

Dielectric Classification and Addition of New Ferroelectric Members by Synthesis for Perovskite Titanate Family

Tetsuro Nakamura, Yue Jin Shan, Mayuko Miyata, Kazuhisa Kobashi*,
Yoshiyuki Inaguma* and Mitsuru Itoh*

Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University,
2753 Ishii-Cho, Utsunomiya 321-8585, Japan

*Materials and Structure Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta,
Midori, Yokohama 226-8503, Japan

(Received September 23, 1998)

For nonconducting perovskite titanates ATiO_3 and $\text{A}'_{1/2}\text{A}''_{1/2}\text{TiO}_3$, 5 ferroelectric members were discriminated from 17 quantum paraelectric members via average mass of A ions $m(\text{A})$: ferroelectric for $m(\text{A}) > 110$ a.u. and quantum paraelectric for $m(\text{A}) < 100$ a.u. An intuitive explanation of the origin of the discrimination is given concerned with the ferroelectric soft modes in perovskite ATiO_3 . Based on the above discrimination, trial synthesis of ferroelectric candidate substances are presented.

Key words : Perovskite titanate, Displacive-type ferroelectrics, Quantum paraelectrics, Ferroelectric criterion, Mass-inequality

I. Introduction

Perovskite titanates ATiO_3 and $\text{A}'_{1/2}\text{A}''_{1/2}\text{TiO}_3$ are characterized by the following common conditions.

- 1) The structure is composed of 3-dimensional oxygen sharings among the $[\text{TiO}_6]$ -octahedra, building up a $[\text{TiO}_3]_{\infty}$ -network, and the A ions occupy its cuboctahedral spaces, compensating the negative charge of the $[\text{TiO}_3]_{\infty}$ -network.
- 2) The size of each titanium ion is quite suitable for rattling at the center of the individual $[\text{TiO}_6]$ -octahedron.
- 3) The mass of each titanium ion $m(\text{Ti}) = 47.9$ a.u. is approximately equal to that of the 3-oxygen ions¹¹ $3m(\text{O}) = 48.0$ a.u..
- 4) Presence of a strong local electric field on each titanium ion coupled with its collinear oxygen ion O_t according to Slater's correction of Lorentz field.¹² These conditions gave the perovskite titanates a high dielectric permittivity¹³ and a big chance to undergo a displacive-type ferroelectric phase transformation. However, only the five of the twenty two perovskite titanates show some ferroelectricity as interpreted below.

It has been confirmed by the present authors⁴ that the average mass of A ions $m(\text{A})$ in nonconducting perovskite titanates, ATiO_3 and $\text{A}'_{1/2}\text{A}''_{1/2}\text{TiO}_3$, is a good criterion which discriminates the 5 kinds of ferroelectrics,⁵ PbTiO_3 , BaTiO_3 , CdTiO_3 , $\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3$, and $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ where $m(\text{A}) > 110$ a.u., from the 17 kinds of quantum paraelectrics,^{6,7} SrTiO_3 ,⁷ CaTiO_3 ,⁸ $\text{La}_{1/2}\text{Na}_{1/2}\text{TiO}_3$,⁹ $\text{Ln}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ ($\text{Ln} = \text{Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$),^{10,12} $\text{La}_{1/2}\text{K}_{1/2}\text{TiO}_3$ and $\text{Y}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ where $m(\text{A}) < 100$ a.u.. This is visually shown in Fig. 1 and the data of individual substances are listed in Table 1.⁴ Such a clear discrimination of ferroelectrics versus quantum paraelectrics in perovskite

titanates as in Fig. 1 suggests that the cause of this discrimination via $m(\text{A})$ originates in some dynamic entity. In the following section we will propose a dynamic origin why the mass of A ion $m(\text{A})$ influences on the ferroelectricity appearance in the perovskite titanates. In the next place, if we assume that the content in Fig. 1 is true, we can prepare some novel ferroelectric perovskite titanates by making use of Fig. 1. This has been done, and the two trial points, $\text{Bi}_{1/2}\text{Ag}_{1/2}\text{TiO}_3$ and $\text{Tl}_{1/2}\text{Na}_{1/2}\text{TiO}_3$, are already plotted in Fig. 1. They will be interpreted in the later section.

