

Stability of layered alkali-metal oxides $A_{0.5}CoO_2$ and $A_{0.5}FeO_2$ ($A=Li, Na, K, Mg, Ca, Sr$)

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Layered alkali-metal cobaltites, A_xCoO_2 , have attracted much attention due to remarkable properties originated from their two-dimensional (2D) structures. For example, Li_xCoO_2 has been used as a cathode material in commercialized lithium-ion batteries, and Na_xCoO_2 exhibits remarkable thermoelectricity [1]. Challenges are being made to search for new combinations of A-cations and Co or other metals, aiming at further improving known materials properties or exploring new functions of materials. However, the stability of the 2D structures that are responsible for remarkable properties has not been systematically understood. In fact, it is reported that Li_xCoO_2 is transformed from the layered structure to the spinel structure in some cases [2]. Lack of the understanding might make any proposals for new materials groundless. In this study, we systematically examined the stability of 2D layered structure of $A_{0.5}CoO_2$. Furthermore, it is also important to find substitutional elements for Co which is rare and expensive. Thus, as a first step, we chose Fe and reveal the stability of layered structure of $A_{0.5}FeO_2$ as well. Preliminary examinations in this study imply that $Na_{0.5}FeO_2$, which can be synthesized from abundant iron oxides and sea salt, would exhibit comparable thermoelectricity to $Na_{0.5}CoO_2$.

We carried out first principles calculations in order to obtain the total energies of both $A_{0.5}CoO_2$ and $A_{0.5}FeO_2$ with two crystal structures, the layered structure and spinel structure. We chose several typical elements, namely, Li, Na, K, Mg, Ca, and Sr for A. Then, we calculated the energy difference as

$$\Delta E = E_{\text{layer}} - E_{\text{spinel}}$$

where E_{layer} and E_{spinel} are total energies of layered and spinel structures, respectively. The calculation were carried out with the generalized gradient approximation (GGA) to density functional theory (DFT) using these initial structures determined by X-ray diffraction and powder neutron diffraction [3, 4].

As shown in Fig. 1, when ionic radius of A are small as for Li or Mg, ΔE turned out to be positive, indicating that spinel structure is more stable than the layered structure. On the other hand, ΔE became negative when Na, K, Ca, or Sr, was chosen for A, stabilizing the layered structure. In addition, it is found that ΔE decreases with the increase in ionic radius of A. In order to reveal the mechanism behind the stabilization of the layered structure, we analyzed strain of bonds and its impact on total energy with

additional first principles calculations with artificially changed lattice constants. Comparing bond lengths in layered and spinel structures, bond length of A-O changed with the ionic radius of A in both structures. In contrast, it is found that bond length of Co-O or Fe-O was much increased, or strained, in the spinel structure when ionic radius of A increased while it remained almost unchanged in the layered structure.

These can be easily explained from viewpoints of crystal structures: Co-O or Fe-O bonding has no other way than being strained when ionic radius of A and, in turn, bond length of A-O is changed since ions are packed in three dimensional manner in spinel structure. In contrast, in the 2D layered structure, even if thickness of A layer is increased due to increased ionic radius of A, thickness of CoO₂ or FeO₂ layer can be virtually unchanged since A layers and CoO₂ or FeO₂ layers are stacked alternately upon forming a 3D crystal. Although in-plane components of Co-O or Fe-O bonds are somewhat strained, presence of A vacancies, which are present when A content is smaller than unity, plays a role to relieve in-plane strain. These packing geometry determine the relative stability of the 2D layered structure as a function of ionic radius of A. The additional first principles calculations supported these explanations.

Finally, there is no remarkable differences in stability between A_{0.5}CoO₂ and A_{0.5}FeO₂ not only relative to the spinel phases but also relative to mixture of binary oxides, which implies the layered cobaltites and ferrites would be synthesized if those new materials has a potential to acquire promising properties, as Na_xFeO₂ does.

Reference

- [1] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B*, **56** (1997) R12685-R12687.
- [2] R. J. Gummow, D. C. Liles, and M. M. Thackeray, *Mater. Res. Bull.* **28** [3] (1993) 235-246.
- [3] Q. Huang, M. L. Foo, R. A. Pascal, Jr., J. W. Lynn, B. H. Toby, H. W. Zandbergen, and R. J. Cava, *Phys. Rev. B*, **70**, (2004) 184110.
- [4] M. Gateshki, V. Petkov, S. K. Pradhan and T. Vogt, *J. Appl. Crystallogr.* **38** [5] (2005) 772-779.

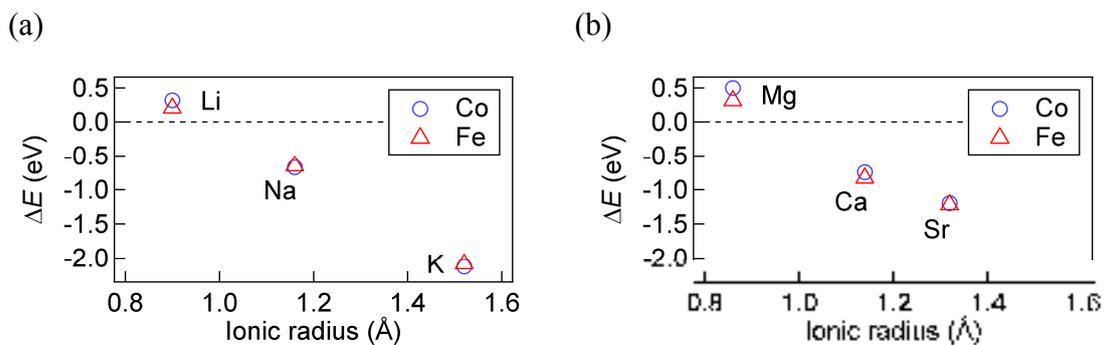


Fig. 1 Energy difference between 2D layered structure and spinel structure when A is (a) monovalent cation and (b) divalent cation.