Ionic Conductivity, Structural, IR and Raman Spectroscopic Data of Olivine, Sr$_2$PbO$_4$, and Na$_2$CuF$_4$ Type Lithium and Sodium Chlorides Li$_2$ZnCl$_4$ and Na$_2$MgCl$_4$ (M = Mg, Ti, Cr, Mn, Co, Zn, Cd)

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Dedicated to Prof. Dr. Albrecht Rabenau on the occasion of his 65th birthday

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Lithium Zinc Chloride. Sodium Chlorides. Olivine and Sr$_2$PbO$_4$ Type. Ionic Conductivity, X-Ray

1. Introduction

The spinel type (cF56) lithium chlorides Li[LiM]Cl$_4$ (M = Mg, Ti, V, Cr, Mn, Fe, Co and Cd) [1–4] have been found to be fast lithium ion conductors (see refs. [3–5] and further refs. cited therein). The mechanism of conduction, as, for instance, the pathways of the ions in the structure and the lattice sites (tetrahedral or octahedral) involved, however, is not fully clear so far (see, for example, [5, 6]). In addition to the chloride spinels there are ternary lithium and sodium chlorides crystallizing in other structures as Li$_2$ZnCl$_4$, Na$_2$ZnCl$_4$, and Na$_2$CoCl$_4$ [7, 8] (olivine type (oP28)), Na$_2$MgCl$_4$ (M = Mg, Mn, Fe, Cd) [9, 10] (Sr$_2$PbO$_4$ type (oP14)), and Li$_2$VCl$_4$ [11] and Na$_2$CrCl$_4$ (M = Mg, Mn, Fe, Cd) [9, 12] (Suzuki type (cF60)). The question arises whether these compounds are likewise fast ionic conductors and, if not, for what reasons the spinels solely reveal such high conductivity.

Therefore, we studied the ionic conductivity of the olivine and Sr$_2$PbO$_4$ type lithium and sodium halides and characterized these compounds by X-ray, thermoanalytical, IR and Raman spectroscopic methods. Furthermore we tried to synthesize hitherto unknown ternary chlorides. The results obtained on the Suzuki type lithium halides Li$_2$MCl$_8$ (M = Fe, Ni, Co) are reported elsewhere [13].

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2. Experimental

The starting materials MCl$_4$ (M = Mg, Mn, Fe, Co, Ni, Cu) were obtained by dehydration of the respective hydrates (Fluka) in a stream of dry HCl at temperatures of 200–400 °C. Commercial “anhydrous” ZnCl$_2$ (Fluka) and CdCl$_2$ (Merck) were dried in the same manner. The anhydrous chlorides MCl$_4$ (M = Mg, Mn, Fe, Cd) obtained were purified by sublimation in vacuo. VCl$_3$ was prepared via disproportionation of VC$_1$ (Ventron) to VCl$_3$ and VCl, at about 700 °C [14]. Pure CrCl$_3$ was prepared by reaction of CrCl$_3$ (Fluka) with excess chromium (Ventron) at about 600 °C for several days and subsequent vacuum sublimation.

The ternary compounds were obtained by fusing stoichiometric amounts of the halides MCl$_4$ and NaCl or LiCl (both Merck), slow cooling to a temperature of about 20–40 °C below the eutectic or peritectic temperature and subsequent heating for 1–4 weeks. Na$_2$TiCl$_4$ and Na$_2$CrCl$_4$ were prepared by fusing NaCl with TiCl$_3$ (Fluka) and Ti (Ventron) and with CrCl$_3$ (Fluka) and Cr (Ventron), respectively. The samples were allowed to cool slowly to 400 °C and then were annealed for 2 weeks at this temperature. Na$_2$CoCl$_4$ was obtained by quenching a sample from 360 °C to ambient temperature as described by van Loon et al. [7]. The chlorides under investigation are extremely hygroscopic. They must be handled under a dry argon atmosphere.

