

Synthesis and Conductivities of Sulfate/Selenate Phases Related to Nasicon: $\text{Na}_x\text{M}'(\text{II})_x\text{M}''(\text{III})_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$

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The synthesis of Na containing Nasicon-type phases of the form $\text{Na}_x\text{M}'(\text{II})_x\text{M}''(\text{III})_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$ ($\text{M}' = \text{Mg, Zn, Cd, Mn}$; $\text{M}'' = \text{Al, Cr, Fe, In, Yb}$; $0 \leq x \leq 1.75$; $0 \leq y \leq 3$) is reported. The conductivities of a range of samples have been measured, with the highest value observed at 200°C being $2 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ for $\text{Na}_{1.75}\text{Mg}_{1.75}\text{Cr}_{0.25}(\text{SO}_4)_3$. The range of x for which single phase samples are observed depends on the nature of M' and M'' , and on the value of y . Attempts to increase the Na content, and so increase the conductivity, by partially substituting the (S, Se)O₄ groups by PO₄ or SiO₄ have proved unsuccessful. © 1993 Academic Press, Inc.

Introduction

The system $\text{Na}_{1-x}\text{Zr}_2\text{Si}_3\text{P}_{3-x}\text{O}_{12}$ and related materials, commonly referred to as Nasicons, have attracted considerable interest since the report of fast ion conduction in phases of this form (1, 2). The conduction properties result from the facile migration of Na ions along channels formed within a rhombohedral framework of corner-sharing ZrO_6 octahedra and (Si/P)O₄ tetrahedra. Prior to the discovery of fast ion conduction in this system, mixed metal sulfates of the form $\text{NaM}'(\text{II})\text{M}''(\text{III})(\text{SO}_4)_3$ were reported by Perret *et al.* (3, 4). Although these materials exhibit similar structural characteristics, their conductivities have not been reported. In a previous paper, we reported the synthesis and electrical properties of a corresponding Li-containing series of sulphates and selenates, $\text{Li}_x\text{M}'(\text{II})_x\text{M}''(\text{III})_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$ (5), and we now describe the synthesis and conductivities of the related Na series, $\text{Na}_x\text{M}'(\text{II})_x\text{M}''(\text{III})_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$ ($\text{M}' = \text{Mg, Zn, Cd, Mn}$; $\text{M}'' = \text{Al, Cr, Fe, In, Yb}$; $0 \leq x \leq 1.75$;

$0 \leq y \leq 3$). These materials represent a significant extension to the materials previously reported (3, 4), and an important objective of the study was the synthesis of new phases with different Na contents. In this respect, we show that it is possible to vary the Na content above and below 1.0, and we also report the successful synthesis of analogous selenates and mixed sulfate/selenates.

Experimental

A number of $\text{Na}_x\text{M}'(\text{II})_x\text{M}''(\text{III})_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$ samples containing several different $\text{M}'(\text{II})$ and $\text{M}''(\text{III})$ cations, and various values of x and y , were prepared. Two synthetic procedures were employed for the sulfate phases ($y = 0$): Method 1 for $\text{M}'' = \text{Al, Cr}$, and Method 2 for $\text{M}'' = \text{Fe, In, Yb}$.

Method 1

The sulfates Na_2SO_4 , $\text{M}'\text{SO}_4$ ($\text{M}' = \text{Mg, Zn, Cd}$), and $\text{M}''_2(\text{SO}_4)_3$ were first dissolved in hot distilled water. After evaporation of the solution to dryness, the solid was ground and heated to 500°C in air for 12 hr. In the case

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of $M' = \text{Cd}$, a slightly higher temperature of 550°C was used, but for this series a Nasicon-type phase was obtained only for $M'' = \text{Cr}$.

