

## Raman and infrared spectroscopy of $\text{Sr}_2B'\text{UO}_6$ ( $B' = \text{Ni}; \text{Co}$ ) double perovskites

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### ABSTRACT

Temperature dependent normal modes and lattice thermal expansion of  $\text{Sr}_2B'\text{UO}_6$  ( $B' = \text{Ni}, \text{Co}$ ) double perovskites were investigated by Raman/infrared spectroscopies and synchrotron X-ray diffraction, respectively. Monoclinic crystal structures with space group  $P2_1/n$  were confirmed for both compounds, with no clear structural phase transition between 10 and 400 K. As predicted for this structure, the first-order Raman and infrared spectra show a plethora of active modes. In addition, the Raman spectra reveal an enhancement of the integrated area of an oxygen stretching mode, which is also observed in higher-order Raman modes, and an anomalous softening of  $\sim 1 \text{ cm}^{-1}$  upon cooling below  $T^* \sim 300 \text{ K}$ . In contrast, the infrared spectra show conventional temperature dependence. The band profile phonon anomalies are possibly related to an unspecified electronic property of  $\text{Sr}_2B'\text{UO}_6$  ( $B' = \text{Ni}, \text{Co}$ ).

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### 1. Introduction

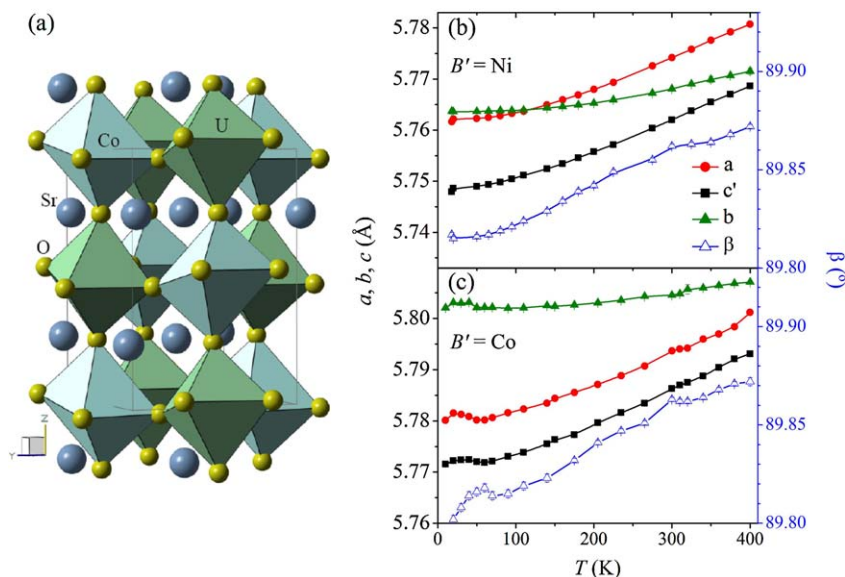
The general stoichiometric formula  $A_2B'B''\text{O}_6$  of double perovskites is derived from the perovskite  $\text{ABO}_3$ , where the  $B$  site is occupied by two cations  $B'$  and  $B''$ . These compounds may be classified as ordered or disordered, depending on the degree of long range order of  $B'$  and  $B''$ . Ordered double perovskites typically occur when these ions show substantial charge and/or size differences. The ideal double perovskite structure has cubic symmetry with space group  $Fm\bar{3}m$ . However, size incompatibilities between  $A$ ,  $B'$ , and  $B''$  ions with respect to the ideal structure distort the lattice, leading to a symmetry reduction to either rhombohedral, tetragonal, orthorhombic, or monoclinic unit cells. The distortions are mostly related to rotations of the  $B'\text{O}_6$  and  $B''\text{O}_6$  octahedra. Interest on these materials has been renewed after a large tunnelling magnetoresistance was found for  $\text{Sr}_2\text{FeMoO}_6$  and

other related compounds [1–7], which was associated with half-metallic ferrimagnetic ground states. For the case of the  $\text{A}_2\text{FeReO}_6$ , novel phenomena arising from the large orbital moment of Re were also found [1,8–12]. These discoveries illustrate the rich and still largely unexplored physics that may be found in double perovskite structures, which may be revealed as the large number of distinct possibilities for  $A$ ,  $B'$  and  $B''$  ions are further explored. In particular, as shown in the above mentioned case of  $B' = \text{Fe}$  and  $B'' = \text{Re}$ , the magnetic properties of the system may be dominated by a  $B''$  ion which may be weakly or even non-magnetic outside the double perovskite structure.

Previous work on uranium-containing double perovskites ( $B' = \text{Co}, \text{Mn}, \text{Fe}, \text{Ni}, \text{Zn}; B'' = \text{U}$ ) showed that these compounds crystallize in either partly or fully ordered monoclinic structures (space group  $P2_1/n$ , see Fig. 1(a)) [13,14]. Neutron powder diffraction in  $\text{Sr}_2\text{CoUO}_6$  revealed a non-collinear magnetic arrangement of the Co moments below  $T_N = 10 \text{ K}$  [13], suggesting partly frustrated exchange interactions in this system. Magnetic susceptibility measurements in  $\text{Sr}_2\text{NiUO}_6$  showed magnetic ordering below  $T_N = 21 \text{ K}$  [14]. The effective paramagnetic moments tend to deviate from the corresponding spin-only moments for  $B'^{2+}$  cations, suggesting either unquenched orbital  $B'^{2+}$  moments [13] or partial charge

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**Figure 1.** (a) Crystal structure of Sr<sub>2</sub>CoUO<sub>6</sub>. Temperature dependence of the monoclinic unit cell parameters of Sr<sub>2</sub>B'UO<sub>6</sub> for (b) B' = Ni, and (c) B' = Co.

disproportionation  $B^{2+} + U^{6+} \rightleftharpoons B^{3+} + U^{5+}$  [14], with possible contribution of U<sup>5+</sup> moments to the magnetic properties of this system. Overall, an unambiguous physical picture has not been attained for these systems yet, and further study is clearly necessary to elucidate their properties.

