

Structural Analysis of Molten NaClO₃ and KClO₃ by T-O-F Pulsed Neutron Diffraction

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The short range structure of NaClO₃ and KClO₃ melts was investigated by time-of-flight neutron scattering experiments. The near neighbor Cl-O and O-O distances in the ClO₃⁻ ion were evaluated at 0.147 nm and 0.235 nm for NaClO₃ melt, respectively, the corresponding values for KClO₃ melt being 0.149 nm and 0.239 nm. At this time the coordination number of O around Cl was almost equal to 3. The arrangements of Na⁺ and K⁺ ions relative to ClO₃⁻ ions were discussed and the optimized structure of NaClO₃ and KClO₃ melts was determined.

KEYWORDS: PND, melt, structure, NaClO₃, KClO₃

§1. Introduction

The structure of NaClO₃ and KClO₃ crystals and their aqueous solutions has so far been examined by Raman spectroscopy, reporting that basic structural units such as XY₃ trigonal pyramids (tp) exist in these media and the structure obtained was little influenced by the kinds of coexisting alkali metal ions.¹⁻⁴⁾ It is of much interest to investigate whether the stable chlorate ions really exist in the melts, whether the specific interionic correlations are observed as medium range orderings, whether the structural changes are detected between crystal and melt, and whether the lone pair of electrons on Cl atom affects the short range structure. Interpretation of diffraction data was made according to the radial distribution analysis in *r*-space and the correlation method in *Q*-space. Utilizing this result as the initial values of structural parameter, the semi-empirical molecular orbital calculation techniques called MOPAC were carried out to predetermine the location of alkali metal ions against to the ClO₃⁻ radicals as well as to utilize the MOPAC results as the initial structural parameters in both analyses.

§2. Experimental

Sodium chlorate and potassium chlorate were dehydrated at temperatures lower than their melting points under reduced pressure for 8 hours, melted, and rapidly quenched. The sample was sealed under vacuum in a fused silica cell (8 mm in inner diameter, 40 mm in height and 0.4 mm in wall thickness). TOF neutron diffraction measurements were carried out using the High Intensity Total scattering spectrometer (HIT-II) installed at a pulsed neutron source in High Energy Accelerator Research Organization at Tsukuba, Japan.⁵⁾ Neutron detectors were arranged to be located at the scattering angles of 150°, 90°, 50°, 30°, 25°, 20°, and 15°, respectively, through the banks of which the intensities of scattered neutrons were measured by the time-of-

flight method.⁶⁾ The structure factor $S(Q)$ was obtained according to Eq. (2.1), from measured scattering data which were corrected for background, absorption by the sample and the cell, multiple and incoherent scatterings, and normalized with a vanadium rod as a reference material,

$$S(Q) = \frac{I_S}{I_V} \frac{b_{Vi}^2 + \Delta_{Vi}(\lambda)}{b_{Sc}^2} - \frac{1}{b_{Sc}^2} (\Delta_{Sc}(\lambda) + \Delta_{Si}(\lambda)) - \frac{b_{Si}}{b_{Sc}^2}, \quad (2.1)$$

where λ is the wavelength of neutron, I_S the real scattering intensity of sample, I_V the scattering intensity of vanadium rod, b_{Sc} and b_{Si} the coherent and incoherent scattering amplitudes of sample,⁷⁾ b_{Vi} the incoherent scattering amplitude of vanadium, Δ_{Si} and Δ_{Vi} the incoherent multiple scatterings of sample and vanadium, respectively.

§3. Results and Discussion

3.1 Neutron Diffraction

The interference function $Q \cdot i(Q)$, the correlation function $G(r)$, and the radial distribution function $D(r)$ are defined by Eqs. (3.1)-(3.3), respectively.

$$Q \cdot i(Q) = Q \cdot [S(Q) - 1] \quad (3.1)$$

$$G(r) = 1 + (2\pi^2 r \rho_0)^{-1} \times \int_0^{Q_{max}} Q \cdot i(Q) \sin(Qr) dQ \quad (3.2)$$

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{Q_{max}} Q \cdot i(Q) \sin(Qr) dQ, \quad (3.3)$$

where ρ_0 is the number of stoichiometric units per unit volume and Q_{max} the maximum value of Q reached in the scattering experiment. The total structure factor $S(Q)$ from 0 to 400 nm⁻¹ for NaClO₃ and KClO₃ melts was obtained by combining $S(Q)$ of each bank as illus-

trated in Fig. 1. The so-called pre-peak in $S(Q)$ was observed for neither NaClO_3 nor KClO_3 melt, which is often observed in amorphous materials with medium or long range ordering and suggests the existence of the network structure at the correlation distance r corresponding to the pre-peak, therefore no specific structural correlation between two ClO_3^- 's appears to be formed.

