A New Pyrochlore System, $Pb(Ti_x \cdot Sn_{1-x})O_3$, and Its Transition to a Perovskite System

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A series of pyrochlore compounds of $Pb(Ti_x \cdot Sn_{1-x})O_3$, was aqueously prepared. They were characterized in terms of inhomogeneously distributed Ti and Sn ions in the equivalent lattice positions. In the composition range where the value x was between 0.00 and 0.45, monophasic pyrochlore was crystallized. In the composition range of $x \gtrsim 0.45$, however, the pyrochlore phase more or less coexisted with a noncrystalline substance whose composition was supposed to be Pb/(Ti+Sn) mole ratio <1.0. The process of thermal transition from the pyrochlore-type $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$ to the perovskite-type system was traced by two lines of measurements of the pyrochlore, *i.e.*, the lattice constant and the degree of fluctuation of interplanar spacings, and by measurements of the tetragonal lattice strain of the resultant perovskite. The results showed that the transition occurred preferentially at Ti-rich microregions in the matrix lattice, in which a measurable fluctuation of the Sn: Ti ratio was detected.

The pyrochlore family, like the perovskite group, draw our attention in view of its ferroelectricity and/or high permittivity. The ferroelectric properties of cadmium pyroniobate, $Cd_2Nb_2O_7$, were discovered some time ago.[1] Recently it has been reported that the anion-deficient pyrochlore $Bi_2Zn_{4/3}Ta_{2/3}O_6$ is ferroelectric below 570 °C,[2] and unusual dielectric properties have been found at low temperatures for the Pb_2BiNbO_6 pyrochlore.[3] On the other hand, numerous studies have been successful in preparing $A^{2+}B^{4+}O_3$ perovskites (A: Ba, Pb, Sr, Cd, and Ca; B: Ti, Zr, Sn, and Hf). Among them, however, no attempts to prepare any single phases with a composition of $PbSnO_3$ have yet been successful under an atmospheric pressure. In the present study, two new pyrochlore compounds, $PbSnO_3$ and $Pb(Ti_x \cdot Sn_{1-x})O_3$ were aqueously prepared with a strong expectation as to their ferroelectricity. The present interest was directed to the thermal transition from the solid-solution-type pyrochlore into the perovskite. The degree of the inhomogeneous distribution of Ti and Sn ions in the equivalent lattice positions of the pyrochlore during the transition was estimated; it could be a useful parameter for the analysis of the transition characteristics.

Experimental

Materials. $Pb(CH_3CO_2)_2 \cdot 3H_2O$ was dissolved into a 5 M NaOH solution, and then this solution was neutralized by means of a 3 M HNO_3 solution. A mixed solution of $TiCl_4$ and $SnCl_4$ with a desired mole ratio was added to the neutralized solution to obtain a white precipitate. After this mixture has stood for a while, a light yellow precipitate appeared. This precipitate was repeatedly washed with water to remove any adsorbed Na^+ and Pb^{2+} and was then oven-dried at 130 °C for 1 day. Experiments were repeated by varying the mole ratio of $TiCl_4/SnCl_4$; more than 30 types of materials were thus obtained.

Chemical Analyses. Chemical analyses for Pb and Na were undertaken for one specimen of $x=0.4$ as-dried, which was readily soluble in a dilute HCl solution. In the determination of its composition on the basis of the chemical analysis data, therefore, the presence of its adsorbed water was taken into account. The Na content in the specimen solution was analyzed using a frame photometer (type EP-3, Shimadzu Co.). The drop-by-drop addition of a 0.3 M solution of cupron (α-benzoinoxime) to the specimen solution led to the quantitative formation of a pale-yellow mixed precipitate of cupron-Ti and cupron-Sn, leaving the cupron-Pb complex solution behind. The resultant precipitate was filtered and washed with diluted acid until all the adsorbed cupron-Pb complex had been removed. The collected solution of the cupron-Pb complex was then titrated with a standard EDTA solution in order to determine the Pb content. The water content in the dried specimen was determined from the weight loss up 650 °C.

