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

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1 Introduction

It is known that the rock salt (B1) structure of binary compounds transforms to the CsCl (B2) structure under high pressure. Recently, the B1-to-B2 transition has been reported in the two-legged spin ladder structure Sr₃Fe₂O₅, an intergrowth compound composed of alternate stacking of the SrO rock salt block and the (SrFeO₂)₂ ladder block along the c axis [1]. Notably, this is a first compound that exhibits the B1-to-B2 transition in intergrowth compound.

In this study, we investigated the presence of pressure-induced structural transitions in one-dimensional (1D) compounds A₂MO₃ (A = Sr, Ca; M = Cu, Pd). The crystal structure is shown in Figure 1a. A₂MO₃ is an intergrowth structure of the AO rock salt blocks and the 1D chains of corner-shared MO₂ squares (or one-legged ladders), and adopt the Immm space group. All examined A₂MO₃ compounds exhibit the same type of structural transitions as Sr₃Fe₂O₅, 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 A₂MO₃ 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 Sr₃CuO₅, 51 GPa for Ca₃CuO₅ and 35 GPa for Sr₂PdO₅ using the NE1A synchrotron beam line of PF-AR. A powder sample of A₂MO₃ 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 Sr₃CuO₅ and Sr₂PdO₅, while a 4:1 methanol:ethanol mixture was used for Ca₃CuO₅. The pressure gradients within the samples were not more than 8 GPa for Sr₃CuO₅, 4 GPa for Ca₃CuO₅ and 1 GPa for Sr₂PdO₅ at maximum pressures applied in this study. The incident X-ray beam was monochromatized to a wavelength of 0.4115 Å for Sr₃CuO₅ and 0.4114 Å for Ca₃CuO₅. For Sr₂PdO₅, the first batch was measured with a wavelength of 0.4115 Å, until the used DAC was broken at 24 GPa. The second batch was measured with a wavelength of 0.4114 Å in a pressure range from 19 GPa to 35 GPa. 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 2θ 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 Pₛ values are 29 GPa for Sr₃PdO₅, 30 GPa for Sr₃CuO₅, and 41 GPa for Ca₃CuO₅. We assumed that this is the same B1-to-B2 transition as observed in Sr₃Fe₂O₅.

The high pressure A₂MO₃ structure was refined using the synchrotron XRD data at 34.7 GPa for Sr₃PdO₅, at 37.4 GPa for Sr₃CuO₅, and at 51.3 GPa for Ca₃CuO₅, assuming the space group Anmmm (as in Sr₃Fe₂O₅) [1]. The atoms are placed at 4j (0.5, 0, z) for A = Sr or Ca, 2a (0, 0, 0) for M = Cu or Pd, 4i (0, 0, z) for O(1), and 2b (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%, χ² = 2.83 for Sr₃PdO₅, R_p = 0.90%, R_wp = 1.20%, χ² = 2.49 for Sr₃CuO₅, and R_p = 0.69%, R_wp = 1.24%, χ² = 1.59 for Ca₃CuO₅.

Now that the proposed high pressure structure of A₂MO₃ is confirmed, we can say that the pressure-induced B1-to-B2 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)(AMO₃)ₙ (n = 1, 2, 3….) with the AO rock salt unit and the (AMO₃)ₙ unit, if synthesized, would exhibit the same type of transition.

Let us now quantitatively compare the B1-to-B2 structural transition between binary systems and the intergrowth systems. Figure 2 shows the empirical relation, where the logarithm of transition pressure Pₛ 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 A₂MO₃ and Sr₃Fe₂O₅ are located just on the line. This means that Pₛ is determined solely by R_A/R_O in the AO block. Insensitivity of the ladder block to Pₛ in turn implies that the ladder subunit at ambient pressure is a favorable form at high pressure. The structural stability

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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 B1-to-B2 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\(_2\)MO\(_3\) 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. 1](image1.png)

Fig. 2: \( P_s \) vs the A-site ion radius (\( R_A \)) to the oxide ion radius (\( R_O \)). \( R_N \) in 6- and 7-fold coordination is used [6], respectively, for the low pressure structure of AO, and A\(_2\)MO\(_3\) (Sr\(_2\)Fe\(_2\)O\(_5\)). 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


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