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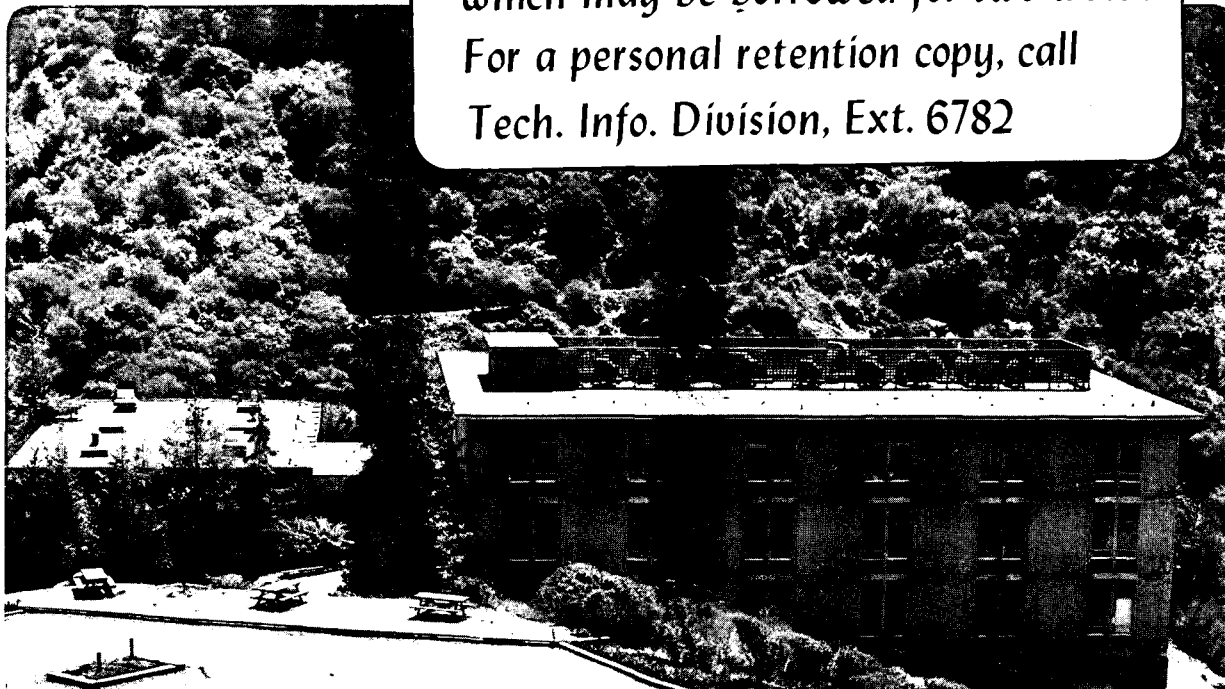
CHEMICAL STABILITY OF NASICON

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Craig Cameron

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CHEMICAL STABILITY OF NASICON

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May, 1981

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ABSTRACT

Nasicon solid electrolytes were tested by immersion in liquid sodium around 300°C. The electrolytes were found to degrade due to chemical reaction with sodium. This reaction changes the lattice parameters of the electrolytes sufficiently to cause fracture. While the rapidity with which the degradation occurs depends on the electrolyte preparation method, the results indicate that a chemical stabilization of Nasicon towards sodium should be sought to make it a useful electrolyte.

1. INTRODUCTION

Nasicons $\text{Na}_{1+x}\text{Si}_x\text{Zr}_2\text{P}_{3-x}\text{O}_{12}$, were first identified by Hong et al. (1) as possible alternatives to sodium- β and β'' solid electrolytes. One important aspect of these ceramic electrolytes is the necessity for chemical stability towards the battery electrodes. It has been noted that while ionic resistivities of a few Ohm-cm can be readily achieved, many Nasicons appear to degrade and crack rapidly when in contact with molten sodium at temperatures around 300°C. The present paper reports the nature of this chemical degradation for specimens with $x \geq 2$.

