SUPERSTRUCTURE OF THE DEFECT PEROVSKITE TYPE COMPOUNDS \( \text{La}_2\text{Ti}_3\text{Nb}_2\text{O}_{12} \)

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Superstructure analysis of the title compound (hereafter call LNO) were carried out by the single-crystal X-ray diffraction making use of SR, with the aid of the electron diffraction. The LNO as well as \( \text{La}_2\text{Ti}_3\text{O}_{12} \) (call LTO) are promising host crystals for the L\( ^{3}\text{I} \) ion intercalation. Both compounds crystallize in double-layered perovskite structure with perfectly vacant sites of \( \text{La}^{3+} \) in the \( z=1/2 \) plane and by two third occupied sites of \( \text{La}^{3+} \) in the \( z=0 \) plane at room temperature. Although reduction of crystal system to which the LNO belongs, from tetragonal space group \( \text{P}4/\text{mmm} \) to orthorhombic and a superstructure doubling the \( a \) and \( b \) dimensions of the fundamental tetragonal unit cell, have been previously reported, no structure refinements have been performed to our knowledge. X-ray diffraction experiment were made using the horizontal-type four-circle diffractometer, utilizing \( \pi \) from a vertical giggler at the beam line 14A of the PF(KEK) in Tsukuba, Japan. The geometry of the reciprocal lattice of the LNO insists on being orthorhombic unlike the LTO is tetragonal, and the refined cell parameters are \( a=0.7817(1), b=0.7836(1) \) and \( c=0.7910(1) \) \( \text{nm} \). Three dimensional diffraction intensity data including the superstructure reflections were collected in the independent reciprocal space within \( \theta \leq 10.00 \) and \( 0 \leq 0.075\text{nm} \). The electron diffraction pattern of the \( h00 \) plane of the LNO contained weak but sharp superstructure reflections and obeyed an extinction rule for the \( C \)-faced lattice. Of five possible space groups, \( \text{Cmmm, C2mm, Cm2m, Cmm2 and C222} \) seems to be the most probable one since in the refinements it gave the lowest conventional \( R \) factor to be 0.048 for all 1150 reflections. The \( R \) factor is 0.044 for 636 fundamental, and 0.069 for 514 superstructure reflections whose intensities are much weaker than the fundamental ones. Refined structure has an alternate shift along the \( b \) axis of \( \text{La}^{3+} \) in the \( z=0 \) plane and suggests the statistical fluctuation of \( \text{Ni}^{3+} \) from the averaged position, which might interact with the local distribution of \( \text{La}^{3+} \) ions in the structure.

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SUPERSTRUCTURE OF METAL HYDROGEN SULFATES. S. Tsyvanyov, C. Werneth, E. Krieritz, Moscow State University, Chemistry Department, 119899 Moscow, Vorojbyev Gory, Russia, Humboldt Universität Berlin, Institut für Anorganische Chemie, Hessische Str. 1-2, 10115 Berlin, Germany

A series of new hydrogen sulfates of general formula \( \text{M}_2\text{H}2\text{SO}_4 \) and \( \text{M}_3\text{H}2\text{SO}_4 \) have been synthesized and structurally characterized in the last few years. The general structural aspects are discussed using the value \( N \) which defines the average number of hydrogen donor functions (OH groups) per \( \text{SO}_4^{2-} \) tetrahedron.

All crystal structures contain \( \text{M}^{1+} \) or \( \text{M}^{2+} \) ions coordinated by \( \text{O} \) atoms with \( \text{CN} \) from 4 to 6 depending mainly on the metal radii. Counterparts consist of simple \( \text{H}_2\text{SO}_4 \) tetrahedra or their combination with \( \text{SO}_4^{2-} \) or \( \text{H}_2\text{SO}_4 \) tetrahedra.

The \( \text{S-O} \) distances correlate with additional structural functions of \( \text{O} \) atoms such as coordination by \( \text{M} \) atom(s), \( \text{H} \)-acceptor, or \( \text{H} \)-donor functions. The \( \text{S-OH} \) distances are generally 0.1 \( \text{Å} \) longer than the \( \text{S-S} \) distances. Both \( \text{S-O} \) and \( \text{S-S} \) distances are slightly longer (by 0.02-0.03 \( \text{Å} \) in \( \text{H}_2\text{SO}_4 \)) as compared to those in the \( \text{H}_2\text{SO}_4 \) unit.

Every \( \text{H}_2 \) atom forms a hydrogen bond \( \text{O} \ldots \text{O} \). The \( N \) value in the formula defines the main features of the hydrogen bonding systems: isolated or extended in one, two or three directions. The connectivity patterns of the \( \text{H} \) bonding systems for the same \( N \) value can vary due to a different distribution of acceptor functions between \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{SO}_4 \) units.

The structures of \( \text{a-NaHSO}_4 \) and \( \text{LiH(H}_2\text{SO}_4)_2 \) \( \text{H}_2\text{SO}_4 \) contain unordered hydrogen bonds characterized by strong \( \text{O} \ldots \text{O} \) interactions at the distances of 2.51 \( \text{Å} \) and 2.44 \( \text{Å} \), respectively.

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NEW MIXED-VALENCE VANADIUM HYDROGEN ARSENATE. Wu-Jen Tsai, Sue-Lein Wang*, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

A new mixed-valence vanadium hydrogen arsenate, \( \text{Rb}_2\text{V}_2\text{O}_7 \) \( \text{HAsO}_4 \) \( \text{H}_2\text{O} \) has been synthesized under hydro-thermal conditions and its structure was determined from single-crystal X-ray diffraction data. Intensity measurements were performed on a CCD area detector system. Crystal data: \( \text{H}_2\text{AsO}_4 \) \( \text{Rb}_2\text{V}_2\text{O}_6 \) monoclinic, \( P2_1/c \), \( a=9.7162(1) \text{Å}, b=11.2839(2) \text{Å}, c=13.8462(2) \text{Å}, \beta=105.843(1)^\circ \), \( V=1490.95(5) \text{Å}^3 \), \( Z=4 \), and \( B=0.0445 \) for 2378 unique reflections. The structure is composed of \( \text{Rb}^+ \) cations, water molecules and \( [\text{V}_2\text{O}_7\text{HAsO}_4\text{H}_2\text{AsO}_4]^4^- \) cluster anions, in which two of the edge-sharing pairs of \( \text{VO}_6 \) octahedra are connected by four \( \text{HAsO}_4 \) and two \( \text{H}_2\text{AsO}_4 \) groups. Variable-temperature powder magnetic susceptibility data confirm the presence of one \( \text{V}^4+ \) and one \( \text{V}^5+ \) ion per formula unit. In this presentation, the hydrothermal synthesis, single-crystal structure, thermal analysis, and magnetic study of \( \text{Rb}_2\text{V}_2\text{O}_7 \) \( \text{HAsO}_4\text{H}_2\text{AsO}_4\text{H}_2\text{O} \) will be given. Structural relationship to \( \text{A}_2\text{M}_2\text{O}_7 \) \( \text{HAsO}_4\text{H}_2\text{AsO}_4\text{H}_2\text{O} \) \( (\text{A} = \text{Cs} \) and \( \text{CsH}_2\text{NH} \) is also discussed.

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REFERENCES