The compounds were characterized by X-ray techniques, thermal analysis, conductivity and spectroscopic measurements. X-ray Guinier powder technique (Huber Guinier 600 system) and high tempera-
ture Guinier technique (Enraf-Nonius Guinier FR 553 camera) were used. For details see [15]. For indexing and interpreting of the X-ray patterns least squares methods ("LSUCR", "ITO" [16, 17]) and the program "LAZY PULVERIX" [18] were used. The DTA (differential thermal analyses) were made in evacuated sealed borosilicate glass tubes with the thermoanalyzer Linseis L62. The electric conductivity of polycrystalline samples was determined by analysis of the complex impedance diagrams. Preparation of suitable specimens and experimental details are described elsewhere [5]. The setup was slightly modified by using a Hewlett-Packard 4192 A LF impedance analyzer. Measurements of the far infrared spectra were performed with a Bruker IFS 114 FT-IR spectrometer in the spectral range from 40 to 700 cm⁻¹. Raman spectra were recorded with a Dilor Omars 89 Raman spectograph (Ar⁺ laser 514.5 nm, spectral slit-width < 3 cm⁻¹, multichannel detector).

3. Results

3.1 Na₂CrCl₄ and Na₂TiCl₄

The X-ray patterns of samples with the composition Na₂CrCl₄ could be indexed in the monoclinic system. The unit cell dimensions a, b and c, however, are characteristic to Sr₂PbO₄ type sodium chlorides (see Table I). We therefore assumed that Na₂CrCl₄ is isostructural with the chlorides Na₂CrF₄ and Na₂CuF₄, which crystallize in a monoclinically distorted Sr₂PbO₄ structure (mP14) (space group P2₁/c) [19, 20]. Calculation of the X-ray intensities of Na₂CrCl₄ using the atom coordinates of these fluorides confirmed this assumption. From the various formulae reported in the literature for the compound observed in the system NaCl–CrCl₃, as Na₂CrCl₄ [21, 22], Na₂CrCl₅ [23–25] and Na₂CrCl₆ [26], the first one is obviously true.

Komarek et al. [27] first described the compound Na₂TiCl₄. X-ray patterns of this compound were indexed and it is shown that Na₂TiCl₄ crystallizes in the ortho-rhombic Sr₂PbO₄ structure (see Table I).

There is no evidence (high-temperature X-ray photographs) for the existence of the ternary compounds Na₂VCl₄, Na₂NiCl₄ and Na₂CuCl₄. Attempts to prepare the compound Na₂FeCl₄ [7] were not successful.

3.2 Phase relationships and X-ray data

From high-temperature X-ray patterns it is shown that olivine type Na₂CoCl₄ is only stable above 340 °C. However, this compound can be quenched to ambient temperature without decomposition. The metastable phase, which rapidly decomposes to NaCl and CoCl₂ above 200 °C, can be preserved at ambient temperature without decomposition for more than one year. Olivine type Li₂ZnCl₄ undergoes a phase transition to a spinel type phase below 215 °C. No phase transitions or low temperature decompositions were observed for Na₂ZnCl₄, Na₂MgCl₄, Na₂MnCl₄, Na₂CdCl₄, and Na₂CrCl₄.

The unit cell dimensions of the chlorides under study are shown in Table I. The data obtained re-

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>ρ</th>
<th>Vₘ Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CoCl₄</td>
<td>1368.3(9)</td>
<td>807.3(9)</td>
<td>641.7(4)</td>
<td>90.0</td>
<td>2.312</td>
<td>106.71 [7]</td>
</tr>
<tr>
<td>Na₂ZnCl₄</td>
<td>1370.3(2)</td>
<td>806.24(7)</td>
<td>641.12(6)</td>
<td>90.0</td>
<td>2.374</td>
<td>106.65 [7]</td>
</tr>
<tr>
<td>Li₂ZnCl₄</td>
<td>1276.4(3)</td>
<td>741.5(1)</td>
<td>610.8(1)</td>
<td>90.0</td>
<td>2.539</td>
<td>87.05 [7]</td>
</tr>
</tbody>
</table>
| Na₂MgCl₄     | 690.5(4)  | 1188.4(5) | 381.2(1) | 90.0 | 2.251 | 94.20 [9]  
| Na₂TiCl₄     | 690.4(3)  | 1189.9(5) | 381.0(2) | 90.0 | 2.251 | 94.20 [9]  
| Na₂MnCl₄     | 694.5(3)  | 1190.8(4) | 385.8(1) | 90.0 | 2.526 | 96.08 [10] |
| Na₂CdCl₄     | 693(1)    | 1186(2)   | 386(2)    | 90.0 | 2.609 | 93.38 [9]  
| Na₂FeCl₄     | 690.1(3)  | 1173.2(4) | 383.0(2) | 90.0 | 3.015 | 99.55 [9]  
| Na₂CrCl₄     | 394.16(6) | 1159.0(2) | 696.5(2) | 92.48(1) | 2.504 | 95.73 [9]  |
semble those given in the literature so far. The lattice constants of the ternary chlorides as well as the mol
volumina do not smoothly correlate with the ionic radii of the bivalent metals as found for the Suzuki
type Li₂MCl₈ (M = V, Fe, Co, Ni) halides [13] (see Fig. 1).