2. EXPERIMENTAL

Nasicon powders with a composition $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ($x = 2$) and with a recently proposed new composition (2) $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$ were fabricated by a sol-gel method. The samples were sintered for 24 hours at 1220°C in air, packed in powder of the same composition. Typically, densities around 95% theoretical were achieved. The polished specimens were then immersed in sodium, kept at 300°C, for periods up to two weeks. These immersions were carried out in a glove box under argon with less than 5 ppm

of oxygen. Some oxidation of the sodium appeared unavoidable, so that the oxygen fugacity in the sodium should be put around 10^{-60} atm (Na/Na₂O equilibrium).

Attempts were made to characterize the microstructures of some electrolytes with transmission electron microscopy at 100 and at 650 kV. However, it was found that Nasicons are very radiation sensitive, precluding a meaningful analysis.

Powdered samples of the specimens were prepared before and after immersion and were examined by X-ray diffractometry. NaCl powder was used as a lattice parameter reference.

3. RESULTS AND DISCUSSION

3.1. X-ray examinations

The X-ray diffractograms from as prepared (A) and immersed (B) material were fitted to a monoclinic and a rhombohedral unit cell. For the rhombohedral phase only single reflections should be observed, while for the monoclinic phase the reduction in symmetry leads to a splitting of the X-ray reflections. This relation between the monoclinic and rhombohedral unit cells is described in Appendix A. A slight splitting of diffraction peaks was observed for the untreated electrolytes of both compositions. However, all main peaks matched the rhombohedral structure well. This indicates that the samples were actually a mixture of rhombohedral and monoclinic phases. A comparison of the diffractograms of as prepared (A) and immersed (B) Na₃Si₂Zr₂PO₁₂ and Na_{3.1}Zr_{1.55}Si_{2.3}P_{0.7}O₁₁ is shown in Fig. 1, illustrating the shifts in the reflections. The data are summarized in Tables I and II. A small amount of ZrO₂ was also detected. The changes in the unit cell parameters that were calculated from the data presented in Tables I and II have been listed in Table III. The monoclinic phases are actually quite close in structure to the rhombohedral ones, as can be observed by comparing columns 2 and 3 in Table II. For Na₃Zr₂Si₂PO₁₂ the reaction with sodium causes a unit cell volume expansion of 2.4%. For Na_{3.1}Zr_{1.55}Si_{2.3}P_{0.7}O₁₁ reaction with sodium leads to the formation of only the rhombohedral phase. While the a and c lattice parameters are affected, the overall unit cell volume decreases by only 0.1%.

The findings indicate that reaction with metallic sodium increases the sodium content of Nasicon electrolytes. This is compatible with the structural data of Hong (1) where, for an increasing sodium content, up to $x = 2.2$, the unit cell volume first increases and then decreases again for $x \geq 2.2$.

The changes in the lattice parameters should lead to cracking of the electrolyte, either by volume expansion of the unit cell for $x = 2$, or by local stresses induced by the anisotropic lattice parameter changes for $x = 2.2$.

3.2. Transmission electron microscope observations.

The thinned, as prepared Nasicon with $x = 2$ was examined by transmission electron microscopy at accelerating voltages of 100 and 650 kV. Rapid damage was observed although the damage rate decreased with increasing accelerator voltages. This permitted the observation of the general

Table I. X-ray data of the composition $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_{12}\text{O}_{42}$.

hkl (monocl.)	hkl (rhomb.)	A (as prepared)		B (sodium immersed)	
		$d_{\text{meas.}} [\text{\AA}]$	$d_{\text{calc.}} [\text{\AA}]$	$d_{\text{meas.}} [\text{\AA}]$	$d_{\text{calc.}} [\text{\AA}]$
200	012	6.5071	6.5025	6.5912	6.5852
$11\bar{1}$		*6.4958	6.4946	*6.5146	6.5145
			6.4749		6.5134
111	104		4.6593	4.6557	4.6690
-		*4.6653	4.6629	*4.6141	4.6169
202		4.6197	4.6306		4.6138
020	110	4.5384	4.5280		4.5975
-		*4.5258	4.5250	*4.5973	4.5960
311				4.5202	4.5957
310	113		3.9101	3.9560	3.9632
021		*3.9069	3.9058	*3.9284	3.9268
		3.8990	3.9036		3.9392
400	024		3.2512	3.2939	3.2941
$22\bar{2}$		3.2524	3.2473	*3.2578	3.2572
		*3.2397	3.2375		3.2567
311	116	2.9441	2.9415	2.9582	2.9585
022			2.9338	2.9302	2.9380
		*2.9406	2.9400	*2.9193	2.9187
$31\bar{3}$		2.9222	2.9220		2.9170
420	214		2.6410		2.6777
131		2.9394	2.6383	2.6612	2.6575
			2.6388		2.6679
$33\bar{1}$	300		2.6127		2.6540
$60\bar{2}$		*2.6122	2.6125	*2.6523	2.6535
		2.6088	2.6083		2.6530