Method 2

Na_2SO_4 , $M'\text{SO}_4$ ($M' = \text{Mg, Zn, Mn, Cd}$), and $M''_2(\text{SO}_4)_3$ were intimately ground and pressed into pellets (1.3 cm diameter, approximately 3–4 mm thick) under a pressure of 4000 kg cm⁻². The pellets were then heated in air for 12 hr, reground, and compacted to pellets, before reheating in air for a further 12 hr. The temperature used depended on the nature of M'' : $M'' = \text{Fe}$, 500°C; $M'' = \text{In}$, 550–600°C; $M'' = \text{Yb}$, 650–700°C. For $M' = \text{Zn}$, the composition $\text{NaZnYb}(\text{SO}_4)_3$ resulted in a multiphase product, with no sign of any Nasicon-type phase, whereas for $M' = \text{Cd}$, only $\text{NaCdIn}(\text{SO}_4)_3$ had the Nasicon structure. Attempts to form similar phases with the larger rare earths Y, Sm, Nd were only partially successful. Nasicon-type phases were observed in multiphase products in the case of $M'' = \text{Y}$ for $M' = \text{Mg}$, or Mn, but for $M'' = \text{Sm, Nd}$, no traces of phases with the required structure were apparent.

The selenates and sulfate/selenates ($y > 0$) were prepared in all cases by Method 1, using appropriate amounts of Na_2SeO_4 , $M'\text{O}$, $M'\text{SO}_4$, $M''(\text{OH})_3$, or $M''(\text{NO}_3)_3$, $M''_2(\text{SO}_4)_3$, and H_2SeO_4 ($M' = \text{Zn, Mg}$; $M'' = \text{Al, Cr, Fe, In, Yb}$), and a reaction temperature of 420°C. In all cases, single phase samples were observed only for $M' = \text{Mg}$, although multiphase samples containing some Nasicon phase were obtained for $M' = \text{Zn}$. In the case of $M'' = \text{Yb}$, it was not possible to synthesise any phase with $y > 0$, and for $M'' = \text{Cr}$ it was only possible to synthesise single phase samples for $y \leq 1.5$. For $M'' = \text{Al, Fe, Cr, and In}$, SeO_4 and SO_4 could be reversibly interchanged by refluxing in dilute H_2SO_4 or H_2SeO_4 , then evaporating to dryness and heating to 420°C to remove any surplus H_2SO_4 or H_2SeO_4 .

Characterization

Given the low temperatures (below that required for decomposition or volatiliza-

tion) employed for the syntheses, and the fact that all materials examined in detail were shown to be single phase by X-ray powder diffraction measurements (Philips PW 1050/70 using Cu $K\alpha$ radiation), the compositions of the products described in this paper can reliably be deduced from the atomic ratios in the relevant starting materials. A detailed neutron powder diffraction study of several materials has confirmed the validity of this and will be reported elsewhere (7).

The observed XRD patterns were similar to that observed for $\text{NaZr}_2(\text{PO}_4)_3$ (1), indicating a rhombohedral cell. The appearance of additional peaks in some XRD traces, most notably (003) as previously noted by Perret *et al.* (4), suggested $R\bar{3}$ symmetry for these phases compared with $R\bar{3}c$ for $\text{NaZr}_2(\text{PO}_4)_3$. Refined cell parameters (hexagonal cell) for a range of samples are given in Table I. It is possible to form a wide range of samples with varying Na contents; i.e., $\text{Na}_x M'_x M''_{2-x}(\text{SO}_4)_{3-y}(\text{SeO}_4)_y$ ($0 \leq x \leq 1.75$), the actual range of x depending on the nature of M' , M'' , and the value of y . In the case of $M'' = \text{In}$ or Yb , the samples with $x < 1.0$ were multiphase, while for $y \geq 1.5$ single phase samples were not formed for $x \geq 1.25$ for any M'' . The highest values of x were observed when $M' = \text{Mg}$. Attempts to further increase x by the partial replacement of SO_4 or SeO_4 groups by PO_4 or SiO_4 using either solid state or hydrothermal techniques proved unsuccessful, with impurity phases being observed in all cases. The replacement of M' by Li^+ or Na^+ ions also failed to allow the incorporation of additional Na^+ into the structure. The possible synthesis of phases of the form $\text{Na}_2 M'(\text{II})N(\text{II})(\text{SO}_4)_3$, where M' and N are different bivalent cations (e.g., Zn and Mg, Mn and Mg), has also been examined, but no Nasicon-type phases were observed.

