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Thermally Induced A′−A Site Exchange in Novel Layered Perovskites $Ag_2[Ca_{1.5}M_3O_{10}]$ (M = Nb, Ta)

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Layered perovskites of the type Ruddlesden−Popper (RP, $A_2'[A_{n-1}M_nO_{3n+1}]$)-, Dion−Jacobson (DJ, $A'[A_{n-1}M_nO_{3n+1}]$)-, and Aurivillius (AU, $Bi_2O_2[A_{n-1}M_nO_{3n+1}]$)-phases,[1] have been widely investigated for their varied and interesting physical properties. They are among the most popular starting reagents for soft-chemical synthesis of novel metastable compounds.[2] These layered compounds (RP, DJ, and AU) have the same general formula for the perovskite blocks (represented within the square brackets), which are made up of perovskite layers *n* octahedra thick. The layers are separated by the A′ cations (alkali, alkaline earth, or rare earth ions) in RP and DJ phases, and Bi_2O_2 layers in AU phases. The functionality of the soft-chemical reactions (i.e., ion-exchange, intercalation/deintercalation, dehydration, exfoliation, and layer-by-layer assembly, etc.) carried out in these oxides is almost exclusively restricted to the interlayer cations or cationic units.[2] By using these routes it is possible to achieve various substitutions of the interlayer cations, which trigger subtle structural distortions that can be exploited to fine-tune the properties.[3,4]

In this communication we report the synthesis and structural characterization of new layered perovskites $Ag_2[A_{1.5}M_3O_{10}]$ (A = Ca, Sr; M = Nb, Ta). These samples were prepared via ion-exchange reactions from $Li_2[A_{1.5}M_3O_{10}]$ precursors, which belong to the recently reported family of layered perovskites $Li_2[A_{0.5n}M_nO_{3n+1}]$.[5] Surprisingly, we also observed that when A = Ca, a topotactic, irreversible "A′−A site exchange" occurs upon heating. We believe this is the first instance of such "ion site exchange" observed in layered perovskites, a discovery which allows one to use soft-chemistry routes to substitute on the A site, in addition to the familiar A′ site substitutions. This capability should lead to the synthesis of new metastable layered perovskites, thereby opening another avenue for tuning the physical properties. As an example of the latter effect we demonstrate the sensitivity of the ionic conductivity to the "A′−A exchange" in this communication.

$Ag_2[Ca_{1.5}Nb_3O_{10}]$ (**I**) was obtained from $Li_2[Ca_{1.5}Nb_3O_{10}]$ by ion-exchange. The composition was confirmed from energy-dispersive X-ray and thermogravimetric analyses (see Supporting Information for details). All of the reflections in the X-ray powder diffraction (XRPD) pattern of $Ag_2[Ca_{1.5}Nb_3O_{10}]$ could be indexed using an orthorhombic cell ($a = 5.5248(2)$ Å, $b = 5.4557(2)$ Å, $c = 28.237(1)$ Å),[6] indicating formation of single-phase compound. Compared to $Li_2[Ca_{1.5}Nb_3O_{10}]$[5a] we found two significant structural changes: (i) a distortion from a tetragonal (A′ = Li) to an orthorhombic unit cell (A′ = Ag) and (ii) a large increase in the *c*-axis length ($\Delta c \cong 2.00$ Å). The former effect can be attributed to the occurrence of octahedral tilting distortions,[3] while the latter effect originates from the replacement of tetrahedrally coordinated Li^+ ions with the larger nine-fold coordinate Ag^+ ions.[7]

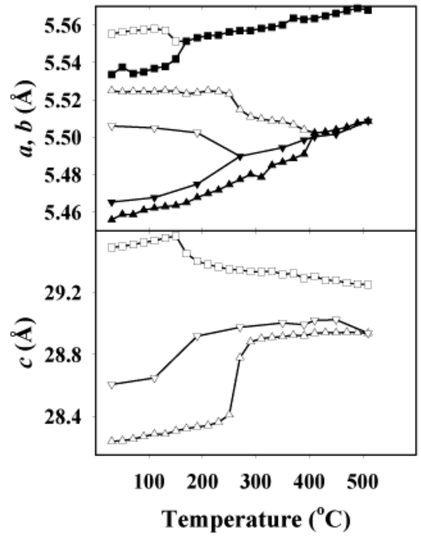

Figure 1. Evolution of lattice parameters of $Ag_2[Ca_{1.5}Nb_3O_{10}]$ (triangles) and $Ag_2[Sr_{1.5}Nb_3O_{10}]$ (squares). In top panel open and filled symbols denote *a* and *b* parameters, respectively. Upward and downward triangles represent heating and cooling cycles, respectively.