3.3 Ionic conductivity

The impedance diagrams of the compounds under investigation are similar to those of lithium halide
spinels [5]. In the case of Na₂MCl₄ (M = Mg, Cr, Mn, Cd) there is evidence of contribution of grain
boundary impedances to the total impedance at low temperatures, which is indicated by a second semicir-
cle in the corresponding impedance diagrams [29]. The specific conductivities and activation energies
for conduction \( \sigma \cdot T = A \cdot e^{-\Delta \mu/kT} \) of the chlorides under investigation are given in Table II. The tem-
perature dependence of the electric conductivity is presented in Fig. 2.

Fig. 1. Mol volumina of the olivine, ▲, Sr:PbO₄, ○, ●, and Na₂CuF₄ type, □, ■, chlorides vs the tetrahedral, ▲, and octa-
 hedral, ○, ●, □, ■, ionic radii [28] of the bivalent metals; low spin, open signs.

Fig. 2. Arrhenius plots (one run of several measurements
on different samples, see Table II) of the specific conduc-
tivity \( \log \sigma \text{[Ω}^{-1}\text{cm}^{-1}] \) vs \( 1/T \) of Sr:PbO₄ type Na₂MgCl₄ (a),
Na₂MnCl₄ (c), Na₂CdCl₄ (d), Na₂CuF₄ type Na₂CrCl₄ (b), and olivine type Na₂ZnCl₄ (e) and Li₂ZnCl₄ (f).
### Table II. Specific conductivities $\sigma [\Omega^{-1} \cdot \text{cm}^{-1}]$ and activation energies $\epsilon_a [\text{kJ} \cdot \text{mol}^{-1}]$ for conduction of olivine, $\text{Sr}_2 \text{PbO}_4$, and $\text{Na}_2 \text{CuF}_4$ type compounds $\text{Li}_2 \text{ZnCl}_4$ and $\text{Na}_2 \text{MCl}_4$ ($\text{M} = \text{Mg, Cr, Mn, Co and Cd}$) at different temperatures (mean values of several measurements).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Compound</th>
<th>$200 , ^\circ \text{C}$</th>
<th>$300 , ^\circ \text{C}$</th>
<th>$400 , ^\circ \text{C}$</th>
<th>$\epsilon_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>$\text{Li}_2 \text{ZnCl}_4$</td>
<td>$3 \cdot 10^{-4}$</td>
<td>$5 \cdot 10^{-5}$</td>
<td>$1 \cdot 10^{-3}$</td>
<td>95 (220–330 °C)</td>
</tr>
<tr>
<td>$\text{Na}_2 \text{CoCl}_4$</td>
<td>$3 \cdot 10^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Sr}_2 \text{PbO}_4$</td>
<td>$1 \cdot 10^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$MgCl$_4$</td>
<td>$5 \cdot 10^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$MnCl$_4$</td>
<td>$5 \cdot 10^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$CdCl$_4$</td>
<td>$5 \cdot 10^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$CrCl$_4$</td>
<td>$8.9 \cdot 10^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td>100 (270–420 °C)</td>
</tr>
<tr>
<td>$\text{Na}_2 \text{CuF}_4$</td>
<td>$1 \cdot 10^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The strong increase of the ionic conductivity and the low activation energy of conduction of $\text{Na}_2 \text{ZnCl}_4$ above 260 °C (see Fig. 2) is probably due to the presence of melt formed by an eutectic reaction of small amounts of NaCl and ZnCl$_2$. There is no indication of a phase transition at this temperature (high-temperature X-ray measurements).

#### 3.4 Vibrational spectra

**Olivine type compounds**

Olivine type compounds crystallize in the space group Pnma ($D_{2h}^{16}$) with four formula units in the primitive unit cell. The crystal structure is strongly related to that of spinels, i.e. hexagonal close packing of the chloride ions instead of a cubic one. Unit cell group analysis yields

$$\Gamma = 11 A_g (\text{Ra}) + 10 A_u + 7 B_{1g} (\text{Ra}) + 14 B_{1u} (\text{IR, T}) + 11 B_{2g} (\text{Ra}) + 10 B_{2u} (\text{IR, T}) + 7 B_{3g} (\text{Ra}) + 14 B_{3u} (\text{IR, T})$$

for the irreducible representations of wavevector $k=0$ vibrational modes [31] (including translations T). Although vibrational spectra of (Fe, Mg)$_2$SiO$_4$ (olivine) and related compounds have been intensively studied in the last years [31–35], there are no IR and Raman data of chloride olivines available in the literature so far.