Determination of a, (c/a)-1, and Δd/d. X-Ray diffraction patterns were obtained at room temperature using a JEOL diffractometer (Nihondenshi Co.) with CuKα radiation in order to determine the lattice constant of pyrochlores and the tetragonal lattice strain, (c/a)-1, of perovskites transformed from a pyrochlore. The lattice constants of the pyrochlores were calculated for typical specimens using 8 of the well-resolved diffraction lines. The result indicated that the estimated accuracy of the lattice constant was ±0.01 Å (see Tables 2 and 3). The lattice constant for other materials was conveniently calculated using the {622} reflection. The tetragonal strain of the perovskites was determined using the {111} and (002) diffraction lines. Further experiments were designed to determine whether each composition of solid-solution-type pyrochlores was microscopically uniform. For this purpose, the magnitude of the fluctuation of the interplanar spacings, $\Delta d/d$, was calculated by observing the reflection angle, θ, and the pure diffraction line broadening, β, relative to a silicon standard according to the $\Delta d/d=\beta\cos\theta/\sin\theta$ equation; for the determination of this, 4 of the well-resolved reflection, {222}, {400}, {440}, and {622}, were chosen. The crystallite size, r, was determined simultaneously using the Walker equation: $\beta=0.9/r \cdot \cos\theta$, with $\beta\cos\theta$ extrapolated to $\sin\theta=0$.

Determination of Degree of Transition. A quantitative determination of the relative amounts of the pyrochlore- and perovskite-phases was made by X-ray diffraction. The perovskite {111} and pyrochlore {222} reflections were used, and their integrated intensity ratio was planimetrically determined. This was compared with the corresponding ratios for a series of pyrochlore-perovskite mixtures.

Thermogravimetry. TG was undertaken at a temperature elevation speed of about 10 °C under the sensitivities of 50 mg/full-scale (Chō Keiryoki Co.) and of 2 mg/full-scale (Rigaku Denki Co.).

Infrared Absorption. The infrared absorption in the wave number range of 1500—4000 cm^{-1} is a way to directly observing the presence of OH^- and H_2O in specimens. A spectrometer (type EPI–S_2, Hitachi Co.) was used to record the spectra of KBr plus specimen disks which were formed after a prolonged evacuation at room temperature to eliminate water adsorbed on KBr and specimen powders.

Results and Discussion

The X-ray diffraction indicated that no crystalline phases other than the pyrochlore one were found in any of the specimens prepared by varying the Ti/(Ti+Sn) mole ratio, x, in the starting mixed solution. TG of all the dried specimens under the sensitivity of 50 mg/full-scale revealed that the majority of dehydration was completed up to about 300 °C, thereafter, no considerable weight changes occurred up to about 1000 °C, at which the temperature volatilization of PbO started (Fig. 1). The DTA profiles of the dried specimens of $x \lesssim 0.45$ gave only heat absorption due to the removal of water, whereas those of $x \gtrsim 0.45$ showed, besides the heat absorption, an exothermic peak at about 550 °C, in which its intensity increased with an increase in the value of x. The latter fact was in harmony with the fact that the intensity of the background of X-ray diffraction also increased with an increase in the value of x. These facts strongly suggest that each specimen of $x \gtrsim 0.45$ more or less involves noncrystalline material, and that its exothermic peak of interest is due to its crystallization to perovskite and/or pyrochlore. Our previous reports[4–7] indicated that in the present manner of aqueous synthesis under the condition of $x=1.0$, "pure" noncrystalline material with a composition of $Pb_{1-y}TiO_{3-y}$ ($y \lesssim 0.3$) resulted, and that this crystallized to the perovskite at about 550 °C. It is thus believed that the compositions of noncrystalline materials coexisting with the pyrochlores are all Pb/(Ti+Sn) mole ratio <1.0. No further discussion will be undertaken of the specimens of $x \gtrsim 0.45$ in the present study.

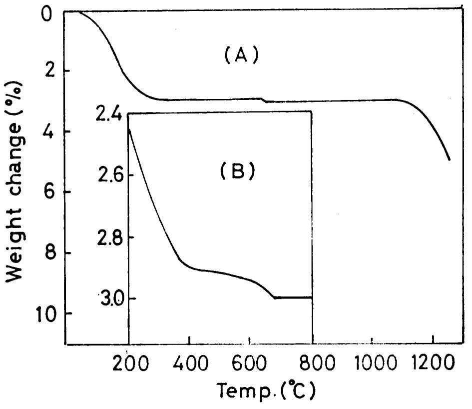

Fig. 1. Thermogravimetric trace of pyrochlore $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$ under the sensitivities of 50 mg/full-scale (A) and 2 mg/full-scale (B).

