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Structural Study of the Lanthanide Phosphonate Family $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]\text{Ln}[\text{hedpH}][\text{hedpH}_2]$ Eva Fernández-Zapico^a, Laura Rocés^{a*}, Santiago García-Granda^a, José R. García^b, Fengyi Liu^c, João Rocha^c
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Keywords: structural characterization, phosphonates, hydrothermal synthesis

Metal phosphonate chemistry has attracted much attention due to the potential applications of these materials in ion-exchange, catalysis, and in sensor devices. Often, metal phosphonates exhibit polymeric structures consisting of chains, layers, or three-dimensional networks, but monomeric structures are also known. In particular, the tunable organic units in diphosphonate $[\text{R}(\text{PO}_3)_2]^{4-}$ allow the construction of metal phosphonate materials with new architectures. One type of these phosphonates is based on 1-hydroxyethane-1,1-diphosphonic acid $[\text{hedpH}_4, \text{H}_2\text{O}_3\text{PC}(\text{OH})(\text{CH}_3)\text{PO}_3\text{H}_2]$, which has been widely used as a strong chelating agent in the preparation of functional metal diphosphonates and found to bind strongly to numerous metal ions. We have recently reported the hydrothermal synthesis and crystal structure of several members in the new family of 1D lanthanide phosphonates $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]\text{Ln}[\text{hedpH}][\text{hedpH}_2]$, where Ln is a trivalent lanthanide metal. The crystal structure of these compound, which crystallize in space group P-1, is built up from one-dimensional covalent lanthanum phosphonate cross-linked chains and $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$ cations. Herein, we report the structural determination by synchrotron X-ray powder diffraction of all the members in this family (Ln: La, Tb, Yb, Sm, Nd, Pr, Gd, Eu, Er). The complete structural study of these compounds and the description of the intricate hydrogen bonding network which holds the chains together will be presented here.

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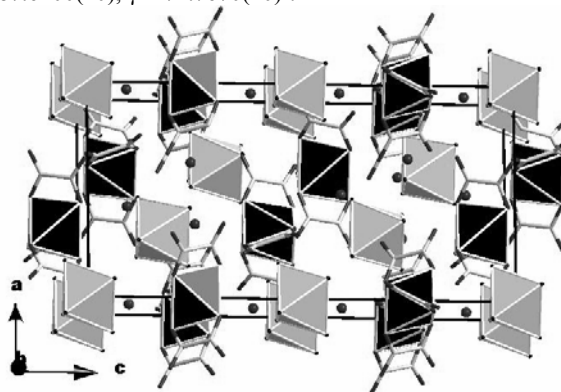
Synthesis and Investigation of Double Complex Salts $[\text{Ir}(\text{NH}_3)_6][\text{M}(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ (M = Fe, Co, Cr) Evgeny Filatov^a, Kirill Yuesenko^a, Evgeniya Vikulova^b, Irida Baidina^a, Yuriy Shubin^a, ^aNikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia. ^bFaculty of Natural Science, Novosibirsk State University, Russia. E-mail: decan@che.nsk.su

Keywords: oxalate complexes, ammine complexes, metal solid solutions

Preparation of novel double complex salts (DCS) simultaneously comprising a platinum group metal and a forth raw transition metal is highly topical fro these compounds can serve as precursors of diverse bimetallic materials. Application of such systems can be exemplified by production of ultrafine particles of metal solid solutions or intermetallides deposited on various supports with the purpose of development of high-performance catalysts [1] having decreased content of noble metals.

Several DCS involving hexaammine cations and tris-oxalate anions are reported in the literature [2, 3]. However, only one study was devoted to the compound combining these ions [3]. The choice of the $[\text{Ir}(\text{NH}_3)_6]^{3+}$ cation was determined by the lack of data on structural features and thermal properties of such compounds.