In the present work, we describe a lattice vibration study of Sr<sub>2</sub>B'UO<sub>6</sub> (B' = Ni, Co) as a function of temperature, by means of Raman and infrared (IR) spectroscopies, complemented by high-resolution synchrotron X-ray powder diffraction (S-XPD) measurements of unit cell parameters. Any possible non-trivial electronic behavior for this system, such as the proposed charge disproportionation [14], should be captured by its vibrational properties. In fact, our Raman spectra show frequency and intensity phonon anomalies at  $T^* \sim 300$  K, suggesting this may be a characteristic temperature for this system. No structural transition has been observed at  $T^*$ . Our results suggest that the detected anomalies in the phonon band profiles may be electronic in origin.

## 2. Materials and methods

Polycrystalline Sr<sub>2</sub>B'UO<sub>6</sub> (B' = Ni, Co) samples were prepared by solid-state reaction, as described in Refs. [13,14]. Raman measurements were performed with a Jobin Yvon T64000 triple grating spectrometer equipped with a cryogenically cooled charge-coupled device detector. The 632.8 nm line of a He–Ne laser was used in the experiments, with power below 2 mW within a spot of  $\sim 50$   $\mu$ m diameter to minimize local heating. A closed-cycle He cryostat was employed. Temperature dependent medium- and far-IR reflectivity spectra of polished pellets were measured between 30 and 5000 cm<sup>-1</sup> in a Fourier transform IR Bruker 113 v with 2 cm<sup>-1</sup> resolution. A gold mirror was used as 100% reference. The sample was mounted on the cold finger of a home-made cryostat for measurements between 4 and 300 K, and the temperature was measured with a Si diode sensor mounted near the sample. High-resolution S-XPD measurements were performed in the XPD beamline of the Brazilian Synchrotron Light Laboratory (LNLS) under reflection geometry. Details of this beamline may be found in Ref. [15]. A monochromatic beam with  $\lambda = 1.3769$  Å, selected by a double crystal Si(111) monochromator, was employed. A Ge(111) analyzer was used for the diffracted beam, yielding instrumental angular resolution down to  $\sim 0.01^\circ$  full width at half maximum in  $2\theta$  [15]. Full diffraction profiles ( $10^\circ < 2\theta < 150^\circ$ ) were measured at  $T = 10,$

150, 300 and 400 K for B' = Co and at  $T = 18$  and 300 K for B' = Ni. The temperature dependence of the unit cell parameters were extracted by measuring a limited but sufficient set of Bragg peaks with the powder samples mounted on the cold finger of a closed-cycle He cryostat. The parameters were refined using the GSAS+EXPGUI suite [16,17].

## 3. Results and analysis

Rietveld analyses of synchrotron X-ray powder diffraction profiles confirm the fully ordered monoclinic ordered double perovskite structure with space group  $P2_1/n$  previously reported for Sr<sub>2</sub>B'UO<sub>6</sub> (B' = Ni, Co) (see Fig. 1(a)) [13,14] at all studied temperatures. Fig. 1(b) and (c) show the temperature dependency of the refined *a*, *b*, *c'* =  $c(2)^{1/2}$ , and  $\beta$  monoclinic unit cell parameters. No structural phase transition takes place in the studied temperature interval ( $10 \text{ K} < T < 400 \text{ K}$ ) for both compounds. On warming, the monoclinic angle  $\beta$  shows a continuous evolution towards  $90^\circ$  for both materials, indicating that a transition to a more symmetric space group would occur at very high temperatures ( $T \gg 400 \text{ K}$ ), as known for perovskite structures. It is interesting to notice that *a* and *c'* present similar temperature behavior, while *b* shows a significantly smaller thermal expansion. Small lattice anomalies seem to take place for B' = Co at  $\sim 60$  K, which might be related to the rise of significant short-range magnetic correlations below this temperature [13].

The normal mode symmetry analysis of the double perovskite structure with space group  $P2_1/n$  is summarized in Table 1. 24 Raman-active modes ( $12A_g + 12B_g$ ) and 33 Infrared-active modes ( $17A_u + 16B_u$ ) are expected. Fig. 2(a) and (b) shows the unpolarized first-order Raman spectra of Sr<sub>2</sub>NiUO<sub>6</sub> and Sr<sub>2</sub>CoUO<sub>6</sub>, respectively, at selected temperatures. For Sr<sub>2</sub>NiUO<sub>6</sub>, 19 modes were detected at 10 K, at 110, 115, 120, 135, 145, 160, 170, 215, 245, 285, 315, 365, 375, 400, 430, 435, 485, 705, and 745 cm<sup>-1</sup>. For Sr<sub>2</sub>CoUO<sub>6</sub>, 20 modes were observed at 12 K, at 100, 110, 115, 130, 145, 155, 170, 215, 245, 255, 285, 315, 365, 375, 380, 405, 510, 575, 650, and 735 cm<sup>-1</sup>. For both compounds, the highest-energy first-order phonon at 735–745 cm<sup>-1</sup> dominates the spectra with a very large relative intensity. The high frequency and large Raman cross section of this mode indicate this is the in-phase stretching vibration of the oxygen octahedra, which is Raman-active even for the cubic double perovskites [18,19]. On warming, some of the observed peaks show

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