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# B1-to-B2 Structural Transitions in Rock Salt Intergrowth Structures

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## 1 Introduction

It is known that the rock salt (*B*1) structure of binary compounds transforms to the CsCl (*B*2) structure under high pressure. Recently, the *B*1-to-*B*2 transition have been reported in the two-legged spin ladder structure $Sr_3Fe_2O_5$, an intergrowth compound composed of alternate stacking of the SrO rock salt block and the $(SrFeO_2)_2$ ladder block along the *c* axis [1]. Notably, this is a first compound that exhibits the *B*1-to-*B*2 transition in intergrowth compound.

In this study, we investigated the presence of pressure-induced structural transitions in one-dimensional (1D) compounds $A_2MO_3$ (A = Sr, Ca; M = Cu, Pd). The crystal structure is shown in Figure 1a. $A_2MO_3$ is an intergrowth structure of the AO rock salt blocks and the 1D chains of corner-shared $MO_2$ squares (or one-legged ladders), and adopt the *Immm* space group. All examined $A_2MO_3$ compounds exhibit the same type of structural transitions as $Sr_3Fe_2O_5$, which provides a unique opportunity to discuss the intrinsic nature of this transition and quantitative comparison with the well-studied binary systems.

## 2 Experiment

A powder sample of $A_2MO_3$ was synthesized by the high temperature ceramic method [2,3].

High resolution powder synchrotron XRD experiments under high pressures were performed at room temperature up to 37 GPa for $Sr_2CuO_3$, 51 GPa for $Ca_2CuO_3$ and 35 GPa for $Sr_2PdO_3$ using the NE1A synchrotron beam line of PF-AR. A powder sample of $A_2MO_3$ was loaded into a 180 μm diameter hole of a pre-indented rhenium gasket of the diamond-anvil cell. Helium was used as a pressure transmitting medium for $Sr_2CuO_3$ and $Sr_2PdO_3$, while a 4:1 methanol:ethanol mixture was used for $Ca_2CuO_3$. The pressure gradients within the samples were not more than 8 GPa for $Sr_2CuO_3$, 4 GPa for $Ca_2CuO_3$ and 1 GPa for $Sr_2PdO_3$ at maximum pressures applied in this study. The incident X-ray beam was monochromatized to a wavelength of 0.4115 Å for $Sr_2CuO_3$ and 0.4114 Å for $Ca_2CuO_3$. For $Sr_2PdO_3$, the first batch was measured with a wavelength of 0.4115 Å, until the used DAC was broken at 24GPa. The second batch was measured with a wavelength of 0.4114 Å in a pressure range from 19 GPa to 35GPa. The obtained synchrotron XRD data were analyzed by the Rietveld method using RIETAN-FP program [4].

## 3 Results and Discussion

The diffraction patterns of these compounds in the low pressure regime could be assigned to the orthorhombic *I*-centered unit cell, consistent with the reported data at ambient pressure. As is expected, the $2\theta$ angles of the reflection peaks gradually increase with increasing pressure, resulting from contraction of the lattice. For all the compounds examined, the further application of pressure finally results in drastic change in the diffraction patterns featured by a discontinuous change in the cell constants and by modified reflection conditions compatible with the orthorhombic *A*-centered lattice. The $P_s$ values are 29 GPa for $Sr_2PdO_3$, 30 GPa for $Sr_2CuO_3$, and 41GPa for $Ca_2CuO_3$. We assumed that this is the same *B*1-to-*B*2 transition as observed in $Sr_3Fe_2O_5$.

The high pressure $A_2MO_3$ structure was refined using the synchrotron XRD data at 34.7 GPa for $Sr_2PdO_3$, at 37.4 GPa for $Sr_2CuO_3$, and at 51.3 GPa for $Ca_2CuO_3$, assuming the space group *Ammm* (as in $Sr_3Fe_2O_5$ [1]). The atoms are placed at 4*j* (0.5, 0, *z*) for A = Sr or Ca, 2*a* (0, 0, 0) for M = Cu or Pd, 4*i* (0, 0, *z*) for O(1), and 2*b* (0, 0.5, 0) for O(2). During the refinements, the occupancy factors were constrained to unity. All the refinements converged well, yielding $R_p$ = 0.75%, $R_{wp}$ = 1.21%, $\chi^2$ = 2.83 for $Sr_2PdO_3$, $R_p$ = 0.90%, $R_{wp}$ = 1.20%, $\chi^2$ =2.49 for $Sr_2CuO_3$, and $R_p$ = 0.69%, $R_{wp}$ = 1.24%, $\chi^2$ = 1.59 for $Ca_2CuO_3$.

