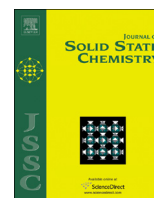




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journal homepage: www.elsevier.com/locate/jsscThe effect of chemical pressure on the structure and properties of A_2CrOsO_6 ($A = Sr, Ca$) ferrimagnetic double perovskiteRyan Morrow^a, Jennifer R. Soliz^{a,b}, Adam J. Hauser^{c,d}, James C. Gallagher^c, Michael A. Susner^{e,f}, Michael D. Sumption^e, Adam A. Aczel^g, Jiaqiang Yan^{f,h}, Fengyuan Yang^c, Patrick M. Woodward^{a,*}^a Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210-1185, USA^b Edgewood Chemical Biological Center, 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010, USA^c Department of Physics, The Ohio State University, Columbus, OH 43210-1185, USA^d California Nanosystems Institute, University of California, Santa Barbara, CA 93106, USA^e Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210-1185, USA^f Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA^g Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA^h Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

The ordered double perovskites Sr_2CrOsO_6 and Ca_2CrOsO_6 have been synthesized and characterized with neutron powder diffraction, electrical transport measurements, and high field magnetization experiments. As reported previously Sr_2CrOsO_6 crystallizes with $R\bar{3}$ symmetry due to $a^-a^-a^-$ octahedral tilting. A decrease in the tolerance factor leads to $a^-a^-b^+$ octahedral tilting and $P2_1/n$ space group symmetry for Ca_2CrOsO_6 . Both materials are found to be ferrimagnetic insulators with saturation magnetizations near $0.2 \mu_B$. Sr_2CrOsO_6 orders at 660 K while Ca_2CrOsO_6 orders at 490 K. Variable temperature magnetization measurements suggest that the magnetization of the Cr^{3+} and Os^{3+} sublattices have different temperature dependences in Sr_2CrOsO_6 . This leads to a non-monotonic temperature evolution of the magnetic moment. Similar behavior is not seen in Ca_2CrOsO_6 . Both compounds have similar levels of Os/Cr antisite disorder, with order parameters of $\eta = 80.2(4)\%$ for Sr_2CrOsO_6 and $\eta = 76.2(5)\%$ for Ca_2CrOsO_6 , where $\eta = 2\theta - 1$ and θ is the occupancy of the osmium ion on the osmium-rich Wyckoff site.

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1. Introduction

Transition metal oxides with the perovskite structure are one of the most heavily studied classes of materials due to their ability to incorporate elements from throughout the periodic table, resulting in properties that span the gamut of modern functional materials. Recently, ordered double perovskites with formula $A_2BB'O_6$ and consisting of a network of corner sharing BO_6 and $B'O_6$ octahedra have been the focus of intense research [1] due to the occurrence of highly spin-polarized electrical transport [2–4], unusual sequences of magnetic phase transitions [5–7], and geometric frustration [8–10]. The ferrimagnetic insulator Sr_2CrOsO_6 has the distinction of possessing the highest known Curie temperature (T_C) amongst double perovskites at 725 K [11]. However, despite the

fact that it has been the subject of numerous theoretical studies [12–14], including one that proposes a canted magnetic structure to explain its unusual non-monotonic magnetic susceptibility temperature dependence [15], Sr_2CrOsO_6 has not been experimentally revisited since the initial publication [11].

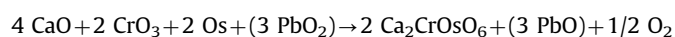
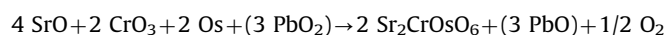
Herein, we revisit the magnetic properties of Sr_2CrOsO_6 with neutron diffraction, electrical transport measurements, and high field magnetization experiments. Additionally, we synthesize and characterize the crystal structure and magnetic properties of Ca_2CrOsO_6 . This compound was prepared by Sleight and Ward in 1962, but its properties have not previously been studied [16]. The results shed light on the way that chemical pressure affects the magnetic interactions and resulting magnetic ground states of these two compounds. Their behavior is compared and contrasted with A_2FeOsO_6 and A_2CoOsO_6 ($A = Sr, Ca$) osmate double perovskites where chemical pressure drives a crossover from an antiferromagnetic to a ferrimagnetic ground state [17–19].