* main peaks

Table II. X-ray data of the composition $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$.

hkl (monocl.)	hkl (rhomb.)	A (as prepared)		B (sodium immersed)	
		$d_{\text{meas.}} [\text{\AA}]$	$d_{\text{calc.}} [\text{\AA}]$	$d_{\text{meas.}} [\text{\AA}]$	$d_{\text{calc.}} [\text{\AA}]$
200			6.4818		
$11\bar{1}$	01.2	*6.4808	6.4793	6.4808	6.4778
		6.4733	6.4750		
111			4.6199	}	
$\bar{2}02$	10.4	4.6160	4.6149		
			4.6087		
				4.5806	4.5805
020			4.5490	}	
$31\bar{1}$	11.0	*4.5493	4.5490		
		4.5439	4.5429		
310			3.9033	}	
021	11.3	3.9003	3.9021		
			3.9030		
400			3.2409	}	
$\bar{2}22$	02.4	*3.2406	3.2397		
		3.2379	3.2375		
311		*2.9222	2.9178	}	
022		2.9156	2.9160		
$\bar{3}13$	11.6	2.9142	2.9145		
			2.9109		
420			2.6395	}	
131	21.4	2.6388	2.6389		
			2.6398		
				2.6447	2.6446
$33\bar{1}$			2.6252	}	
$\bar{6}02$	30.0	2.6260	2.6264		
			2.6217		

* main peaks

Table III. Structural parameters derived from X-ray data.

$\text{Na}_3\text{Si}_2\text{Zr}_2\text{P}_{12}\text{O}_{12}$			
	rhombohedral (Å)	equivalent monoclinic (Å)	monoclinic (Å)
A	a = 9.056 c = 23.205	a = 15.675 b = 9.056 c = 9.334 $\beta = 124.04^\circ$ V = 1645.92 Å ³	a = 15.650 b = 9.056 c = 9.270 $\beta = 123.80^\circ$ V = 1637.62 Å ³
B	a = 9.192 c = 22.670	a = 15.921 b = 9.192 c = 9.234 $\beta = 125.08^\circ$ V = 1658.83 Å ³	a = 15.920 b = 9.195 c = 9.230 $\beta = 124.14^\circ$ V = 1677.42 Å ³
$\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{1.33}\text{P}_{0.7}\text{O}_{11}$			
A	a = 9.098 c = 22.775	a = 15.758 b = 9.098 c = 9.230 $\beta = 124.68^\circ$ V = 1632.60 Å ³	a = 15.730 b = 9.098 c = 9.220 $\beta = 124.50^\circ$ V = 1631.14 Å ³
B	a = 9.161 c = 22.440	a = 15.867 b = 9.161 c = 9.161 $\beta = 125.26^\circ$ V = 1630.95 Å ³	not observed

A = as prepared

B = after immersion

V = unit cell volume referred to rhombohedral cell

microstructure of a sintered sample at 650 kV, as shown in Fig. 2a. The contrast indicates that the individual grains, which are on the order of 0.5 μm, are heavily faulted. A meaningful analysis was, however, not possible, since the sample was made completely amorphous by the electron beam in less than 60 sec, Fig. 2b. Interestingly, the amorphous relic structure showed an image contrast that outlined the boundaries of the original crystalline structure. The nature of some of these grain boundary relics seems to suggest that some grain boundary phase might have been present. This could, however, not be established with certainty.