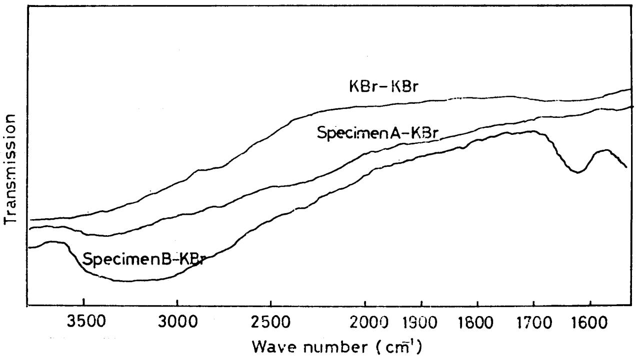

Fig. 2. Infrared absorption spectra of specimens A and B which were obtained by firing pyrochlore $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$ at 800 and 550 °C.

The foregoing results allow us to regard the materials of $x \lesssim 0.45$ as roughly monophasic, even if a very small amount of a noncrystalline substance coexists. The results of chemical analyses for the material of $x=0.4$ as a typical example gave $Pb_{1.05}(Ti_{0.4} \cdot Sn_{0.6})O_3$ as its composition; no measurable content of Na was detected. Thus, its $Pb/(Ti_{0.4}+Sn_{0.6})$ and hence $Pb/(Ti_x+Sn_{1-x})$ mole ratio in general may be taken to be unity within the limits of experimental error. Here we may need to further examine the possibility of the $Pb_2(Ti_{0.4} \cdot Sn_{0.6})_2(O,OH)_7$ composition besides $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$, since the two compositions may both lie within the accuracy of chemical analyses. Fortunately, as will be described later, the pyrochlore of $x=0.4$ was transformed to monophasic perovskite at elevated temperatures. Therefore, a composition of $Pb^{2+}(Ti_{0.4} \cdot Sn_{0.6})_2$-$[O_5 \cdot (OH)_2]$ where the electroneutrality is maintained would be an accepted possibility, since only this composition can be transformed to the $Pb^{2+}(Ti_{0.4} \cdot Sn_{0.6})_2O_6$ by losing one molecule of water from the pyrochlore composition. A close examination was, therefore, done of the weight change at elevated temperatures using a microthermobalance. The results for a thermogravimetric trace of the specimen under the senstivity of 2 mg/full-scale is shown in Fig. 1; a slight weight change occurs over the temperature range from 300 to 620 °C. To ascertain the constituent species which causes the weight change, the infrared absorption spectra of two specimens of $x=0.4$ fired at 800 °C (Specimen A) and 550 °C (Specimen B) were recorded, (Fig. 2). For Specimen B, two kinds of absorptions, in the vicinity of 3400 cm^{-1} due to the stretching vibration mode of OH^{-1} and in the vicinity of 1600 cm^{-1} due to its bending vibration mode, are obvious. For Specimen A, whose relative mole ratio of perovskite/pyrochlore was 0.50, no absorption was detected over the wavelength range of interest. However, it should be stressed that the percent weight change in the temperature range of 300—620 °C (≈0.1 wt%) was far less than the calculated H_2O percentage in $Pb_2(Ti_{0.4} \cdot Sn_{0.6})_2[O_5 \cdot (OH)_2]$ (=2.54 wt%). This fact shows the possible existence of pyrochlore with a composition of $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$ over a temperature range of at least 300—600 °C; the very small amounts of OH^- detected by the infrared absorption technique may arise from either zeolitic water or strongly-absorbed water present. Remarks will be necessary, for dehydration occurred up to ≈300 °C. The lattice constants of two specimens of $x=0.4$ before and after the dehydration were equal within the limits of experimental error. This fact gives negative evidence for the occurrence of pyrochlore with a composition of $Pb_2(Ti_{0.4} \cdot Sn_{0.6})_2[O_5(OH)_2]$.

