Pulsed Neutron Diffraction Study of NaNO₂ and KNO₂ Pure Melts

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The short-range structural parameters for NaNO₂ and KNO₂ pure melts were determined by the time-of-flight neutron diffraction. The precise analyses of structural parameters obtained such as coordination number, interatomic distance, and temperature factor allowed us to conclude that (1) there exist stable NO₃⁻ anions in the melts, (2) NO₃⁻ anions behave like NO₂⁻ anions due to the existence of lone pairs of electrons, (3) the short-range structure of KNO₂ pure melt is similar to that of NaNO₂ pure melt but the cation site relative to anion is a little different from each other in terms of the cation size effect.

Key Words : Pulsed Neutron Diffraction, Local Structure, Pure Melt, NaNO₂, KNO₂

1 Introduction

Structural analyses have continued to be carried out so as to comprehend physico-chemical properties of molten salts since 1960’s. Laboratory-scale X-ray diffractometers and less stable neutron source-detector systems were, however, compelled to be used at the sacrifice of data accuracy. In recent years substantial improvements in the apparatuses, for instance a high-energy monochromatic X-ray beamline at SPRing-8 and a pulsed neutron diffractometer at KEK in Japan, have been established and therefore remeasurements of the melt structure are called upon to be made.

Low melting materials such as alkali nitrite melts as well as alkali nitrate melts have been well studied from 1960’s to 1980’s.¹ In usual, melts exhibit a short-range structure possessing a high degree of ordering just among nearest neighbors like in the corresponding crystalline phase. NaNO₂ is typical dielectric substance and thus it is of much interest to investigate the characteristics of ionic correlations in liquid state. Moreover, attentions are attracted to the comparison in melt structure with NaNO₃. NaNO₂ forms an orthorhombic crystal, the lattice constants of which are a₀ = 0.3569 nm, b₀ = 0.5563 nm, and c₀ = 0.5384 nm.⁷ The sites of Na⁺ and NO₃⁻ ions in the crystal are located like in the NaCl crystal where the near neighbour distances between Na⁺ ion and O atom forming NO₃⁻ ion is 0.2470 nm and that between Na⁺ ion and N atom 0.2590 nm. An NO₃⁻ ion has a V-shaped bond and the bonding angle θ of O-N-O is 115°. On the other hand, KNO₂ belongs to a monoclinic crystal system and the corresponding lattice constants are a₀ = 0.445 nm, b₀ = 0.499 nm, c₀ = 0.731 nm, and β = 114°.⁷ A K⁺ ion is surrounded by four O atoms which originate from four distinct NO₃⁻ ions and the distance between K⁺ ion and O atom is estimated at 0.275 nm.

From the standpoint of structural chemistry, time-of-flight pulsed neutron diffraction experiments were performed on NaNO₂ and KNO₂ pure melts. In the present work the discussion is somewhat focussed upon the structure of KNO₂ pure melt since there have existed several works concerning NaNO₂ pure melt to be examined and investigated for comparison but not for the case of KNO₂ pure melt.

2 Experimental

Since a small amount of water was contained even in the reagent grade chemicals NaNO₂ and KNO₂, both were dehydrated at the temperatures lower than the respective melting points by 50 K for 8 h under reduced pressure 10⁻³ Pa.

The purified and granular salt samples with well-defined densities were introduced into the transparent fused silica cell and pulsed neutron scattering experiments were performed at 593 K for NaNO₂ melt and at 773 K for KNO₂ melt using the High Intensity Total scattering spectrometer (HIIT-II), which is designed to measure the structure factor S(Q) at high rate of data collection over a wide range of momentum transfer Q (from 5 to 300 nm⁻¹ in this work) and installed in the pulsed neutron source of High Energy Accelerator Research Organization, Neutron Science Laboratory at Tsukuba, Japan. The neutron scattering intensities were measured with seven counter banks at angles of 7°, 13°, 20°, 30°, 50°, 90°, and 150° by the time-of-flight method. The S(Q) was obtained from the measured intensity after some corrections such as subtraction of cell intensity, absorption, multiple scattering, normalization with vanadium a standard and so on (see Eq. (1)). These correction procedures have so far been reported in detail elsewhere.⁵⁻¹⁰ The coherent scattering lengths of N, O, Na,
and K elements with natural abundance were taken from the literature.\textsuperscript{11)}

