

Glass Formation And Phase Transitions Of NbF_5 And TaF_5 From 77 To 600 K

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Raman spectroscopy has been used for studying the structural changes observed for the NbF_5 and TaF_5 compounds from LN_2 temperatures up to ~ 200 K above their melting points. Figure 1 gives a schematic diagram of the phase transitions occurring for these systems. It was observed that quenching of the MF_5 ($M=\text{Nb,Ta}$) melts in liquid nitrogen results in formation of glasses, which are stable up to ~ 230 K. Around this temperature the viscosity of the MF_5 glass decreases and a new "metastable" liquid is formed. Further increase of temperature leads to exothermic solidification and formation of *new* crystalline MF_5 solids (β -form) which are stable up to approximately 270-280 K. Then, a room temperature solid \rightarrow solid transition leads to formation of the stable crystalline α -forms. Further heating of the α -solids gives the low viscosity MF_5 melts whose vapor pressure increases with temperature yielding finally an equilibrium gaseous mixture composed of MF_5 monomers and M_2F_{10} dimers⁽¹⁾. Slow cooling of the melts or condensation of the vapors gives the α -solid form.

Raman spectra have been measured at different temperatures for all phases observed (Fig. 1) except the TaF_5 metastable liquid phase. Fig. 2 shows the spectra of the NbF_5 phases. All spectra are characterized by a relative strong band near and above 750 cm^{-1} which corresponds to the Nb-F_t niobium-terminal fluorine atom frequency of the " NbF_6 " octahedral bridged by an edge (s) to other octahedral, like in the case of M_2F_{10} dimers⁽¹⁾. The Nb-F_b , niobium-fluorine atom bridging frequency, near and below 700 cm^{-1} , is definitely seen in the amorphous phases (glass, metastable liquid and melt) as well as in the vapor phase. The spectral behavior for the TaF_5 system is similar.

It appears that the predominant structures of these phases consist mainly of " MF_6 " octahedra having both terminal and bridging fluorine bonds. The bridging may cause dimerization (e.g. the M_2F_{10} gaseous molecule) or polymerization involving either n-mers of edge-bridged octahedra or more open structures with corner bridged octahedra. The spectra of MF_5 melts were not affected by temperature which indicates a increased stability of the octahedral bridged structures. It was only in the vapor phase and at elevated temperatures that the less symmetric MF_5 monomeric species were found.

The low frequency ($<50\text{ cm}^{-1}$) Raman spectra of the glass and the liquid phases of both MF_5 compound show a rapidly falling Rayleigh wing with no shoulder bands. In this frequency region the studied so far inorganic glasses and melts show a rather strong scattering arising from contributions⁽²⁾ of (a) the vibrational Boson peak whose temperature dependence scales with the Bose thermal factor and (b) the quasielastic component on the foot of the Rayleigh pick which is attributed to fast relaxations in the system. The spectra in Fig. 2 indicate that the dynamic properties of the MF_5 amorphous phases are very different from the behavior of the known so far inorganic glass forming systems.

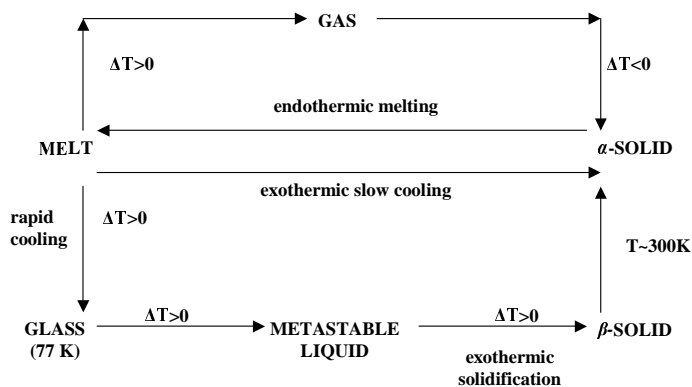


Fig. 1. Phase transitions for the MF_5 ($M= \text{Nb,Ta}$) compounds. Note the rather unusual solidification of the metastable liquid with increasing temperature.

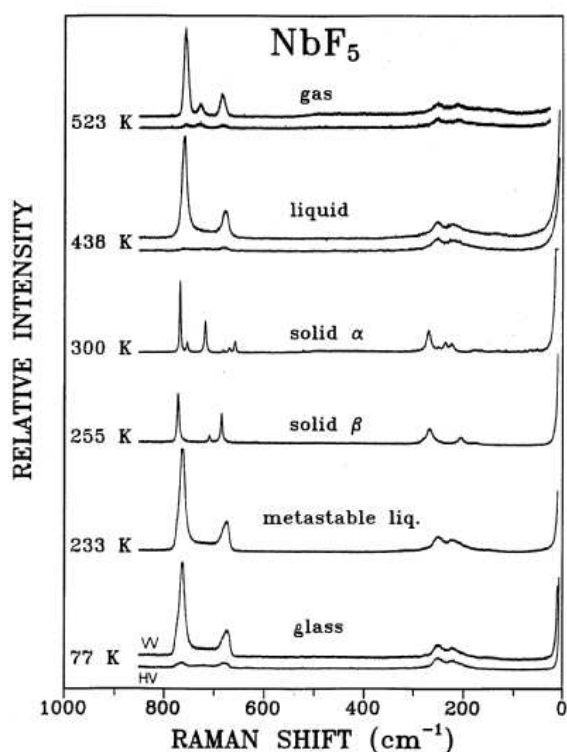


Fig. 2. Raman spectra of all phases observed for NbF_5 in the temperature range 77 – 525 K.

References

1. S. Boshosian and G.N. Papatheodorou, *submitted for publication*.
2. G.N. Papatheodorou and S.N. Yannopoulos, in "*Molten Salts: from Fundamentals to Applications*" NATO ASI Symposium Series 2, ed. M. Gaune-Escard, Kluwer, Boston Vol. 52, 47-106 (2002).