Journal of the European Ceramic Society 19 (1999) 1089–1093
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00380-X
0955-2219/99/$ - see front matter

Changes in Ordered Structure and Dielectric Properties with the A-site and B-site Cation Ratios of Complex Perovskites $(Sr_{1-x}Ba_x)(Sr_{0\cdot 33+y}Ta_{0\cdot 67-y})O_{3-\delta}$

J. Takahashi,* T. Fujii, S. Shimada and K. Kodaira

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University,
Kita-13 Nishi-8 Kita-ku, Sapporo 060-8628, Japan

Abstract

Complex perovskites with large-sized B′-site cations, $(Sr_{1-x}Ba_x)(Sr_{0\cdot 33+y}Ta_{0\cdot 67-y})O_{3-\delta}$ $(0 \leqq x \leqq 1,\ 0 \leqq y \leqq 0\cdot 17)$*, were fabricated to examine the transformation behavior between the (1:1) and (1:2) order types and dielectric property change with A-site cation substitution. The (1:2) type order was found to appear in a limited Ba-rich composition range. Structural strain induced by size difference between the A-site and large-sized B′-site cations might be responsible for the occurrence of the (1:1) type order in perovskite compounds substituted with more than 50%* Sr^{2+} *on the A-site sublattice. Low* ε_r *and positive temperature coefficient of* ε_r *observed for the (1:2) ordered samples were explained by the restricted ion movement in the (1:2) type order array. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: sintering, X-ray methods, dielectric properties, perovskites, functional applications.

1 Introduction

Complex perovskite compounds are classified into two subgroups according to a B-site cation ratio, i.e. $A(B'_{0\cdot 5}B''_{0\cdot 5})O_3$ and $A(B'_{0\cdot 33}B''_{0\cdot 67})O_3$. A large size mismatch or charge discrepancy between unlike B-site cations causes cation ordering on the B-site sublattice.[1] The ordered structure of $A(B'_{0\cdot 5}B''_{0\cdot 5})O_3$ perovskites is very simple. Each B′ and B″ cations are placed on alternate (111) planes of the primitive cubic cell as -B′-B″-B′-B″-. Such a structure is called a (1:1) type order and has the NaCl-type symmetry. On the contrary, for compounds with a B-site cation ratio of 1:2, ordering manner of the B-site cations is rather complicated. A typical cation configuration frequently encountered is a (1:2) type order where one layer of B′-cations and two layers of B"-cations are arranged in a parallel sequence along the [111] direction. Additionally, one can recognize the occurrence of the (1:1) type order in the $A(B'_{0\cdot 33}B''_{0\cdot 67})O_3$ perovskites. For example, a short range ordering of the (1:1) type was found for pure $Pb(Mg_{0\cdot 33}Nb_{0\cdot 67})O_3$ (PMN) where (1:1) type ordered microdomains of ~2–4 nm in size were distributed in a disordered matrix.[2] Although the ordered structure and domain size of PMN were unaffected by long-term annealing, the incorporation of La^{3+} into the Pb^{2+} sublattices could enhance the (1:1) type order.[2]

Changes in the type of the B-site cation ordering with chemical modification on the A- site or B-site sublattice were observed for the $A(B'_{0\cdot 33}B''_{0\cdot 67})O_3$ perovskites.[3–6] The present authors also reported ordering transformation in complex perovskites with large-sized B′- site cations, $A(Sr_{0\cdot 33+y}Ta_{0\cdot 67-y})O_{3-\delta}$, in which the effect of the B-site cation ratio on order type was examined for some selected samples with A = Sr, $Sr_{0\cdot 5}Ba_{0\cdot 5}$ and Ba.[7,8] Besides, for stoichiometric perovskites with $y = 0$, it was found out that A-site substitution with equally charged cations could necessarily changed the B-site order type. Therefore, the B-site order transformation has been examined as a function of the A-site cation ratio (Sr/Ba) and a new factor dominating the order type of the present complex perovskites is proposed in this paper. Furthermore, a strong dependence of dielectric properties on order type has been demonstrated for stoichiometric samples.