As shown from Fig. 3 only 8–9 of the 35 group theoretically allowed IR active normal modes of

![Fig. 3. Far infrared spectra of olivine type chlorides $\text{Li}_2 \text{ZnCl}_4$, $\text{Na}_2 \text{CoCl}_4$ and $\text{Na}_2 \text{ZnCl}_4$ (Bruker IFS 114, Nujol).](image-url)
Olivine type chlorides are observed. In the case of the sodium compounds only the bands near 300 cm\(^{-1}\) are significantly shifted when cobalt is replaced by zinc, while the other frequencies remain almost unchanged. Therefore, these bands must obviously be assigned to vibrations of the M\(^{II}\)Cl\(_4\) tetrahedra, although strong coupling of internal and external modes has to be expected. Because all bands are observed in a narrow frequency range a full separation of internal and external modes as in the case of the respective silicates and borates is not valid for chlorides. A more detailed assignment of the bands observed can only be given on the basis of single crystal data, which are not available at the present time.

Raman spectra of chloride olivines are shown in Fig. 4. The Raman spectrum of Na\(_2\)CoCl\(_4\) could not be measured because this compound decomposed to NaCl and CoCl\(_2\) by the action of laser light, even at liquid nitrogen temperature. As in the case of the far infrared spectra, the Raman spectra reveal much less bands than those (36) predicted by group theory. The spectra of the lithium and sodium compounds are very similar, especially in the region of the main band at about 280 cm\(^{-1}\) indicating that the alkali metal ions are only little involved in the corresponding normal vibrations.

Sr\(_2\)PbO\(_4\) type compounds

Goodyear et al. [10] proposed as possible space groups for Sr\(_2\)PbO\(_4\) type Na\(_2\)MnCl\(_4\) Pbam (D\(_{2h}\)) or Pba2 (C\(_{2v}\)). Since space group Pbam is centro-symmetric and Pba2 is not, vibrational spectroscopy should be a good tool for determining the true space group. Unit cell group analysis yields

\[
\Gamma(D_{2h}) = 6A_g(Ra) + 4A_u + 6B_{1g}(Ra) + 4B_{1u}(IR, T_2) + 3B_{2g}(Ra) + 8B_{2u}(IR, T_v) + 3B_{3g}(Ra) + 8B_{3u}(IR, T_v)
\]

or

\[
\Gamma(C_{2v}) = 10A_1(IR, Ra, T_3) + 10A_2(Ra) + 11B_1(IR, Ra, T_3) + 11B_2(IR, Ra, T_3)
\]

for the irreducible representations of wavevector k = 0 vibrational modes (including translations T).

Far infrared and Raman spectra of Na\(_2\)MCl\(_4\) (M = Mg, Mn, Cd) are presented in Figs. 5 and 6, respectively. The number of group theoretically allowed bands for the space groups Pba2 and Pbam is considerably larger than the number of observed bands. So far both space groups are compatible with the observed spectra. When comparing the corresponding far infrared and Raman spectra of the compounds under investigation, it is apparent that some bands appear at about the same frequencies. However, the mutual exclusion principle seems to be valid because the main bands in the Raman spectra, which can be assigned to the total symmetric stretching modes of the M\(^{II}\)Cl\(_6\) octahedra, are only slightly changed in frequency (235–238 cm\(^{-1}\)) when replacing M\(^{II}\), whereas the corresponding IR bands, i.e. the asymmetric M–Cl stretching modes of the M\(^{II}\)Cl\(_6\) octahedra, are considerably shifted towards higher wavenumbers with decreasing masses of M\(^{II}\). Thus Pbam must be the correct space group as originally claimed for Sr\(_2\)PbO\(_4\) by Trömel [38].

![Fig. 4. Raman spectra of olivine type chlorides Li\(_2\)ZnCl\(_4\) and Na\(_2\)ZnCl\(_4\) (Dilor Omars 89, Ar\(^+\) laser 514.5 nm).](image-url)
Fig. 5. Far infrared spectra of Sr$_2$PbO$_4$ type Na$_2$MgCl$_4$, Na$_2$MnCl$_4$, and Na$_2$CdCl$_4$ and Na$_2$CuF$_4$ type Na$_2$CrCl$_4$ (Bruker IFS 114, Nujol).