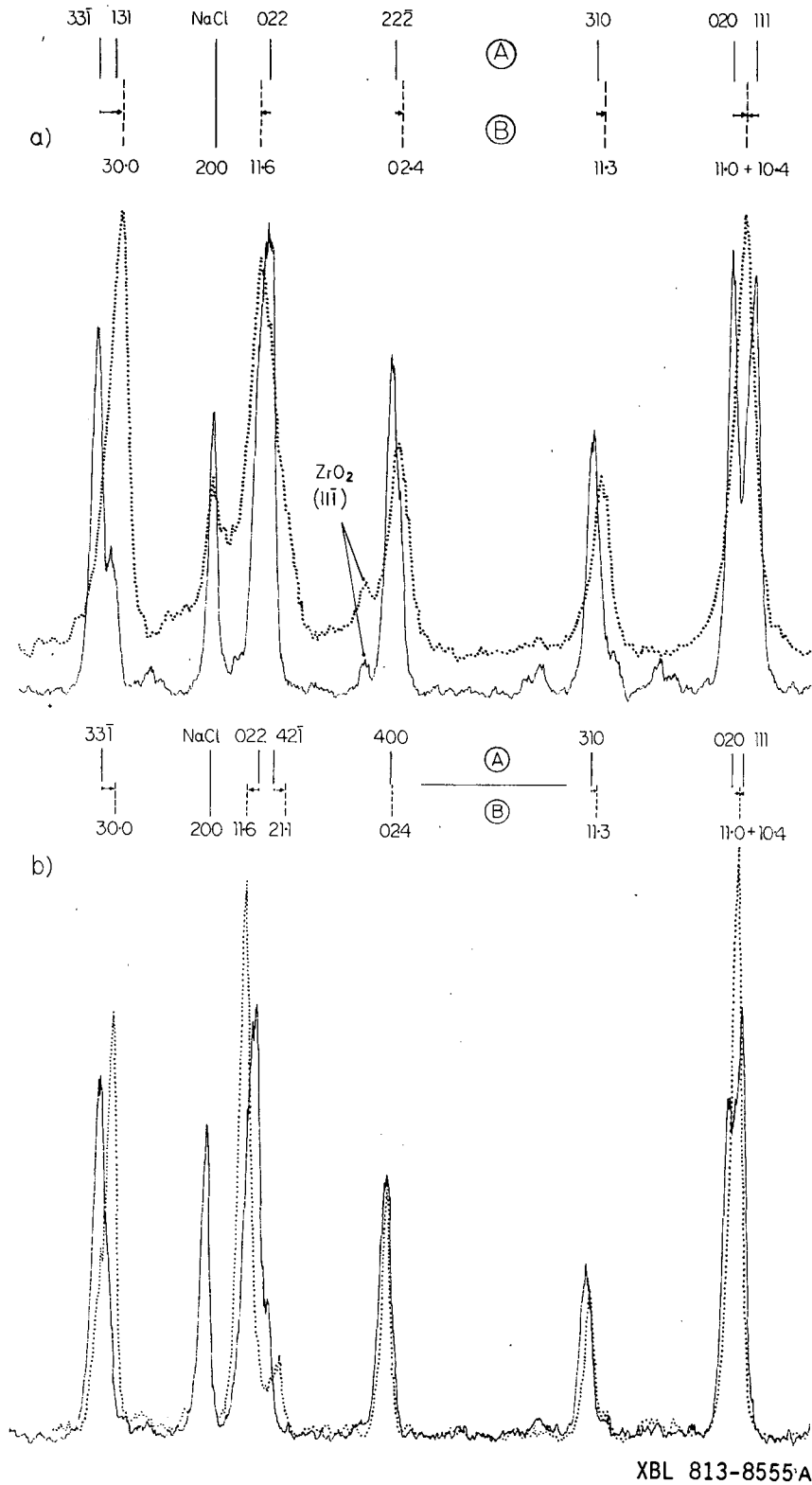
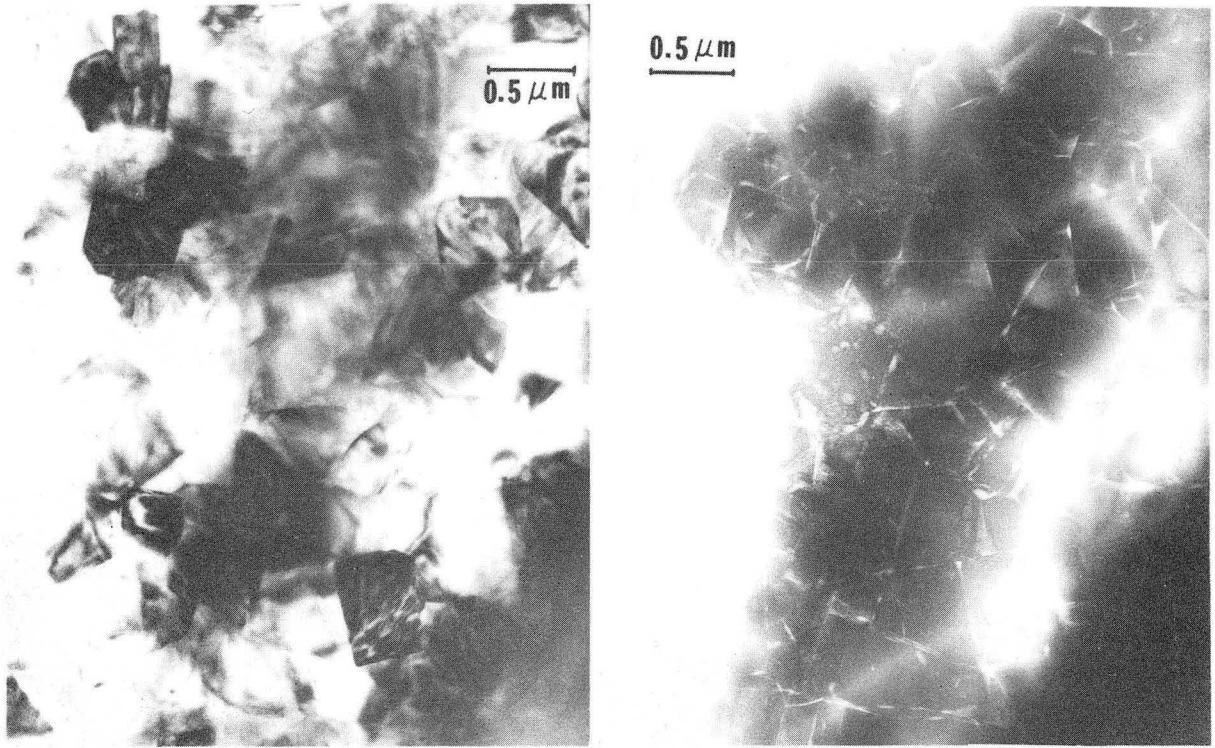
