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Superiority of nitrate decomposition method for synthesis of K_2NiF_4-type $La_xSr_{2-x}MnO_4$ catalysts

R. Karita [a], H. Kusaba [b], K. Sasaki [c], Y. Teraoka [b,*]

[a] Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
[b] Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
[c] Department of Mechanical Engineering Science, Faculty of Engineering, Kyushu University, Motooka, Nishai-ku, Fukuoka 819-0395, Japan

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Abstract

K_2NiF_4-type $La_{0.2}Sr_{1.8}MnO_4$ was synthesized by nitrate (ND) and nitrate/acetate (NAD) decomposition methods as well as solid-state reaction. Single-phase oxide was obtained at 550 °C by the ND method just after the decomposition of $Sr(NO_3)_2$ and at 1000 °C by the NAD method after the decomposition of $SrCO_3$. The K_2NiF_4-type oxide was hardly formed by the solid-state reaction. In the La–Sr–Mn system, an intermediate compound of $SrCO_3$, if present or formed during the decomposition process, interfered with the low-temperature formation of the K_2NiF_4-type oxide because of its high decomposition temperature about 1000 °C. The ND method used only metal nitrates and no starting materials with carbon source, so that the low-temperature synthesis of the K_2NiF_4-type oxide was realized without forming obstinate intermediate compound of $SrCO_3$. The low-temperature synthesis was possible for $La_xSr_{2-x}MnO_4$ with the substitution of La ($0 < x < 0.5$) and not for $La_{0.2}A_{1.8}MnO_4$ (A = Ca and Ba). The effect of A-site cations on the K_2NiF_4-phase formation was discussed from the geometric aspect.
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Keywords: K_2NiF_4-type $La_xSr_{2-x}MnO_4$; Nitrate decomposition method; Lower-temperature synthesis

1. Introduction

Perovskite-type oxides (ABO_3) have been investigating as catalysts, because they show high catalytic activity for the oxidation of CO, hydrocarbons and VOCs as well as the direct decomposition of NO [1]. In addition, perovskites having a well-defined structure are good target materials to verify the relation between catalytic property and solid-state chemistry [1]. Recent development of Pd-containing perovskites such as $La(Fe,Co,Pd)O_3$ with the so-called self-regeneration property [2,3] has recalled the attention to perovskites in the application to automotive catalysis.

K_2NiF_4-type oxides (A_2BO_4) have not been studied so much as catalysts in comparison with perovskites, though they are categorized in relative oxides of $(AO)_n(ABO_3)$; $n = 0$ for perovskite and $n = 1$ for K_2NiF_4-type. Actually, K_2NiF_4-type oxides so far reported as catalytic materials were limited to those with Co, Cu and Ni at B-site [4–14]. Very recently, we reported, for the first time, the catalytic application of Mn-containing K_2NiF_4-type oxides, $La_xSr_{2-x}MnO_4$ [15]. $La_xSr_{2-x}MnO_4$ showed lower catalytic activity for NO–CO reaction than $La_{0.5}Sr_{0.5}MnO_3$ perovskite. When Pd was loaded on them, however, Pd/$La_xSr_{2-x}MnO_4$ was more active and selective to N_2 formation than Pd/$La_{0.5}Sr_{0.5}MnO_3$ and it may be a possible candidate for the three-way catalyst [15].

$La_xSr_{2-x}MnO_4$ have been studied from interests of electronic and magnetic properties, and they were mostly synthesized by solid-state reaction at very high temperatures [16–18]; for examples, the oxide with $x = 1$ was synthesized at 1300 °C in N_2 [16], the oxides with $0 \leq x \leq 1$ at 1400 °C in argon [17], and the oxides with $0 \leq x \leq 0.8$ at 1480 °C in air [18]. Börger et al. succeeded the synthesis of $La_{0.5}Sr_{1.5}MnO_4$ by using freeze-dried acetate precursors and calcination at 1000 °C was necessary to obtain a single-phase oxide [19]. In our previous paper, $La_xSr_{2-x}MnO_4$ ($0 < x \leq 0.5$) was obtained at 800 °C by a simple nitrate decomposition method which was composed of evaporation-to-dryness of aqueous metal nitrates and calcination in air [15]. The simple preparation would

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* Corresponding author. Tel.: +81 92 583 7526; fax: +81 92 583 8853.
E-mail address: teraoka@mm.kyushu-u.ac.jp (Y. Teraoka).