Differential thermal analysis (DTA) of the product did not show any sharp phase transitions before its decomposition temperature (∼700 °C). Nonetheless, we anticipated a decrease in the octahedral tilting distortion upon heating.[8] To investigate this possibility we carried out temperature-dependent X-ray diffraction studies over the temperature range 30−510 °C (both upon heating and cooling). Significantly, we found two clear phase transitions on heating (Figure 1): one near 270 °C and another close to 410 °C. The first transition is accompanied by an abrupt increase in the *c*-axis ($c = 28.410(3)$ Å at 250 °C, $c = 28.903(2)$ Å at 310 °C). The second transition involves the evolution from an orthorhombic unit cell below 410 °C to a tetragonal one at higher temperatures. Analysis of powder pattern obtained at 490 °C ($a = 3.8994(1)$ Å, $c = 29.015(1)$ Å) gives systematic absences corresponding to the extinction symbol $I - - -$. Using a starting model based on the structure of $Ag_2[La_2Ti_3O_{10}]$ (space group $I4/mmm$),[7b] we were unable to obtain a satisfactory fit to the data ($R_p = 15.6\%$; $R_{wp} = 23.0\%$). Upon allowing the Ag^+ and Ca^{2+} ions to mix, the reliability factors decreased sharply ($R_p = 9.4\%$; $R_{wp} = 12.7\%$). The results reveal that ∼60% of the Ca^{2+} ions occupy the nine-fold interlayer site, while the Ag^+ ions are almost equally distributed among the 12-coordinate (A) and 9-coordinate (A′) sites (Figure 2). Thus, the formula of the high-temperature phase can be written as $Ag_{1.1}Ca_{0.9}[Ca_{0.6}Ag_{0.9}Nb_3O_{10}]$ (**II**). The temperature at which this

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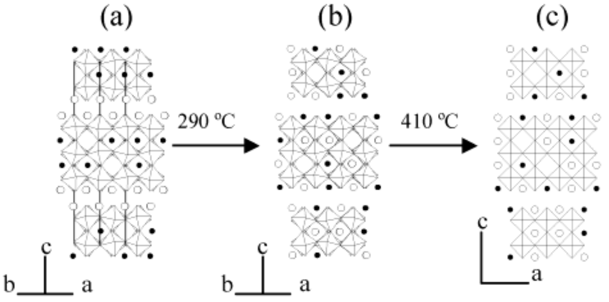

Figure 2. Schematic structures for $Ag_2[Ca_{1.5}Nb_3O_{10}]$ at (a) room temperature, (b) 290 °C, and (c) 490 °C. Open and closed spheres represent Ag^+ and Ca^{2+} ions, respectively.

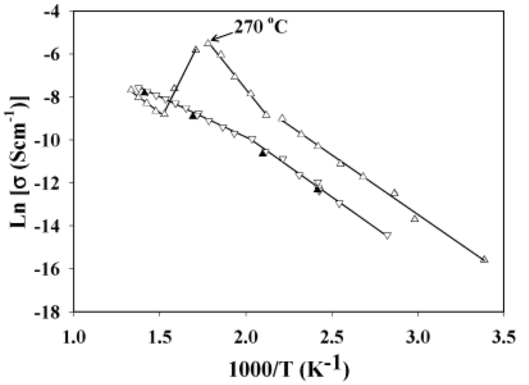

Figure 3. Plot of 1000/T vs ln σ of $Ag_2[Ca_{1.5}Nb_3O_{10}]$. Open upward and downward triangle represent heating and cooling cycles, respectively. Closed triangles denote a second heating cycle.

“A′−A site exchange” occurs also correlates well with the increase in the c-axis observed at 290 °C.[9] Upon cooling **II** transforms back to an orthorhombic unit cell ($a = 5.5020(3)$ Å, $b = 5.4665(3)$ Å, $c = 28.605(1)$ Å) at 280 °C, but the c-axis remains larger than the as-synthesized room-temperature phase ($\Delta c = 0.37$ Å). This behavior is a clear indication that the “A′−A exchange” is not reversible. Furthermore, taking the difference between the a and b parameters as a rough measure of the magnitude of the tilting distortion,[10] we see that the phase obtained after cooling is less distorted, presumably as a result of increasing the average ionic radius of the cation distribution on the 12-coordinate A site.

To confirm our arguments, we investigated the Ag^+-ion conductivity using impedance analysis. The results strongly corroborate our observation: the ionic conductivity decreases by an order of magnitude upon heating above 290 °C (Figure 3).[11] Furthermore, upon cooling, the ionic conductivity does not return to its original value, but it does attain the same slope in the Arrhenius plot ($E_A \approx 0.47$ eV below 180 °C). This behavior suggests that the conduction path for the Ag^+ ions in the interlayer space is the same for **I** and **II**. The decreased conductivity of the latter can be attributed to the decrease in the concentration of Ag^+ ions on the interlayer sites. A second heating cycle followed same trace as observed upon cooling, suggesting that additional thermal treatment does not induce further cation rearrangement.