---

*To whom correspondence should be addressed. Fax: + 81-11-706-6572; e-mail: tkjun@eng.hokudai.ac.jp

2 Experimental

Complex perovskite powders with stoichiometric compositions of $A(Sr_{0{\cdot}33}Ta_{0{\cdot}67})O_3$ and those having oxygen vacancies $A(Sr_{0{\cdot}33+y}Ta_{0{\cdot}67-y})O_{3-\delta}$ $(0 < y \leqq 0{\cdot}17)$ were synthesized by conventional solid-state method from high-purity Ba and Sr carbonates and Ta_2O_5 (>99·9%). The powders were weighed and mixed in distilled water with Y_2O_3 -stabilized ZrO_2 balls in a plastic container. Slurry thus prepared was dried, calcined at 1150°C for 6 h and pressed into green compacts. Sintering of the compacts was conducted at 1500–1600°C for 24 h with a heating rate of $150\,Ch^{-1}$, which was followed by furnace cooling of about $400\,Ch^{-1}$ down to 1000 C. Some selected samples were annealed at given temperatures in air. Sample compositions examined in this study are listed in Table 1.

The order type in each sintered sample was detected from its X-ray powder diffraction (XRD) profile. For samples consisting of both types of ordering, a ratio of each order type, (1:2) to (1:1), was estimated from a relative X-ray intensity of the (400) and (204) reflections of the corresponding cubic (1:1) and hexagonal (1:2) ordered phases. The relative permittivity (ε_r) and loss tangent of sintered samples at 1 MHz were measured as a function of temperature up to 150°C by 3-probe method using a digital LCR meter.

3 Results and Discussion

3.1 Effects of chemical modification on ordered structure

Stoichiometric (M_4T) and oxygen-deficient ($M_{4{\cdot}5}T$~M_6T) samples with their A-site cation ratios ranging from Sr:Ba = 5:5 to 0:10 were fabricated by sintering at 1550°C for 24 h in air. Figure 1 shows changes in order type with increasing A-site Ba^{2+} content for the M_4T and $M_{4{\cdot}5}T$ samples. For the M_4T samples, the substitution with more than 60% Ba^{2+} caused the partial formation of the (1:2) type order and then the (1:1) type order completely diminished at $A = Sr_{0{\cdot}2}Ba_{0{\cdot}8}$. Oxygen-deficient $M_{4{\cdot}5}T$ samples were found to include both types of the B-site ordering after complete substitution with Ba^{2+}.

Table 1. Compositions of complex perovskites $(Sr_{1-x}Ba_x)(Sr_{0{\cdot}33+y}Ta_{0{\cdot}67-y})O_{3-\delta}$ examined in this study

Sample type	y-*value*	*Ideal formula*[a]	*Abbreviation*[b]
Stoichiometric	0	$A(Sr_{0{\cdot}33}Ta_{0{\cdot}67})O_3$	M_4T
Oxygen-deficient	0·05	$A(Sr_{0{\cdot}38}Ta_{0{\cdot}62})O_{2{\cdot}92}$	$M_{4{\cdot}5}T$
Oxygen-deficient	0·10	$A(Sr_{0{\cdot}43}Ta_{0{\cdot}57})O_{2{\cdot}86}$	M_5T
Oxygen-deficient	0·14	$A(Sr_{0{\cdot}47}Ta_{0{\cdot}53})O_{2{\cdot}80}$	$M_{5{\cdot}5}T$
Oxygen-deficient	0·17	$A(Sr_{0{\cdot}50}Ta_{0{\cdot}50})O_{2{\cdot}75}$	M_6T

[a] $A = (Sr_{1-x}Ba_x)$:$0 \leqq x \leqq 1{\cdot}0$.

[b] e.g. $M_4T \Rightarrow (SrO + BaO):Ta_2O_5 = 4:1$.

The examination of heating and annealing temperature effect on the stability of ordered structure was conducted for some selected samples. Results are indicated in Fig. 2. (heating duration is 24 h in each run). Open marks (△,▽ and ○) in Fig. 2 are for the samples heated at 1500, 1550 or 1600°C. Annealing at 1400, 1450 and 1500°C (closed marks) was conducted for a sample preheated at 1550°C. Completely ordered structure of the (1:2) type obtained in the M_4T sample with $A = Sr_{0{\cdot}2}Ba_{0{\cdot}8}$ was stable under any heating conditions. However, a slight reduction in the fraction of the hexagonal (1:2) phase was observed after annealing at lower temperatures for samples where both the (1:2) and (1:1) ordered phases coexisted. The results obtained in Figs 1 and 2 indicated that the control of order type in the present complex perovskites could be achieved not by simple heat-treatment but chemical modification on the A-site sublattice.