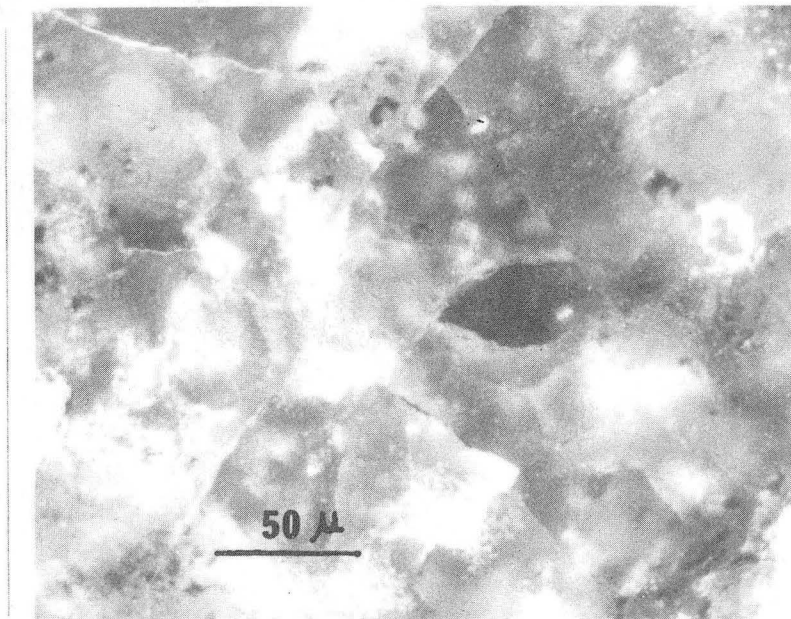


