83 (M^+, $-CH_2CH_2-OCOCH_3$, 100); $[\alpha]_D$ -48.6 (*c* 2.2, $CHCl_3$); Anal. Calcd for $C_8H_{10}O_4$: C, 56.47 H, 5.92; Found. C, 56.48; H, 5.94.

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Ordering Behavior in A-Site Modified $Pb_{1-x}Bi_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ and $Pb_{1-x}La_x(Mg_{(1+x)/3}Ta_{(2-x)/3})O_3$ Ceramics

Young-Sik Hong, Chi-Hwan Han, Hyu-Bum Park, and Si-Joong Kim*

Department of Chemistry, Korea University, Seoul 136-701, Korea

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Complex perovskite compounds, A(B'B")O_3, exhibit a different ordering behavior depending on the charge and size differences of B-site cations.[1-3] Among them, the order-disorder phenomena in lead-based Pb(B'B")O_3 ceramics have been extensively investigated because the dielectric properties of the ceramics are closely related to the degree of the ordering of B-site cations. The degree of ordering can be controlled in some ceramics such as $Pb(Sc_{1/2}Ta_{1/2})O_3$ and $Pb(Sc_{1/2}Nb_{1/2})O_3$ by thermal annealing.[2,4,5] Generally, the presence of the ordering in A(B'B")O_3 perovskites has been expected by considering the electrostatic and mechanical forces, generated by the differences in ionic valence and in ionic radii of the B' and B" ions. In addition, the degree of ordering in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), firstly observed by Krause *et al.*, can be only enhanced by incorporation La^{3+} into Pb^{2+} sites in PMN lattices.[6-8]

In this study, we have investigated the charge and size effects of donor dopants on the degree of ordering in perovskite type $Pb_{1-x}Bi_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PBiMN) and $Pb_{1-x}La_x(Mg_{(1+x)/3}Ta_{(2-x)/3})O_3$ (PLaMT) ceramics.

Experimental

To fabricate the polycrystalline samples of perovskite phases with minimal pyrochlore impurities, the columbite precursor method was used.[9] The appropriate amounts of MgO and Nb_2O_5 or Ta_2O_5 powder were mixed by ball-milling in ethanol for 12 h. After drying, the mixture was calcined at 1000 °C for 4 h. The columbite precursors ($MgNb_2O_6$ and $MgTa_2O_6$) were then mixed with the required amounts of PbO, Bi_2O_3, La_2O_3 and MgO powder, and calcined in a covered alumina crucible at 800 °C for 2 h at a heating rate of 200 °C/h.

The calcined powders were mixed with 2 wt.% poly (vinyl alcohol) added as a binder and cold-pressed into cylindrical pellets. Following binder burnout at 600 °C, the pel-

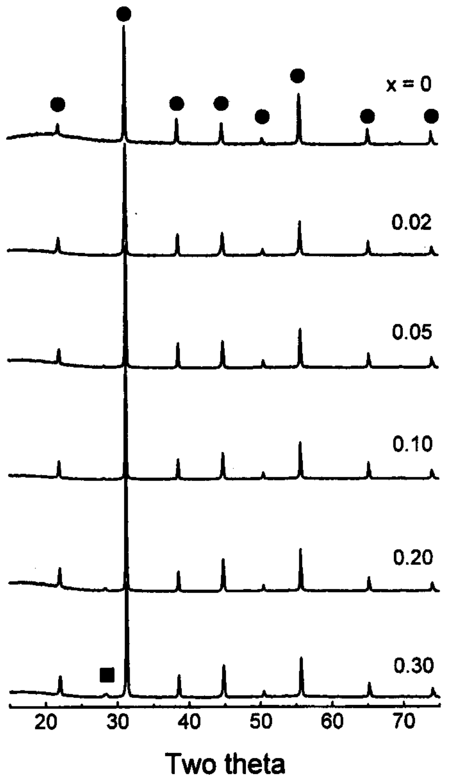

Figure 1. The X-ray diffraction patterns of $Pb_{1-x}Bi_x(Mg_{(1+x)/3}-Nb_{(2-x)/3})O_3$ ceramics sintered at 1100 °C. (●: perovskite phase and ■: pyrochlore phase)

lets were sintered in a covered Pt crucible for 2 h at 1150 and 1250 °C for PBiMN and PLaMT, respectively. To suppress the PbO loss, the calcined powders with the same composition were used during the sintering. The degree of ordering was calculated quantitatively from the intensity of powder X-ray diffraction data using CuK_α radiation.