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2. Material and methods

Polycrystalline samples (mass = 1.6 g) were prepared by solid state reaction of stoichiometric quantities of SrO (99.9% pure, Sigma Aldrich), CaO (99.9% pure, Sigma Aldrich), CrO₃ (99.99% pure, Sigma Aldrich), and Os metal (99.98% pure, Alfa Aesar). Reactants were ground in an argon glove box and then placed in a high density alumina tube that was sealed in a silica ampoule (40 mL volume, 3 mm wall thickness) along with a separate vessel containing PbO₂ that decomposed into PbO and acted as an in-situ source of O₂ gas. One quarter mole excess O₂ gas was produced in this way in order to ensure full oxidation of the reactants. The sealed tubes were heated to 1000 °C for Sr₂CrOsO₆ and 950 °C for Ca₂CrOsO₆ and held for 48 hours in a box furnace located within a fume hood as an additional precaution. Great caution must be used as heating osmium in the presence of oxygen can produce toxic OsO₄ gas. Larger batch sizes or ampoules with thinner walls may produce conditions resulting in rupture of the sealed tube at elevated temperatures. The following equations were used for these reactions.



Laboratory X-ray diffraction measurements were conducted on a Bruker D8 Advance instrument equipped with a Ge(111) monochromator in order to verify composition and cation ordering. Time of flight neutron powder diffraction (NPD) data were collected on the POWGEN [20] beamline at Oak Ridge National Laboratory (ORNL). Sr₂CrOsO₆ was measured using the JANIS cryofurnace with high and low d spacing frames of 0.2760–3.0906 Å and 2.2076–10.3019 Å at 5 K and 500 K as well as single intermediate d spacing frames of 1.1038–6.1811 Å at 50 K intervals. Ca₂CrOsO₆ was measured in the Powgen Automatic Changer (PAC) environment at 10 K and 300 K with frames of 0.2760–4.6064 Å and 2.2076–15.3548 Å at each temperature. Rietveld refinements were conducted using the GSAS EXPGUI software package [21,22]. Additional neutron powder diffraction data was collected on Sr₂CrOsO₆ using ORNL's HB-1A instrument with a constant wavelength of λ = 2.367 Å. The HB-1A sample of approximately 5 g was comprised of three combined batches of material. Diffraction patterns were collected at T = 4 and 300 K using a closed cycle refrigerator, and the instrument collimation was 40°-40°-40°-80°.

Sr₂CrOsO₆ and Ca₂CrOsO₆ powders were pressed and sintered at 1000 °C and 950 °C, respectively, in evacuated sealed ampoules in order to produce bar shaped polycrystalline pellets for electrical measurements. Silver paint was applied to attach copper leads to the pellets. DC resistivity data was collected over a temperature range of 140–400 K for Sr₂CrOsO₆ and 70–335 K for Ca₂CrOsO₆ using the four-point probe method in a Quantum Design model 6000 physical property measurement system (PPMS). The samples were too resistive for accurate measurements at lower temperatures. No magnetic field was applied during the measurements. Additionally, no corrections were made for porosity.

The field dependence of the magnetization of Sr₂CrOsO₆ and Ca₂CrOsO₆ pellets was measured using the Vibrating Sample Magnetometer (VSM) option of the PPMS with the maximum field of 140 kOe at 5, 300, and 400 K for Sr₂CrOsO₆ and at 5 and 300 K for Ca₂CrOsO₆. Higher magnetic fields (± 350 kOe) were used to measure the hysteresis loops of Sr₂CrOsO₆ at 4.5 K and 295 K using the VSM at the National High Magnetic Field Laboratory (NHMFL).

Magnetic susceptibility of a pelletized Sr₂CrOsO₆ sample was obtained using a LakeShore VSM. The sample was heated to 800 K and then cooled in a 15 kOe field to field cool the sample. The field cooled susceptibility curve was then measured in field strength of

1 kOe in the temperature range from 300 to 800 K. An analogous set of measurements was conducted for Ca₂CrOsO₆ within the temperature range 300 to 600 K.