Ionic Conductivity Measurements

Ionic conductivities were determined from a.c. impedance measurements in the

TABLE I
 UNIT CELL DIMENSIONS

Sample composition	a (Å)	c (Å)	V (Å ³)
NaZnAl(SO ₄) ₃	8.253(4)	21.90(1)	1292
NaMgAl(SO ₄) ₃	8.329(5)	21.78(1)	1308
NaMgAl(SO ₄) _{2.5} (SeO ₄) _{0.5}	8.355(7)	21.88(2)	1323
NaMgAl(SO ₄) _{1.5} (SeO ₄) _{1.5}	8.444(7)	22.20(2)	1371
Na _{2.25} Mg _{2.25} Al _{1.75} (SeO ₄) ₃	8.343(8)	22.43(3)	1352
Na ₅ Mg ₅ Al _{1.5} (SeO ₄) ₃	8.364(6)	22.62(2)	1370
Na _{7.75} Mg _{7.75} Al _{1.25} (SeO ₄) ₃	8.439(7)	22.60(2)	1394
NaMgAl(SeO ₄) ₃	8.599(7)	22.36(2)	1432
NaZnFe(SO ₄) ₃	8.403(4)	22.14(1)	1354
NaMnFe(SO ₄) ₃	8.584(6)	22.17(2)	1415
Na _{2.25} Mg _{2.25} Fe _{1.75} (SO ₄) ₃	8.249(8)	22.20(3)	1308
Na ₅ Mg ₅ Fe _{1.5} (SO ₄) ₃	8.274(7)	22.36(3)	1326
Na _{7.75} Mg _{7.75} Fe _{1.25} (SO ₄) ₃	8.400(7)	22.12(3)	1352
NaMgFe(SO ₄) ₃	8.493(3)	21.98(1)	1373
Na _{1.25} Mg _{1.25} Fe _{0.75} (SO ₄) ₃	8.534(5)	21.94(2)	1384
NaMgFe(SO ₄) _{2.5} (SeO ₄) _{0.5}	8.541(3)	22.04(1)	1392
NaMgFe(SO ₄) _{1.5} (SeO ₄) _{1.5}	8.578(3)	22.40(1)	1428
Na _{1.25} Mg _{1.25} Fe _{0.75} (SO ₄) _{1.5} (SeO ₄) _{1.5}	8.703(5)	22.31(1)	1463
Na _{2.25} Mg _{2.25} Fe _{1.75} (SeO ₄) ₃	8.520(9)	22.97(2)	1444
Na ₅ Mg ₅ Fe _{1.5} (SeO ₄) ₃	8.560(8)	23.00(3)	1459
Na _{7.75} Mg _{7.75} Fe _{1.25} (SeO ₄) ₃	8.619(8)	22.94(2)	1476
NaMgFe(SeO ₄) ₃	8.733(8)	22.72(2)	1501
Na _{1.25} Mg _{1.25} Fe _{0.75} (SeO ₄) ₃	8.851(8)	22.51(2)	1527
Na _{2.25} Zn _{2.25} Cr _{1.75} (SO ₄) ₃	8.132(7)	22.05(2)	1263
Na ₅ Zn ₅ Cr _{1.75} (SO ₄) ₃	8.154(6)	22.23(2)	1280
Na _{7.75} Zn _{7.75} Cr _{1.25} (SO ₄) ₃	8.190(7)	22.24(2)	1292
NaZnCr(SO ₄) ₃	8.251(6)	22.27(2)	1313
NaCdCr(SO ₄) ₃	8.229(6)	23.09(2)	1354
Na _{2.25} Mg _{2.25} Cr _{1.75} (SO ₄) ₃	8.157(6)	22.14(2)	1276
Na ₅ Mg ₅ Cr _{1.5} (SO ₄) ₃	8.187(6)	22.20(3)	1289
Na _{7.75} Mg _{7.75} Cr _{1.25} (SO ₄) ₃	8.284(7)	22.14(2)	1316
NaMgCr(SO ₄) ₃	8.360(6)	22.09(2)	1337
Na _{1.25} Mg _{1.25} Cr _{0.75} (SO ₄) ₃	8.456(6)	21.98(2)	1361
Na _{1.5} Mg _{1.5} Cr _{0.5} (SO ₄) ₃	8.540(7)	21.89(3)	1383
Na _{1.75} Mg _{1.75} Cr _{0.25} (SO ₄) ₃	8.612(7)	21.85(2)	1403
NaMgCr(SO ₄) _{2.5} (SeO ₄) _{0.5}	8.436(8)	22.08(2)	1361
Na _{1.75} Mg _{1.75} Cr _{0.25} (SO ₄) _{2.5} (SeO ₄) _{0.5}	8.665(8)	22.01(2)	1431
NaMgCr(SO ₄) _{1.5} (SeO ₄) _{0.5}	8.496(8)	22.57(3)	1411
NaZnIn(SO ₄) ₃	8.493(6)	22.60(2)	1412
NaMnIn(SO ₄) ₃	8.712(7)	22.53(3)	1481
NaCdIn(SO ₄) ₃	8.600(6)	23.08(2)	1478
NaMgIn(SO ₄) ₃	8.619(6)	22.23(2)	1430
Na _{1.2} Mg _{1.2} In _{0.8} (SO ₄) ₃	8.630(3)	22.23(1)	1434
Na _{1.5} Mg _{1.5} In _{0.5} (SO ₄) ₃	8.645(3)	22.11(1)	1431
NaMgIn(SO ₄) _{1.5} (SeO ₄) _{1.5}	8.718(5)	22.62(3)	1489
Na _{1.25} Mg _{1.25} In _{0.75} (SO ₄) _{1.5} (SeO ₄) _{1.5}	8.728(8)	22.48(2)	1483
NaMgIn(SeO ₄) ₃	8.926(8)	22.83(2)	1575
NaMnYb(SO ₄) ₃	8.857(5)	22.96(2)	1560
NaMgYb(SO ₄) ₃	8.723(6)	22.64(2)	1492
Na _{1.3} Mg _{1.3} Yb _{0.7} (SO ₄) ₃	8.692(5)	22.45(1)	1469
Na _{1.5} Mg _{1.5} Yb _{0.5} (SO ₄) ₃	8.678(5)	22.23(2)	1450

