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Layer Perovskites: A Critical Arena for Testing Concepts of Layer Rigidity

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Using high resolution x-ray diffraction data, we show that the composition dependence of the normalized basal-spacing, $d_N(x)$, of the bi-layer alkali perovskites, $Cs_xRb_{1-x}[LaNb_2O_7]$, measured over the range $0 \leq x \leq 1$, can be quantitatively accounted for with the anharmonic Lennard-Jones (aLJ) model which incorporates deformations of *both* the host layers and the guest ions. With the same independently determined value of the Rb/Cs stiffness constant ratio, 1.73, used in previous studies of $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$, the tri-layer perovskites, the aLJ model yields a very good one-parameter fit to $d_N(x)$ for the bi-layer perovskites. The single fitting parameter, $\beta = [d(0) - t]/[d(1) - t]$ where t is the host layer thickness, yields a t value of 7.73Å in very good (3%) agreement with the value 7.97Å deduced from structural studies.

Keywords: layered perovskites; layer rigidity; anharmonic Lennard-Jones

INTRODUCTION

One of the most fundamental challenges in research on intercalated layered solids has been the development of a layer rigidity model which correctly accounts for the composition dependence of the basal spacing, $d(x)$, of binary solid-solution compounds of the general form $A_xB_{1-x}[L]$ where A

(B) is the larger (smaller) gallery cation and [L] represents the host layer structure. The finite layer rigidity model[1,2] in which only the host layers are flexible while the guest ions are rigid has been successfully applied to a range of lamellar compounds including graphite, dichalcogenides and 2:1 silicate clays with *fixed* layer structures.[2] However, the solid solution alkali layer perovskites[3] offer a more challenging arena to test layer rigidity concepts because the thickness and hence the rigidity of the perovskite host layer is *stepwise variable*. These layer perovskites have the general chemical formula $A_xB_{1-x}[C_{n-1}D_nO_{3n+1}]$ where the $[C_{n-1}D_nO_{3n+1}]$ host layers themselves consist of a stack of n sheets of corner connected DO_6 perovskite octahedra. Using high resolution x-ray diffraction data, we have recently shown[4] that the composition dependence of the normalized basal-spacing,[5] $d_N(x) = [d(x) - d(0)]/[d(1) - d(0)]$, of the tri-layer (n=3) alkali perovskites, $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$, measured over the range $0 \leq x \leq 1$, could best be accounted for using the anharmonic Lennard-Jones (aLJ) model.[6] This model incorporates deformations of *both* the host layers and the guest ions as well as an anharmonic interaction between them. More restrictive layer rigidity models were shown to be inadequate. [Here, $d(x)$ is the basal spacing at composition x.] To further validate the aLJ model, its applicability to other (thinner) alkali layer perovskites must be established. Accordingly, we now report an investigation of $Cs_xRb_{1-x}[LaNb_2O_7]$, the bi-layer (n=2) compounds, which have also been studied over the full range $0 \leq x \leq 1$.

EXPERIMENTAL DETAILS

Mixed-alkali niobates were prepared by solid state reactions as described elsewhere.[7] The high resolution (0.0024 $Å^{-1}$) x-ray diffractometer used to acquire the diffraction data reported here has also been described elsewhere.[8] All observed powder pattern reflections were fit with a gaussian line shape to determine their positions. The basal spacing of each sample was obtained from a q-plot[5] containing at least three ($00l$) reflections.

Crystal Structure

The bi-layer perovskites crystallize in the orthorhombic Imcm structure (space group #74) with the lattice parameters of the pure rubidium end-member being a= 5.4941Å, b=5.4925Å and c=21.9901Å.[9] This structure is illustrated schematically in Fig. 1.