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enlarge the possibility of investigation of $La_xSr_{2-x}MnO_4$ in many applications including catalysis, so that clarification of the preparation by the nitrate decomposition method is an important issue to be investigated.

In this paper, we focused on elucidating the superiority of the nitrate decomposition method and the effects of A-site cations in the synthesis of $La_{0.2}A_{1.8}MnO_4$ (A = Ca, Sr and Ba).

2. Experimental

In the synthesis of $La_{0.2}A_{1.8}MnO_4$ (A = Ca, Sr and Ba) by the nitrate decomposition (ND) method, metal nitrates of $La(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ were used as starting materials. After evaporation-to-dryness of a mixed aqueous solution containing appropriate amounts of metal nitrates, the residue was calcined first at 350 °C for 2 h and then 500–1200 °C for 10 h in air. In order to investigate the effect of acetate precursor, $La_{0.2}Sr_{1.8}MnO_4$ was prepared by evaporation-to-dryness of mixed aqueous solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ and nitrates of La and Sr, followed by the two-step calcination in air (nitrate/acetate decomposition method). In solid-state reaction, La_2O_3, $SrCO_3$ and $MnCO_3$ were mixed for 30 min in a mortar and calcined at each temperature for 10 h in air.

Crystalline phases in the products were identified by powder X-ray diffraction (XRD) using Cu Kα radiation (Rigaku RINT2200). Thermogravimetric analysis (TG) was carried out at a heating rate of 10 °C min^{-1} in air (Shimadzu DTG-60H). Fourier transformed infrared spectroscopy (FT-IR) was recorded on a Shimadzu IR-Prestige 21 spectrometer at room temperature by the KBr method.

3. Results and discussion

3.1. Synthesis of K_2NiF_4-type $La_xSr_{2-x}MnO_4$

In our previous paper [15], $La_xSr_{2-x}MnO_4$ ($0 \leq x \leq 0.8$) were prepared by the ND method at 800 °C, and single-phase oxides with a tetragonal K_2NiF_4-type structure were obtained at $x = 0.1$, 0.2 and 0.4. When x exceeded 0.5, by products of La_2O_3 ($x \geq 0.5$) and $SrMnO_{3-\delta}$ ($x = 0.8$) were observed. For the oxide with $x = 0$ (Sr_2MnO_4), XRD pattern was completely different from that of the K_2NiF_4-type oxide and agreed with the reported pattern of α-Sr_2MnO_4 [20]. α-Sr_2MnO_4 was reported to transform into K_2NiF_4-type structure above 1600 °C [20] and to be a mixture of SrO and $Sr_7Mn_4O_{15}$ [21]. There results indicate that, in the ND synthesis at 800 °C, the substitution of La for Sr is indispensable for $La_xSr_{2-x}MnO_4$ to crystallize in K_2NiF_4-type structure and that the solubility limit of La is just below $x = 0.5$.

Fig. 1 shows XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ prepared by the ND method. When the precursor was calcined at 500 °C, only $Sr(NO_3)_2$ was identified as a crystalline phase. When the calcination temperature increased to 550 °C, $Sr(NO_3)_2$ was decomposed and a single-phase K_2NiF_4-type oxide was obtained. The oxide was stable even after calcination at 1200 °C. It has turned out that K_2NiF_4-type $La_{0.2}Sr_{1.8}MnO_4$ can be synthesized at calcination temperature as low as 550 °C.

