stable. Above 600°C, both phases were formed by some solid-state reactions. The thermodynamical relevance of the stability of the perovskite phase to temperature and composition is discussed. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Single crystals of $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) with the perovskite structure can be synthesized by the PbO flux method and exhibit an unusually high dielectric constant, a high resistivity and a high Curie temperature. It is difficult, however, to prepare PZN powders by a conventional solid-state reaction from the mixed oxides. Matsuo[1] reported the full development of the PZN perovskite phase by heating the mixed oxides to 900°C under a high pressure of 2·5 GPa. The perovskite structure in the PZN was, however, not stable. When reheated above 700°C at atmospheric pressure, the structure decomposed into a mixture of pyrochlore phase, PbO and ZnO, indicating that the structure is in a stable state only during the high pressure preparation procedure. The single crystal by a flux method was also decomposed above 600°C.[2] The stability of several ABO_3 compounds has been analyzed by considering the tolerance factor and electronegativity difference between cations and anions which describe the degree of ionic character of the bonds.[3] Wakiya *et al.*[4] considered that both the steric hindrance of the lone pair of Pb in the perovskite lattice and the mutual interactions between the lone pair and Zn with a small electronegativity difference from oxygen inhibit the formation of the stable perovskite PZN.

$Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) powders with a single perovskite phase have been prepared by the columbite method.[5] Yoshikawa and Uchino[6] reported that perovskite PFN powders are rather easily prepared by a chemical method from nitrate solutions and that trivalent Fe^{3+} cations can construct a more ionic perovskite structure compared to a covalent pyrochlore structure. One would expect similar stabilizing effect of Fe^{3+} cations on the perovskite structure in the PZN–PFN binary system. In general, phase stabilities are determined by thermodynamic parameters—temperature, composition and pressure. It is interesting to investigate some specified combinations of temperature and composition to stabilize the perovskite structure for practical use and determine whether the perovskite compounds are thermodynamically stable.

The present work was undertaken to prepare homogeneous powders in order to avoid the effects of kinetic factors on the formation of the perovskite phase. A series of xPZN·$(1-x)$PFN powders were prepared from mixed nitrate solutions by a precipitation method.

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2 Experimental

2.1 Preparation of niobium precursor solutions and xPZN·(1−x)PFN powders

Oxalate-free niobium precursor solutions were prepared from aqueous niobium oxalate solutions by hydrolysis with ammonia water. The resulting hydrated niobia was dissolved in a nitric acid solution with hydrogen peroxide. Niobium exists as peroxo-complex ions in the precursor solutions. Details of the preparation method were described in a previous paper.[6]

Clear precursor solutions of 0·047 M xPZN·(1−x) PFN (x = 0·0 to 1·0) with Pb^{2+}, Zn^{2+}, Fe^{3+} and peroxo-Nb complex ions were prepared by mixing the niobium precursor solutions with the corresponding nitrates for subsequent precipitation and hydrolysed by diethylamine (DEA) being poured into 1000 ml of the PZFN precursor solution. All the components were successfully precipitated from the PZFN precursor solutions by maintaining the final pH value above 10·5. The precipitates were washed with 500 ml of water and then dried at 80°C for 12 h.

To confirm the precipitation of all the elements from the mixed nitrate solutions, the as-dried powders were quantitatively analyzed by inductively coupled plasma atomic emission spectroscopy. Fifty mg of the as-dried powders with x = 0 and x = 1 were dissolved in a hydrofluoric acid–nitric acid mixture that was diluted to 5000 ml and then analyzed.

2.2 Characterization

The as-dried powders were investigated by thermogravimetric analysis and differential thermal analysis (TGA-DTA): 80 mg of the as-dried powders were placed in a platinum holder and measured at a heating rate of 10°C min^{-1} in air with alumina powders as the reference. For calcination, an electric furnace was allowed to equilibrate at the desired calcining temperature. One gram samples of the as-dried powders were heated in the furnace for 1 h. The calcined powders were then characterized by X-ray diffraction (XRD) (CuK_α radiation). The relative intensities of the (110) perovskite peak and the (222) pyrochlore peak were measured. The percentage of the perovskite phase was calculated using the following equation:

$$\% \text{ perovskite} = \text{Ipero}/(\text{Ipero} + \text{Ipero}) \times 100$$