Compounds $[\text{Ir}(\text{NH}_3)_6][\text{M}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (M = Fe, Cr) are isostructural and crystallize in a trigonal space group P-3c1 with unit cell parameters $a = 12.6128(7)$, $c = 20.8480(22)$ Å and $a = 12.608(7)$, $b = 21.180(14)$ Å, respectively. The compound $[\text{Ir}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$ does not contain water of crystallization and belongs to a triclinic space group P1 with parameters $a = 7.5630(2)$, $b = 9.6046(3)$, $c = 11.8116(4)$ Å, $\alpha = 84.7950(10)$ Å, $\beta = 87.6100(10)$, $\gamma = 71.7670(10)^\circ$.



Thermal decomposition of the title compounds has been studied. Final products of thermal decomposition are single-phase cubic closed-packed metal solid solutions $\text{Ir}_{0.5}\text{Fe}_{0.5}$ ($a = 3.745(4)$ Å) and $\text{Ir}_{0.5}\text{Co}_{0.5}$ ($a = 3.710(3)$ Å). Thermolysis of $[\text{Ir}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ affords a solid solution $\text{Ir}_x\text{Cr}_{1-x}$ ($x \sim 0.5$, $a = 2.690(2)$, $b = 4.291(4)$ Å) and a small amount of chromium oxide..

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The Structures and Kinetics of Lithium Magnesium Alanates Hilde Grove, Ole Martin Løvvik, Bjørn C. Hauback, *Physics Department, Institute for Energy Technology, Kjeller, Norway.* E-mail: hilde.grove@ife.no

Keywords: Hydride structure, neutron powder diffraction, X-ray powder diffraction.

Safe storage and transportation are one of the limiting factors for a wide use of hydrogen as an energy carrier. Solid compounds like metal hydrides contribute a promising alternative for traditional hydrogen storage. The 4 wt % hydrogen capacity for NaAlH_4 containing Ti-catalyst, showed about 10 years ago [1] the potential for reversible hydrogen storage in complex hydrides. In the search for novel materials for hydrogen storage the mixed alanate $\text{LiMg}(\text{AlD}_4)_3$ has been considered [2-3]. LiMgAlD_6 was synthesized by using the ball milling technique. $3\text{LiAlD}_4 + \text{MgCl}_2 \rightarrow 2\text{LiCl} + \text{LiMg}(\text{AlD}_4)_3$. The product was recrystallized in diethyl ether/toluene to increase the crystallinity and to remove LiCl. The sample

was heated under dynamic vacuum; at 130°C deuterium is released and LiMgAlD_6 is formed: $\text{LiMg(AlD}_4)_3 \rightarrow \text{LiMgAlD}_6 + 2\text{Al} + 3\text{D}_2$. At 180°C LiMgAlD_6 decomposes: $\text{LiMgAlD}_6 \rightarrow \text{LiD} + \text{MgD}_2 + \text{Al} + 3/2\text{D}_2$. The first reaction is endothermic; the second exothermic, indicating that $\text{LiMg(AlD}_4)_3$ is not thermodynamic stable. $\text{LiMg(AlD}_4)_3$ crystallizes in the monoclinic space group $P2_1/c$ with cell parameters: $a = 8.37 \text{ \AA}$, $b = 8.74 \text{ \AA}$, $c = 14.30 \text{ \AA}$ and $\beta = 124.83^\circ$. The structure consists of isolated AlD_4 tetrahedra that are connected by octahedral Mg and Li atoms. LiMgAlD_6 crystallizes in the trigonal space group $P321$ with cell parameters: $a = 7.98 \text{ \AA}$ and $c = 4.38 \text{ \AA}$. The structure consists of isolated AlD_6 octahedra tied together by hexa-coordinated Li and Mg atoms. A small amount of TiCl_3 was added to $\text{LiMg(AlD}_4)_3$ and mixed using the ball milling technique. The effect of addition of TiCl_3 was also studied for LiMgAlD_6 .