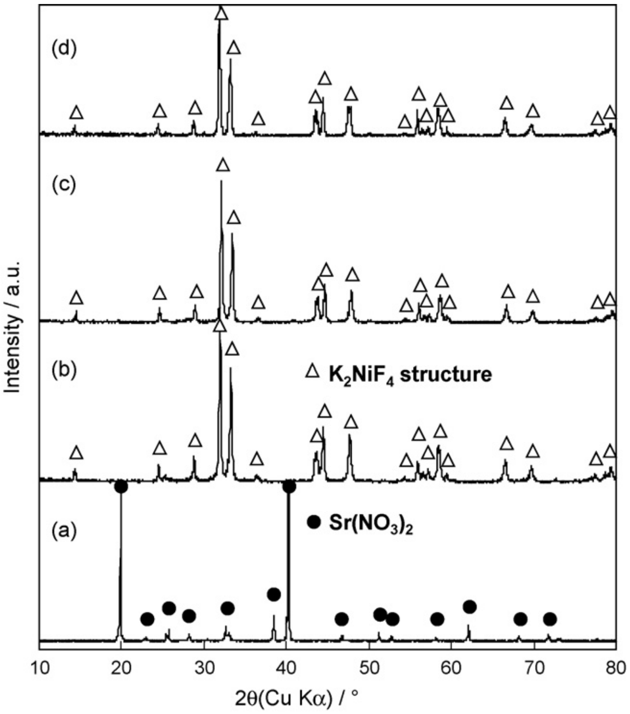

Fig. 1. XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ synthesized by nitrate decomposition method and calcined at (a) 500 °C, (b) 550 °C, (c) 800 °C and (d) 1200 °C.

In Fig. 2(A), TG curve of the evaporated-to-dryness precursor of $La_{0.2}Sr_{1.8}MnO_4$ was shown together with those of La, Sr and Mn nitrates. The precursor underwent several-step decomposition (weight loss) up to about 300 °C (first stage), gradual decomposition up to about 550 °C (second stage), and sharp decomposition (third stage) to reach the constant weight above 650 °C. Among metal nitrates of raw materials, $Sr(NO_3)_2$ was more stable or difficult to decompose than La and Mn nitrates. As shown in Fig. 2(B), sharp IR bands assignable to nitrate ion were observed at 1382, 813 and 736 cm^{-1} after calcination at 400 °C, and they were completely disappeared after calcination at 600 °C. These results, coupled with the XRD results, indicate that, in the ND synthesis, crystallization of K_2NiF_4-type oxide takes place just after or simultaneously with the decomposition of $Sr(NO_3)_2$.

Comparing the decomposition behavior of the precursor with those of metal nitrates, the decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ to MnO_2 took place in the first stage and the partial decomposition of $La(NO_3)_3 \cdot 6H_2O$ did in the first and second stages. The completion temperature of the third-stage decomposition was close to that of $La(NO_3)_3 \cdot 6H_2O$ but lower than that of $Sr(NO_3)_3$. Table 1 lists completion temperatures of the decomposition (T_{DC}) of the precursors of $La_xSr_{2-x}MnO_4$ ($x = 0, 0.2$) and the mixture of La and Sr nitrates. T_{DC} progressively decreased with increasing the La content, indicating that the decomposition of $Sr(NO_3)_2$ is enhanced by the co-presence and decomposition of $La(NO_3)_3 \cdot 6H_2O$. Since T_{DC} of the precursor of $x = 0$ without La (639 °C) was lower than that of neat $Sr(NO_3)_2$ (732 °C), the decomposition of $Sr(NO_3)_2$ in the precursor is also enhanced by the co-present MnO_2 which is a decomposition product of $Mn(NO_3)_2 \cdot 6H_2O$. There results show that the decomposition of $Sr(NO_3)_2$ is enhanced in the precursor and this is a reason why the