Fig. 1. Comparison of as prepared (A) and sodium immersed (B) electrolyte diffraction patterns. NaCl was used as a standard. a) $\text{Na}_3\text{Si}_2\text{Zr}_2\text{PO}_{12}$. b) $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$. Solid lines: as prepared; dotted lines: after immersion in Na, for 16 days at 300°C.



XBB 807 8749

Fig. 2. (a) Transmission electron micrograph of Nasicon with $x = 2$ observed in the 650 kV microscope. (b) The electron irradiation rapidly destroys the crystalline nature of the sample. Note the grain boundary relics.



XBB 807 8654

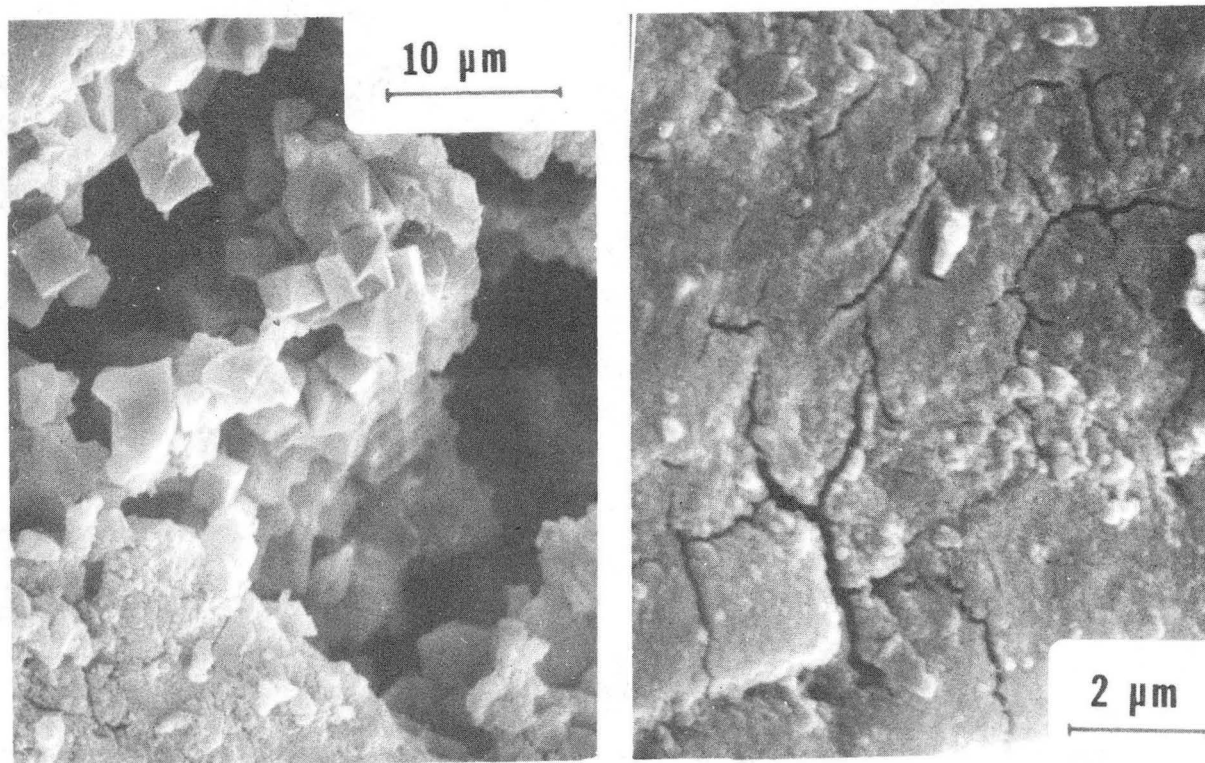
Fig. 3. Optical micrograph of a Nasicon sample with $x = 2$, after 2 weeks in sodium at 300°C. A crack pattern has formed.