range $5\text{--}5 \times 10^5$ Hz using a Hewlett Packard 4800A vector impedance meter. Pellets (13 mm diameter, ≈ 1 mm thick) of each sample were obtained by pressing at 4000 kg cm^{-2} and sintering in air at the temperatures used in the initial synthesis. Densities of the pellets ranged from between 62% of the theoretical for $\text{NaMgAl}(\text{SeO}_4)_3$ to 82% for $\text{NaZnFe}(\text{SO}_4)_3$; in general the higher values were obtained for the Fe-, In-, and Yb-containing samples. Both planar faces of the pellets were coated with silver paint, and the pellets were then sandwiched between metal electrodes, which were also coated with silver paint. Although similar results could be obtained using gold foil electrodes, confirming the ionically blocking nature of the silver-coated electrodes, the use of silver paint was preferred. Measurements were made in air between 60°C and 300°C , the actual temperature range examined being determined by the conductivity of the sample, since for the samples with low conductivities ($\approx 10^{-7} \Omega^{-1} \text{cm}^{-1}$), measurements below 150°C were less reliable. Prior to any measurements being made, the pellets were heated to 300°C to ensure the removal of adsorbed water. The complex-plane impedance spectra could be fitted to a single semi-circle, and extrapolation to the real axis determined the bulk resistance. Conductivity data for a range of samples are given in Table II. A change in activation energy, from ΔH_1 (low temperature) to ΔH_2 (high temperature), occurred for several samples at temperatures between 100°C and 160°C , and both values are given in Table II. It is likely that the remaining samples, for which only one ΔH value is given, also undergo a similar change in activation energy, but the low conductivities prevented satisfactory measurements being taken below 150°C . A similar change in activation energy has been observed in the related Li-containing series, $\text{Li}_x\text{M}'_x\text{M}''_{2-x}(\text{SO}_4)_3$ (5). Figure 1 shows the variation of $\log \sigma T$ with $1/T$ for $\text{Na}_{1.75}\text{Mg}_{1.75}\text{Cr}_{0.25}(\text{SO}_4)_3$, which is reproducible and is typical of the data obtained.