Recently a number of the anion-deficient pyrochlores,

TABLE 1. COMPOSITIONS AND PHASES OF MATERIALS AT 300 AND 900°C
Compositions are indicated without taking the presence of "water" into consideration

$x=\frac{\mathrm{Ti}}{\mathrm{Ti+Sn}}$ (Mole fraction)	Phases present	
	Specimen fired at 300 °C	Specimen fired at 900 °C
$x<0.35$	Pyro.—$Pb(Ti_x \cdot Sn_{1-x})O_3$	$Pb_2SnO_4+SnO_2$ +Pero.—$Pb(Ti_{x'} \cdot Sn_{1-x'})O_3$
$0.35 \lesssim x < 0.45$	Pyro.—$Pb(Ti_x \cdot Sn_{1-x})O_3$	Pero.—$Pb(Ti_x \cdot Sn_{1-x})O_3$
$0.45 \lesssim x < 0.85$	Pyro.—$Pb(Ti_{x'} \cdot Sn_{1-x'})O_3$ +Noncryst.—$Pb_{1-y}(Ti_{x''} \cdot Sn_{1-x''})O_{3-y}$	Pero.—$Pb(Ti_{x'} \cdot Sn_{1-x'})O_3$ +Pero.—$Pb_{1-y}(Ti_{x''} \cdot Sn_{1-x''})O_{3-y}$
$x \gtrsim 0.85$	Noncryst.—$Pb_{1-y}(Ti_x \cdot Sn_{1-x})O_{3-y}$	Pero.—$Pb_{1-y}(Ti_x \cdot Sn_{1-x})O_{3-y}$

such as Pb_2BiNbO_6,[8] and $Bi_3A_2^{2+}TaO_9$, where A=Mg, Zn, and Ca,[8] and $Pb_2Cd_{1/2}Mn_{1/2}TaO_6$[8] and Pb_2Sb^{3+}-$B^{5+}O_6$, where B=Nb and Ta,[8] have been reported. In view of the fact that many of these pyrochlores involve Pb, the existence of the oxygen-deficient pyrochlore system $Pb(Ti_x \cdot Sn_{1-x})O_3$ in the present study may be accepted. The $Pb(Ti_x \cdot Sn_{1-x})O_3$ composition in general indicates that the structure is oxygen-deficient with respect to a standard type of pyrochlore, $A_2B_2O_7$, where lattice positions available are fully occupied. In the standard pyrochlore structure, the configuration of the BO_6 octahedral is complicated, the O–B–O chains lying on a zig-zag line along the <110> direction. In this structure the seventh set of oxygen are not essential to the stability of the structure. Therefore, the number of oxygen ions in the $A_2B_2O_7$ pyrochlore may be reduced to 6. Our pyrochlores can also be such a case.

In summary, the compositions and phases of materials prepared aqueously and then fired at 300 °C are summarized in Table 1 in relation to the mole ratio, x. The X-ray diffraction data of $PbSnO_3$ and $Pb(Ti_{0.45} \cdot Sn_{0.55})O_3$, both fired at 300 °C, are listed in Table 2. It may be seen from the table that they have cubic symmetry, for which more strict proof will be presented later. Figure 3 shows the lattice constant, a, as a function of the x value. No anomaly is found in the plot. The materials precipitated aqueously and then dried were heat-treated at elevated temperatures, and then quenched in air down to room temperature. The results of phase analyses for the materials fired at 900 °C are shown in the third column in Table 1. The pyrochlore of x=0.0, *i.e.*, $PbSnO_3$, decomposed into Pb_2SnO_4 and SnO_2 at about 800 °C. This fact indicates that if a solid-solid reaction between PbO and SnO_2 could occur in the vicinity of 800 °C, there can be no single stable phases of the $PbSnO_3$ composition. On the other hand, restricted monophasic pyrochlores of $0.35 \lesssim x \lesssim 0.45$ were transformed into monophasic perovskites, the starting temperature being about 600 °C.