Results and Discussion

The XRD patterns of $Pb_{1-x}Bi_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PBiMN) ceramics sintered at 1150 °C for 2 h are shown in Figure 1. Three facts are noticeable in these XRD patterns as the substituent content increases from 0 to 30 at.%. First, all the XRD peaks are shifted to slightly higher diffraction angles even though the ionic radius of Bi^{3+} ion (1.03 Å) is smaller than that of Pb^{2+} ion (1.20 Å). This fact indicates that the unit cell volume is nearly not affected by the ionic radius of Bi^{3+} ion. Second, all the diffraction patterns of PBiMN are indexed by the cubic structure. Lastly, no superlattice lines are detected at any compositions, indicating that the B-site ions are randomly distributed.

The XRD patterns of PLaMT ceramics sintered at 1250 °C for 2 h are shown in Figure 2. Three trends are also apparent in these XRD patterns with increasing La^{3+} content. First, a series of extra peaks are appeared at 2θ angles of 19.06°, 36.98°, and 49.28° for 5 at.% La^{3+}-modified PMT ceramic and their relative intensities are progressively increased with La^{3+} content is increased. These extra peaks are from the ordered structure and are indexed as (111), (311), and (331) superlattice reflections for the 1 : 1 ordered lattice. Second, all the XRD peaks are shifted to higher diffraction angles, indicating that the unit cell volume is decreased. Third, the peak intensities for the pyrochlore phase corresponding to $Pb_2Ta_2O_7$ (JCPDS No. 19-705) or $Pb_3Ta_4O_{13}$ (22-674) are increased with increasing La^{3+} content from 0 at.% to 30 at.%, and the La_3TaO_7 (38-1418) phase is appeared in the samples of La^{3+} contents of 40 at.% and 50 at.%.

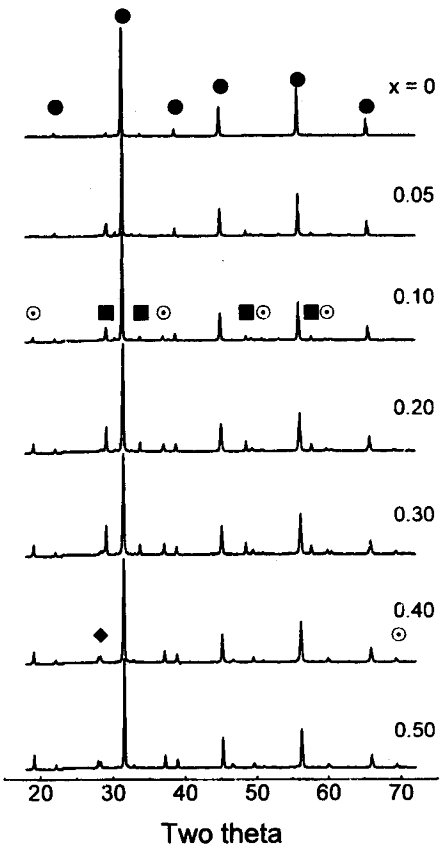

Figure 2. The X-ray diffraction patterns of $Pb_{1-x}La_x(Mg_{(1+x)/3}-Ta_{(2-x)/3})O_3$ ceramics sintered at 1250 °C. (●: Fundamental line, ⊙: Superlattice line, ■: Pyrochlore phase, and ◆: La_3TaO_7)

It is observed, as shown in Figure 1 and Figure 2, that only PLaMT ceramics exhibit the superlattice lines due to the 1 : 1 ordering. To compare the size and charge effects of dopants, the unit cell volume is plotted as a function of dopant content in Figure 3. Three series of $Pb_{1-x}(Na/La)_x(Mg_{1/3}Nb_{2/3})O_3$ (PNLMN),[10] $Pb_{1-x}La_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PLaMN),[11] and $Pb_{1-x}Nd_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PNdMN)[11] ceramics are compared.