Discussion

The highest conductivity was recorded for $\text{Na}_{1.75}\text{Mg}_{1.75}\text{Cr}_{0.25}(\text{SO}_4)_3$ ($2.3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 200°C , $1.6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 300°C) and the latter value is similar to the corresponding value ($2.9 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$) reported for $\text{Na}_{1.8}\text{Zr}_2\text{P}_{2.2}\text{Si}_{0.8}\text{O}_{12}$ (1). The activation energies are also comparable (50 kJ mol^{-1} and 30 kJ mol^{-1} , respectively). Unfortunately, the sulfate/selenate systems studied appear restricted to a maximum Na content of 1.75 per formula unit, which limits the potential for further increasing the conductivity. The measured conductivities of the samples will be lower than the true bulk values due to the generally porous nature of the pellets, which is a difficult problem to overcome, since higher sintering temperatures would cause decomposition.

The range of M' and M'' cations which form $\text{NaM}'\text{M}''(\text{SO}_4)_3$ Nasicons appears, at least partly, to reflect the radii of the octahedral M'^{2+} and M''^{3+} ions. For example, although it has proved impossible to prepare the phases $\text{NaMgSm}(\text{SO}_4)_3$ or $\text{NaMgNd}(\text{SO}_4)_3$ [octahedral radii $\text{Sm}^{3+} 0.96 \text{ \AA}$, $\text{Nd}^{3+} 0.98 \text{ \AA}$ (6)] with a Nasicon-type structure, the analogous phases containing the smaller rare earths Yb and Y [$\text{Yb}^{3+} 0.87 \text{ \AA}$, $\text{Y}^{3+} 0.90 \text{ \AA}$ (6)] have been synthesized, albeit with some impurities for the latter.

In the case of $M' = \text{Cd}^{2+}$, octahedral radius 0.95 \AA , it is possible that there is at least some of the Cd in the channel sites. This seems likely given the large Cd^{2+} radius and its similarity to that of Na^+ [1.02 \AA], and possible support for this is found in the unit cell volume of $\text{NaMnIn}(\text{SO}_4)_3$, which is larger than that of $\text{NaCdIn}(\text{SO}_4)_3$ despite the fact that Mn^{2+} is smaller than Cd^{2+} . However, the large size of Na^+ suggests that only low concentrations of this ion would be possible in the octahedral sites, and octahedral vacancies may therefore be present.

It is interesting to note that the highest Na content in the sulfate/selenate phases is significantly lower than in the silicate/phosphate analogues, for which Na_4Zr_2

TABLE II
CONDUCTIVITIES ($\Omega^{-1}\text{cm}^{-1}$) AND ACTIVATION ENERGIES (kJ mol^{-1})