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Structural phase transitions in $\text{Sr}_2\text{ScReO}_6$

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Keywords: Re-containing double perovskites, structural phase transition, magnetism of Re^{+5}

In double perovskites A_2MReO_6 , where A – an alkaline-earth ion and M – a non-magnetic two – or three-valence cation such as Zn^{2+} , Mg^{2+} or Sc^{3+} , only the Re ion is relevant to the unusual magnetism in these compounds [1, 2]. Structural thermal behaviour of these compounds, which can be connected with magnetic and transport properties, is not yet investigated. In our work, high-temperature structure investigations of $\text{Sr}_2\text{ScReO}_6$ were performed at beamline B2 (HASYLAB DESY, Germany) in Debye-Scherrer mode using the on-site readable image-plate detector OBI and a STOE furnace. All diffraction patterns have been analyzed by using the software package WinPLOTR [3]. Two phase transitions with a change of symmetry of the crystal structure from monoclinic (S.G. $P2_1/n$) to tetragonal (S.G. $P4/mnc$) and then to cubic (Fm-3m) have been detected at elevated temperatures. These phase transitions were also proved by DSC measurements. Low-temperature investigations of $\text{Sr}_2\text{ScReO}_6$ are in progress.

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MS17 P12

X-ray Induced Water Order-Disorder Transition in Hydrated Cesium Cobalt Oxide

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Keywords: X-ray Induced, Order-Disorder Transitions, Water Structure

Metal cobalt oxides, A_xCoO_2 (A= Li, Na, K, Rb, Cs), with layered structure have been attracting wide attention for the past two decades. Li_xCoO_2 is one of the most important intercalation compounds for secondary lithium ion batteries. Na_xCoO_2 is recognized to be a potential candidate for thermal electric power materials and non-cuprites superconductors. A_xCoO_2 compounds have a layered structure, with the CoO_2 layers consisting of CoO_6 octahedra sharing common edges and forming a triangular Co–O sublattice. Open and polarizable framework structure makes the compounds adaptable by chemical modification. The superconductivity of hydrated $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ oxide was found and immediately targeted by research scientists owing to its unusual bilayer-hydrate (BLH) structure. In the coupling strength of CoO_2 layers might be varied by the replacement of different ionic size alkalis resulting in the change of c-axis lattice constant. The influence of coupling strength between CoO_2 layers on superconductivity, therefore, can be possibly studied when the process of controlling the interlayer spacing is developed. The bilayer-hydrate of $\text{Cs}_{0.2}\text{CoO}_2 \cdot 0.63\text{H}_2\text{O}$ with a greatest interlayer spacing $d_{10.0(2)} \text{ \AA}$ among alkali cobalt oxides has been grown in crystal form. Magnetic susceptibility measurement of $\text{Cs}_{0.2}\text{CoO}_2 \cdot 0.63\text{H}_2\text{O}$ displays a paramagnetic behavior down to 1.9 K. We find that X-ray powder diffraction patterns of $\text{Cs}_{0.2}\text{CoO}_2 \cdot 0.63\text{H}_2\text{O}$ changed according to various X-ray dosages during the XRD measurement. The water ordering in $\text{Cs}_{0.2}\text{CoO}_2 \cdot 0.63\text{H}_2\text{O}$ is sensitive to X-ray irradiation. The relative diffraction intensity vary is strongly dependent on the amount of water contain and the location at interfacial position. We will report the X-ray dosage dependent crystal structure of $\text{Cs}_{0.2}\text{CoO}_2 \cdot 0.63\text{H}_2\text{O}$ in the meeting.

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Investigation of $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ (KNN) near the Morphotropic Phase Boundaries

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Keywords: morphotropic phase boundary, sodium potassium niobate, neutron and X-ray scattering

PZT is commonly regarded as the leading piezoelectric material for a wide range of applications, and one which all others must be assessed against. However, there are growing concerns over the toxicity and environmental issues of lead-based substances, which is why attention has turned to other lead-free piezoelectric materials, one of which is Sodium Potassium Niobate (KNN).

The newer lead-free materials are united with PZT in that they exhibit a region in their phase diagrams where there appears to be a sudden change in crystal structure. This region has been termed the Morphotropic Phase Boundary (MPB) and appears to coincide with the maximum piezo-response of these materials. Of particular interest in $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ (KNN) is the presence of three morphotropic phase boundaries (MPB) that occur at $x \sim 0.18$, $x \sim 0.35$, and $x \sim 0.48$ [1].