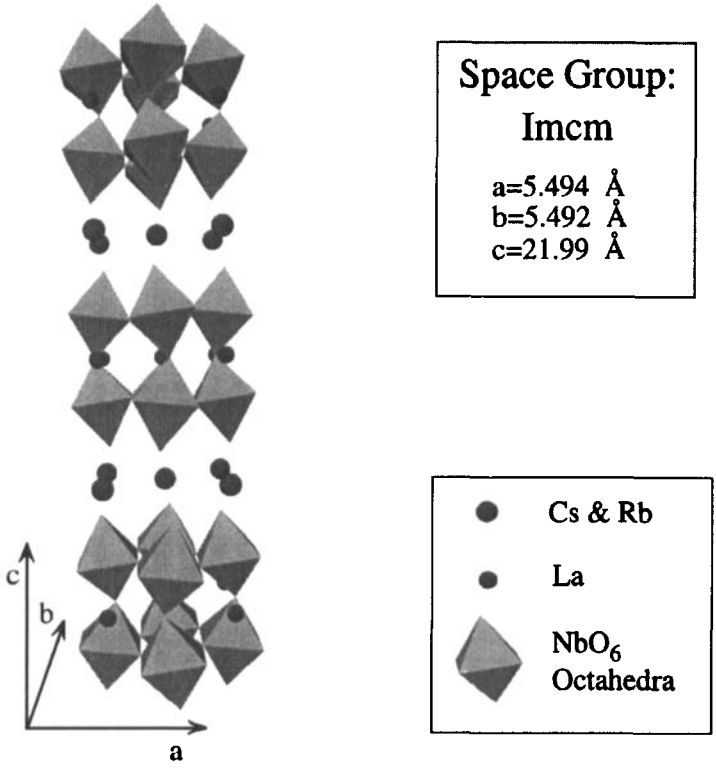

FIGURE 1. Schematic diagram of the crystal structure of the bi-layer alkali perovskites, $Cs_xRb_{1-x}[LaNb_2O_7]$. The lattice parameters shown are for the rubidium endmember compound with x = 0.

Notice from Fig. 1 that the NbO_6 octahedra form a corner connected but tilted structure which provides pockets within which the alkali gallery cations can nestle. This structure provides a basal spacing which is 1/2 of the c-axis repeat distance.

RESULTS AND DISCUSSION

In Fig. 2 we show the x = 0.5 indexed x-ray powder diffraction pattern of $Cs_xRb_{1-x}[LaNb_2O_7]$. This pattern has been fully indexed on the Imcm space group as indicated. Also shown in the inset of Fig. 2. is the composition (x) dependence of the high resolution scans of the (00 12) reflections. Note that these reflections shift continuously to lower q with

increasing Cs content. Also note that only single reflections are observed evidencing a pure phase structure.

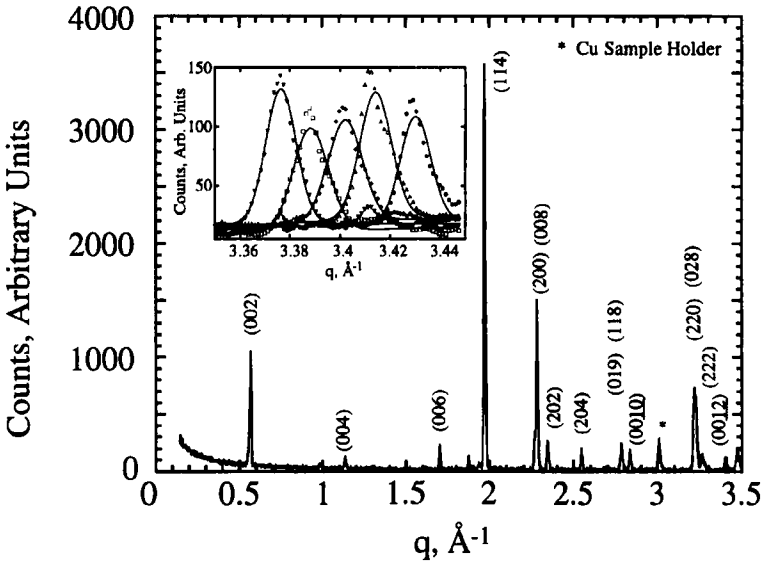

FIGURE 2. The powder diffraciton pattern of $Cs_xRb_{1-x}[LaNb_2O_7]$, x=0.5. Inset - high resoulution scans of the (00 12) reflections for various values of x [from left to right x = 1.0, 0.7, 0.5, 0.3, 0.0]. The solid lines are Gaussian least squares fits to the data.

