GLASS FORMATION AND PHASE TRANSITIONS OF NbF₅ AND TaF₅ FROM 77 TO 600 K

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ABSTRACT

Raman spectroscopy is used for characterizing a series of new phases formed by quenching molten MF₅ (M = Nb, Ta) to liquid nitrogen temperatures. At ~77 K contraction of the melt volume occurs which is followed by the formation of a clear MF₅ glass that remains stable up to ~230 K. Around this temperature the glass viscosity decreases and a new metastable liquid is formed, which by further temperature increase leads to an exothermic solidification resulting in a new β-MF₅ crystalline solid. Near room temperature a solid transformation of β-MF₅ gives the known α-MF₅ monoclinic modification composed of tetramers having four “MF₆” octahedra bound by vertices. For all phases including the amorphous (melt, glass, metastable liquid) the crystalline (α- and β- forms) and the vapor, the Raman spectra show a rather common high frequency band (at ~760 and ~755 cm⁻¹ for NbF₅ and TaF₅ respectively) which is attributed to the M-F terminal stretching of the bridged octahedra. Based on the literature physicochemical data and the Raman spectroscopy systematics a structural model is proposed for the amorphous phases of MF₅ composed from a variety of cyclic and/or chain “MF₆” octahedra bound by vertices in cis and/or trans configurations.

INTRODUCTION

A large number of metal halide melts upon cooling have a tendency to form glasses. Typical examples are the zinc chloride and bromide salts (1) as well as certain fluorides used as components of ZBLAN (2,3). Simultaneous studies of the melt and the glass are helpful for understanding the physicochemical properties of these amorphous phases and for correlating their structural peculiarities (4).

Most structural studies of molten metal halides, involve metals with low valences (4). Divalent and trivalent halides have been extensively studied, data on a few tetravalent halides are available while studies on pentavalent halides are very scarce. The original purpose of this work was to use Raman spectroscopy in order to study the structural correlation between the molten, gaseous and crystalline phase of MF₅ (M = Nb, Ta). In the course of our work it was found that these salts have a glass forming ability. For each system two new amorphous phases (a glass and a metastable liquid) have been found and a new allotropic crystalline phase (β-MF₅) was stabilized at low temperatures. Raman spectra of these phases have been measured and are correlated to the structure of the amorphous phases.
EXPERIMENTAL

High purity NbF$_5$ and TaF$_5$ were obtained by slow sublimation of the corresponding dried commercial (Alfa-Johnson Matthey) materials. The handling of chemicals and filling of the optical cells took place in a controlled nitrogen atmosphere glove box with water content of less than 1 ppm. The Raman set up, the optical furnace and the procedures for measuring spectra at high temperatures have been described elsewhere (4). For the low temperature spectral measurements a liquid-nitrogen- cooled pyrex glass optical “Dewar type” cryostat was constructed. Within the cryostat a copper metal block sample holder was placed which had openings for the optical paths and was wound with insulated copper wire allowing temperature variation and control in the temperature range 77-290 K. The Raman cells were made from fused silica tubing (~4 nm OD, ~3mm ID, ~2 cm long) and could be placed in both the cooled copper block or the high temperature furnace.

New Amorphous and Crystalline Phases

A series of visual experiments were first carried out showing the complexity of the phases existing for the NbFs and TaFs salts. An optical cell containing the $\alpha$-NbF$_5$ crystalline solid (5) was heated to ~50 K above its melting point (352 K) and was then quenched into a Dewar containing liquid nitrogen. The melt was solidified forming a transparent glass possessing a well defined internal meniscus due to volume contraction. Warming the sample outside the Dewar resulted slowly in the disappearance of the meniscus and the formation of a rather fluid metastable liquid. This change started to occur 50-100 K below room temperature and then with further increase of temperature the metastable liquid was crystallized “exothermically” by warming up the cell. As shown in the next section the solid formed is a new allotropic crystalline modification ($\beta$-NbF$_5$) which near 273 K transforms to the known $\alpha$-NbF$_5$.

Similar was the behavior of TaF$_5$, which also forms an isostructural to $\alpha$- NbF$_5$ crystalline modification (5) and has a higher m.p. (370 K). Exception was the formation of the metastable liquid which was formed in a smaller temperature range and then was rapidly solidified to $\beta$-TaF$_5$. Thus, in the case of TaF$_5$ it was not possible to stabilize the metastable liquid for Raman measurements. The thermal cycle involving the phases for both the NbF$_5$ and TaF$_5$ salts is shown schematically in Figure 1.
Figure 1. Phase transitions of MF$_5$ (M= Nb, Ta) salts. For our experiments all transitions occur in the “heating” direction indicated above. The regular melting transition $T_m$ was reversible. Precise determination of the glass transition region $T_g^*$ the solidification $T_m^*$ and the solid phase $T_s$ transition temperatures was not possible with our system. Thus some of these transitions might be also reversible.