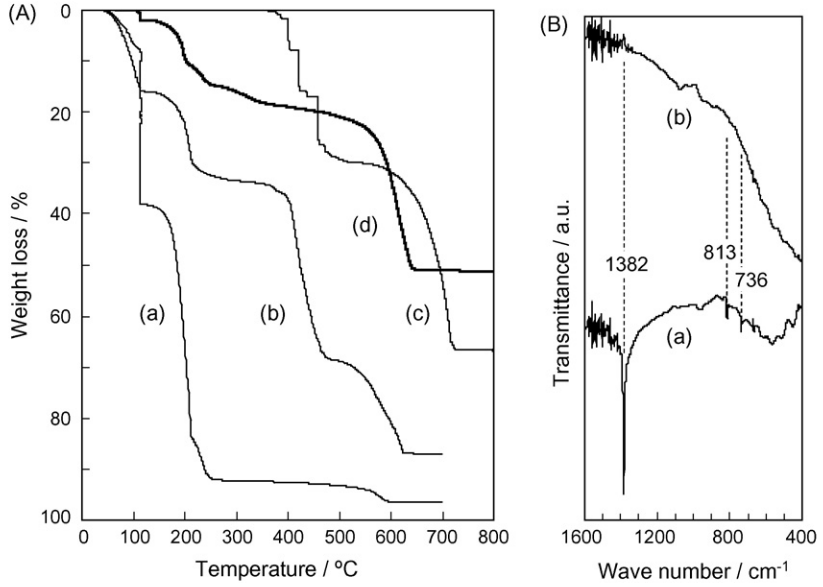

Fig. 2. (A) TG curves of (a) $Mn(NO_3)_2{\cdot}6H_2O$, (b) $La(NO_3)_3{\cdot}6H_2O$, (c) $Sr(NO_3)_2$ and (d) the evaporated-to-dryness precursor of $La_{0.2}Sr_{1.8}MnO_4$. (B) FT-IR spectra of the precursor decomposed at (a) 400 °C and (b) 600 °C.

K_2NiF_4-type oxide is formed at temperatures lower than the decomposition temperature of $Sr(NO_3)_2$.

Fig. 3 shows XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ synthesized with the procedure same as the ND method but with different starting materials of Mn acetate and nitrates of La and Sr (nitrate/acetate decomposition method). $SrCO_3$ was observed in addition to K_2NiF_4-type oxide after calcination at 800 °C, and single-phase K_2NiF_4-type oxide was obtained after calcination at 1000 °C. When carbon source, Mn acetate in this case, is present in the starting materials, Sr nitrate react with CO_2 to convert into thermodynamically more stable $SrCO_3$, and the K_2NiF_4 phase is formed above 1000 °C which is close to the decomposition temperature of $SrCO_3$ [19].

XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ synthesized by the solid-state reaction using La_2O_3, $MnCO_3$ and $SrCO_3$ as starting materials are shown in Fig. 4. The observed crystalline phases depended on the calcination temperature. The formation of perovskite phases took place in preference to that of K_2NiF_4 phase, and $SrCO_3$ and La_2O_3 were almost disappeared after calcination at 1000 °C. The formation of K_2NiF_4 phase, however, was hardly observed even after calcination at 1200 °C. This contrasts with the preparation by the nitrate and nitrate/acetate decomposition methods, and indicates the advantage of the preparation method using mixed aqueous solution and evaporation-to-dryness.

Table 1
Temperature of the decomposition completion (T_{DC}) of the precursor of $La_xSr_{2-x}MnO_4$ ($x = 0$, 0.2) and mixtures of La and Sr nitrates

Sample	T_{DC} (°C)
$Sr(NO_3)_3/La(NO_3)_3{\cdot}6H_2O$ (molar ratio)	
1/0	732
3/1	687
1/1	666
1/3	639
0/1	630
Precursor of $La_xSr_{2-x}MnO_4$	
$x = 0$	639
$x = 0.2$	650

From the results shown above, it can be concluded that the following two requirements are at least necessary to realize the low-temperature synthesis of $La_xSr_{2-x}MnO_4$. One is to utilize the evaporation-to-dryness of mixed aqueous solution which would give smaller-sized and therefore reactive intermediates such as La_2O_3. Another is not to use carbon-containing raw materials in order to prevent the formation of the obstinate intermediate compound of $SrCO_3$. The nitrate decomposition method fulfils both requirements and makes it possible to synthesize $La_xSr_{2-x}MnO_4$ at temperature as low as 550 °C.

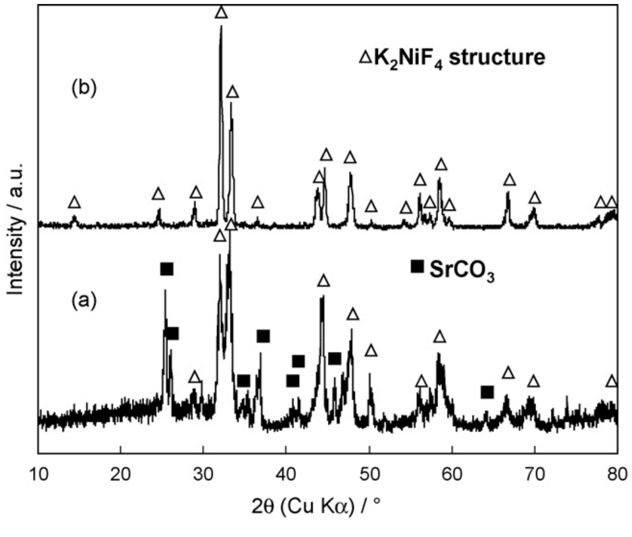

Fig. 3. XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ synthesized by nitrate/acetate decomposition method and calcined at (a) 800 and (b) 1000 °C. Starting materials were $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$ and $Mn(CH_3COO)_2{\cdot}4H_2O$.