II. Effect of $m(\text{A})$ Upon the Amplitude of Last Mode -An Intuitive Explanation-

In order to correlate the mass of A ion with the appearance of ferroelectricity in perovskite titanate ATiO_3 , we must mention for the ferroelectric soft modes¹³ of the cubic perovskite titanate and discuss on the mass-inequality of a classical harmonic oscillator composed of two particles, because the effects of mass-inequality on the ferroelectric soft modes ($|\mathbf{k}| = 2\pi/\lambda = 0$) are supposed to be analogous to those on the two-particle system.

According to the soft mode theory,¹³ there are three independent ferroelectric soft modes of transverse optical phonons at the zone-center ($\mathbf{k} = 0$) in the \mathbf{k} -space of the cubic perovskite structure ATiO_3 . They are 1) Last mode A-TiO_3 , a collective vibration mode between the A ions and their counter $[\text{TiO}_3]_{\infty}$ -network, 2) Slater mode Ti-O_3 , a collective vibration mode between the Ti ions and their counter octahedral-oxygen-network inside the $[\text{TiO}_3]_{\infty}$ -net-

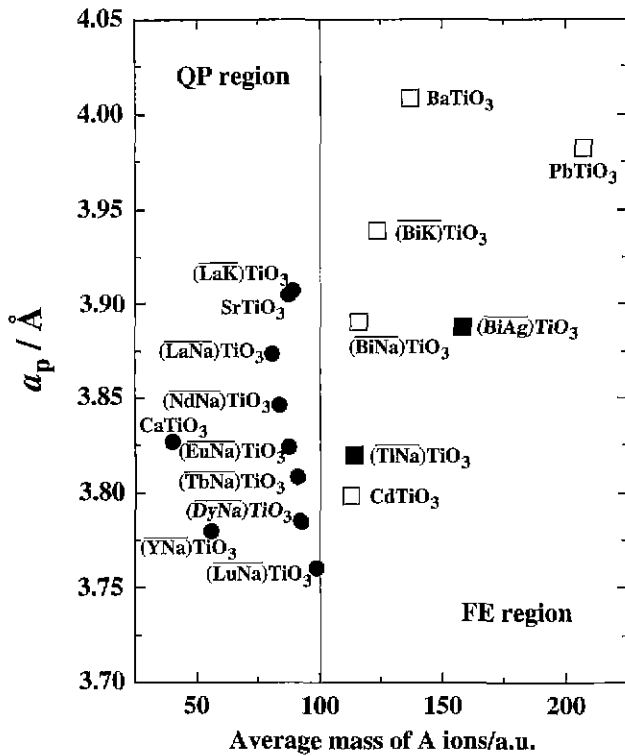


Fig. 1. Perovskite parameter vs. average mass of A ions for perovskite titanates ATiO_3 and $(\text{A}'_{1/2}\text{A}''_{1/2})\text{TiO}_3$. Solid circles (●) and open squares (□) indicate quantum paraelectrics and ferroelectrics, respectively. Trial candidate ferroelectric substances are indicated by solid squares (■). "QP region" and "FE region", respectively, denote quantum paraelectric and ferroelectric regions.

work, and 3) a deformation mode of octahedral-oxygen-network via vibration of O_t versus 2O_n inside the $[\text{TiO}_6]_c$ -network. In these three ferroelectric normal modes of vibration, only the Last mode A-TiO_3 is directly connected with the mass of A ion.

To demonstrate the mass-inequality effect on the ferroelectric modes, we imagine a classical one-dimensional oscillator made of two particles with masses M and m , bound together by a harmonic force with its constant C . On subtraction of the coordinates of the motion of their center of gravity for the two particles, we obtain a Newtonian equation of their relative motion with the reduced mass $\mu = Mm/(M+m)$,

$$\mu \frac{d^2x}{dt^2} = -Cx \quad (1)$$

Requiring the solution of Eq. (1) in the form

$$x = x_0 \cos \omega t \quad (2)$$

we obtain

$$C = \mu \omega^2 \quad (3)$$

It is important to note that in this relative coordinate expression x , the center of gravity of the two particles generally oscillates for $M \neq m$, and it agrees on $x=0$ only

when $M=m$. On application of the equipartition law of thermal energy to this oscillator, we can calculate its amplitude x_0 as functions of the temperature T , angular frequency ω and masses of the particles as follows,

$$(\text{kinetic energy}) + (\text{potential energy}) = kT = \frac{1}{2} Cx_0^2 \quad (4)$$

from Eqs. (3) and (4) it follows that

$$x_0 = \sqrt{\frac{2kT}{C}} = \sqrt{\frac{2kT}{\omega^2} \left(\frac{1}{m} + \frac{1}{M} \right)} \quad (5)$$

If we keep the condition of Eq. (3), it appears that x_0 in Eq. (5) is only a function of T and involves no mass dependence, however, the effective amplitude increases with a factor proportional to $(M-m)/(M+m)$. This is shown as follows.