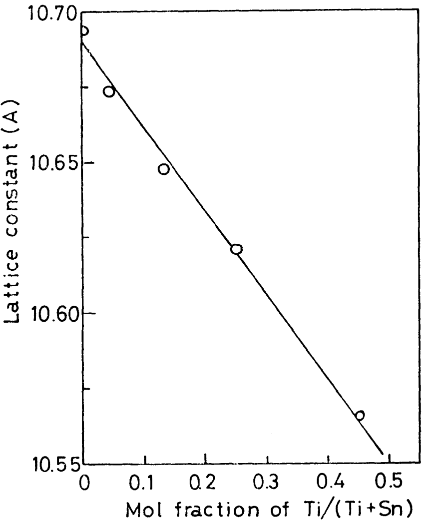

Fig. 3. Lattice constant as a function of x in pyrochlore $Pb(Ti_x \cdot Sn_{1-x})O_3$.

TABLE 2. X-RAY DIFFRACTION DATA OF PYROCHLORES $PbSnO_3$ AND $Pb(Ti_{0.45} \cdot Sn_{0.55})O_3$ FIRED AT 300°C

$PbSnO_3$			
d(Å)	I/I(%)	hkl	a(Å)
3.083	100	222	10.680
2.671	42	400	10.684
2.459	10	331	10.706
1.889	51	440	10.686
1.612	50	622	10.693
1.541	18	444	10.681
1.220	17	662	10.679
1.195	17	840	10.688
			Av. 10.682±0.013

$Pb(Ti_{0.45} \cdot Sn_{0.55})O_3$			
d(Å)	I/I(%)	hkl	a(Å)
3.056	100	222	10.565
2.639	40	400	10.556
2.427	10	331	10.579
1.860	40	440	10.573
1.590	35	622	10.573
1.525	10	444	10.566
1.213	10	662	10.574
1.182	10	840	10.572
			Av. 10.570±0.012

The $Pb(Ti_{0.4} \cdot Sn_{0.6})O_3$ composition was chosen to study the transition characterisitics of a solid-solution-type pyrochlore. The material was fired at a series of temperatures in order to measure the lattice constant of the pyrochlore phase. Table 3 gives the lattice constants of the pyrochlores fired at 720 and 870 °C, at which temperatures the extents of the transition were about 50 and 90% respectively. The pyrochlore phase held cubic symmetry during the transition. It is noticeable that the lattice constant, a, varies continuously during the transition. (Fig. 4). To ascertain the cause of such "anomalous" transition characteristics,

Table 3. X-Ray diffraction data of materials of pyrochlore-type obtained by firing pyrochlore $Pb(Ti_{0.4}\cdot Sn_{0.6})O_3$ at 720 and 870 °C

Material fired at 720 °C		Material fired at 870 °C	
hkl	*a*(Å)	*khl*	*a*(Å)
222	10.613	222	10.677
400	10.610	400	10.676
331	10.614	331	10.677
440	10.613	440	10.675
622	10.615	622	10.675
444	10.617	444	10.677
662	10.614	662	10.676
840	10.614	840	10.677
Av. 10.614±0.004		Av. 10.676±0.001	

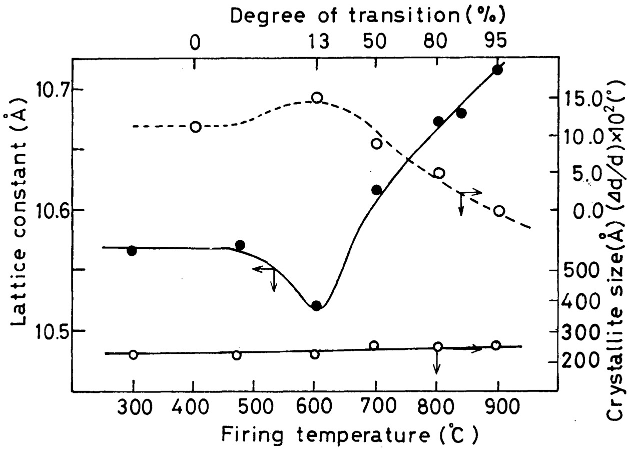

Fig. 4. Variations of $\Delta d/d$ and *a* of materials of pyrochlore-type obtained by firing pyrochlore $Pb(Ti_{0.4}\cdot Sn_{0.6})O_3$, with firing temperature.

