A NEW FAMILY OF HIGH Na^+-ION CONDUCTIVITY SOLID ELECTROLYTES

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Previously, high cationic conductivity of layered phases $Na_x(M,Ti)O_2$ (P2-type, $P6_3/mmc$, x≈0.6-0.7, M = Ni, Co, Cr, Li) was discovered in this laboratory. Heterovalent cations Ti(4+) and M (3+, 2+ or 1+) were distributed at random over the oxygen octahedra, and this feature was considered as an essential reason for Na^+ disordering over the interlayer prisms and high Na^+ ion mobility. This idea received further support from the recent reports on sodium ordering in the P2-type Na_xCoO_2 bronzes where "heterovalent cations" in octahedra were actually the same element and, thus, charge distribution within the octahedral layer might be easily adjusted to the sodium distribution in the interlayer.

In the present work, however, a series of P2-type compounds is reported where ordered distribution of the heterovalent octahedral cations is combined with sodium disorder and high sodium ion conductivity.

$Na_2MM'TeO_6$ compounds (MM' = Ni_2, Co_2, Zn_2, Mg_2, LiFe) have been prepared by solid-state synthesis at 780-820°C in air. In contrast to the $Na_x(M,Ti)O_2$ berthollides, the new compounds are stoichiometric: sodium content (x) cannot be varied by Te(6+)/M(2+) substitutions, obviously, due to the great difference in their oxidation states. Single-phase ceramics with 55-85 % theoretical density have been prepared by hot pressing at 800°C and studied by the electrochemical impedance spectroscopy and dc polarization techniques. Oxygen content was confirmed by redox titration. According to the Rietveld analysis of the X-ray data, all the compounds are superlattices of the P2 type with ordered arrangement of M, M' and Te on the octahedral sites. Three different superlattices with $a=a_0\sqrt{3}$, where $a_0 \approx 3$ Å, have been found (see the Table). Nevertheless, the sodium distribution over the non-equivalent trigonal prisms is disordered, and hot-pressed ceramics exhibit high and purely ionic conductivity, well comparable with that of β-alumina: 4-11 S/m at 300°C (see the Table). In contrast to the structurally related sodium cobalt bronzes (that are semiconductors, metals or even superconductors) the new compounds contain elements in their stable oxidation states and are electronic insulators. Their electron transport numbers are negligible, except that for the Co compound ($t_e = 10^{-3}$ at 300ºC), obviously due to admixture of Co(3+).

Electrochemical alkali cation extraction has been performed in $Na_2Ni_2TeO_6$ and its ion-exchange product, $Li_2Ni_2TeO_6$. These phases are prospective electrode components for Li-ion batteries.

Compositions and parameters of $Na_2MM'TeO_6$

Composition	Space group	a, Å	b, Å	c, Å	σ(300°C), S/m	Ea, эВ
$Na_2Zn_2TeO_6$	$P2_12_12_1$	5.2784	9.144	11.2895	7.0	0.48
$Na_2Ni_2TeO_6$	$P6_3/mcm$	5.204		11.138	10.8	0.55
$Na_2Co_2TeO_6$	$P6_322$	5.289		11.215	4.4	0.52
$Na_2Mg_2TeO_6$	$P6_322$	5.254		11.255		