3 Results

Structure factors, \(S(Q)\)'s, measured at each detector bank were obtained from Eq. (1). Interference function, \(Q \cdot i(Q)\), was derived from Eq. (2). The total pair distribution function, sometimes called the correlation function, \(G(r)\), was calculated by Fourier transformation of the \(Q \cdot i(Q)\). The structure factor, \(S(Q)\), the interference function, \(Q \cdot i(Q)\), the radial distribution function, \(D(r)\) and the correlation function, \(G(r)\), are defined in the forms,

\[
S(Q) = \frac{I_s N_s}{I_c N_c} \sum \frac{b_s^2 + \Delta_s(\lambda)}{b_s^2} - \frac{1}{b^2} |\Delta_s(\lambda) + \Delta_c(\lambda)| - \frac{b_w^2}{b_c^2}
\]

\[
Q \cdot i(Q) = Q (S(Q) - 1)
\]

\[
D(r) = 4\pi r^2 P_s \left( \frac{2r}{\pi} \right) \int_0^{Q_{\max}} Q \cdot i(Q) \sin(Q r) dQ
\]

\[
G(r) = 1 + (2\pi^2 r^2 P_s)^{-1} \int_0^{Q_{\max}} Q \cdot i(Q) \sin(Q r) dQ
\]

where \(I_s\) is the real scattering intensity of sample, \(I_c\) the scattering intensity of vanadium cell, \(N_s\) and \(N_c\) the numbers of scattering atoms in sample and vanadium, \(b_s\) and \(b_w\) the coherent and the incoherent scattering amplitude of sample, \(b_{w}\) the incoherent scattering amplitude of vanadium, \(\Delta_s\) and \(\Delta_c\) the coherent multiple scattering of sample and vanadium, respectively, \(P_s\) the number of stoichiometric units per unit volume, \(Q_{\max}\) the maximum of \(Q\) reaching in this scattering experiment.

The total structure factors, \(S(Q)\)'s, were obtained by smoothly combining \(S(Q)\) of each bank from \(Q_{\min}\) to \(500\ \text{nm}^{-1}\) for KNO\(_3\) melt, in which the accuracy in \(S(Q)\) at each bank is dependent on the range of \(Q\). The resultant synthetic \(S(Q)\) in the whole range showed the less fluctuation at higher \(Q\) values, as shown in Fig. 1. The first sharp diffraction peak is observed at about \(Q = 15.5\ \text{nm}^{-1}\) and the second peak around \(Q = 61.5-62.0\ \text{nm}^{-1}\), after which the oscillation in \(S(Q)\) declined noticeably with increasing \(Q\). The so-called prepeak in \(S(Q)\), characteristic of the diffraction patterns for glasses and liquids with medium range order, was not recognized at all in these melts. This fact implies that KNO\(_3\) melt is composed of discrete cations and anions, and no correlation exists among ions, vacant sites, clusters and so on.

4 Discussion

4.1 Radial distribution function \(D(r)\) and correlation function \(G(r)\)

So as to attain structural information such as \(G(r)\) and \(D(r)\) in the real space, Fourier transformations of \(S(Q)\)'s were made. Figure 2 depicts the correlation function \(G(r)\) of KNO\(_3\) pure melt at 773 K, in which a reasonable inference of atomic pairs were made from consulting the ionic or crystal radii by Shannon,\textsuperscript{12)} the crystallographic data\textsuperscript{13)} and the results so far reported.\textsuperscript{14)} The typical peak appeared at about \(r = 0.125\ \text{nm}\) and it was thought to be due to N-O nearest neighbor (intra-ionic) correlation. After the peak a lot of correlations such as O-O (intra-ionic), K-N, K-O, K-K, O-O (inter-ionic), N-N, and so on were intricately piled up with one another and it made the peak assignments too difficult in real space. Beyond \(r = 0.35\ \text{nm}\, G(r)\) fluctuated monotonously in the very vicinity of unity and gradually abated.