For both systems the thermal visual cycle experiments were also carried in the cryostat where the Raman spectra were measured. With the exception of the regular melting $T_m$ (Fig. 1) all other transitions took place in the direction of the arrows (Figure 1). The range of $T_g^*$ appears to be rather large and the $T_m^*$ and $T_s$ temperature are used only to indicate the approximate temperature range of the corresponding phase transition. These uncertainties are mainly due to our failure to control accurately the cryostat. Obviously a more precise DTA/DSC analysis is needed in order to determine the transition temperatures and the reversibility of the transformations.

Characterization of Phases by Raman Spectroscopy

The Raman spectra of the various NbF$_5$ and TaF$_5$ phases formed upon heating the quenched glass are shown in Figs 2 and 3. The $\alpha$-MF$_5$ (M= Nb,Ta) crystalline modification has been studied before by vibrational spectroscopy and assignments have been made for both compounds (6). The new $\beta$-MF$_5$ forms show Raman patterns different than those of the $\alpha$-MF$_5$, but due to the lack of crystal structure data no assignments can be made. The spectra of the amorphous phases (glass, metastable liquid and melt) are isomorphous indicating that the predominant vibrational frequencies are common for all these phases.
Figure 2. Raman spectra of the NbF$_5$ phases upon heating the quenched glass at LN$_2$ temperatures. Spectral conditions: LL = 514.5 nm; w = 20-100 mW; ss = 3-6 cm$^{-1}$; sr = 0.5 cm$^{-1}$.

Figure 3. Raman spectra of the TaF$_5$ phases upon heating the quenched glass at LN$_2$ temperatures. Spectral conditions as in Figure 2.
The upper part in Figures 2 and 3 include the vapor phase spectra which according to our recent measurements are characterized by a dimer (band D:M$_2$F$_{10}$)-monomer (band M:MF$_5$) gaseous equilibrium (7). The M$_2$F$_{10}$ dimer structure consists of two edge bridged octahedra (Figure 4a) and the high frequency band (~756 and 752 cm$^{-1}$ for Nb$_2$F$_{10}$ and Ta$_2$F$_{10}$ respectively) is a terminal M-F stretching vibration. The crystal structure of the $\alpha$-MF$_5$ modification is made of isolated tetramers each composed of four octahedra “MF$_6$” bridged to each other in a cis configuration (Figure 4b). Again the highest Raman vibrational frequency has been assigned to the terminal M-F stretching (6). It seems that the spectra of all MF$_5$ phases shown in Figs 2 and 3 have a high intensity Raman band at high frequencies in the region of the M-F stretching, indicating that the “MF$_6$” octahedra are the predominant units in building up the structure of all these phases.

![Figure 4](https://example.com/figure4.png)

Figure 4. Octahedral “MF$_6$” sharing either an edge or cis and/or trans vertices to form different structures. Only the equatorial fluorides are shown at the vertices of the squares; the two axial fluorides are perpendicular above and below the central atom of the square and are not shown. (a) edge-bridged dimer (found in the vapor phase, ref. 7), (b) cyclic tetramer, (found in $\alpha$-MF$_5$, ref.5) only a cis configuration is possible; (c) cis cyclic octamer (d) trans cyclic octamer; (e) mixed cis/trans cyclic octamer; (f) cis linear chain; (g) trans linear chain and (h) mixed cis/trans linear chain. Only a few cyclic structures and symmetric combination of linear chain structures are shown. Non-linear (space) structures can be easily formed by shifting the bridging vertex around the octahedra and thus creating complex 3D structures with random space orientation.

**Structure of the Amorphous Phases**

Table I summarizes certain physicochemical properties of the NbF$_5$ and TaF$_5$ compounds in the melt and $\alpha$-crystalline phases. For the melts the viscosities and
Trouton's constants suggest the presence of highly associated species. Upon melting the molar volume increase by $-1/3$, indicating that the structures of the tetramer rings in the solid (5) change drastically on going into the melt.

The two intense polarized Raman bands of all amorphous phases have positions and relative intensities close to the two main frequencies of the vapor phase dimer (Table II). These bands are assigned to the M-F stretching frequency (as above) and the M-F-M bridging frequency of the octahedra participating in the bridged structures both in the vapor and the amorphous phases. Apart from the gas phase dimer (Figure 4a) and the tetramer (Figure 4b) in the crystal other closed structures like hexamers, octamers (Figure 4c,d,e) etc or open structures like chains (Figure 4f,g,h) could possibly be formed by bridging "MF$_6$" octahedra. The main characteristic of these structures (Figure 4) is that each octahedron has two bridged fluorides to other octahedra and four terminal fluorides in equatorial or axial configurations. This would imply that the terminal and bridging frequencies lay respectively in the same energy region for all these structures. In other words when the "MF$_6$" octahedra with terminal and bridging fluorides are preserved, the frequency shifts from structure to structure are not expected to be large.