Sample composition	σ_{473}	ΔH_1	ΔH_2
NaZnAl(SO ₄) ₃	9.6×10^{-8}	93	
NaMgAl(SO ₄) ₃	2.3×10^{-7}	80	
NaMgAl(SO ₄) _{2.5} (SeO ₄) _{0.5}	6.0×10^{-7}	71	
NaMgAl(SO ₄) _{1.5} (SeO ₄) _{1.5}	4.1×10^{-7}	76	
NaMgAl(SeO ₄) ₃	3.8×10^{-7}	73	
NaZnFe(SO ₄) ₃	7.9×10^{-6}	64	53
NaMnFe(SO ₄) ₃	2.6×10^{-6}	85	66
Na _{0.75} Mg _{0.75} Fe _{1.25} (SO ₄) ₃	1.1×10^{-6}	73	56
NaMgFe(SO ₄) ₃	9.0×10^{-6}	72	53
Na _{1.25} Mg _{1.25} Fe _{0.75} (SO ₄) ₃	8.1×10^{-5}	69	53
NaMgFe(SO ₄) _{2.5} (SeO ₄) _{0.5}	2.4×10^{-6}	75	64
NaMgFe(SO ₄) _{1.5} (SeO ₄) _{1.5}	1.6×10^{-6}	76	62
Na _{1.25} Mg _{1.25} Fe _{0.75} (SO ₄) _{1.5} (SeO ₄) _{1.5}	2.5×10^{-5}	78	60
NaMgFe(SeO ₄) ₃	2.2×10^{-6}	78	64
Na _{1.25} Mg _{1.25} Fe _{0.75} (SeO ₄) ₃	9.7×10^{-6}	82	62
NaZnCr(SO ₄) ₃	8.7×10^{-8}	95	
NaCdCr(SO ₄) ₃	1.9×10^{-8}	109	
Na _{0.75} Mg _{0.75} Cr _{1.25} (SO ₄) ₃	2.0×10^{-7}	77	
NaMgCr(SO ₄) ₃	6.7×10^{-7}	77	
Na _{1.25} Mg _{1.25} Cr _{0.75} (SO ₄) ₃	1.8×10^{-5}	77	59
Na _{1.5} Mg _{1.5} Cr _{0.5} (SO ₄) ₃	8.6×10^{-5}	72	54
Na _{1.75} Mg _{1.75} Cr _{0.25} (SO ₄) ₃	2.3×10^{-4}	79	50
NaMgCr(SO ₄) _{2.5} (SeO ₄) _{0.5}	1.1×10^{-7}	75	
Na _{1.75} Mg _{1.75} Cr _{0.25} (SO ₄) _{2.5} (SeO ₄) _{0.5}	1.2×10^{-4}	68	50
NaMgCr(SO ₄) _{1.5} (SeO ₄) _{1.5}	5.4×10^{-6}	75	61
NaZnIn(SO ₄) ₃	1.1×10^{-7}	77	
NaMnIn(SO ₄) ₃	5.8×10^{-7}	67	
NaCdIn(SO ₄) ₃	1.8×10^{-7}	81	
NaMgIn(SO ₄) ₃	2.2×10^{-6}	72	52
Na _{1.2} Mg _{1.2} In _{0.8} (SO ₄) ₃	3.1×10^{-5}	73	48
Na _{1.5} Mg _{1.5} In _{0.5} (SO ₄) ₃	1.9×10^{-4}	69	44
NaMgIn(SO ₄) _{1.5} (SeO ₄) _{1.5}	3.0×10^{-6}	76	58
Na _{1.25} Mg _{1.25} In _{0.75} (SO ₄) _{1.5} (SeO ₄) _{1.5}	3.3×10^{-5}	72	55
NaMgIn(SeO ₄) ₃	1.3×10^{-5}	80	55
NaMnYb(SO ₄) ₃	2.8×10^{-6}	78	58
NaMgYb(SO ₄) ₃	6.1×10^{-6}	68	49
Na _{1.3} Mg _{1.3} Yb _{0.7} (SO ₄) ₃	6.9×10^{-5}	68	46
Na _{1.5} Mg _{1.5} Yb _{0.5} (SO ₄) ₃	2.0×10^{-4}	66	46

(SiO₄)₃ can be prepared. This may relate to the different distribution of cation charges in the two classes of Nasicon, in particular the short S–O bond distances which induce subtle structural differences such as reduced O–O distances (7). However, Madelung energy calculations, using a program which also estimates anion polarization en-

ergies (8), suggested that electrostatic arguments alone do not provide a satisfactory account for the difference. For example, using appropriate structural parameters (7, 9), the sums of Madelung and polarization energies were calculated to be NaM'M''(SO₄)₃ [142538 kJmol⁻¹], the hypothetical composition "Na₂M'₂(SO₄)₃" [142145 kJmol⁻¹],

