

REPORT

HC-928 "Fine crystal structure features of the new mixed-valence tellurite/manganite compounds showing unique physical properties and absolutely unusual valency of manganese"

It was carried out high resolution synchrotron powder diffraction studies of $\text{LiMn}_2\text{TeO}_6$ and related nonstoichiometric compositions (16 samples) at ID31 at room temperature and 1 sample at several helium and 4 samples at several nitrogen temperatures. The measured series of samples combined by the fact that they are complex oxides of transition and alkali-earth metals and have a low-dimensional crystal and magnetic structures. Crystal structure of $\text{LiMn}_2\text{TeO}_6$ corresponds a new triclinic structure type (*PI*) derived from orthorhombic $\text{Li}_2\text{TiTeO}_6$ with another variant of the cations ordering. A simultaneous analysis of high resolution synchrotron powder diffraction and neutron diffraction data allowed to clarify the positions of Mn, Li and O atoms. Precise definition of Mn and O positions allows to determine MnO_6 octahedra distortions and in a result Mn oxidation states for all independent position of Mn ions for comprehension of magnetic properties. The position of Li ions determines the transport properties of this system. Also we studied of the deviations from stoichiometry in both sides of $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratio by different synthesis methods, resulting in reduced distortion and transitions to monoclinic or orthorhombic symmetry.

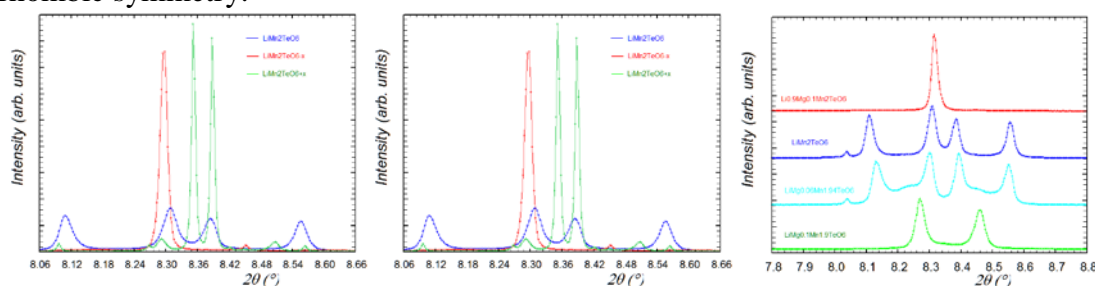


Fig.1. Multiplet {112} which contains 4 components in triclinic, 2 – in monoclinic, and is not split in the orthorhombic system. (a) - comparison of the stoichiometric $\text{LiMn}_2\text{TeO}_6$ composition (blue) and its oxidation (green), and reduction products (red); (b) - comparison of $\text{LiMn}_2\text{TeO}_6$ (blue), and substitution products: $\text{Li}_{1.1}\text{Mn}_{1.9}\text{TeO}_6$ (green), and $\text{Li}_{0.9}\text{Mn}_{2.1}\text{TeO}_6$ (red); (c) - comparison of $\text{LiMn}_2\text{TeO}_6$ (blue) and magnesium substitution products with lithium or manganese: $\text{Li}_{0.9}\text{Mg}_{0.1}\text{Mn}_2\text{TeO}_6$ (red) - orthorhombic, $\text{LiMg}_{0.06}\text{Mn}_{1.94}\text{TeO}_6$ (cyan) - triclinic with a monoclinic impurity, $\text{LiMg}_{0.1}\text{Mn}_{1.9}\text{TeO}_6$ (green) - monoclinic.

Other first interesting physical results of mathematical processing of the obtained experimental data are the following.

Room-temperature investigation of $\text{Na}_2\text{Ni}_2\text{TeO}_6$

This compound is interested for its very high solid-state sodium ion conductivity and unusual magnetic properties. From the laboratory powder XRD data, its crystal structure was shown to be a superstructure of the well known hexagonal layered *P2* type with $P6_3/mcm$ symmetry. Other $\text{Na}_2\text{M}_2\text{TeO}_6$ ($\text{M} = \text{Co}, \text{Zn}, \text{Mg}$) have very similar lattice parameters but another space group, $P6_322$, due to a different stacking mode of the same layers. However, careful inspection of the XRD pattern of $\text{Na}_2\text{Ni}_2\text{TeO}_6$ revealed a weak reflection (101) forbidden in $P6_3/mcm$ and anomalous broadening of the (001) reflections. This might indicate presence of stacking faults or admixture of the $P6_322$ polytype as a separate phase. It was expected that the problem might be solved by the synchrotron XRD study due to its much higher resolution and sensitivity. Indeed, the synchrotron XRD study unambiguously showed that “broadened (001) reflections” are actually split into two distinct reflections from different layered phases (Fig. 2). In addition, several weak reflections specific for the $P6_322$ polytype (and also to the Ni_3TeO_6 impurity) were detected. This permitted separate refinement of lattice constants of the two polytypes within one sample (Table 1).