The peak assignment of first peak in \(D(r)\) curve of molten KNO\(_3\) as demonstrated in Fig. 3 is, in general, carried out so as to be due to the nearest neighbor unlike ion pair correlation by taking into account the

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**Fig. 1** Total structure factor \(S(Q)\) of KNO\(_3\) pure melt at 773 K.

**Fig. 2** Correlation function \(G(r)\) of KNO\(_3\) pure melt at 773K.

**Fig. 3** Radial distribution function \(D(r)\) and scaled function \(D(r)/r\) of KNO\(_3\) pure melt at 773 K.
sum of ionic radii, the area of the peak reflecting the coordination number, and the shape of the corresponding scaled function $D(r)/r$ with or without good symmetry. In order to obtain the radial distribution function $D(r)$ and study the first coordination, Fourier transformation was first made on the structure factor $S(Q)$. Determination of atomic pair correlations is often performed on the scaled function defined by $D(r)/r$, since it is essentially expressed as a sum of unique Gaussian-type functions corresponding to individual pair correlations. According to the analysis of first peak in $D(r)$ the coordination number was roughly calculated to be 2 in each melt, indicating that this was due to not the cation-anion correlation but the intra-ionic correlation N-O. As matters stand, the determination of structural parameters by radial distribution analyses was, however, rather difficult in r-space, except for parameters of near neighbors.

4.2 Interference function $Q\cdot i(Q)$

For better understanding the melt structure, the structural parameters for each atomic pair are needed to be refined by the correlation method in the $(Q, Q\cdot i(Q))$ space, using the non-linear least squares regression of Eq. (5),

$$Q\cdot i(Q) = \sum_{i,j} n_{ij} b_{ij} \exp(-B_{ij} Q^2) \sin(Qr_{ij}/r_0) / \sum b^2$$  \hspace{1cm} (5)

where $n_{ij}$, $r_0$, and $B_{ij}$ refer to the average coordination number, the average interatomic distance, and the temperature factor for the atomic pair $ij$, respectively. Each atomic pair was presumed to be Gaussian distributed, centered at $r_0$ with a mean square displacement $2B_{ij}$. The initial values of the structural parameters were preset to be equal to those in preliminary $D(r)$ or $G(r)$ analysis. The relatively short range parameters, for example, for N-O, O-O, K-N, and K-O pairs, were calculated from the $Q\cdot i(Q)$ data at large $Q$ region. As for the other K-K, O-O (second coordination), and N-N correlations, the $Q\cdot i(Q)$ data over the entire range were available. The comparison between the $Q\cdot i(Q)$ observed and that calculated from the least squares fitted parameters for KNO$_2$ pure melt at 773 K on the basis of Eq. (5) was shown in Fig. 4. In order to determine the validity of model structure, the following parameter is often introduced where $R$ is the degree coincidence in fitting of two reduced intensity functions, observed and calculated, which is defined by Eq. (6).

$$R = \frac{\sum |Q\cdot i(Q)_{obs} - Q\cdot i(Q)_{calc}|}{\sum |Q\cdot i(Q)_{calc}|}$$  \hspace{1cm} (6)

As can be seen from Fig. 4, the observed $Q\cdot i(Q)$ was well reproduced by the least squares fitted parameters which are tabulated in Table 1. The existence of nitrite ions is confirmed from short-range structural parameters of atomic pairs such as N-O and O-O. The structural changes between NaNO$_2$ and KNO$_2$ melts are thought to be due to the difference in cationic radii of Na$^+$ and K$^+$. The comparison of interatomic distance $r_0$ in pure melts and crystals of NaNO$_2$ and KNO$_2$ is listed in Table 2.

![Figure 4](image_url)  
**Fig. 4** Comparison between the $Q\cdot i(Q)$ observed and that calculated from the least squares fitted parameters for KNO$_2$ pure melt at 773 K.