In order to correlate the relative displacement x of the two particles with their individual displacements x_m and x_M from their center of gravity, we describe the motions of the two particles with separate Newtonian equations:

$$m \frac{d^2x_m}{dt^2} = f = -C_m x_m \quad (6)$$

$$M \frac{d^2x_M}{dt^2} = F = -C_M x_M \quad (7)$$

where C_m and C_M are harmonic constants. We will require again a solution of steady oscillation with the same angular frequency ω of a sinusoidal form $x_m = x_m^0 \cos \omega t$ and $x_M = x_M^0 \cos \omega t$. Thus, it follows from Eqs. (6) and (7) that

$$-m\omega^2 x_m = -C_m x_m = f \quad (8)$$

$$-M\omega^2 x_M = -C_M x_M = F \quad (9)$$

and furthermore we obtain from Eqs. (8), (9) and (3) that

$$C_m = m\omega^2 = \frac{M+m}{M} C \quad (10)$$

$$C_M = M\omega^2 = \frac{M+m}{m} C \quad (11)$$

Note in Eqs. (10) and (11) that the constants C_m and C_M are not equal and $C_m < C_M$ for $m < M$, even though the particles with masses m and M are bound together by the same force in the description Eqs. (6) and (7). Now, we must put the condition

$$f = -F \quad (12)$$

for steady oscillation of the two particles in Eqs. (6) and (7), or (8) and (9). Dividing both sides of Eq. (8) with those of Eq. (9) and use Eq. (12), we obtain an important relationship

$$\frac{x_m}{x_M} = -\frac{M}{m} \quad (13)$$

This shows that the displacement of the lighter particle x_m is wider than that of the heavier one x_M , and their directions are always opposite. From the definitions of x , x_m and x_M , together with Eq. (13), we obtain the relations

Table 1. Scaling Parameters for Ferroelectric and Quantum Paraelectric Perovskite Titanates

Chemical formula		Perovskite parameter/Å a_p	Average radius/Å $r(A)$	Average mass/a.u. $m(A)$	Transition- or arrival-temperature/K T_t or T_a	Maximum dielectric constant ϵ_{\max} or ϵ_a
BaTiO ₃	FE	4.009	1.42	137.3	$T_t \sim 398$ K	$\epsilon_{\max} \sim 10000$
PbTiO ₃	FE	3.982	1.29	207.2	763	~ 15000
CdTiO ₃	FE	3.798*	1.10	112.4	50-60 ¹⁾ , 77*	$\sim 2900^*$
Bi _{1/2} K _{1/2} TiO ₃	FE	3.939	1.34	124.0	653	~ 3500
Bi _{1/2} Na _{1/2} TiO ₃	FE	3.891	1.18	115.5	593	~ 2300
SrTiO ₃	QP	3.905	1.26	87.62	$T_a \sim 4$ K	$\epsilon_a \sim 20000$
CaTiO ₃	QP	3.827	1.12	40.08	~ 30	370
La _{1/2} K _{1/2} TiO ₃ *	QP	3.907	1.335	89.00	~ 30	100.6
La _{1/2} Na _{1/2} TiO ₃	QP	3.873	1.170	80.95	~ 30	134.2
Pr _{1/2} Na _{1/2} TiO ₃	QP	3.845	1.153	81.95	~ 40	125.3
Nd _{1/2} Na _{1/2} TiO ₃	QP	3.838	1.145	83.61	~ 60	114.7
Sm _{1/2} Na _{1/2} TiO ₃	QP	3.824	1.130	86.67	~ 50	112.2
Eu _{1/2} Na _{1/2} TiO ₃	QP	3.824	1.123	87.48	~ 50	111.8
Gd _{1/2} Na _{1/2} TiO ₃	QP	3.819	1.117	90.12	~ 60	102.2
Tb _{1/2} Na _{1/2} TiO ₃	QP	3.808	1.110	90.96	~ 70	95.5
Dy _{1/2} Na _{1/2} TiO ₃	QP	3.785	1.104	92.75	~ 40	76.9
Ho _{1/2} Na _{1/2} TiO ₃	QP	3.781	1.098	93.96	~ 50	62.3
Er _{1/2} Na _{1/2} TiO ₃	QP	3.776	1.092	95.13	~ 70	51.0
Tm _{1/2} Na _{1/2} TiO ₃	QP	3.769	1.087	95.96	~ 60	49.3
Yb _{1/2} Na _{1/2} TiO ₃	QP	3.764	1.083	98.02	~ 70	46.7
Lu _{1/2} Na _{1/2} TiO ₃	QP	3.760	1.079	98.98	~ 70	45.5
Y _{1/2} Na _{1/2} TiO ₃ *	QP	3.780	1.10	55.94	~ 60	70.0