From the data of Fig. 2. we can construct a plot of the composition dependence of the normalized basal spacing, $d_N(x)$, defined in the introduction. [The normalized basal spacing allows the intercomparison of the basal expansion of a number of diverse layered solid solutions as described by Solin and co-workers.[4,8]]. A plot of the normalized basal spacing for the bi-layer perovskites, $Cs_xRb_{1-x}[LaNb_2O_7]$, is shown in Fig. 3. For comparison, we have also been included in Fig. 3. previously reported results[4] for the tri-layer perovskites, $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$.

As can be seen from Fig. 3., the $d_N(x)$ for the n=3 perovskites exhibits the superlinear response typical of most layered solids[1] while that of the n=2 compounds is almost, but not exactly, Vegard law[10] like.

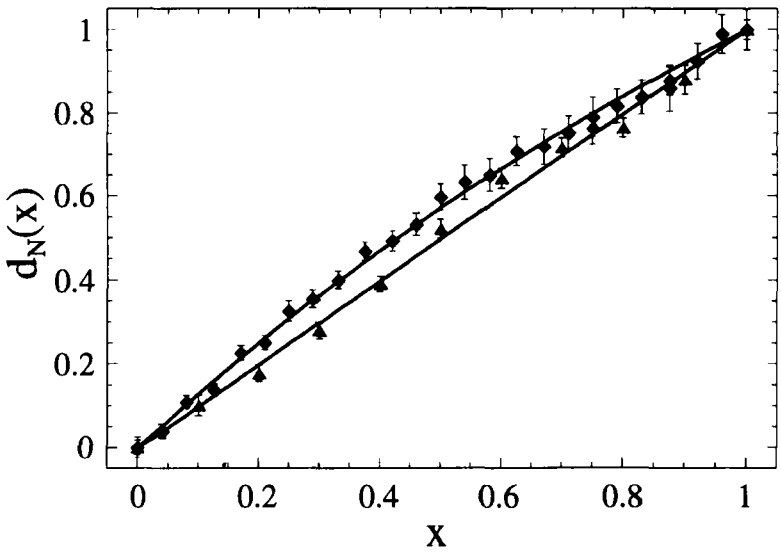

FIGURE 3. The composition dependence of the normalized basal spacing of $Rb_{1-x}Cs_x[LaNb_2O_7]$ (triangles) and $Rb_{1-x}Cs_x[Ca_2Nb_3O_{10}]$ (diamonds). The solid lines are computed from the aLJ model (Eq. 1).

Solin et al.[4] have recently shown that the aLJ model was the only layer rigidity model considered to date which could account for the n=3 layer perovskite basal spacing data. In that model, the normalized basal spacing is given by the expression

$$[d_n(x)]_{LJ} = \frac{\left[\frac{x+\alpha\beta^{14}(1-x)}{x+\alpha\beta^{8}(1-x)}\right]^{1/6} - \beta}{1-\beta} \qquad (1)$$

where $\alpha = K_B / K_A$ is the stiffness constant ratio of the gallery ions and $\beta = h_B^0 / h_A^0$ is the ratio of the equilibrium gallery heights. Now if we define the host layer thickness to be t, then the parameter β can be rewritten as

$$\beta = \frac{h_B^0}{h_A^0} = \frac{d(0)-t}{d(1)-t}. \qquad (2)$$

In our previous study of the tri-layer perovskites,[4] we have used Eq. 1 to fit the normalized basal spacing with β as the only adjustable parameter. The Rb/Cs stiffness constant ratio, α = *1.73*, was determined from the

known compressibilities of the ions.[11] The fit we obtained is reproduced in Fig. 3. and yielded a value of $\beta_3 = 0.924 \pm 0.002$ from which (see Eq. 2) we find $t_3 = (12.5 \pm 0.5)$Å. This value is in good (4%) agreement with the value of 11.96Å obtained from x-ray structure analysis. Using the same procedure, and the same Rb/Cs stiffness constant ratio, we have fit the data for the bi-layer perovskites. This fit is also shown as a solid line in Fig. 3. and yields a value of $\beta_2 = 0.950 \pm 0.003$ from which we find, using Eq. 2, that $t_2 = (7.7 \pm 0.2)$Å. This is also in good (3%) agreement with the x-ray structure value of 7.97Å. Thus the aLJ layer rigidity model is applicable to both the bi-layer and tri-layer perovskites, a fact which lends strong support to its validity.

Acknowledgments

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