The effect of chemical modification on the ordered structure of $A(B'_{0{\cdot}33}B''_{0{\cdot}67})O_3$ type complex perovskites

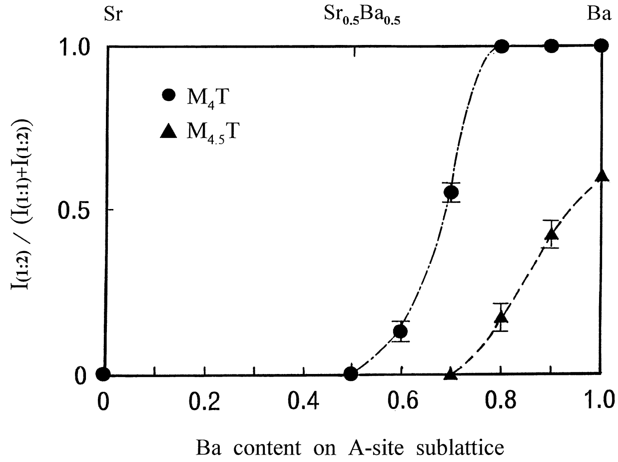

Fig. 1. Ordering transformation with A-site Ba^{2+} content for M_4T and $M_{4{\cdot}5}T$ samples.

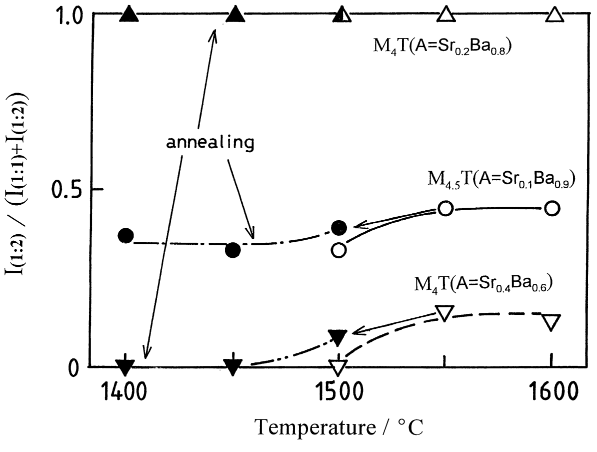

Fig. 2. Effect of heating and annealing temperature on stability of ordered phases.

has been extensively investigated. Most of them, however, were focused on the modification on the B-site sublattice. In general, the (1:1) type order tends to be favorable as the fraction of B^{2+} deviated from a stoichiometric value of 0·33 to larger ones in $A(B^{2+}_{0\cdot33+y}B^{5+}_{0\cdot67-y})O_{3-\delta}$. In the case of the A-site substitution with aliovalent cations such as La^{3+} for Pb^{2+} in PMN[2], it also inevitably causes an increase in the B^{2+} fraction towards $B^{2+}/B^{5+}=1/1$. In the present study, it can be seen in Fig. 1 that the equally charged A-site cation species definitely dominates the type of the B-site cation ordering. The complex perovskites examined in this study are somewhat different from others in a structural view point that very large Sr^{2+} cations partially occupy the octahedral B-site. This occupancy might produce substantial strain in perovskite structure. If local charge imbalance was permitted in the structure, the strain is minimized in an array of alternating Sr^{2+} and Ta^{5+} layers, i.e. the (1:1) ordering. Besides, the size of the A-site cation necessarily correlates with the structural strain to be involved. Then, a factor of size ratio between the A-site and larger B′-site cations, $SR=(R_A-R_{B'})/R_A$ where R_A and $R_{B'}$ are the ion radii of the 12-fold A^{2+} and 6-fold B'^{2+} cations, respectively, was introduced as an indicator determining which order type the perovskite compound would take. These factors were estimated to be 0·25, 0·28, 0·35 and 0·28 for the hexagonal (1:2) type ordered perovskites of $Ba(Sr_{0\cdot33}Ta_{0\cdot67})O_3$, $Sr(Ca_{0\cdot33}Ta_{0\cdot67})O_3$, $Ba(Ca_{0\cdot33}Nb_{0\cdot67})O_3$, and $Sr(Ca_{0\cdot33}Ta_{0\cdot67})O_3$, respectively. For those with the (1:1) type order in the present study, $Sr(Sr_{0\cdot33}Ta_{0\cdot67})O_3$ and $(Sr_{0\cdot5}Ba_{0\cdot5})(Sr_{0\cdot33}Ta_{0\cdot67})O_3$, the corresponding SR factors are 0·17 and 0·21. The lower the SR factor is, the larger the structural strain becomes. In order to determine a critical SR factor differentiating the (1:2) and (1:1) type orders, a similar examination was conducted for slightly modified complex perovskites $Sr[(Sr_{1-z}Ca_z)_{0\cdot33}Ta_{0\cdot67}]O_3$. The Ca-substituted perovskites with $z=0\cdot3$ and 0·5 were found to be ordered with the (1:1) type and the SR factors were 0·20 and 0·22, respectively. A sample with $z=0\cdot7$ and the SR factor of 0·24 showed a mixture of both order types. The complete (1:2) ordered structure was recognized at $z=0\cdot9$ and $SR=0\cdot27$. In conclusion, the transformation of the order type in such complex perovskites with large-sized B′ cations probably occurs in a range of $0\cdot23<SR<0\cdot25$.