*Our unpublished work.

among the amplitudes:

$$x_0 = x_m^0 - x_M^0 = \left(1 + \frac{m}{M}\right)x_m^0 = -\left(1 + \frac{M}{m}\right)x_M^0 \quad (14)$$

Thus, it follows from Eqs. (4) and (14) that

$$x_m^0 = x_0 \frac{M}{M+m} = \sqrt{\frac{2kT}{C}} \frac{M}{M+m} \quad (15)$$

$$-x_M^0 = x_0 \frac{m}{M+m} = \sqrt{\frac{2kT}{C}} \frac{m}{M+m} \quad (16)$$

The normalized amplitudes x_m^0/x_0 from Eq. (15) and $-x_M^0/x_0$ from Eq. (16) are plotted in Fig. 2 against the mass ratio M/m of the two particles. x_m^0/x_0 of the lighter particle increases as M/m increases and approaches to unity as M/m tends to infinity. While, $-x_M^0/x_0$ of the heavier particle decreases as M/m increases and approaches to zero as M/m tends to infinity. Fig. 3 shows the time dependence of the displacements x_m and x_M from their center of gravity for the two particles. When the masses of the two particles are equal, $m=M$, the amplitudes of the individual particles are equal to $1/2x_0$ from Eqs. (15) and (16);

$$\left|x_m^0\right|_{m=M} = \left|x_M^0\right|_{m=M} = \frac{1}{2}x_0 = \frac{1}{2}\sqrt{\frac{2kT}{C}} \equiv \Delta \quad (17)$$

While, if $m < M$, $|x_m^0/x_0| > 1/2$ and $|x_M^0/x_0| < 1/2$ as indicated in Figs. 2 and 3. It is noted in Fig. 3 that even though the total amplitude $x_0 = (2kT/C)^{1/2}$ is kept at a constant value, the net amplitude for the case (b) $m < M$ is wider

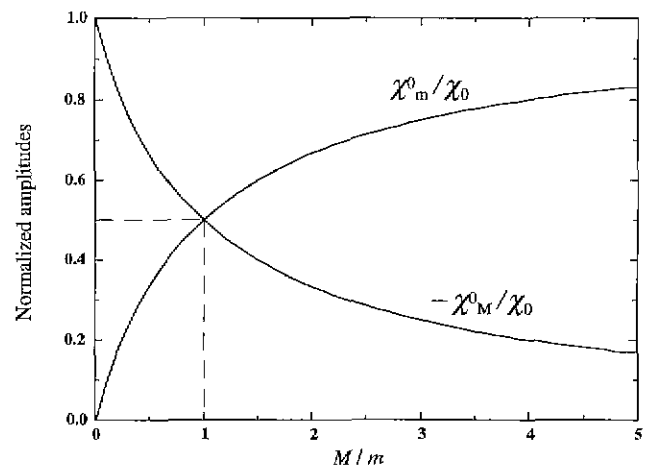


Fig. 2. M/m -dependence of the normalized amplitudes x_m^0/x_0 and $-x_M^0/x_0$.

