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Na_2CrO_4(I) SOLID SOLUTIONS: CRYSTAL CHEMISTRY, DEFECTS AND IONIC CONDUCTIVITY

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ABSTRACT

In the system Na_2CrO_4-$CaCrO_4$ a field of solid solutions $Na^+_{2-x}Ca^{2+}_x\square_x CrO_4$ was found extending up to 40% $CaCrO_4$, i.e. 20% cation vacancies ($\square$). These defects are the reason for a remarkable ionic conductivity with a maximum of $\sigma = 10^{-1}$ $(\Omega\cdot cm)^{-1}$ at 7.5% $\square$ and at 500°C. In the chromate and the corresponding selenate system four new phases were found: $Na_6Ca(CrO_4)_4$, $Na_4Ca(CrO_4)_3$, $Na_4Ca(SeO_4)_3$ and high-$CaSeO_4$.

METHODS

$CaCrO_4$ was precipitated from aqueous solutions of Na_2CrO_4 and $CaCl_2$. Then mixtures of $CaCrO_4$ and Na_2CrO_4 were molten for 3 min. in Pt crucibles at 950°C and quenched in air or liquid N_2 (weight losses 1/2%) or slowly cooled in the furnace (weight loss 2%).

The resulting phases were identified by X-ray powder diffraction (Norelco Diffractometer) or Guinier Camera (AEG) with silicon NBS-SRM 640 as internal standard. High temperature Debye Scherrer patterns were calibrated with α-Al_2O_3 (a = 4.775 and c = 13.036 Å at 500°C; a = 4.759 and c = 12.992 Å at 20°C).

For thermal analysis a Du Pont Thermal Analyzer 1090/910 with microcomputer, DSC-cell ($\leq$ 700°C) and 1200°C cell was employed. (For temperature calibration c.f. ref.1). In addition a hot stage (Leitz Company, $\leq$ 1350°C) was used with a polarizing microscope.

Ionic conductivities could be determined by impedance measurements (2) since the Na_2CrO_4(I)ss exhibit no significant electronic conductivity (c.f. ref.3).

THE SYSTEM Na_2CrO_4-$CaCrO_4$

Various methods were used to determine the Na-rich part of the phase diagram Na_2CrO_4-$CaCrO_4$. DTA, DSC and high temperature X-ray (Fig.1) results are included in Fig.2. In addition the phases found by X-ray powder diffraction after quenching or slow cooling were identified. The two polymorphs of Na_2CrO_4 are called Na_2CrO_4(III) and Na_2CrO_4(I) in analogy to the isostructural

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modification of Na_2SO_4,(III) and (I). The latter has a strongly disordered structure (4).

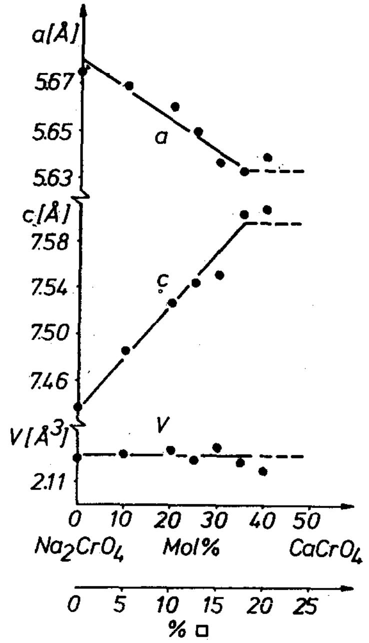

Fig.1 Lattice parameters of Na_2CrO_4(I)ss at 500°C

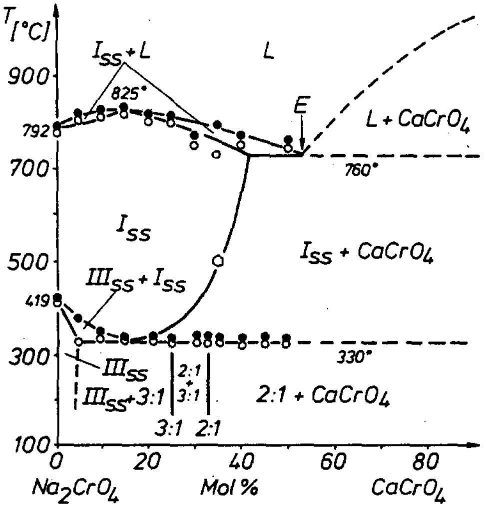

Fig.2

The system Na_2CrO_4-$CaCrO_4$

○ High temperature X-ray results

● DTA and DSC, heating

○ DTA and DSC, cooling

The system is characterized by a large field of solid solution of Na_2CrO_4(I) and by two low temperature compounds 2:1 = $Na_4Ca(CrO_4)_3$ and 3:1 = $Na_6Ca(CrO_4)_4$. Their small stability ranges below 300°C were not determined in detail. During investigations in the corresponding system Na_2SeO_4-$CaSeO_4$ the isostructural $Na_4Ca(SeO_4)_3$ and a new modification of $CaSeO_4$ with scheelite structure were found (Table 1). The latter was obtained by sintering a pellet at 400°C for 5 days with subsequent quenching. The 3:1 selenate could not be prepared. In contrast to the corresponding Na_2SO_4(I)ss (ref.4) the Na_2CrO_4(I)ss could not be quenched.

Table 1

Lattice parameters of new compounds

Complete powder data were sent to JCPDS for publication in the Powder Data file

Compound	Symmetry	a (Å)	c (Å)
$Na_4Ca(CrO_4)_3$	hexagonal	16.315	22.747
$Na_4Ca(SeO_4)_3$	hexagonal	16.348	22.853
$CaSeO_4$	tetragonal	5.047	11.664

IONIC CONDUCTIVITY

The large field of the solid solutions $(Na_{2-2x}Ca_x\square_x)CrO_4$ implies a massive concentration of cation vacancies $\square$. They provide "hopping paths" for the remaining Na^+ ions and are the basis of a remarkable ionic conductivity (Fig.3).

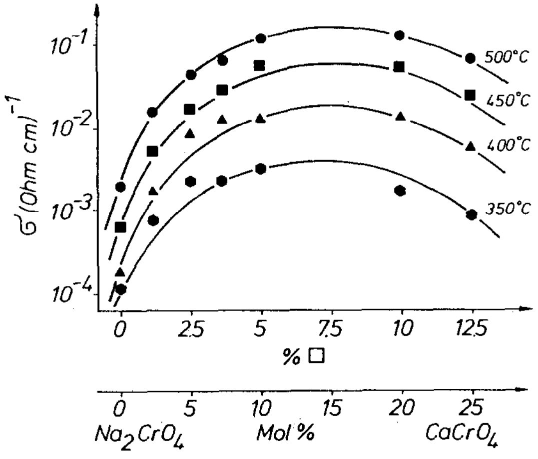

Fig.3 Ionic conductivity of Na_2CrO_4(I)ss

Starting from pure Na_2CrO_4, the conductivity increases strongly and reaches its maximum at about 7.5% vacancies. The following decrease is probably due to defect clustering. The maximum value measured was $\sigma = 10^{-1}$ $(\Omega\ cm)^{-1}$ at 500°C.

A comparison with the isostructural solid solutions of Na_2SO_4(I) shows a surprising agreement, since also for these materials the maxima of the conductivity curves appear at 7.5% vacancies (3). Due to decomposition reactions corresponding investigations in the system Na_2SeO_4-$CaSeO_4$ were not possible.

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