In PNLMN ceramics, the unit cell volume is decreased whereas the average charge of A-site cation is constant as the amount of dopant is increased. On the contrary, in PBiMN ceramics, the unit cell volumes is nearly constant despite that the average charge of A-site cations is increased. In PLaMT, PLaMN, and PNdMN ceramics,[11] the average charge of A-site is increased and the unit cell volume is decreased with the amount of dopant is increased.

It can be concluded from the comparison that the 1 : 1 ordering can be increased by the substitution with a high valent A^{3+} ion such as La^{3+} and Nd^{3+} ions. That is, the ordered composition has one to one composition in B site

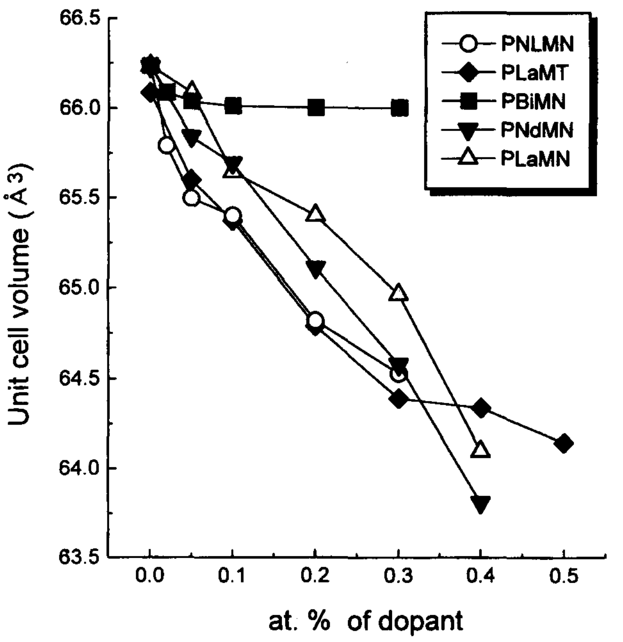

Figure 3. Lattice parameter versus at.% of dopants for various ceramics.

such as $Pb(Mg_{1/2}Nb_{1/2})O_3$, which shows negative charge relative to the disordered $Pb(Mg_{1/3}Nb_{2/3})O_3$. Thus, charge imbalance are developed as the 1 : 1 ordering is increased. Therefore, the degree of ordering can be enhanced by the substitution of A^{3+} donor for Pb^{2+} ion.

However, in PBiMN ceramics, the ordering is not observed by XRD pattern even though the Bi^{3+} donor substitutes Pb^{2+} ion. This may be considered as follows: one is that the change of unit cell volume is small and thus a mechanical driving force for ordering is small with increasing Bi^{3+} contents. For example, the $Sr(B'_{1/3}B''_{2/3})O_3$ system shows greater degree of ordering than the $Ba(B'_{1/3}B''_{2/3})O_3$ one, which is attributed to the smaller ionic radius of Sr^{2+} ion.[4] The other is that the large polarizability of the Bi^{3+} ion may also influence the ordering as in the case of $Pb(B'_{1/3}B''_{2/3})O_3$ system. This system has been shown the disordered structure due to the large polarizability of Pb^{2+} ion.[7]

In addition, the superlattice lines in PLaMT show the same tendencies with those in PLaMN and PNdMN ceramics.[8,11] Only a observed difference is the intensities of superlattice lines compared with the fundamental lines. From a theoretical calculation of intensity ratio of (111) superlattice line and (200) fundamental line, $I_{s(111)}/I_{f(200)}$, as shown in Figure 4, the ordering site is certainly confined to the B-site in PLaMT ceramics because the difference of atomic scattering factor of f_{Ta}-f_{Mg} in B-site is quite larger than that of f_{Pb}-f_{La} in A-site. Unlike this, in PLaMN and PNdMN ceramics, the ordering site is rather ambiguous because the difference of f_{Nb}-f_{Mg} is similar to that of f_{Pb}-f_{La} or f_{Pb}-f_{Nd}.[8]