than that of the case (a) $m=M$. This excess amplitude Δx_m^0 in Fig. 3(b) which is caused by the mass-inequality is evaluated to be

$$\Delta x_m^0 \equiv x_m^0 - \Delta = \frac{M-m}{M+m} \Delta \quad (18)$$

The areas where $|\Delta x_m^0| > \Delta$ in Fig. 3(b) are quite important because they can introduce various physical and chemical interactions into the relevant oscillator by accessing the lighter ion to the nearest-neighbor ion,

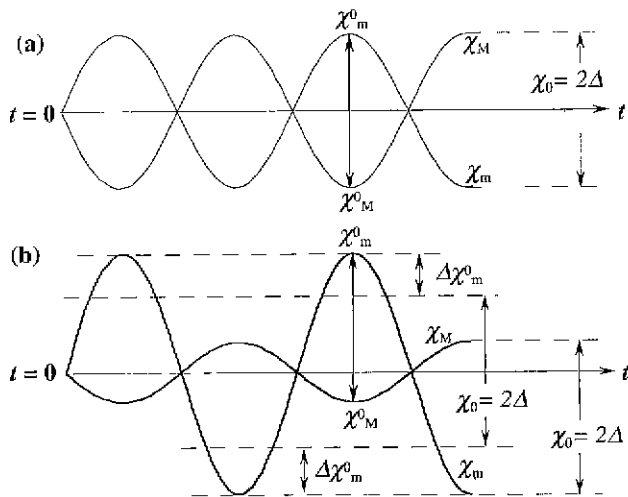


Fig. 3. Comparison of the individual amplitudes x_m^0 and x_M^0 between the cases (a) $m=M$ and (b) $m<M$.

especially in the solid state. Returning to the perovskite titanates $ATiO_3$, the mass-inequality between the A-site ions and the $[\text{TiO}_3]_B$ -network can produce an excess amplitude in the $[\text{TiO}_3]_B$ -network for the case $M(A) > m(\text{TiO}_3)$, introducing some energetic interactions or anharmonicity into Last's mode, destroying the stability of the mode, and finally it induces $ATiO_3$ to be a ferroelectric phase transition. Thus, the Last's mode has a possibility to be a trigger for the ferroelectric phase transformations. The Slater's mode Ti-O_3 , however, can not be a trigger of the ferroelectric phase transformations, because $m(\text{Ti})=3m(\text{O})$ and the mode is always very close to harmonic, $\Delta x_m^0/\Delta=(M-m)/(M+m)=0$, and stable. The origin of the discrimination in Fig. 1 must come from the excess amplitude $\Delta x_m^0/\Delta=(M-m)/(M+m)$ in the ferroelectric soft modes.

III. Trial Synthesis of Ferroelectric Candidates

According to the suggestions in Fig. 1, several candidate ferroelectric perovskite titanates, which have mass-inequalities in Last's mode $A\text{-TiO}_3$, have been selected by choosing A ions or $A'A''$ ion pairs so that their average mass of A ions $m(A)$ satisfy

$$m(A) > 110 \text{ a.u.} > m(\text{TiO}_3) = 95.8 \text{ a.u.} \quad (19)$$

and their average radius of A ions $r(A)$ in 8-coordination¹⁴ satisfy simultaneously

$$r(A) \geq 1.10 \text{ \AA} = r(\text{Cd}^{2+}) \quad (20)$$

to form a perovskite structure.

The selected candidate substances for $ATiO_3$ -type are RaTiO_3 , HgTiO_3 , AuTiO_3 , YbTiO_3 and EuTiO_3 , and those for $(A'_{1/2}A''_{1/2})TiO_3$ -type are $(\text{La}_{1/2}\text{Ag}_{1/2})TiO_3$, $(\text{Bi}_{1/2}\text{Ag}_{1/2})TiO_3$, $(\text{Tl}_{1/2}\text{Na}_{1/2})TiO_3$, etc. HgTiO_3 has been recently synthesized by Prof. G. Demazeau, Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, Université Bordeaux I,

as a rhombohedral perovskite structure under very high pressure (80 kbar-900°C). This is an ongoing work and the results will be reported in the separate paper. The candidate compounds EuTiO_3 , $(\text{La}_{1/2}\text{Ag}_{1/2})TiO_3$, $(\text{Bi}_{1/2}\text{Ag}_{1/2})TiO_3$ and $(\text{Tl}_{1/2}\text{Na}_{1/2})TiO_3$ have been prepared by the present authors.