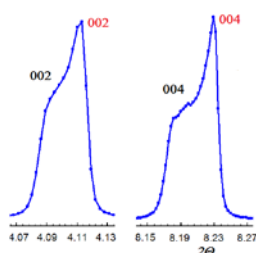


Fig. 2. Selected parts from the XRD pattern of $\text{Na}_2\text{Ni}_2\text{TeO}_6$ with 00l reflections: black hkl are from the $P6_322$ phase and red hkl, from the main $P6_3/mcm$ phase. Intensity scales are different for different doublets. The 002 doublet is actually much stronger

Table 1. Hexagonal lattice parameters of $\text{Na}_2\text{Ni}_2\text{TeO}_6$

	Phase	Space group	a , Å	c , Å
Laboratory XRD	“Single”	$P6_3/mcm$	5.2074(1)	11.1558(4)
ESRF	Major	$P6_3/mcm$	5.2072(9)	11.1673(18)
	Minor	$P6_322$	5.1988(13)	11.2190(8)

Room-temperature investigation of $\text{Li}_3\text{Ni}_2\text{SbO}_6$ and $\text{Na}_3\text{Co}_2\text{SbO}_6$

These two compounds are interested for their possible use as electrode materials for lithium-ion or sodium-ion batteries and for their unusual magnetic properties. Both are superlattices of the well-known rhombohedral layered $\alpha\text{-NaFeO}_2$ type (O3 type) with honeycomb arrangement of magnetic cations. Their laboratory XRD patterns were indexed with high figures of merit in the trigonal space group $P3_1I2$. However, by analogy with some similar phases, monoclinic symmetry might be suggested.

Indeed, XRD profile refinements of $\text{Li}_3\text{Ni}_2\text{SbO}_6$ within two models, $P3_1I2$ and $C2/m$, showed some preference to the latter. However, the monoclinic symmetry could not be proved unambiguously because no splitting of the trigonal reflections could be observed with a laboratory XRD instrument. For $\text{Na}_3\text{Co}_2\text{SbO}_6$, the powder neutron diffraction refinement was only performed within the $C2/m$ model, and possibility of trigonal symmetry was not tested at all.

Owing to much better resolution of the synchrotron instrument, this splitting of several reflections was actually observed in the present work and, thus, the monoclinic model was proved unambiguously for both compounds. Lattice parameters from the different experiments are in reasonable agreement (Table 2).

Table 2. Monoclinic lattice parameters of $\text{Li}_3\text{Ni}_2\text{SbO}_6$ and $\text{Na}_3\text{Co}_2\text{SbO}_6$

Experiment	Refinement method	a , Å	b , Å	c , Å	β , °
$\text{Li}_3\text{Ni}_2\text{SbO}_6$					
Laboratory XRD	Profile refinement, no splitting	5.1828(2)	8.9678(3)	5.1578(2)	109.695(2)
ESRF (run 1)	Search for distinct peaks, refinement with CELREF3	5.1836(4)	8.9719(3)	5.1560(4)	109.680(7)
ESRF (run 2)		5.1840(4)	8.9710(3)	5.1562(4)	109.670(8)
$\text{Na}_3\text{Co}_2\text{SbO}_6$					
Powder neutron diffraction	Profile refinement, no peak splitting	5.3681(2)	9.2849(4)	5.6537(2)	108.506(4)
ESRF	Search for distinct peaks, refinement with CELREF3	5.3656(6)	9.2794(3)	5.6540(5)	108.490(8)

Low-temperature investigation of $\text{Na}_{3.9}\text{Co}_{1.05}\text{TeO}_6$

The room-temperature structure of this phase was solved from the laboratory powder XRD data and showed to be a novel monoclinic structure type. Subsequent investigation of its static and dynamic magnetic properties revealed two anomalies at about 220 K and 110 K that might be associated with structural transitions. To elucidate this point, the low-temperature synchrotron XRD study was performed. However, temperature dependence of the lattice parameters did not show any structural anomaly.

Thus, the experiment No. **HC- 928** was carried out in full. The numerous experimental data are received. The first mathematical processing of experimental data yielded new physical results. Due to the features of the objects of research in this case the joint SR-neutron analysis appeared the most effective. At present the main part of experimental results is in a data processing and preparation the publication.