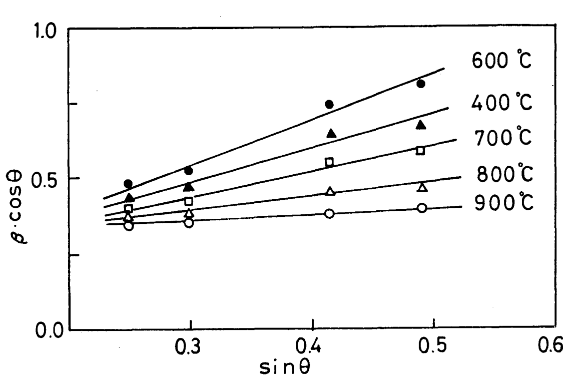

Fig. 5. Plots of $\beta\cos\theta$ vs. $\sin\theta$ of materials of pyrochlore-type obtained during transition from pyrochloro Pb-$Ti_{0.4}\cdot Sn_{0.6})O_3$ into perovskite one.

the magnitude of the fluctuation of the interplanar spacings and crystallite size of pyrochlores were determined. Figure 5 shows the plots of $\beta\cos\theta$ *vs.* $\sin\theta$ for the pyrochlores. The linearity of the plots is fairly good; the slopes give the $\Delta d/d$ value. Care must be taken that no diffraction line broadening due to crystallite size reduction contributes to the $\Delta d/d$ value. The $\Delta d/d$ value and the crystallite size are shown together in Fig. 4 as a function of the firing temperature. The $\Delta d/d$ value decreases continuously with the progress of the transition after a slight increase at an early stage of the transition. It should be noted that the $\Delta d/d$ value of the pyrochlore at the final stage of the transition is nearly zero, mainly because its diffraction lines are very sharp. Therefore, the interpretation of the pyrochlore fired at 870 °C in terms of cubic symmetry (Table 3) is valid. Accordingly, one might expect that all the pyrochlores treated in the present study have an exactly cubic symmetry even if their diffraction lines were unsharp in some cases.

It is very important to note that a decrease in $\Delta d/d$ follows an increase in *a* during the transition. There are two ways of interpreting the fluctuation of the interplanar spacings characteristic of the materials. One is based on the presence of an inhomogeneous strain, and the other, on its composition fluctuation. The literature[9,10] has indicated that the application of mechanical stress to polycrystalline solids causes an inhomogeneous strain. Throughout the formation process of the pyrochlores, however, there are not external environments enough for any residual stress or microstress to occur so as to create an inhomogeneous strain. One possibility to be considered is an internal stress stemming from a difference in the ionic radii of Ti^{4+} and Sn^{4+} ions. However such a stress, even if could be developed, may be quickly removed *via* free surfaces during the formation process of the materials. Therefore, it seems reasonable to give the interpretation in terms of composition fluctuation for $\Delta d/d$. A more rigorous proof for this will be described later. The majority of the composition fluctuation may occur as a result of the clustering of Sn ions in the B-positions of the $A_2B_2O_6$ pyrochlore in the formation process, by which an inhomogeneous distribution of Sn and Ti ions may result. The clustering tendency of Sn ions seems in harmony with the fact that an Sn-rich composition was apt to crystallize in a pyrochlore-type structure. The foregoing discussion suggests that a decrease in $\Delta d/d$ above 600 °C (see Fig. 4) occurs as a result of either Sn-rich or Ti-rich sides of the composition being missing. The accompanying increase in the lattice constant, *a*, above that temperature allows us to choose a preferential lack of a Ti-rich composition in the pyrochlore phase from among the two possibilities; a Sn-rich composition thus comes to predominate in the pyrochlore phase remaining. This feature of the two parameters, *a* and $\Delta d/d$, during the transition is also indicative of the validity of the interpretation based on composition fluctuation for $\Delta d/d$, because if the $\Delta d/d$ value is due to an inhomogeneous strain, its decrease has to proceed without varying the lattice constant. Here it is important to evaluate the actual range of the composition fluctuation of pyrochlores. The $\Delta d/d$ value was used with the data of Fig. 3 for this purpose. The composition range of, for example, $Pb(Ti_{0.4}\cdot Sn_{0.6})O_3$ fired at 300 °C was calculated as x=0.364—0.436 (average of x=0.4). In summary, it seems reasonable that the transition from the solid-solution-type pyrochlore to the perovskite occurs favorably in Ti-rich microregions. To confirm this line of thought definitely, it is useful to trace the tetragonal lattice strain, $(c/a)-1$, of the resultant