Based on this consideration, the dependence of order type on A-site cation species in the present complex perovskites was explained as follows. For stoichiometric samples, the structural strain induced by the occupancy of large-sized Sr^{2+} in the B-site might be minimized at A = Ba where the charge imbalance between Sr^{2+} and Ta^{5+} predominates to produce the (1:2) type order. On the other hand, if the Ba^{2+} cations were considerably substituted with much smaller Sr^{2+}, the increasing strain possibly forces the B-site ordering to be transformed to the (1:1) type which has less strain.

By combining with the results obtained for oxygen-deficient samples, a map of order type can be given in Fig. 3 for the present complex perovskites heated at 1550°C for 24 h. Open and closed circles represent the (1:1) and (1:2) type order, respectively. Partially closed circles correspond to a mixture of both ordering types. It was concluded that the mixed ordering region extended towards Ba-rich compositions in A-site cation ratio and the complete (1:2) type order was recognized in a very restricted composition range.

3.2 Dielectric properties of stoichiometric perovskites

A change in ε_r of the (1:1) ordered perovskites, $A(Sr_{0\cdot33+y}Ta_{0\cdot67-y})\ O_{3-\delta}$ ($A=Sr$, $Sr_{0\cdot5}Ba_{0\cdot5}$), with B-site cation ratio has been already reported elsewhere.[8] It was monotonously decreased as the y-value (oxygen deficiency) increased. However, the effect of order type on the dielectric properties of those samples was not examined. To evaluate the order type effect only, dielectric measurement was conducted for stoichiometric M_4T samples. Figure 4 shows changes in ε_r and temperature coefficient of ε_r ($TC\varepsilon_r$) against the Ba^{2+} content on the A-site sublattice. Open and closed marks correspond to the values obtained for the (1:1) and (1:2) type order, respectively, and partially closed ones for those having mixed ordered phases. Surprisingly, both ε_r and $TC\varepsilon_r$ are strongly dependent on order type. The ε_r of the $Sr(Sr_{0\cdot33}T_{0\cdot67})O_3$ sample with complete (1:1) ordered structure is slightly increased with an increasing Ba^{2+} up to $A=Sr_{0\cdot5}$

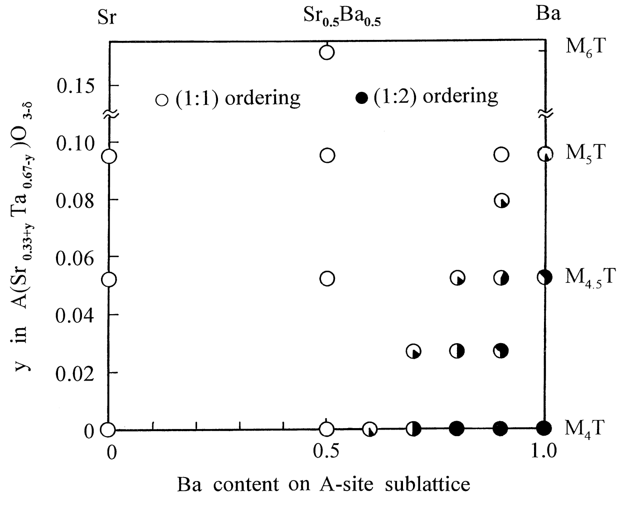

Fig. 3. Effect of chemical modification on order type of complex perovskites $(Sr_{1-x}Ba_x)(Sr_{0\cdot33+y}Ta_{0\cdot67-y})O_{3-\delta}$.