3 Results and Discussion

XRD analysis revealed that the yellow precipitates obtained from the PZFN precursor solutions were all amorphous. SEM observations showed that these powders do not have a well-developed grain morphology and consisted of agglomerates of small particles ranging in diameter from 30 to 40 nm. Specific surface areas determined by the BET method were 137, 134, 91, 66, and 52 $m^2\ g^{-1}$ for the powders with x = 0, 0·25, 0·50, 0·75, and 1·0, respectively. The surface areas decreased with increasing x values. This is consistent with the SEM observations. Larger values of the specific surface areas in iron-rich compositions are attributed to the ultrafine hydrate iron oxide precipitates. The hydrogen peroxide involved in the precursor solution oxidizes the iron hydroxide precipitated from the mixed solution during hydrolysis. This oxidation partially substitutes the hydroxide groups with peroxo groups in the iron hydroxide and prevents the iron hydroxide from agglomerating between hydroxide groups.[7] Table 1 shows the chemical analysis data. These as-dried powders have good compositional homogeneity close to the stoichiometry of $Pb(Zn_{1/3}Nb_{2/3})O_3$ or $Pb(Fe_{1/2}Nbi_{1/2})O_3$.

Figure 1(A) shows the TGA-DTA curves for the powder with x = 0·20. The TGA shows a 9 ∼ 10% weight loss below 500°C due to the physical desorption of water, exothermic pyrolysis of the DEA organics trapped inside powders and dehydration of the hydrated precipitates with endothermic effects on the DTA curves. A sharp exothermic peak was observed at ∼ 460°C on the DTA curve. Similar exothermic peaks were observed on DTA curves for all the other powders. An XRD analysis was performed on the powders heated in the TGA-DTA apparatus before and after the exothermic peak temperature. The XRD pattern before the peak temperature shows only a broad peak around $2\,\theta = 29°$, while both the pyrochlore and perovskite phases were detected for the powders quenched from 550°C to room temperature [Fig. 1(B)]. Thus, the exothermic effects essentially determine the heat of crystallization of the pyrochlore and perovskite phases from the amorphous powders because a weight loss did not occur in the relevant temperature range. The percentages of the perovskite phase crystallized at 50°C are given in Table 2. These percentages decrease with increasing x values and decrease abruptly at x = 0·5.

To investigate these crystallization behaviors in detail, the as-dried powders with x = 0·4 and x = 0·5 were calcined from 400 to 600°C for 30 min and 1 h in the electric furnace and then the XRD intensities of the peaks of the perovskite and pyrochlore phases were measured (Fig. 2). For the powder with x = 0·4 [Fig. 2(A)], the intensities of the crystallized perovskite were increased with increasing temperature, while the intensities of the simultaneously crystallized pyrochlore were small and did not increase with increasing temperature. In the figure the differences in the amount of crystallized perovskite between 30 min and 1 h are observed below 475 and above 600°C. This is because dehydration of the hydrates and/or hydroxides in the powder was not finished for 30 min below 475°C; above 600°C, some solid-state reactions may start instead of the crystallization. For the powders with $x=0{\cdot}50$ [Fig. 2(B)], the perovskite intensities decreased between 450°C and 575°C, while pyrochlore increased. These decreases in the crystallized perovskite mean that the perovskite phase is thermodynamically metastable in the crystallization temperature range (from 450 to 575°C), so the temporarily crystallized perovskite rapidly converts to the more stable pyrochlore phase. Above 575°C, the perovskite intensities began to increase by some solid-state reactions. That is, above the temperature, the perovskite phase becomes thermodynamically stable.

Table 1. Chemical analysis of as-dried powders (normalized molar ratio)

Element	*PZN*		*PFN*	
	Formula	*Measured*	*Formula*	*Measured*
Pb	1·00	1·00	1·00	1·00
Zn	0·33	0·34 ± 0·01	—	—
Fe	—	—	0·50	0·51 ± 0·01
Nb	0·67	0·67 ± 0·01	0·50	0·52 ± 0·02

Table 2 shows the percentage of perovskite in the as-dried powders calcined at 700 and 800°C. It is a function of temperature and strongly dependent upon composition. For the powders with $x=0\sim0{\cdot}65$, raising the calcination temperatures promotes perovskite formation. A certain increase in the percentage perovskite for the $x=0{\cdot}65$ powder with increasing temperature suggests that the perovskite phase is thermodynamically stable above 700°C. The formation of the perovskite and pyrochlore phases above the crystallization temperature range will be controlled by the solid-state reactions and the rate of the solid-state reactions may be extremely slow in comparison with the rate of crystallization.