$\text{NaZr}_2(\text{PO}_4)_3$ [105114 kJmol^{-1}], and $\text{Na}_2\text{Zr}_2(\text{PO}_4)_2(\text{SiO}_4)$ [90748 kJmol^{-1}]. Not only do the sulfate phases have a higher lattice energy than the phosphate/silicates, but a reduced destabilization also results from the incorporation of additional Na^+ ions with charge balance on the octahedral sites. The most plausible explanations may therefore be associated with entropy effects, and the more stringent synthetic constraints which apply to the sulfate materials. To avoid decomposition, a maximum temperature of 700°C could be employed in the present study for the synthesis of the sulphate phases, whereas temperatures of 1100°C are typically used for phosphate/silicate Nasicons. Entropy considerations suggest that the high level of disorder on the Na^+ sublattice of the latter compounds, which results in stabilization at high temperatures, is significantly reduced for the low temperature synthesis of the sulfates.

The variation of unit cell parameters with Na content is also of interest. In the case of $M' = \text{Mg}$, for all the cases examined a increases with increasing Na content over the whole range. The c parameter appears, however, to go through a maximum at a Na content of around 0.5 (a representative plot

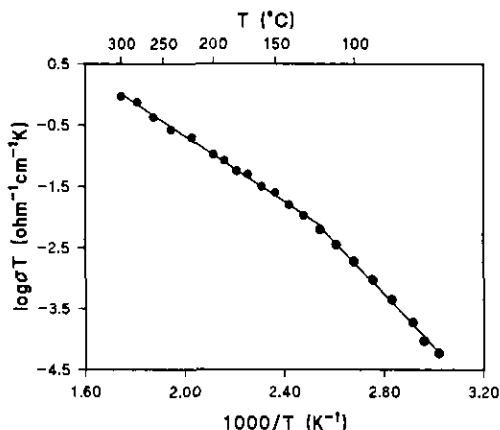


FIG. 1. The variation of $\log \sigma T$ with $1/T$ for $\text{Na}_{1.75}\text{Mg}_{1.75}\text{Cr}_{2.25}(\text{SO}_4)_3$ showing the change in activation energy at around 135°C .

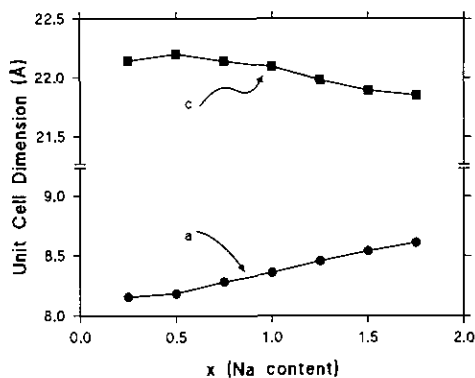


FIG. 2. The variation of the cell parameters with x in $\text{Na}_x\text{Mg}_x\text{Cr}_{2-x}(\text{SO}_4)_3$ ($0 \leq x \leq 1.75$).

for $\text{Na}_x\text{Mg}_x\text{Cr}_{2-x}(\text{SO}_4)_3$ is shown in Fig. 2). In the case of $M' = \text{Zn}$, the c parameter does not go through a maximum, but becomes approximately constant above $x = 0.5$. A possible explanation for this cell parameter behavior might be related to the fact that there are two Na sites (maximum occupancy of 0.5) for space group $R\bar{3}$, and up to $x = 0.5$ one site is preferentially occupied, with the second site becoming occupied only above $x = 0.5$.

An interesting feature of the conductivity measurements is the change in activation energy at ca. $100\text{--}160^\circ\text{C}$, which is consistent with the occurrence of a structural transition. In order to try to rationalize this, neutron diffraction data at different temperatures have recently been collected. Refinement of this data is currently in progress, and the results will be published elsewhere (7).

The substitution of Na^+ by Ag^+ and K^+ has also now been demonstrated in these phases, and the synthesis and conductivities of these new materials will be reported elsewhere.

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