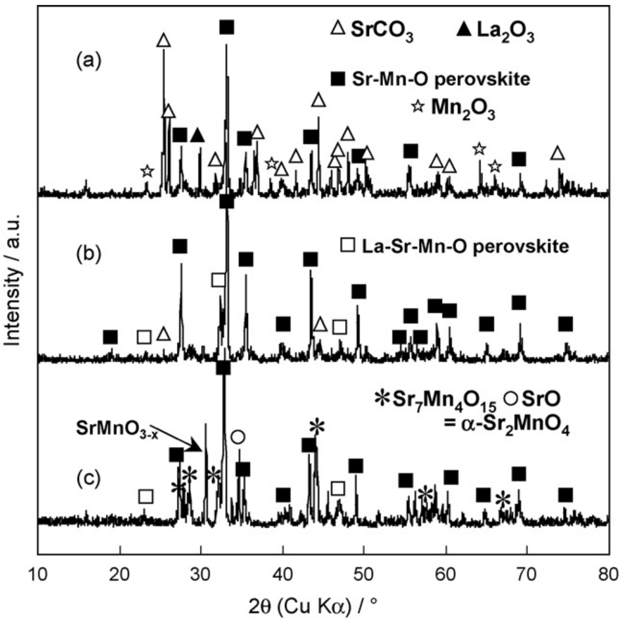

Fig. 4. XRD patterns of $La_{0.2}Sr_{1.8}MnO_4$ synthesized by solid-state reaction and calcied at (a) 800 °C, (b) 1000 °C and (c) 1200 °C. Starting materials were La_2O_3, $SrCO_3$ and $MnCO_3$.

3.2. Effect of A-site cations in the synthesis of Mn-based K_2NiF_4-type oxides

Figs. 5 and 6 show XRD patterns of $La_{0.2}Ca_{1.8}MnO_4$ and $La_{0.2}Ba_{1.8}MnO_4$, respectively. As for the Ca system, the K_2NiF_4 phase was formed at 550 °C, but the reaction was not completed even after calcination at 1200 °C because CaO was still present. In the case of Ba system, on the other hand, the K_2NiF_4 phase was not formed after calcination at 800 and 1000 °C. The formation of $Ba_3Mn_2O_8$ and $BaMnO_3$ phases is preferential to that of the K_2NiF_4 phase in the La–Ba–Mn–O system. These results clearly indicate that the formation of the K_2NiF_4-phase in $La_{0.2}A_{1.8}MnO_4$ depended on the kind of alkaline earth meal cations (A), and Sr with intermediate ionic radius is the most suitable to the K_2NiF_4-phase formation.

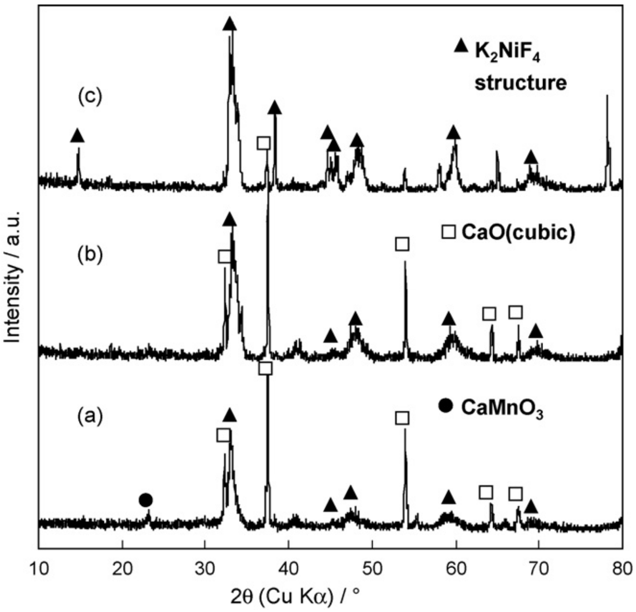

Fig. 5. XRD patterns of $La_{0.2}Ca_{1.8}MnO_4$ synthesized by nitrate decomposition method and calcined at (a) 550 °C, (b) 800 °C and (c) 1200 °C.