### Table 1  
Coordination number $n_{ij}$, interatomic distance $r_0$, temperature factor $B_0$, and root mean squares displacement $\langle \Delta r_0^2 \rangle^{1/2}$/nm

<table>
<thead>
<tr>
<th>i-j</th>
<th>$n_{ij}$</th>
<th>$r_0$/nm</th>
<th>$B_0$/10$^{-5}$nm$^2$</th>
<th>$\langle \Delta r_0^2 \rangle^{1/2}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-O</td>
<td>2</td>
<td>0.125</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>O-O</td>
<td>2</td>
<td>0.25</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Na-N</td>
<td>2</td>
<td>0.211</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Na-O</td>
<td>4</td>
<td>0.239</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td>O-O</td>
<td>4</td>
<td>0.321</td>
<td>0.018</td>
<td>0.019</td>
</tr>
<tr>
<td>Na-N</td>
<td>2</td>
<td>0.465</td>
<td>0.026</td>
<td>0.023</td>
</tr>
<tr>
<td>N-N</td>
<td>2</td>
<td>0.554</td>
<td>0.032</td>
<td>0.025</td>
</tr>
</tbody>
</table>

### Table 2  
Comparison of interatomic distance $r_0$ in pure melts and crystals of NaNO$_2$ and KNO$_2$:

<table>
<thead>
<tr>
<th>System</th>
<th>i-j</th>
<th>$r_0$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>melt</td>
<td>crystal</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>N-O</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>O-O</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>Na-N</td>
<td>0.211</td>
</tr>
<tr>
<td></td>
<td>Na-O</td>
<td>0.232</td>
</tr>
<tr>
<td></td>
<td>O-O</td>
<td>0.321</td>
</tr>
<tr>
<td></td>
<td>Na-Na</td>
<td>0.465</td>
</tr>
<tr>
<td></td>
<td>N-N</td>
<td>0.554</td>
</tr>
<tr>
<td></td>
<td>N-O</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>O-O</td>
<td>0.207</td>
</tr>
<tr>
<td>KNO$_2$</td>
<td>K-N</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td>K-O</td>
<td>0.282</td>
</tr>
<tr>
<td></td>
<td>O-O</td>
<td>0.330</td>
</tr>
<tr>
<td></td>
<td>K-K</td>
<td>0.448</td>
</tr>
<tr>
<td></td>
<td>N-N</td>
<td>0.568</td>
</tr>
</tbody>
</table>

*: Distance of Nearest pair in unit cell
indicating that there are conspicuous differences in the interatomic distances within the second coordination shell and the outer shells. The nitrite ion is thought to be rigid and stable in the molten state. On melting, the distances of unlike ion pairs such as Na-N and K-N in melts become rather short in comparison with those in crystals, but those of like ion pairs such as Na-Na, N-N, and K-K are estimated to be larger than in crystals. Consequently, this phenomenon rationally explains thermal expansion on crystal melting. The local structure of NaN$_3$ and KNO$_2$ pure melts reconstructed from the refined parameters is geometrically illustrated in Fig. 5 where the symbol of Lp refers to the lone pair of electrons, suggesting that the position of cation relative to anion differs from melt to melt. It should be also stressed that NO$_2^-$ ion is of V-shape but it possesses a part with high electron density, due to the lone pair of electrons. Thus, it is imagined with ease that no ion can approach the NO$_2^-$ ion from the Lp site.

5 Conclusions

The optimized short-range structural parameters for NaN$_3$ and KNO$_2$ pure melts were obtained and the precise analyses of the parameters allowed us to conclude that (1) there exist stable NO$_2^-$ anions in the melts, (2) NO$_2^-$ anions behaves as if they were NO$_3^-$ anions due to the existence of lone pairs of electrons, (3) the short-range structure of KNO$_2$ pure melt is similar to that of NaN$_3$ pure melt but the cation site relative to anion is a little different from each other mainly in terms of the cation size effect.

References