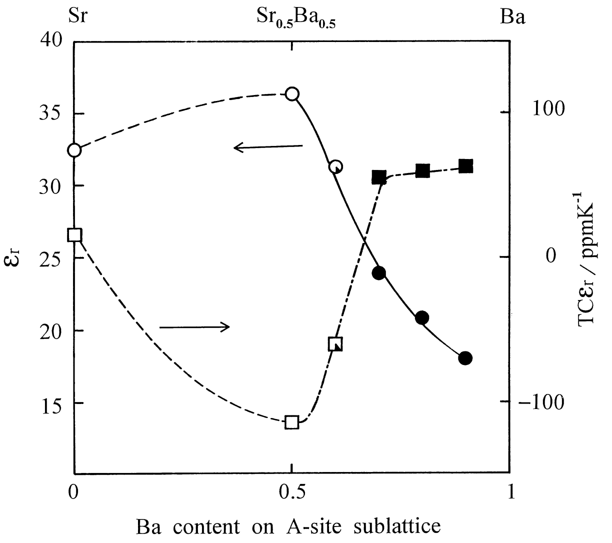

Fig. 4. Changes in ε_r and $TC\varepsilon_r$ of stoichiometric samples with A-site Ba^{2+} content.

$Ba_{0.5}$ which is a general tendency observed for Ba^{2+} substitution for Sr^{2+} in a structure. The tendency was drastically inversed when the (1:2) type order formed, resulting in a very low value of $\varepsilon_r = 18$ for a sample with $A = Sr_{0.1}Ba_{0.9}$. This suggested that the (1:2) type ordered array considerably restricts the ion movement against applied electric field, compared with the (1:1) ordering.

Reaney *et al.*[9] summarized the $TC\varepsilon_r$ of Ba- and Sr-based complex perovskites as a function of the tolerance factor and tried to explain the large $TC\varepsilon_r$ change by the linkage manner of the BO_6 octahedra in the perovskite structure.[9] The present authors also examined the dielectric property change of some complex perovskites with a serial cation substitution.[10,11] From those studies, a qualitative but fundamental correlation between a $TC\varepsilon_r$ change and structural strain involved in a perovskite structure was deduced, assuming that the temperature dependence of the macroscopic polarizability (α_m) of a material could be changed by crystal structure.[12] If a perovskite compound has a very highly symmetrical structure in which the BO_6 octahedra interlink straightforward with each other, a negative temperature dependence of α_m predominated to cause a negative $TC\varepsilon_r$. On the other hand, in a perovskite structure with tilting of the octahedra, α_m would hardly change or inversely increase with temperature due to release of the strain involved, leading to a positive $TC\varepsilon_r$.

As is mentioned in 3·1, $Ba(Sr_{0.33}Ta_{0.67})O_3$ probably contains the least strain in the structure. This preferably leads to the formation of the (1:2) type order of the B-site cations due to large charge discrepancy. But once the B-site cations could be arranged in the (1:2) type order array, it becomes less tolerable for ion movement than the (1:1) ordered array. The restricted ion movement can be loosened with increasing temperature, resulting in an increase in ε_r. This consideration might be acceptable for the explanation of low ε_r and positive $TC\varepsilon_r$ values obtained in the (1:2) ordered perovskites. On the contrary, an increase in the strain induced by the substitution of Sr^{2+} for the A-site Ba^{2+} caused the transformation of the B-site ordering to the (1:1) type. The ions in the (1:1) ordered array could be moved more easily by the applied electric field, giving higher ε_r and negative $TC\varepsilon_r$. The latter was again increased for $Sr(Sr_{0.33}$-$Ta_{0.67})O_3$ up to about $+15\,ppm/K^{-1}$. This change suggested increasing structural strain in the perovskite compound, which was supported by the fact that XRD patterns of the (1:1) ordered $Sr(Sr_{0.43}Ta_{0.57})O_{3-\delta}$ sample could be identified with a very slightly strained cubic perovskite having a space group of $F\bar{4}3m$. Thus it was clearly concluded that the order type in the complex perovskites essentially affected their dielectric properties.