3. Results and discussion

Sr₂CrOsO₆ crystallizes in the *R* $\bar{3}$ space group as reported previously [11], while Ca₂CrOsO₆ crystallizes in the monoclinic *P*2₁/*n* space group common to double perovskites with a tolerance factor smaller than approximately 0.97 [23]. Cr/Os cation ordering for both compounds was determined from laboratory XRD data in order to take advantage of the substantial X-ray scattering contrast between Cr and Os, as well as to avoid unwanted correlations with the magnetic moments while analyzing the neutron diffraction data. The order parameter, which is defined as $\eta = 2\theta - 1$ where θ is the occupancy of the cation on its assigned site (i.e. the Cr occupancy on the Cr-rich octahedral site), was found to be 80.2(4)% for Sr₂CrOsO₆ and 76.2(5)% for Ca₂CrOsO₆.

The results from neutron powder diffraction are given in Tables 1 and 2 for Sr₂CrOsO₆ and Ca₂CrOsO₆ respectively, while the refined NPD patterns are shown in Figs. 1 and 2. The calculated bond valence sums [24] for chromium are 3.27 (5 K) and 3.38 (500 K) for Sr₂CrOsO₆, while they are 3.21 (10 K) and 3.22 (300 K) for Ca₂CrOsO₆. These results support the assignment of Cr³⁺ in these materials, indicating that Os is in the 5+ oxidation state. These conclusions are supported by direct comparison to the M–O bond lengths in related perovskites with these oxidation states [11,17,25,26]. Other than the change in symmetry driven by the change in octahedral tilting, the most significant variance between the two is the reduction in the Cr–O–Os bond angle from 170.8° in Sr₂CrOsO₆ to an average of 153.2° in Ca₂CrOsO₆ (at low temperatures). An increased bending of the B–O–B' bonds is the expected response to increasing chemical pressure when the stiffness of the B/B'–O bonds is higher than that of the A–O bonds.

It is interesting to note that the continuous evolution of the Cr–O–Os bond angle in Sr₂CrOsO₆ with temperature, as shown in Fig. 3, typical of rhombohedral perovskites approaching the cubic phase transition [27]. The symmetry of Sr₂CrOsO₆ is rhombohedral at 500 K, which is presumably quite close to a structural phase transition, given the earlier report of cubic symmetry at 540 K [11].

The electrical transport of Sr₂CrOsO₆ and Ca₂CrOsO₆ is given in Fig. 4 showing linear behaviors on a T^{-1/4} scale which is consistent with a variable range hopping transport model as has been reported in related double perovskite osmates [28, 29]. The resistivity of Sr₂CrOsO₆ increases from 8.6 × 10² Ω cm at 300 K to

Table 1

Neutron powder diffraction parameters obtained from Rietveld refinement for Sr₂CrOsO₆ at 5 and 500 K.

| Temperature (K) | 5 | 500 |
|---------------------------|--------------------|--------------------|
| Space Group | <i>R</i> $\bar{3}$ | <i>R</i> $\bar{3}$ |
| <i>a</i> (Å) | 5.5200(1) | 5.5300(1) |
| <i>c</i> (Å) | 13.4403(3) | 13.5242(6) |
| <i>V</i> (Å) ³ | 354.662 | 358.2(1) |
| <i>R</i> _{wp} | 2.74% | 3.60% |
| Cr–O (× 6, Å) | 1.964(2) | 1.952(1) |
| Os–O (× 6, Å) | 1.944(2) | 1.958(1) |
| ∠Cr–O–Os (deg) | 170.82(5) | 176.5(1) |
| Sr <i>z</i> | 0.2500(3) | 0.2502(7) |
| O <i>x</i> | 0.3350(6) | 0.3323(8) |
| O <i>y</i> | 0.1958(3) | 0.1770(6) |
| O <i>z</i> | 0.4162(2) | 0.4166(4) |

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