To investigate the generality of this behavior we prepared and studied $Ag_2[Ca_{1.5}Ta_3O_{10}]$ and $Ag_2[Sr_{1.5}Nb_3O_{10}]$. Diffraction studies reveal a similar “A′−A site exchange” in $Ag_2[Ca_{1.5}Ta_3O_{10}]$. However, the 270 and 410 °C transitions seen in **I** occur almost simultaneously in $Ag_2[Ca_{1.5}Ta_3O_{10}]$ (~350 °C). In contrast, no such transition occurs in $Ag_2[Sr_{1.5}Nb_3O_{10}]$ (Figure 1). This observation suggests that the likely driving force behind this transition is the superior fit (with respect to the smaller Ca^{2+} ion) of Ag^+ to the 12-coordinate A site. In $Ag_2[Sr_{1.5}Nb_3O_{10}]$ the Sr^{2+} and Ag^+ ions are of similar size, and electrostatic considerations favor a structure with the monovalent Ag^+ on the interlayer sites. Neutron diffraction measurements are underway to determine the full structural details for each compound as a function of temperature. Such information is essential to understand the different slopes observed in the 1000/T versus ln σ plots, and establish the mechanisms of the observed phase transitions.

In conclusion, we have prepared $Ag_{1.1}Ca_{0.9}[Ca_{0.6}Ag_{0.9}Nb_3O_{10}]$ and $AgCa[Ca_{0.5}AgTa_3O_{10}]$ for the first time. These compounds belong to the layered perovskite family where Ag^+ ions occupy both the A and A′ sites of the RP structure. This result demonstrates a method for utilizing soft-chemical routes to substitute onto the A sites within the perovskite blocks. We strongly believe, on the basis of the size, charge, and coordination preferences of the A′ and A cations, similar “A′−A site exchange” phase transitions could be utilized in other layered perovskite systems, thus providing a new synthetic tool for tuning the structure and associated properties of layered perovskites.

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Supporting Information Available: Synthesis, experimental procedures, X-ray diffraction, and typical thermal analysis data of $Ag_2[A_{1.5}M_3O_{10}]$ (A = Ca, Sr; M = Nb, Ta) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1957**, *10*, 538; **1958**, *11*, 54. (b) Dion, M.; Ganne, M.; Tournoux, M. *Mater. Res. Bull.* **1981**, *16*, 1429. (c) Gopalakrishnan, J.; Bhat, V. *Inorg. Chem.* **1987**, *26*, 4299. (d) Jacobson, A. J.; Johnson, J. W.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 3727. (e) Dion, M.; Ganne, M.; Tournoux, M. *Rev. Chim. Miner.* **1986**, *23*, 61. (f) Aurivillius, B. *Ark. Kemi* **1949**, *1*, 463, 499; **1950**, *2*, 519.

(2) Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* **2002**, *14*, 1455 and references therein.

(3) Aleksandrov, K. S. *Crystallogr. Rep.* **1995**, *40*, 251.

(4) (a) Colla, E. L.; Reaney, I. M.; Setter, N. *J. Appl. Phys.* **1993**, *74*, 3414. (b) Hwang, H. Y.; Palstra, T. T. M.; Cheong, S. W.; Batlogg, B. *Phys. Rev. B* **1995**, *52*, 15046. (c) Woodward, P. M. *Acta Crystallogr. B* **1997**, *53*, 44. (d) Woodward, P. M. *J. Appl. Crystallogr.* **1997**, *30*, 206. (e) Lufaso, M. W.; Woodward, P. M. *Acta Crystallogr. B* **2001**, *57*, 725.

(5) (a) Bhuvanesh, N. S. P.; Crosnier-Lopez, M. P.; Bohnke, O.; Emery, J.; Fourquet, J. L. *Chem. Mater.* **1999**, *11*, 634. (b) Bhuvanesh, N. S. P.; Crosnier-Lopez, M. P.; Duroy, H.; Fourquet, J. L. *J. Mater. Chem.* **1999**, *9*, 3093.

(6) Although the powder XRPD pattern obtained at room temperature could be indexed on an orthorhombic cell, we found significant peak-broadening for some of the Bragg reflections. On this basis a small monoclinic distortion cannot be ruled out. Similar peak-broadening and lowering of symmetry to monoclinic crystal systems has been reported in other RP phases, which has been attributed to subtle octahedral tiltings (Olafsen, Å.; Fjellvag, H.; Hauback, B. C. *J. Solid State Chem.* **2000**, *151*, 46 and references therein). Further work is required to establish the accurate structure of this phase.

(7) (a) Toda, K.; Watanabe, J.; Sato, M. *Mater. Res. Bull.* **1996**, *31*, 1427. (b) Toda, K.; Watanabe, J.; Sato, M. *Solid State Ionics* **1996**, *90*, 15.

(8) Hervoches, C. H.; Snedden, A.; Riggs, R.; Kilcoyne, S. H.; Manuel, P.; Lightfoot, P. *J. Solid State Chem.* **2002**, *164*, 280.

(9) Although the size of 9-coordinate Ca^{2+} ions (1.31 Å) is smaller than that of Ag^+ (1.44 Å), the cationic repulsions between Ca^{2+} and Ag^+ ions compared to that between two Ag^+ ions, occupying the interlayer space, would result in increased c parameter. The sizes of the ions were calculated as in reference: Brown, I. D. *Chem. Soc. Rev.* **1978**, *7*, 359.

(10) Marezio, M.; Remeika, J. P.; Dernier, P. D. *Acta Crystallogr. B* **1970**, *26*, 2008.

(11) The nature of the structural changes associated with change in the slope at 180 °C is not clear from the powder XRPD patterns.

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