The volume fraction of pyrochlore phase is increased with increasing La^{3+} content from 0 at.% to 30 at.%. It is suggested that the increase of ordering is directly related to the instability of the perovskite structure, since the Mg-rich composition relatively causes a Ta-rich composition in the disordered state.[7,8] The excess Ta_2O_5 in the disordered states

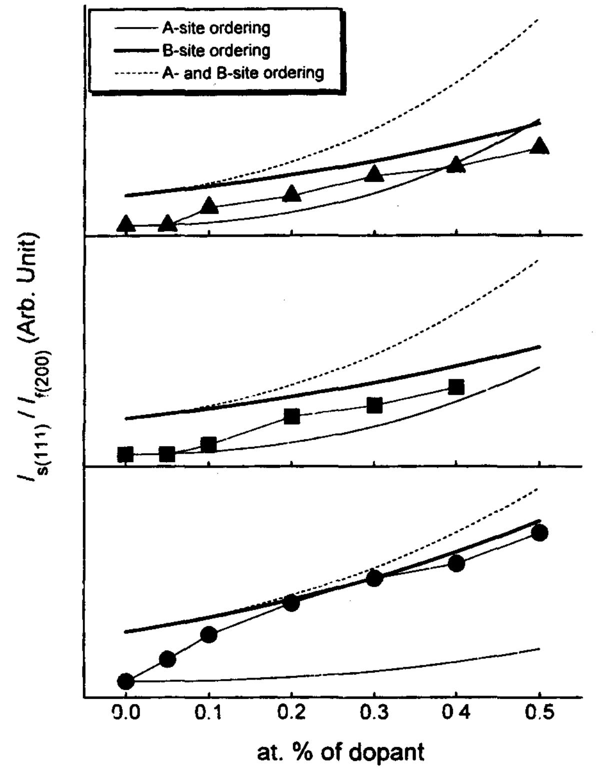

Figure 4. Relative integrated intensity of the superlattice reflection to the fundamental reflection for PLaMN (▲), PNdMN (■), and PLaMT (●) ceramics.

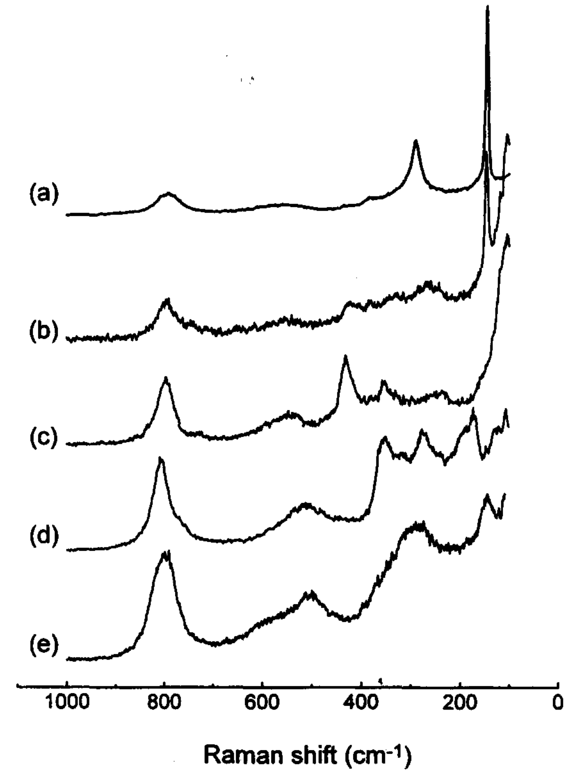

Figure 5. Raman spectra for selected composition. (a) $Pb(Mg_{1/3}Ta_{2/3})O_3$, (b) $Pb_{0.7}La_{0.3}(Mg_{1.3/3}Ta_{1.7/3})O_3$, (c) $Pb_{0.5}La_{0.5}(Mg_{1.5/3}$-$Ta_{1.5/3})O_3$, (d) $Pb(Yb_{1/3}Nb_{2/3})O_3$, and (b) $Pb_{0.7}Bi_{0.3}(Mg_{1.3/3}Nb_{1.7/3})O_3$