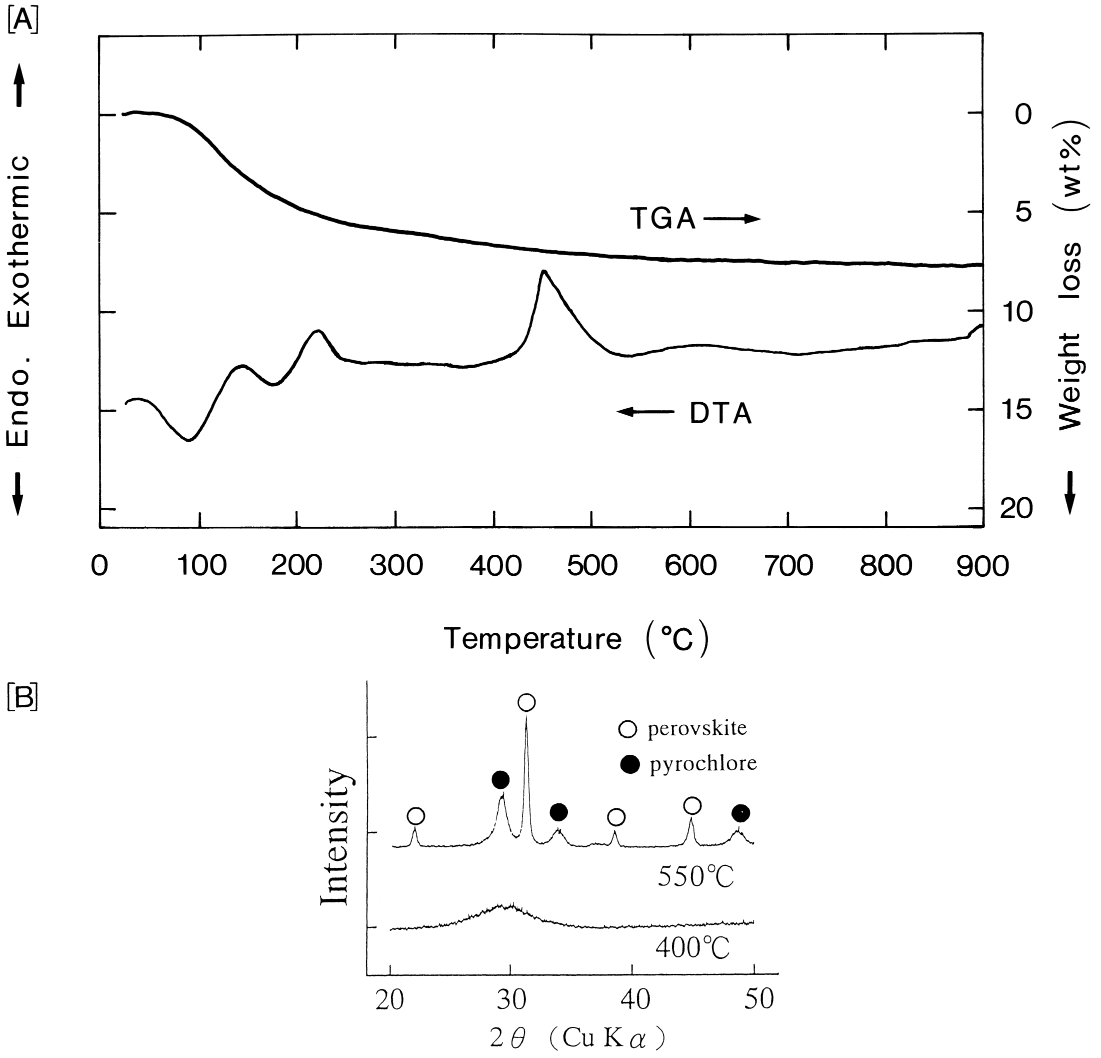

Fig. 1. TGA-DTA curves and XRD patterns of powders with $x=0{\cdot}2$.