EuTiO_3 was obtained by reacting $\text{Eu}_2\text{O}_3(4\text{N})$ and $\text{TiO}_2(3\text{N})$ at 1473 K in a hydrogen atmosphere. It was a colourless cubic perovskite with $a=3.905 \text{ \AA}$. Its dielectric constant ϵ , ranging 5000-3000 and loss angle $\tan \delta$ ranging 0.4-0.2 show an appreciable frequency dependence for $f=5 \text{ kHz}$ -600 kHz at 300 K. Its resistivity $\rho/\Omega\text{m}$ at 54 kHz changes from 6×10^3 at 90 K to 7×10^2 at 390 K. It was quite difficult to obtain a nonconducting EuTiO_3 .

$(\text{La}_{1/2}\text{Ag}_{1/2})TiO_3$ was obtained by reacting $\text{La}_2\text{O}_3(3\text{N})$, $\text{AgNO}_3(3\text{N})$ and $\text{TiO}_2(3\text{N})$ at 1273 K for 2-3 times $\times 8$ hrs and final sintering at 1423 K for 6 hrs in air. It was a colorless single phase, cubic perovskite with $a=3.880 \text{ \AA}$, but its chemical composition determined by ICP analysis was $\text{La}_{0.88}\text{Ag}_{0.26}\text{TiO}_3$ with the average mass of A ions $m(A)=108.6 \text{ a.u.}$ Dielectric behavior of this A-site deficient perovskite titanate was a quantum paraelectric. Details of this topic will be presented in AMF-2 conference on December 7-11, 1998 at Singapore.

$(\text{Bi}_{1/2}\text{Ag}_{1/2})TiO_3$ was synthesized by reacting $\text{Bi}_2\text{O}_3(4\text{N})$, $\text{Ag}_2\text{O}(2\text{N})$ and $\text{TiO}_2(3\text{N})$ at 1323 K for 10 min under 5 GPa with a cubic-anvil-type high pressure apparatus. The mixture of raw materials were sealed in a gold capsule. The capsule was covered by a NaCl disks at the top and bottom. The covered capsule was placed into a pyrophyllite container equipped with an interval graphite tube heater. The obtained compound was a yellow pseudo cubic perovskite with $a=3.887 \text{ \AA}$. A D-E hysteresis curve was observed for this compound at room temperature by use of a hand made Sawyer-Tower circuit at 50 Hz and 1.9 kV/cm. Therefore, $(\text{Bi}_{1/2}\text{Ag}_{1/2})TiO_3$ may be a ferroelectric member.

$(\text{Tl}_{1/2}\text{Na}_{1/2})TiO_3$ was synthesized by reacting TlNaO_2 and $\text{TiO}_2(3\text{N})$ at 1248 K for 30 seconds under 5.5 GPa with a cubic-anvil-type high pressure apparatus. TlNaO_2 was prepared beforehand by reacting $\text{Tl}_2\text{O}_3(3\text{N})$ and $\text{NaNO}_3(3\text{N})$ at 973 K in an oxygen atmosphere. The obtained compound has a tetragonal perovskite structure with $a=3.816 \text{ \AA}$ and $c=3.830 \text{ \AA}$, although it contained a small amount of impurity phases. Its dielectric properties are under examination.

IV. Summary

It is pointed out that the average mass of A ions $m(A)$ is a good criterion, which classified the 22 kinds of non-conducting perovskite titanates, $ATiO_3$ and $A'_{1/2}A''_{1/2}TiO_3$, into the 5 kinds of ferroelectrics via $m(A) > 110 \text{ a.u.}$, and the 17 quantum paraelectrics via $m(A) < 100 \text{ a.u.}$ The reason why $m(A)$ is a good criterion was intuitively explained, by analogy with the simple harmonic oscillator of two-particles, that the presence of a mass-inequality

in Last's mode $A\text{-TiO}_3$, one of the ferroelectric soft mode in perovskite ATiO_3 , gives a normalized excess amplitude $\{m(A)-m(\text{TiO}_3)\}/\{m(A)+m(\text{TiO}_3)\}$ in Last's mode. This excess amplitude gives the mode an anharmonicity and loses the stability of the mode, causing a trigger of the displacive-type ferroelectric phase transition for ATiO_3 . Making use of the criterion $m(A)$ to a strategy for ferroelectric synthesis in perovskite titanates, several candidate substances were examined.