Now that the proposed high pressure structure of $A_2MO_3$ is confirmed, we can say that the pressure-induced *B*1-to-*B*2 transition generally occurs in the rock salt/spin-ladder intergrowth compounds and is not restricted to iron oxides and/or two-legged ladder structure . Namely, we can propose that $(AO)(AMO_2)_n$ ($n$ = 1, 2, 3…) with the AO rock salt unit and the $(AMO_2)_n$ *n*-legged spin ladder unit, if synthesized, would exhibit the same type of transition.

Let us now quantitatively compare the *B*1-to-*B*2 structural transition between binary systems and the intergrowth systems. Figure 2 shows the empirical relation, where the logarithm of transition pressure $P_s$ shows a linear dependence on ratio of the cation/anion radius, $R_A/R_O$. It is remarkable that the critical pressures for the binary compounds AO, the intergrowth compounds $A_2MO_3$ and $Sr_3Fe_2O_5$ are located just on the line. This means that $P_s$ is determined solely by $R_A/R_O$ in the AO block. Insensitivity of the ladder block to $P_s$ in turn implies that the ladder subunit at ambient pressure is a favorable form at high pressure. The structural stability of the ladder subunit under high pressure is understandable because it should have high compressibility along the out-of-plane direction as a result from the complete absence of apical oxygen.

In summary, we demonstrated that the pressure-induced *B*1-to-*B*2 transition generally occurs in the rock salt/spin-ladder intergrowth compounds. It is remarkable that the critical pressures $P_s$ for the intergrowth compounds are determined solely by $R_A/R_O$, showing quantitatively the same trend as the binary AO compounds, which make it possible to predict $P_s$ of other related compounds.. For more details of the study, see the reference [5].

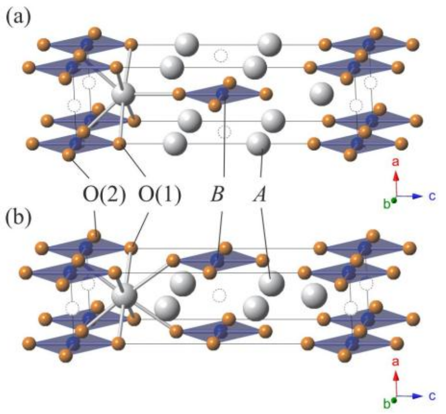

Fig. 1: The $A_2MO_3$ structures (a) at low pressure ($P < P_s$) and (b) at high pressure ($P_s < P$). White, blue, and orange spheres represent A, M and O atoms, respectively.

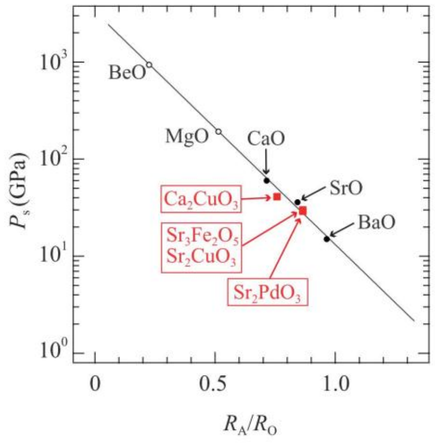

Fig. 2: $P_s$ vs the A-site ion radius ($R_A$) to the oxide ion radius ($R_O$). $R_A$ in 6- and 7-fold coordination is used [6], respectively, for the low pressure structure of AO, and $A_2MO_3$ ($Sr_3Fe_2O_5$). Experimental (black closed circles) and theoretical (black open circles) values for binary systems AO (A = Ca, Sr, Ba) are from the references [7-9]. Red Closed squares represent the data obtained in this study.

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References

[1] T. Yamamoto *et al.*, J. Am. Chem. Soc. 133 (2011) 6036.
[2] M. T. Weller and D. R. Lines, J. Solid State Chem. 82 (1989) 21.
[3] Y. Nagata *et al.*, J. Alloys Compounds 346 (2002) 50.
[4] F. Izumi et al., Solid State Phenom. 130, 15(2007).
[5] T. Yamamoto *et al.*, J. Inorg. Chem. 50 (2011) 11787.
[6] R. Shannon, J. Acta Crystallogr. 32 (1976) 751.
[7] L. Liu and W. A. Bassett, J. Geophys. Res. 77 (1972), 4934.
[8] R. Jeanloz *et al.*, Science 206 (1979) 829.
[9] Y. Sato and R. J. Jeanloz, Geophys. Res. 86 (1981) 11773.

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