Figure 3 shows the schematic free energy-temperature relations among perovskite, pyrochlore plus corresponding oxides, and amorphous powders in order to explain the behavior of the formation of the perovskite phase. For the powders with $x \leqq 0{\cdot}40$ [Fig. 3(A)], the energy level of the perovskite is assumed to be lower than the total energy of the pyrochlore phase plus the corresponding oxides above 450°C. When components of the oxides in the amorphous powder activated upon heating to ~450°C by losing the hydroxide group inhibiting their movement, they will mainly form a stable perovskite phase by the crystallization as observed experimentally at TG-DTA data. Simultaneously, a small amount of crystallized pyrochlore was experimentally observed. There was probably a chemical inhomogeneous local part in the powder, where the formation of the metastable pyrochlore phase is favored. In general, the nucleation rate is governed by the net driving force $(\Delta Gc + \Delta Gb + \Delta Gs)$, where ΔGc is the change of chemical free energy representing the driving force for the bulk transformation, ΔGb is the surface energy of nuclei generated, and ΔGs is the elastic energy associated with the molar volume change.[8] If $(\Delta Gb + \Delta Gs)$ of the metastable phase is smaller than that of the stable phase, the nucleation rate of the metastable phase can be larger than that of the stable phase. ΔGb and ΔGs are related to the kinetic factors—the mobility of ions, the number of nucleation sites, chemical homogeneity, surface tension, etc. Unfortunately, the lack of the requisite information on these phases prevents quantification of these effects. However, if the pyrochlore phase is metastable, raising the calcination temperatures should not promote pyrochlore crystallization, as shown in Fig. 3(A).

As the x values increase, the Zn contents in the perovskite will increase. The free energy level of the perovskite phase increases and the cross point in the Fig. 3(A) shifts to higher temperature. For the powders with $x \geqq 0{\cdot}50$ [Fig. 3(B)], the perovskite phase becomes metastable at the crystallization temperature. When the chemical composition of the as-dried powders is homogeneous, however, it is favored for the nucleation of perovskite rather than that of the pyrochlore. Therefore, certain amounts of the metastable perovskite phase may

Table 2. Percentages of perovskite phase for xPZN·$(1-x)$PFN powders

DTA	*Calcination temperature*		
x	*550°C*	*700°C*	*800°C*
0·00	87	93	98
0·25	80	84	96
0·40	77	80	89
0·50	28	53	71
0·65	25	40	50
0·75	21	24	25
0·85	0	1	1
0·90	0	0	1
0·92	0	0	1
0·95	0	0	0
1·00	0	0	0