3.3. Structure of chemically degraded Nasicons

After two weeks of immersion, the mechanical strength of the Nasicons had decreased dramatically, and a layer of brown discoloration had proceeded from the sample surface.

An optical micrograph of a chemically degraded Nasicon, $x = 2$, is shown in Fig. 3. Discoloration as well as cracking has occurred. The electrolyte shows many cracks that are intersecting each other nearly perpendicularly. Such crack patterns can also be found in glazes that do not match the substrate thermal expansion (3). This crack pattern can thus be seen as evidence for the degradation of Nasicon by the stresses introduced by the lattice parameter changes.

Scanning electron microscopy of fracture regions of chemically attacked Nasicon surfaces are shown in Fig. 4. The detailed morphology of the degradation and microcrack pattern suggests that the chemical attack proceeded preferentially along grain boundaries.



XBB 808 9254

Fig. 4. Scanning electron micrograph of Nasicon with $x = 2$, immersed for 2 weeks in sodium at 300°C . The microcracks and degradation suggests an intergranular attack.

3.4. Conclusions

The experiment clearly showed that Nasicons with $x = 2$ and $x = 2.2$ are chemically attacked by sodium at 300°C . This chemical attack leads to cracking, and makes the material unsuitable for use in solid electrolyte

batteries in which one of the storage electrodes is sodium metal. The apparent difference in resistance to sodium reported by other workers (4), thus indicates that stabilization of Nasicons should be sought by altering its chemical composition by incorporation of, as yet unidentified, impurities in its lattice.

4. ACKNOWLEDGEMENTS

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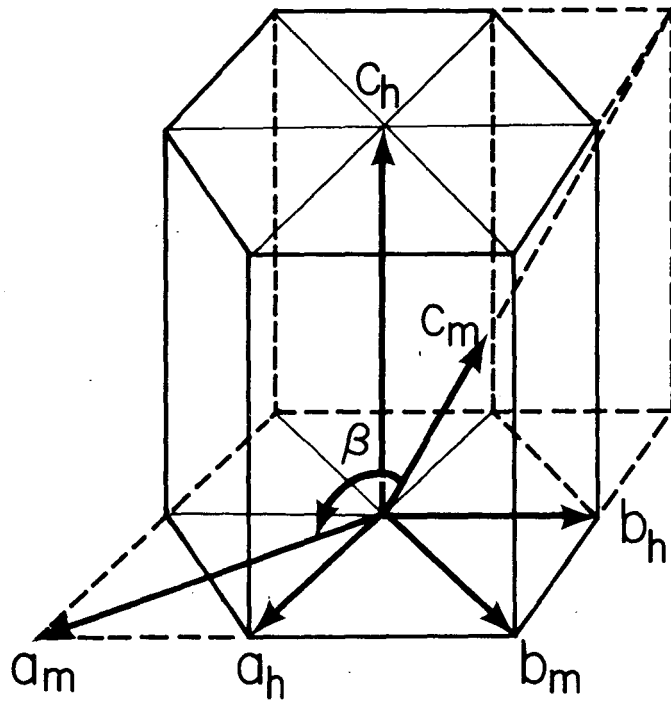
APPENDIX A

The relation between the rhombohedral and the equivalent unit cell is described with the aid of Fig. 5. The rhombohedral structure is described in the 4-axis hexagonal system; the parameters are a_h and c_h . The equivalent monoclinic structure has the lattice parameters a_m, b_m, c_m and the angle β . The relationship between the lattice parameters is then:

$$a_m = \sqrt{3} a_h; \quad b_m = a_h; \quad c_m = \frac{1}{3} \sqrt{3a_h^2 + c_h^2}$$

$$\beta = 180^\circ - \arctan \left(\frac{c_h}{\sqrt{3} a_h} \right)$$

The distortion of the rhombohedral structure towards a non-equivalent monoclinic structure leads to a lowering of the cell symmetry and thus to a diffraction peak splitting. The previously equivalent monoclinic reflections are then no longer equivalent, and a diffraction peak splitting should then occur. The correspondence has been indicated in Table III.



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Fig. 5. Relation of the rhombohedral and equivalent monoclinic unit cells.

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