Fig. 6. Raman spectra of Sr$_2$PbO$_4$ type Na$_2$MgCl$_4$, Na$_2$MnCl$_4$, and Na$_2$CdCl$_4$, and Na$_2$CuF$_4$ type Na$_2$CrCl$_4$ (Dilor Omars 89, Ar$^+$ laser 514.5 nm), for Na$_2$CdCl$_4$ see also [37].
Na$_2$CrCl$_4$

Na$_2$CuF$_4$ type compounds crystallize in the space group P2$_1$/c (C$_{2h}^+$) [19] with two formula units in the primitive unit cell. Unit cell group analysis yields

$$
\Gamma = 9 \mathbf{A}_g (\text{Ra}) + 12 \mathbf{A}_u (\text{IR}, T_x) + 9 \mathbf{B}_g (\text{Ra}) + 12 \mathbf{B}_u (\text{IR}, T_{x,y})
$$

for the irreducible representations of wavevector $k=0$ vibrational modes (including translations T). As shown from Figs. 5 and 6, respectively, only some of these vibrations can be observed in the IR and Raman spectra.

Whereas the Raman spectrum of Na$_2$CuF$_4$ type Na$_2$CrCl$_4$ is quite different from those of both olivine and Sr$_2$PbO$_4$ type chlorides, its far infrared spectrum is surprisingly similar to those of olivine chlorides, but not to those of the undistorted Sr$_2$PbO$_4$ type compounds as expected, in particular because of the presence of two bands near 300 cm$^{-1}$, which have been assigned to vibrations of M$^2$Cl$_4$ tetrahedra in the case of the olivine type compounds (see above). Larkworthy et al. [39] observed two bands in the IR spectra of K$_2$NiF$_4$ type Cs$_2$CrCl$_4$ and one band in those of other chlorochromates at about 300 cm$^{-1}$, which they assigned to stretching vibrations of short Cr—Cl bonds in distorted octahedral CrCl$_6$X$_2$ (X = Cl, H$_2$O) and square planar CrCl$_4$ units. Therefore, in our opinion, the far infrared spectrum of Na$_2$CrCl$_4$ supports the results of the X-ray measurements, namely that this compound possesses the monoclinically distorted Sr$_2$PbO$_4$ structure because the CrX$_6$ entities of this structure (Na$_2$CuF$_4$ type) are strongly distorted (Jahn-Teller-effect) and, hence, can better be described as planar CrX$_4$ units with two additional X atoms at considerably longer distances.

4. Discussion and Conclusion

The ionic conductivities of olivine, Sr$_2$PbO$_4$, and Na$_2$CuF$_4$ type ternary sodium chlorides are about three orders of magnitude lower than those of lithium chloride spinels [3–5]. Appreciable conductivities come up only just below the melting points. Even the conductivity of Li$_2$ZnCl$_4$ is two orders of magnitude lower (at 300 °C) than those of the spinels. In the case of the Sr$_2$PbO$_4$ type Na$_2$MCl$_4$, the conductivities increase in the order Mg < Mn < Cd. This may be either a result of increasing covalency or decreasing lattice energy. The latter is supported by the fact that the mol volume increases (and the activation energies for conduction decrease) in the same order (see Tables I and II).

In the past, several attempts have been made to answer the question why lithium halide spinels reveal such a high ionic conductivity and what is the contribution of tetrahedrally and octahedrally coordinated lithium ions [5, 6]. In this context it is of interest to note the considerably lower ionic conductivity of olivine type Li$_2$ZnCl$_4$ than that of the inverse lithium spinels with both tetrahedrally and octahedrally coordinated lithium ions. Since in the olivine structure lithium ions are situated only in octahedral sites, one could conclude that tetrahedrally coordinated lithium ions exhibit higher mobility than the octahedrally coordinated ones.

This presumption is confirmed by other experimental results. Thus, for example, substitution of lithium by sodium in Li$_2$–Na$_2$MCl$_4$ (M = Mn, Cd) spinel solid solutions [40], which is expected to take place in octahedral sites, only results in a small effect on the electric conductivity [29]. Furthermore the conductivity of spinel type Li$_2$ZnCl$_4$, with lithium ions only in octahedral sites (normal spinel), is two orders of magnitude smaller than those of the inverse chloride spinels.

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