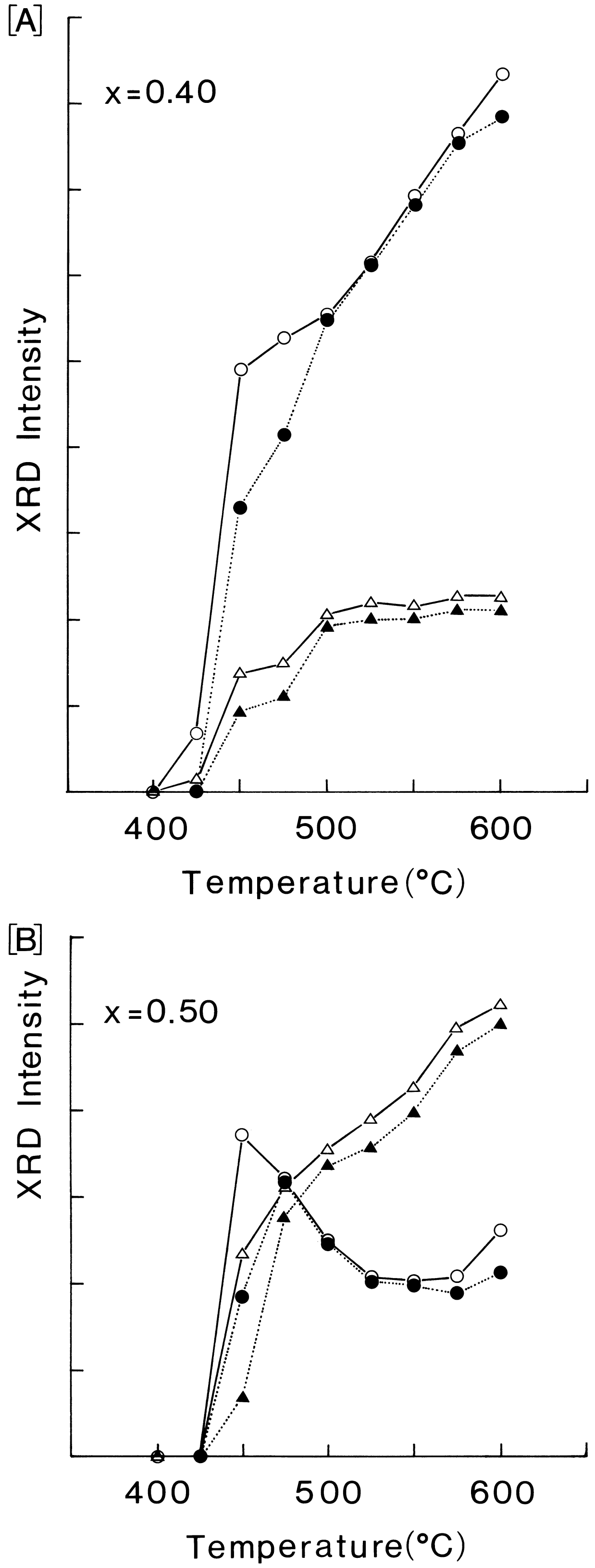

Fig. 2. XRD intensities of calcined powders: ●, perovskite (30 min.); ○, perovskite (1 h); ▲, pyrochlore (30 min.); △, pyrochlore (1 h).

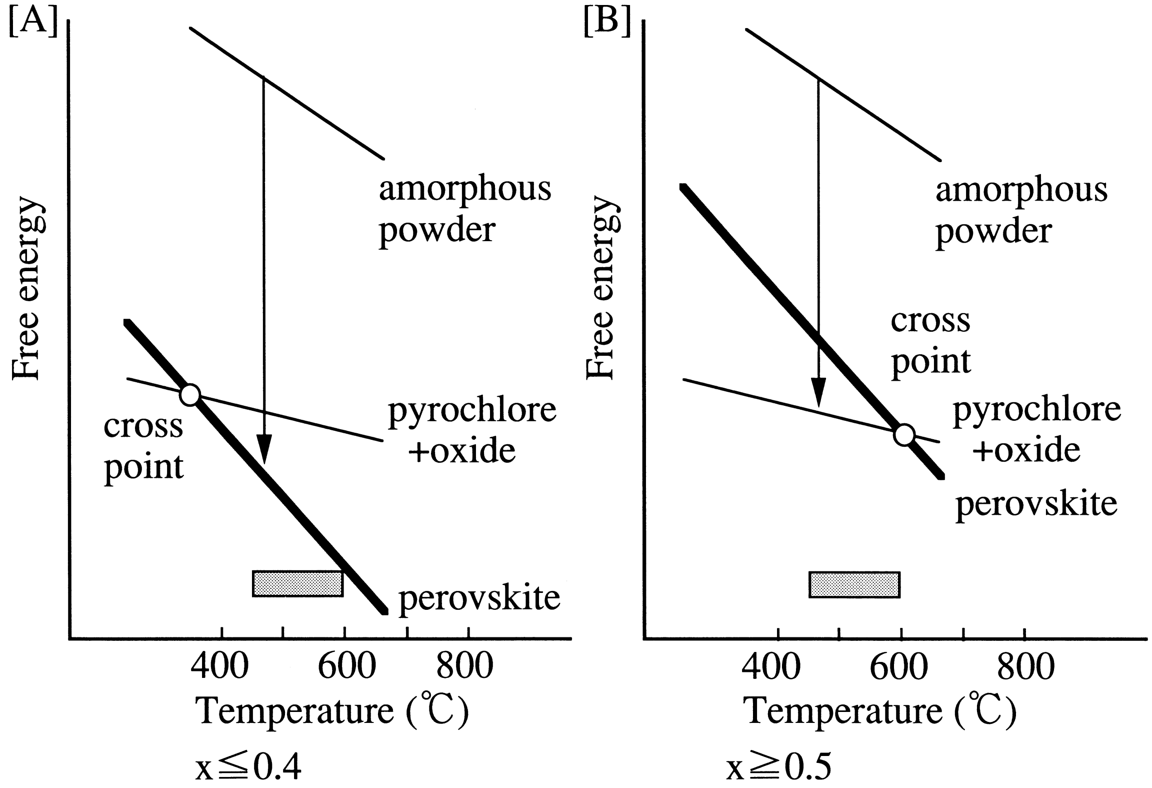

Fig. 3. Schematic representation of free energy–temperature relations among crystals and powder of the same composition.

be temporarily crystallized. These kinetic effects on the formation of the metastable phase, however, will be lowered by raising the calcination temperatures. Indeed, the stability of perovskite phase decreased from 475 to 550°C by reduction of the metastable crystallization or by decomposition of the temporarily crystallized perovskite as shown in Fig. 2(B). For the powders with $x = 0{\cdot}5$, the cross point is probably at ~575°C because the amount of perovskite begins to increase at 575°C.

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