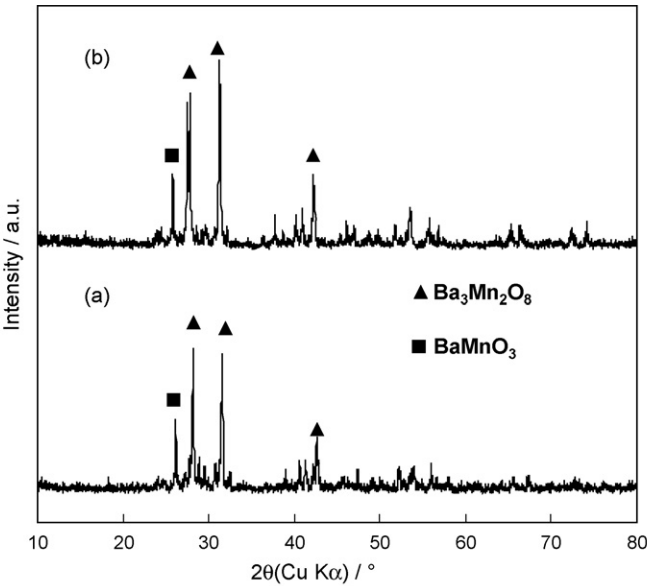

Fig. 6. XRD patterns of $La_{0.2}Ba_{1.8}MnO_4$ synthesized by nitrate decomposition method and calcined at (a) 800 °C and (b) 1000 °C.

The geometric effect on the formation of perovskite-type oxide has been discussed by the tolerance factor (t) using ionic radii of A cation (r_A), B-site cation (r_B) and O^{2-} anion (r_O) which was proposed by Goldshumidt [22]:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \tag{1}$$

The tolerance factor is also applicable to the K_2NiF_4-type oxide and the range of the K_2NiF_4-phase formation was reported to be $0.87 \leq t \leq 0.99$ [23]. Tolerance factors of $La_xA_{2-x}MnO_4$ (A = Ca, Sr and Ba, $0 \leq x \leq 0.5$) were calculated by using Shannon's ionic radii [24]. Apparent t values were calculated based on the following chemical formulae without the formation of oxide ion vacancy and equations for the calculation of average ionic radius.

$$La_x{}^{3+}A_{2-x}{}^{2+}Mn_x{}^{3+}Mn_{1-x}{}^{4+}O_4 \tag{2}$$

$$r_A = \left(\frac{x}{2}\right) r(La^{3+}) + \left\{1 - \frac{x}{2}\right\} r(Sr^{2+}) \tag{3}$$

$$r_B = x\, r(Mn^{3+}) + (1 - x)\, r(Mn^{4+}) \tag{4}$$

Here $r(La^{3+})$ and $r(Sr^{2+})$ are ionic radii of La^{3+} and Sr^{2+} in nine-fold coordination, and $r(Mn^{3+})$ and $r(Mn^{4+})$ are those of Mn^{3+} and Mn^{4+} in six-fold coordination. In our previous paper [15], the composition of Mn^{3+} and Mn^{4+} in $La_xSr_{2-x}MnO_4$ (x = 0.1, 0.2 and 0.4) was determined by iodometry, and the actual formula were shown in Table 2. Based on the measured Mn^{3+}/Mn^{4+} composition, the actual tolerance factors were calculated for these oxides. Calculated t factors are plotted as a function of x

Table 2
Actual chemical formula of $La_xSr_{2-x}MnO_4$ ($x = 0.1$, 0.2 and 0.4)

$x = 0.1$	$La_{0.1}Sr_{1.9}Mn_{0.27}{}^{3+}Mn_{0.73}{}^{4+}O_{3.92}$
$x = 0.2$	$La_{0.2}Sr_{1.8}Mn_{0.22}{}^{3+}Mn_{0.78}{}^{4+}O_{3.99}$
$x = 0.4$	$La_{0.4}Sr_{1.6}Mn_{0.24}{}^{3+}Mn_{0.76}{}^{4+}O_{4.08}$

Calculated from data in reference [15].