4 Conclusion

The effect of chemical modification on order type transformation was studied for complex perovskites with large-sized B′-site cation, $(Sr_{1-x}Ba_x)(Sr_{0.33+y}Ta_{0.67-y})O_{3-\delta}$. The (1:2) type order of the $Ba(Sr_{0.33}Ta_{0.67})O_3$ perovskite was transformed to the (1:1) ordered structure by the A-site cation substitution with Sr^{2+} for Ba^{2+} through a mixed ordering region. The occurrence of the (1:2) type or (1:1) type order could be rationalized by a size ratio factor, $SR = (R_A - R_{B'})/R_A$ where R_A and $R_{B'}$ are radii of the A-site and B′-site cations in the perovskite structure, respectively. An order type map of the present complex perovskites showed that the mixed ordering region extended towards Ba-rich composition in the A- site cation ratio and the complete (1:2) type order appeared in a very limited composition range. Changes in ε_r and $TC\varepsilon_r$ were found to be closely related to the order type. Low ε_r and positive temperature coefficient of ε_r observed for the (1:2) ordered samples were explained by the restricted ion movement in the (1:2) type order array.

References

1. Galasso, F. S., Perovskites and High Tc Superconductors. Gordon and Breach Science, New York, 1990, pp. 11–58.
2. Chen, J., Chan, H. M. and Harmer, M., Ordering structure and dielectric properties of undoped and La/Na-doped $Pb(Mg_{0.33}Nb_{0.67})O_3$. *J. Am. Ceram. Soc.*, 1989, **72**, 593–598.
3. Lee, C., Chou, C. and Tsai, D., Effect of La/K A-site substitutions on the ordering of $Ba(Zn_{1/3}Ta_{2/3})O_3$. *J. Am. Ceram. Soc.*, 1997, **80**, 2885–2890.

4. Akbas, M. A. and Davies, P. K., Cation ordering transformations in the $Ba(Zn_{1/3}Nb_{2/3})O_3$—$La(Zn_{2/3}Nb_{1/3})O_3$ System. *J. Am. Ceram. Soc.*, 1998, **81**, 1061–1064.
5. Chai, L. and Davies, P. K., Formation and structural characterization of 1:1 ordered perovskites in the $Ba(Zn_{1/3}Ta_{2/3})O_3$—$BaZrO_3$ system. *J. Am. Ceram. Soc.*, 1997, **80**, 3193–3198.
6. Du, Y. and Nowuck, A. S., Structural transitions and proton conduction in non-stoichiometric $A_3B'B''_2O_9$ perovskite-type oxides. *J. Am. Ceram. Soc.*, 1995, **78**, 3033–3039.
7. Takahashi, J., Kodaira, K., Ota, T. and Takahashi, M., Synthesis and dielectric properties of complex perovskites with different oxygen vacancies in the system SrO–Ta_2O_5, Proceedings of Electroceramics IV, Aachen, 1994, pp. 135–138.
8. Takahashi, J., Fujii, T., Shimada, S. and Kodaira, K., Ordered structure and dielectric properties of oxygen-deficient complex perovskites $(Ba_{1-x}Sr_x)(Sr_{0\cdot33+y}Ta_{0\cdot67-y})O_{3-\delta}$, Proceedings of PacRim II, Cairns, in press.
9. Reaney, I. M., Colla, E. L. and Setter, N., Dielectric and structural characteristics of Ba- and Sr-based complex perovskites as a function of tolerance factor. *Jpn. J. Appl. Phys.*, 1994, **33**, 3984–3990.
10. Takahashi, J., Kageyama, K., Fujii, T., Yamada, T. and Kodaira, K., Formation and microwave dielectric properties of $Sr(Ga_{0\cdot5}Ta_{0\cdot5})O_3$-based complex perovskites. *J. Mater. Sci. Mater. in Electronics*, 1997, **8**, 79–84.
11. Fujii, T., Takahashi, J., Shimada, S. and Kageyama, K., Changes in the crystal structure and dielectric properties of the complex perovskites $Sr(Ga_{0\cdot5}Ta_{0\cdot5})O_3$ with A-site cation substitution. *J. Ceram. Soc. Jpn.*, 1998, **106**, 669–675 (in Japanese).
12. Bosman, A. J. and Havinga, E. E., Temperature dependence of dielectric constants of cubic ionic compounds. *Phys. Rev.*, 1963, **129**, 1593–1600.