can easily react with PbO to form PbO-Ta_2O_5 related compounds, as expected from the corresponding phase diagram.[12,13] However, the pyrochlore phase is not formed with La^{3+} contents 40 at.% and 50 at.%. This may be ascribed as the change of B-site compositions. For example, in $Pb_{1-x}La_x(Mg_{(1+x)/3}Ta_{(2-x)/3})O_3$ for x=0.50, the pyrochlore phase is not observed because the 1 : 1 ordering promotes a more homogeneous distribution as in the case of $Pb(Sc_{1/2}Ta_{1/2})O_3$.

The Raman spectra for selected compositions are shown in Figure 5. For unmodified PMT, it exhibits the same feature as that for PMN.[14] The band at 290 cm^{-1}, assigned to the O-B-O bending modes, are split to three band with increasing La^{3+} content, which may be ascribed to the lowered local symmetry by the 1 : 1 ordering. The Raman spectrum for $Pb_{1/2}La_{1/2}(Mg_{1/2}Ta_{1/2})O_3$, having the highest degree of 1 : 1 ordering, has five relatively sharp Raman bands at *ca.* 798, 548, 432, 358, and 238 cm^{-1}. This is very similar to those of ordered $Pb(Yb_{1/2}Nb_{1/2})O_3$, which has been known to have an ordered perovskite structure, except in the peak frequencies.[5] However, PBiMN ceramics show no changes with the Bi^{3+} content is increased.

In conclusion, we suggest that the increase of the ordering can be explained as the effect of electrostatic charge compensation by incorporating La^{3+} in PMT lattices. However, the effect of mechanical forces due to the reduction of unit cell volume and polarizability of A-site ion must be considered as in the case of PBiMN ceramics. In PLaMT ceramics, the 1 : 1 ordering led to a mixture of Mg-rich region and Ta-rich region, resulting in the formation of pyrochlore phases.

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Rhodium-Catalyzed Coupling Reaction of 2-Vinylquinolines with Terminal Alkenes *via* C-H Bond Activation

Yeong-Gweon Lim and Jung-Bu Kang

1st R&D Center (1-4-5), Agency for Defense Development, Yuseong P.O. Box 35-1, Taejon 305-600, Korea

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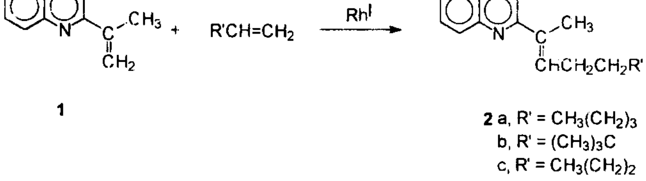
The formation of C-C bonds by activation of C-H bonds is of particular value. Especially vinylic C-H bond activation of the alkenes has been investigated.[1] Alkylation at the vinylic position of alkenes *via* C-H bond activation by transition metal complexes has been reported by us,[2] Trost *et al.*[3] and Murai *et al.*[4] In this report, we describe that 2-vinylquinolines react with terminal alkenes at the β-position in the presence of the Rh(I) complex as a catalyst to give the highly selective cross coupled β-alkylated products.

2-Isopropenylquinoline **1** reacted with 1-hexene (3 equiv.) in the presence of Wilkinson complex (10 mol%) in toluene at 110 °C for 21 h to give the alkylated product **2a** as a mixture of *cis* and *trans* isomers in 65% yield (Run 1). The reaction rate was also found to be a function of the alkene concentration. The reaction rate increased as the alkene concentration: 10 equiv. and 20 equiv. of 1-hexene gave 86% and 94%, respectively (Run 3 and 5).

In the case of neohexene, **1** reacted with 5 equiv. of neohexene in the presence of Wilkinson complex (10 mol%) in toluene at 110 °C for 20 h to give the corresponding



Scheme 1.