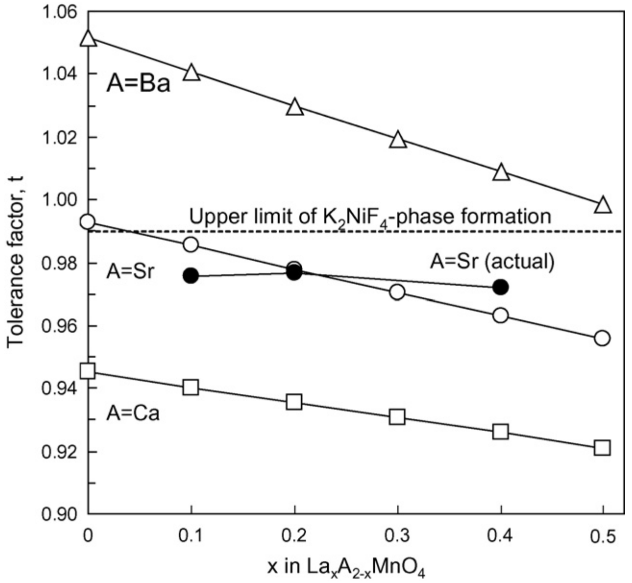

Fig. 7. Tolerance factors of $La_xA_{2-x}MnO_4$ (A = Ca, Sr and Ba, $0 \leq x \leq 0.5$) as a function of La content (x). Open and closed symbols are apparent and actual tolerance factors, respectively. See text for details.

in Fig. 7. For apparent t factor of $La_xSr_{2-x}MnO_4$, the t value of $x = 0$ is slightly above the upper limit of K_2NiF_4-phase formation, and La substitution caused a decrease in t value and entrance into the formation range even at $x = 0.1$. As stated above, the decomposition of the precursors of $x = 0$ and 0.2 completed at nearly same temperatures, but the K_2NiF_4-phase was formed not for $x = 0$ but for $x = 0.2$. It can be speculated that the incorporation of La is geometrically favorable to form the K_2NiF_4-type oxide. The t value of $La_{0.2}Ba_{1.8}MnO_4$ was too large to form the K_2NiF_4 phase, which is consistent with the experimental result. The t value of $La_{0.2}Ca_{1.8}MnO_4$ was within the range of the K_2NiF_4-phase formation, but smaller than that of the corresponding Sr system. This may be a reason for the difficulty in the single-phase formation. It should be noted that actual t values of single-phase K_2NiF_4-type oxides was kept at around 0.97 by changing Mn^{3+}/Mn^{4+} composition. It is not sure whether the constant t value has implication with the single-phase formation or not, but it is true that the single-phase $La_xSr_{2-x}MnO_4$ have the t value close to the upper limit of the K_2NiF_4-phase formation.

4. Conclusions

By the nitrate decomposition method, $La_{0.2}Sr_{1.8}MnO_4$ could be synthesized at temperature as low as 550 °C just after the decomposition of $Sr(NO_3)_2$. The decomposition of $Sr(NO_3)_2$ was enhanced in the precursor as compared with neat $Sr(NO_3)_2$. When Mn acetate and nitrates of La and Sr were used as starting materials, the single-phase K_2NiF_4-type oxide was obtained at 1000 °C by way of the appearance of the intermediate compound of $SrCO_3$ at 800 °C. By the solid-state reaction using La_2O_3, $MnCO_3$ and $SrCO_3$, the K_2NiF_4-type oxide was never obtained even after calcination at 1200 °C. From these results, it can be concluded that low temperature synthesis of $La_{0.2}Sr_{1.8}MnO_4$ is realized only by the nitrate decomposition method because of the prevention of $SrCO_3$ formation and the well mixing state of precursor materials. The substitution of La for Sr in $La_xSr_{2-x}MnO_4$ was indispensable to form the K_2NiF_4-type oxide at lower temperatures, and the low-temperature synthesis was never realized in $La_{0.2}A_{1.8}MnO_4$ (A = Ca and Ba). The effect of A-site cations on the K_2NiF_4-phase formation may be understood from the geometric consideration.

Acknowledgement

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