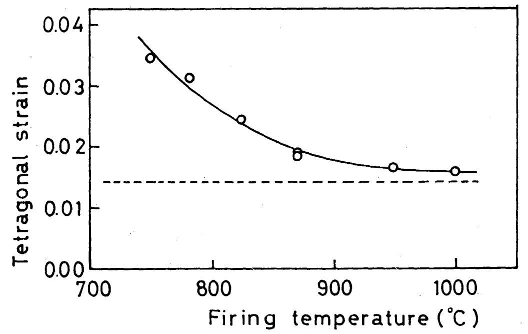

Fig. 6. Tetragonal lattice strain of materials of perovs kite-type obtained during transition from pyrochlore $Pb(Ti_{0.4}\cdot Sn_{0.6})O_3$ to perovskite one.

perovskite during the transition. Figure 6 shows the result; the dotted line shows the literature value[11] of the tetragonal strain of $Pb(Ti_{0.4}\cdot Sn_{0.6})O_3$ perovskite. As may be seen, the tetragonal strain of our perovskite lies in the vicinity of 0.04 at an early stage of the transition and then goes down to the literature value, 0.014, as the transition proceeds. This means that the composition of the resultant perovskite is Ti-richer at an early stage of the transition, thus fitting the foregoing interpretation of the transition characteristics of the solid-solution-type pyrochlore.

It is noticeable that a slight increase in $\Delta d/d$ occurs up to 600 °C, along with a slight decrease in the lattice constant, a (Fig. 4). A probable interpretation for this may be worked out by postulating that the as-dried solid solution contains a very small quantity of a noncrystalline material with a value of x slightly higher than that of the host. This line of thought may be supported by the fact that material with a high value of x is apt to become amorphous (Table 1). If this consideration is valid, and if its crystallization to pyrochlore proceeds near 500—600 °C, there can occur an increase in $\Delta d/d$ accompanying a decrease in the lattice constant, a, in the restricted temperature range of interest.

Some discussion may be needed regarding the displacement of the constituent ions, especially that of the Pb ions of the pyrochlore during the transition. Only when the displacement is "inhomogeneous", it can contribute to the $\Delta d/d$ value. Even if such a type of displacement could occur during the transition, however, the $\Delta d/d$ value has to go to a higher level than that before the transition without the lattice constant being varies. The results show in Fig. 4 and contrary to this requirement.

Further examinations were designed to trace the thermal-decomposition process of the monophasic pyrochlore $PbSnO_3$ by measurements along the same lines. These examinations may serve for checking whether the "anomalous" transition behavior is characteristic of the solid-solution-type pyrochlore. Figure 7 shows the two parameters, a and $\Delta d/d$, of the pyrochlore phase as a function of the firing temperature or of the extent of decomposition. No variations in the two are found up to at least 950 °C, at which temperature the extent of the decomposition reached about 63%; the $\Delta d/d$ value was zero before and throughout the transition, as had been expected. This fact can be taken as positive evidence for the foregoing way of understanding of the transition characterisitics of the solid-solution-type pyrochlore $Pb(Ti_x\cdot Sn_{1-x})O_3$ in general, and also as negative evidence for the occurrence of the displacement of the constituent ions of the pyrochlore during thetransition.

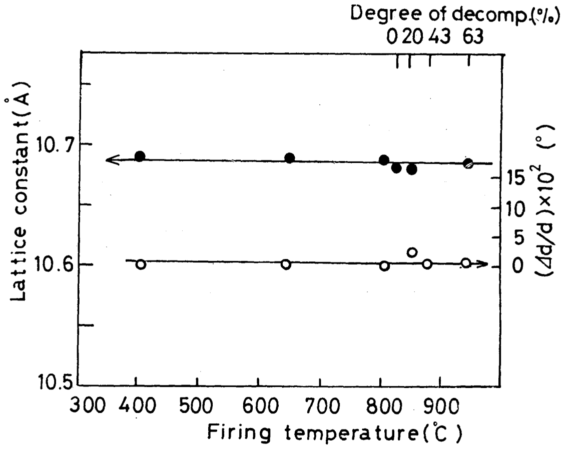

Fig. 7. Trace of $\Delta d/d$ and a of pyrochlore $PbSnO_3$ during thermal decomposition.

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