References

1. T. Nakamura, P. H. Sun, Y. J. Shan, Y. Inaguma, M. Itoh, I. S. Kim, J. H. Sohn, M. Ikeda, T. Kitamura and H. Konagaya, "On the Perovskite-Related Materials of High Dielectric Permittivity with Small Temperature Dependence and Low Dielectric Loss," *Ferroelectrics* **196**(1-4), 205-209 (1997).
2. J. C. Slater, "The Lorentz Correction in Barium Titanate," *Phys Rev.* **78**(6), 748-761 (1950).
3. J-H. Sohn, Y. Inaguma, M. Itoh and T. Nakamura, "Cooperative Dielectric Interaction of the Perovskite-Related Layered Solid Solution System $\text{Sr}_{n-1}(\text{Sn}, \text{Ti}_{1-x})_n\text{O}_{3n+1}$ ($n=1, 2$ and ∞)," *Ferroelectrics* **166**(1-4), 149-158 (1995).
4. T. Nakamura, Y. J. Shan, P. H. Sun, Y. Inaguma and M. Itoh, "Discrimination of Ferroelectrics from Quantum Paraelectrics among Perovskite Titanates ATiO_3 and $A'_{1/2}A''_{1/2}\text{TiO}_3$," *Ferroelectrics* (1998) in print.
5. E. Nakamura, "Table SIE-2, Common Two-Dimensional Survey of Contents for III/16a and III/28a"; pp.23-24; J. Harada, M. Okuyama, T. Ikeda, M. Adachi, "Data S II-1, Perovskite-type Oxides"; pp.71-81, LANDOLT-BORN-STEIN, Numerical Data and Functional Relationships in Science and Technology, New Series III/28a. Edited by T. Mitsui and E. Nakamura, Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong 1989.
6. John H. Barrett, "Dielectric Constant in Perovskite Type Crystals," *Phys Rev.* **86**(1), 118-120 (1952).
7. K. A. Muller and H. Burkard, "SrTiO₃: An Intrinsic Quantum Paraelectric Below 4K," *Phys Rev. B* **19**(7), 3593-3602 (1979).
8. I. S. Kim, M. Itoh and T. Nakamura, "Electrical Conductivity and Metal-Nonmetal Transition in the Perovskite-Related Layered System $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ ($n=1, 2$ and ∞)," *J. Solid State Chem.* **101**(1), 77-86 (1992).
9. Y. Inaguma, J. H. Sohn, I. S. Kim, M. Itoh and T. Nakamura, "Quantum Paraelectricity in a Perovskite $\text{La}_{1/2}\text{Na}_{1/2}\text{TiO}_3$," *J. Phys. Soc. Jpn.* **61**(10), 3831-3832 (1992).
10. P. H. Sun, T. Nakamura, Y. J. Shan, Y. Inaguma and M. Itoh, "High Temperature Quantum Paraelectricity in Perovskite-Type Titanates $\text{Ln}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ and Tb)," *Ferroelectrics* **200**, 93-107 (1997).
11. Y. J. Shan, T. Nakamura, Y. Inaguma and M. Itoh, "Preparation and Dielectric Characterizations of the Novel Perovskite-type Oxides $\text{Ln}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ ($\text{Ln}=\text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Lu)," *Solid State Ionics* **108**(1-4), 123-128 (1998).
12. T. Nakamura, Y. J. Shan, P. H. Sun, Y. Inaguma and M. Itoh, "The cause of High-temperature Quantum Paraelectricity in some Perovskite Titanates," *Solid State Ionics* **108**(1-4), 53-58 (1998).
13. T. Nakamura, T. Sakudo, Y. Ishvashi and Y. Tominaga, "Displacive Type Ferroelectrics versus Soft Mode"; Chap. 1, Sec. 1.6, pp.32-46; "Lattice Vibration and Soft Mode"; Chap. 2, Sec. 2.2 pp.72-87; "Displacive-type Ferroelectric Phase Transition"; Chap. 4, pp.159-173, KyoYuDenTai To KoZoSoTeni (Ferroelectricity Involved in Structural Phase Transitions). Edited by Terutaro Nakamura, Printed by Tasuji Yoshino, Shokabo, Tokyo, 1988.
14. R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.* **A32**(part 5), 751-767 (1976).