Table I. Physicochemical Properties of Solid and Molten MF$_5$ (M= Nb, Ta) Salts

| Property | NbF$_5$ | TaF$_5$ | Property | NbF$_5$ | TaF$_5$
|----------|---------|---------|----------|---------|---------|
| Crystal structure | C$_{2v}$ - C2/m monoclinic | C$_{2h}$ - C2/m monoclinic | $\Delta V_f$ | 31.25% | 33.49%
| Vapor structure | NbF$_5$/Nb$_2$F$_{10}$ equilibrium | TaF$_5$/Ta$_2$F$_{10}$ equilibrium | $\eta$, at m.p. | 91.4 | 70.30
| m.p. | 79 (352) | 97 (370) | $\sigma$, at m.p. | 1.63.10$^5$ | 1.56.10$^4$
| b.p. | 234(507) | 229(502) | $\Delta H_f$ | 12.9±0.5 | 18.4±1.0
| $\rho$, a-MF$_5$ at 300 K | 3.54 | 5.19 | $\Delta S_f$ | 34.5 | 50.9
| $\rho$, melt at m.p. | 2.697 | 3.888 | Trouton$^{(d)}$ | 102 | 108
| [gr.cm$^{-3}$] | | | J.K$^{-1}$.mol$^{-1}$ | | |

$^{(a)}$ Data collected from: i. G.J. Janz "Molten Salt Handbook" Academic Press, New York (1967); ii. D. Brown "The Chemistry of Niobium and Tantalum" in "Comprehensive Inorganic Chemistry" Vol. 3, ed. A.F. Trotman-Dickenson, Pergamon Press, Oxford 1973.

$^{(b)}$ The symbols used are: $\rho$, density; $\Delta V_f$ = 100($V_r$-$V_s$)/$V_n$, the molar volume change upon melting; $\eta$, viscosity; $\sigma$, specific conductance; $\Delta H_f$ enthalpy of fusion; $\Delta S_f$ entropy of fusion.

$^{(d)}$ Trouton's constant corresponds to the entropy of vaporizations which for most liquids is $-85$ J K$^{-1}$.mol$^{-1}$.

Geometrical estimation of the volumes of the dimer, tetramer, octamers and chain structures (Fig. 4) as well as other structures like trimer, pentamers and hexamers give the trends of volume changes expected upon melting the $\alpha$-crystal containing the tetramers. By taking into account and including in the volume the center voids in the cyclic structures and the side voids of the chain structures it can be shown (8) that the large volume changes upon melting (i.e. by 1/3 volume increase-Table I) are justified by having the tetramers (in the $\alpha$-solid) to be transformed in the melt to either large cyclic or and to chain structures. In such a transformation the "MF$_6$" octahedra are bridged to either cis and/or trans configurations and do not change much their vibrational energies and the terminal and bridging frequencies do not shift.
Table II. Terminal and Bridging Frequencies (cm⁻¹) of “MF₆” Octahedra

|          | Glass | m-liquid | melt | vapor (a) | Glass | melt | vapor (b) |
|----------|-------|----------|------|-----------|-------|------|-----------|
| M-F₀ (b) | 762   | 761      | 759  | 756       | 756   | 754  | 752       |
| M-F₆ (a) | 674   | 676      | 677  | 683       | 683   | 684  | 690       |

(a) dimer (7); (b) M-F terminal; (c) M-F-M bridging

Thus, the association in the melt supported by the physicochemical properties (Table I), the volume changes upon melting and the main Raman bands observed suggest for the melt a mixed network (chain) and cyclic like structure composed of vertex bridged “MF₆” octahedral. Presumably similar are the basic units building up the glass and the metastable liquid structures. However, the visually observed volume changes (contraction and formation of internal meniscus-see experimental description) on going from the melt into the glass and then to metastable liquid indicate rearrangements of the ring and chain sizes so to form more compact structures in the glass.

Figure 5. Temperature dependence of Raman spectra of molten NbF₅ and TaF₅. Spectral conditions as in Fig. 2 and 3. Spectra were measured at VV and HV configurations every 40 to 50°C above melting point, but no substantial differences were observed.
Furthermore, the similarities of the spectra for all amorphous phases suggest that the size of the cyclic structures and/or the length of chain structures do not affect the terminal and bridging frequencies of the basic octahedral “MF$_6$” units. The Raman spectra of molten MF$_5$ measured at different temperatures are in support of this view (Fig. 5). Apart from an expected band broadening the spectra are practically independent of temperature. In the same temperature region the fluidity increases indicating structural changes (less polymerization; i.e.: smaller rings, shorter chains) which do not change the vibrational modes of the “octahedral” basic unit and thus do not alter the overall spectra.

Finally, it should be pointed out that the cyclic structures are neutrally charged. On the other hand, the chain structures have ending “MF$_6$” octahedral units which could be charged either positively (e.g. the terminal octahedron is edge bridged to the chain) or negatively (e.g. the terminal octahedron is vertex bridged to the chain and possess an additional terminal fluoride). By charging the endings of the chains one would expect that the melt should be slightly ionized and this is indeed what the specific conductivities of the melt suggest (Table I).

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