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Crystallized Hydrates in GaX_3–H_2O Binaries and their Vibrational Spectra

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Summary Systematic studies of liquid–solid equilibria in the binaries GaX_3–H_2O (X=Cl, Br) show the existence of several hydrates the vibrational (i.r. and Raman) spectra of which indicate a change in the co-ordination around gallium.

Diagrams for GaX_3–H_2O binaries have been established by thermal analysis following crystallization treatments. In the binary $GaCl_3$–H_2O, only the monohydrate $GaCl_3,H_2O$ has been characterized. It is a compound with a congruent melting point. Solutions in the range 0—50% (moles $GaCl_3$) form glasses and are difficult to crystallize, and hence the diagram in this range (Figure 1) is very ill defined.

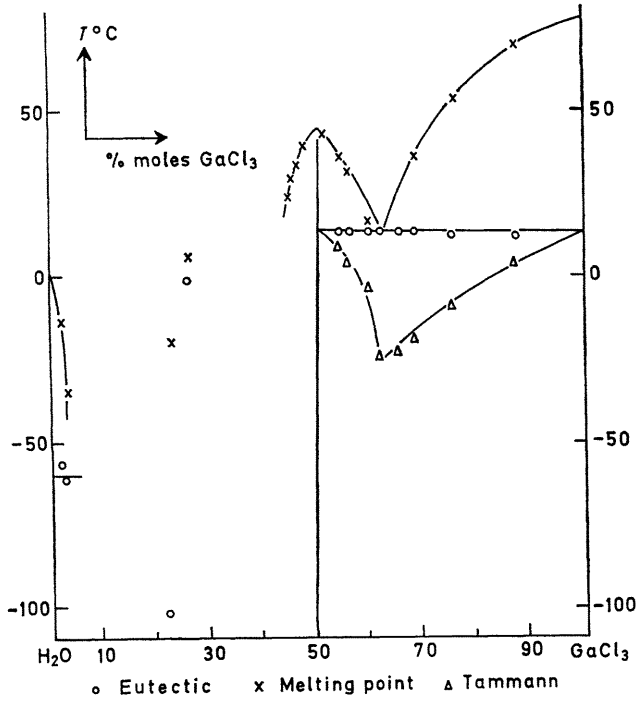

Figure 1. *Binary* $GaCl_3$–H_2O.

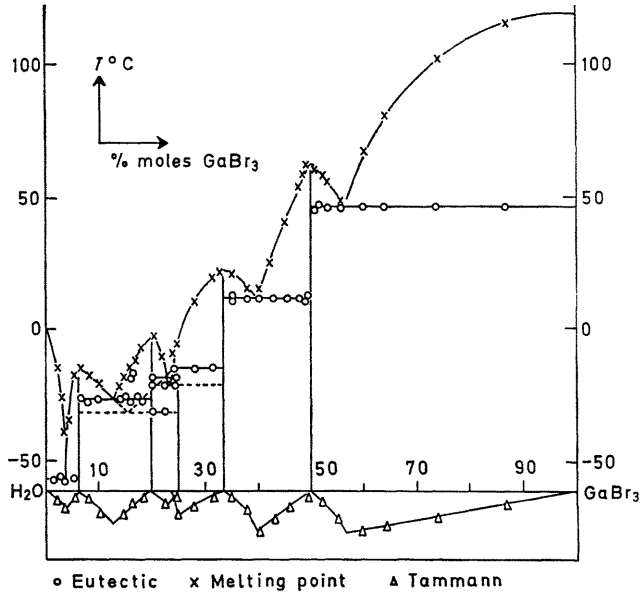

Figure 2. *Binary* $GaBr_3$–H_2O.

The binary $GaBr_3$–H_2O shows five definite hydrates at 1,2,3,4, and 15 H_2O. They have congruent melting points, except for the trihydrate. The hexahydrate has not been characterized but its occurrence is not rejected.

A study of the i.r. (200—4000 cm^{-1}) and Raman (0—500 cm^{-1}) spectra of the adducts $GaCl_3,H_2O$ and $GaBr_3$ with

1,2,4, and 15 H_2O gives indications concerning the environment of the gallium. For the two monohydrates and the dihydrate of $GaBr_3$, i.r. and Raman spectra are characteristic of a H_2O–GaX_3 arrangement with four-co-ordination around the gallium. For the dihydrate, they show that its formula must certainly be $(GaBr_3,H_2O)H_2O$ (Table).

For the other hydrates studied, i.r. and Raman spectra may be interpreted on the basis of six-co-ordination around gallium.

I.r. spectra in the fundamental vibration range of the water molecule show the presence of two types of water molecule for the dihydrate and the pentadecahydrate. Some are co-ordinated on the gallium, others outside the "skeleton." The existence of particularly short hydrogen bonds might be characterized by the triplet found around 2900—2600—1900 cm^{-1} in the i.r. spectra of the dihydrate and tetrahydrate.

TABLE. *Assignments of the* O–$GaX_3(C_{3v})$ *"skeleton" in* $GaCl_3,H_2O$, $GaBr_3,H_2O$, *and* $(GaBr_3,H_2O)H_2O$

$GaCl_3,H_2O$			$GaBr_3,H_2O$			$(GaBr_3,H_2O)H_2O$	
I.r.	Raman	Assignments	I.r.	Raman	Assignments	I.r.	Raman
			440—410	—	ν(Ga–O)	470—430	—
410	418	ν(Ga–O) + $\nu_{deg.}(GaCl_3)$	305	310	$\nu_{deg.}(GaBr_3)$	310	316
390	404		295	290		295	300
360	364	$\nu_s(GaCl_3)$	225	230	$\nu_s(GaBr_3)$	230	233
	169	$\delta(GaCl_3)$	—	120	$\delta(GaBr_3)$	—	120
	128						

ν_s symmetric stretching vibration of the pyramidal group GaX_3.
$\nu_{deg.}$ degenerate stretching vibration of the pyramidal group GaX_3.
δ bending vibration of the pyramidal group GaX_3.

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