The correlation function $G(r)$ for NaClO_3 and KClO_3

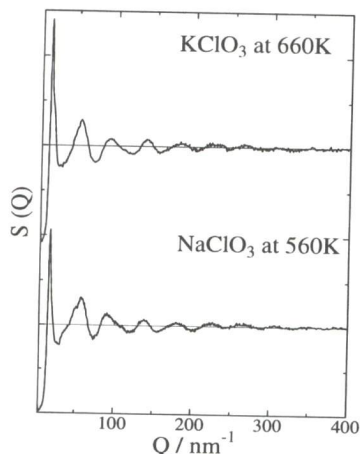


Fig. 1. Total structure factor $S(Q)$ for NaClO_3 and KClO_3 melts.

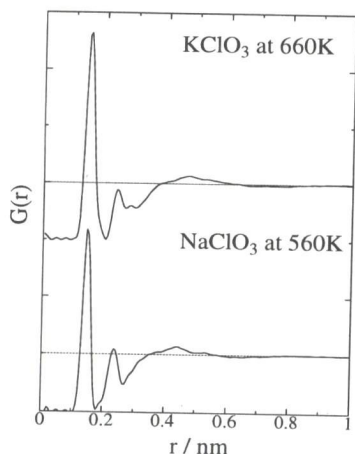


Fig. 2. Correlation function $G(r)$ for NaClO_3 and KClO_3 melts.

melts is shown in Fig. 2. The first peak appearing at about $r = 0.14$ nm in the $G(r)$ was thought to be due to the first nearest neighbor Cl-O pair in the ClO_3^- unit. The peak is very sharp and clear, indicating the good stability of first coordination shell. In the same way, the second and third peaks at about $r = 0.23$ - 0.28 nm correspond to the first nearest neighbor O-O in the ClO_3^- unit and M-O or M-Cl pairs (M=Na, K).⁸⁾ With increasing interatomic distance, the values of $D(r)$ increased along the line corresponding to the average molecular density of the melt, and then the nearest neighbor coordination number is evaluated to be about 3 from integration of the

first peak area in $D(r)$. In order to refine the short-range structure of the melt the structural parameters for each atomic pair are needed to be optimized in Q -space by the correlation method,⁹⁾ using the nonlinear least-squares fitting of Eq. (3.4),

$$Q \cdot i(Q) = \left[\sum_i \sum_j n_{ij} b_i b_j \exp(-B_{ij} Q^2) \sin(Q r_{ij}) / r_{ij} \right] / \left(\sum_i b_i \right)^2, \quad (3.4)$$

where n_{ij} , b_i , B_{ij} , and r_{ij} are the average coordination number, the scattering length, the temperature factor, and the average interatomic distance for pair ij , respectively. Each atomic pair was supposed to be Gaussian distributed and centered at r_{ij} with a mean square displacement $2B_{ij}$, and the initial values of the structural parameters were predetermined to be equal to those in $D(r)$ or $G(r)$ analysis.

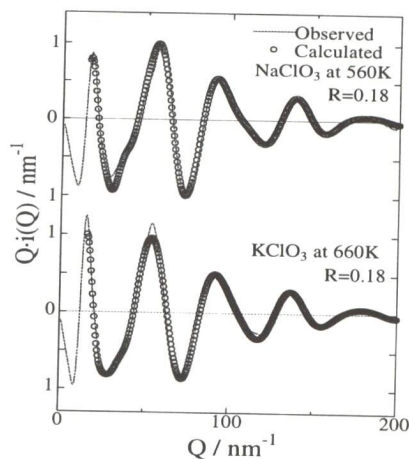


Fig. 3. Interference function $Q \cdot i(Q)$ for NaClO_3 and KClO_3 melts.

Figure 3 illustrates the comparisons between the observed $Q \cdot i(Q)$ and that calculated from the least squares fitted parameters.^{10,11)} The geometrically optimized structure of NaClO_3 melt is shown in Fig. 4. The optimized short-range structural parameters of NaClO_3 and KClO_3 melts and the interatomic distances of the crystals for comparison are listed in Tables I and II. These results indicate the existence of stable ClO_3^- trigonal pyramids in these melts, also taking into account the molecular orbital calculation described afterwards.⁴⁾ The Cl-O and O-O distances forming the ClO_3^- trigonal pyramids in NaClO_3 and KClO_3 crystals⁴⁾ were evaluated at 0.145-0.149 nm and 0.236-0.238 nm, respectively. The corresponding values in NaClO_3 and KClO_3 melts were equal to about 0.147-0.149 nm and 0.235-0.239 nm, respectively. The bond angles of $\angle\text{O-Cl-O}$ for the ClO_3^- trigonal pyramids in NaClO_3 and KClO_3 crystals were calculated to be about 106.4° - 106.8° , being 105.2° - 105.8° for the melts. These findings indicate that the average

shape of the ClO₃⁻ trigonal pyramids in melts is almost unchanged with either elongation or contraction of about 1%. In contrast, the interatomic distances of Na-O and Na-Cl pairs were elongated by about 7-11%. Thus on melting, the alkali chlorates appear to dissociate into alkali cations and chlorate anions without formation of O²⁻ anions.

Table I. Least squares fitted structural parameters of molten NaClO₃ at 560 K.

i-j	n _{ij}	r _{ij} / nm (melt)	r _{ij} / nm (crystal)	b _{ij} / nm ²
Cl-O	3.18	0.1477	0.1455	8.52-E5
O-O	2.13	0.2350	0.2380	9.13-E5
Na-O	2.55	0.2412	0.2580	1.11-E3
Na-Cl	3.13	0.3270	0.3457	1.27-E3
Na-Na	6.90	0.4367	0.4173	1.32-E3
Cl-Cl	6.49	0.6214	0.5903	1.75-E3
∠OClO	—	105.8°	106.8°	—

Table II. Least squares fitted structural parameters of molten KClO₃ at 660 K.

i-j	n _{ij}	r _{ij} / nm (melt)	r _{ij} / nm (crystal)	b _{ij} / nm ²
Cl-O	3.05	0.1491	0.1490	8.41-E5
O-O	1.47	0.2393	0.2360	9.63-E5
K-O	2.75	0.2856	0.3201	5.68-E3
K-Cl	3.08	0.3758	0.3923	1.12-E3
K-K	4.11	0.4587	0.4301	1.36-E3
Cl-Cl	4.19	0.6700	0.6380	1.52-E3
∠OClO	—	105.2°	106.4°	—

3.2 MOPAC

The semi-empirical molecular calculation (PM3-MOPAC) using the MOPAC97 program (winMOPAC) installed on the Windows machine, was applied to confirm the results given as the inter-radical structural parameters of Cl-O and O-O by PND in this work. It should be stressed that inter-radical interactions are left out of consideration. It was reported that alkali ions such as Na⁺ and K⁺ are located at the side of lone-pair electron of ClO₃⁻ trigonal pyramids in the crystal.⁴⁾ Calculations were made until the model structure was in the most stabilized energy state, that is geometrically optimized. The geometrically optimized structure of NaClO₃ melt is illustrated in Fig. 4. This finding described that the chlorate ion was regarded as a tetrahedron rather than a trigonal pyramid by taking into account the lone-pair of electrons which occupied a tetrahedral site instead of O atoms. The bond length of Cl-O and bond angle of ∠O-Cl-O were in fair agreement with the experimental structural data (0.14 nm and 106°), although the other bond lengths were a little different from the experimental ones. Finally, when MOPAC was adopted to the calculation of the NaClO₃ unit, the Na⁺ was found to be located at the opposite side of the lone-pair of electrons. This is due to that freedom of space and mobility of ions were increased by melting and Na⁺ was more affected

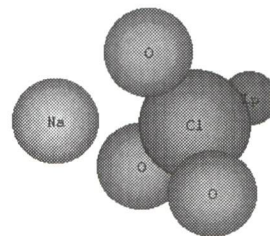


Fig. 4. Geometry optimized structure of NaClO₃ melt by PM3-MOPAC calculation. LP: lone pair electrons on Cl atom.

by the lone-pair electrons of Cl atom and a fractional charge of O atom (-1.5) in the ClO₃⁻ unit. It is thus semi-quantitatively interpreted by the MOPAC calculations that the alkali ions moved to the side of O atom. In addition, the kind of alkali ions caused no effect on the structure.

§4. Conclusion

According to TOF pulsed neutron diffraction (PND) and semi-empirical orbital calculation (PM3-MOPAC method), the short-range structure of NaClO₃ and KClO₃ melts has been investigated. The results obtained in the present work are that the intra-radical structure of ClO₃⁻ in NaClO₃ and KClO₃ melts consists of trigonal pyramids having the Cl atom in the center, three O atoms and lone-pair of electrons on the Cl atom. The near neighbor Cl-O and O-O distances in the ClO₃⁻ ions were evaluated at 0.147 nm and 0.235 nm for NaClO₃ melt, respectively, the corresponding values for KClO₃ melt being 0.149 nm and 0.239 nm. On melting, alkali ions were influenced by the fractional charge of O atom and the existence of lone-pair of electrons and moved to the site opposite to lone-pair of electrons on Cl atom.

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