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**EPMA STUDY OF “NASICON” SOLID ELECTROLYTE**


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Electron probe micro analysis was performed on “NASICON” solid electrolyte. The mobile sodium ions move towards the electron beam and get converted into atoms. Results are presented.

Key Words: NASICON, solid electrolyte, ion mobility

**INTRODUCTION**

Electron probe micro analysis (EPMA) is usually employed for elemental analysis. Recently [1] that technique was employed as charge supply electrode to the fast ion conductors, viz. beta alumina and NASICON. These ion conductors have mobile cations. When they are subjected to electron bombardment, electrons are trapped by mobile cations and transformed into atoms [2]. Here the electron beam itself serves as cathode. Sodium X-ray counts of polycrystalline beta alumina were reported [3] to be increased gradually during the electron bombardment. NASICON solid electrolyte was also subjected to electron bombardment. EPMA curve was taken and sodium deposition on NASICON was photographed. Results are presented in this short communication.

**EXPERIMENTAL**

NASICON powders were synthesized from calculated quantities of AR Grade Na2CO3, ZrO2, SiO2 and NH4H2PO4 to achieve a final composition corresponding to Na3Zr2 Si2 PO12. The mixture was ball milled as acetone slurry for 16 hours. The product was slowly dried and decomposed at 170°C for 16 hours. Remaining powder was then calcined at 900°C for 4 hours. The powder was then ground in a agate mortar for uniformity and calcined again at 1100°C for 4 hours. The fully decomposed powder was then vibromilled so as to obtain the particle size around 1 to 3 μm. Pellets of suitable dimension could be pressed out from this powder in a floating steel die set-up.

Sodium (K-K+) X-ray counts were collected throughout the electron bombardment time on NASICON using EPMA technique, available as accessory in scanning electron microscope instrument (JEOL JSM 35 CF). The electron beam was fixed corresponding to sodium wavelength to a selected point on the surface of the pellet and also scanned over the area of the pellet. Regions of sodium precipitation and deposition were picked out and photographed. In this case, there was no need to have a conductive coating on the pellet. EPMA probe itself is used as cathode and the mobile ions are discharged at this electrode.

**RESULTS**

Sodium accumulation and deposition in Nasicon sintered compact, three dimension conducting grains are randomly oriented. Fig.1 reveals the deposition of white droplets of sodium on NASICON compact.

In Fig.2, the deposition of sodium is highlighted. Fig.3 depicts the characteristic X-ray per second (CPS) versus time.

![Image](image-url)
This graph can be used to evaluate the quantities of the ionic and atomic deposits. The expression for time dependence of sodium accumulation done in (1) is given by

\[ Q = a \left[ 1 - \exp(-bt) \right] + Q_0 \exp(-bt) \]

where:
- \( a = \frac{m_0}{k_1} \)
- \( b = k_2 + \frac{\ln n}{k_3} \)
- \( t = \text{time} \)
- \( E = \text{strength of the electrical field} \)
- \( n = \text{concentration of major carrier} \)
- \( k_1 = \text{ionic conductivity} \)
- \( k_2 = \text{constant characteristic of the experimental conditions} \)
- \( k_3 = \text{another constant} \)
- \( Q_0 = \text{the value of } Q \text{ at } t = 0 \)

At infinite time, saturation limits are reached and this corresponds to the value of \( a \). Using the above expressions and from Fig. 3, the values of \( a, b \) and \( Q_0 \) are calculated and given below:

\[ a = 94275 \quad b = 0.0374 \quad Q_0 = 14030 \]

From the standard sample of sodium carbonate pellet, counts per second were obtained and % of sodium was evaluated and tabulated (Table I).

<table>
<thead>
<tr>
<th>Time in secs</th>
<th>Percentage of Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>16.5</td>
</tr>
<tr>
<td>60</td>
<td>39.6</td>
</tr>
<tr>
<td>90</td>
<td>60.0</td>
</tr>
<tr>
<td>120</td>
<td>70.0</td>
</tr>
<tr>
<td>150</td>
<td>81.8</td>
</tr>
<tr>
<td>180</td>
<td>89.0</td>
</tr>
<tr>
<td>200</td>
<td>99.3</td>
</tr>
</tbody>
</table>

From the Table it is seen that accumulation tends to saturation after 200 sec which is evident from the Fig. 3 also.

CONCLUSION: NASICON solid electrolyte was subjected to electron bombardment and typical ion mobility curve was presented. Sodium accumulation with time was calculated from the standard sample and it agrees well with the experimental ion mobility curve.

REFERENCES: