THE FORMATION OF FLUOROOXOGERMANATES IN ALKALI METAL NITRATE MELTS

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Attempts were made to isolate fluorooxogermanates, whose formation in nitrate melts was indicated potentiometrically[1]. The stability of fluorooxogermanates in nitrate melts depends on the melt temperature and on the effect of the cation. In addition to the already known compound, $K_4[Ge_2F_{10}O]$, a new compound, $Na_2[GeF_4O]$, was also obtained from nitrate melts. In addition, conditions were found for the formation of both the tetragonal and of the hexagonal modification of GeO_2 in nitrate melts.

This work is a continuation of a study of the formation and isolation of new compounds from nitrate melt medium[1], uing a procedure in which the formation of new substances in the nitrate melt was first demonstrated potentiometrically and these substances were then isolated.

This work was carried out to employ similar methods to study the possible formation and isolation of fluorooxogermanates, which have not yet been thoroughly studied, and to consider possible applications. First, we carried out a potentiometric study of fluorogermanates in nitrate melts and indicated the formation of anions with probable[2] composition $[Ge_2F_{10}O]^{4-}$, $[Ge_4F_6O_9]^{8-}$, and $[Ge_2F_2O_5]^{4-}$. The potassium salt of the first of these anions is already known and is prepared by the thermal decomposition of $K_2[GeF_5OH]$, formed in aqueous solution[3].

EXPERIMENTAL

The chemicals employed, $NaNO_3$, KNO_3, $LiNO_3$, $Pb(NO_3)_2$, Na_2CO_3, $NaOH$, 38—40% hydrofluoric acid, dimethylsulphoxide, ethanol, and methanol were the commercial substances of *p.a.* purity (Lachema, Brno) and GeO_2 was of semiconductor purity (The Single Crystal Research Institute, Turnov).

Na_2GeF_6 was prepared by dissolving GeO_2 in concentrated hydrofluoric acid in a teflon vessel. After addition of sodium fluoride, the crystals of Na_2GeF_6 were filtered off, washed with ethanol and dried at 70°C.

Na_2GeO_3 was prepared either by dissolving a stoichiometric amount of GeO_2 in an aqueous

NaOH solution with subsequent evaporation until crystallization occurred, filtering off and washing with ethanol, or by melting a stoichiometric amount of GeO_2 and Na_2CO_3 at 1 100°C.

Sodium, germanium and, in Na_2GeF_6, fluorine were determined in both the starting compounds. For Na_2GeO_3 (166·6) calculated: 27·60% Na, 43·58% Ge; found: 27·18% Na, 43·40% Ge. For Na_2GeF_6 (232·6) calculated: 19·77% Na, 31·21% Ge, 49·02% F; found: 20·23% Na, 31·16% Ge, 49·31% F.

Germanium was determined by alkalimetric titration after addition of mannitol using phenol red indicator[4]. Fluorine was determined using a Crytur type 0·9-17 ion selective electrode using a PHM 62 pH-meter (Radiometer, Copenhagen); alkali metals were determined by atomic absorption and lead gravimetrically as lead chromate. After removal of extraneous nitrates, the amount of nitrate in the compounds was determined spectrophotometrically[5].

The $NaNO_3 + KNO_3$ melt was prepared by melting an equimolar mixture of the two nitrates recrystallized from aqueous solutions, the $NaNO_3 + LiNO_3$ melt was prepared by melting an eutectic mixture of the two compounds (100·6 g of recrystallized $NaNO_3$ and 99·4 g $LiNO_3$), and the $NaNO_3 + Pb(NO_3)_2$ melt by melting an eutectic mixture of the two components (115·4 g of recrystallized $NaNO_3$ and 84·6 g $Pb(NO_3)_2$). Fusing was carried out in a teflon vessel at a temperature of 300—310°C. The melt was dried using a stream of dry pure oxygen for at least 1 hour; this time was prolonged to 3·5 hours for the melt containing $LiNO_3$. Weighed amounts of the initial compounds were carefully poured into the dried melt and the reaction vessel was stored in the furnace during the whole experimental period (usually several days). The temperature was regulated using a Zeparis regulator; a Fe–constantan thermocouple was used as a sensor. The precipitate was separated from the liquid melt by filtration through an S1 glass filter tempered to the melt temperature. Nitrates were removed from the product in several ways depending on the type of melt. The mixture of sodium and lithium nitrates was extracted using a Soxhlet extractor and predried methanol, the mixture of sodium and lead nitrates was extracted using dimethylsulphoxide at laboratory temperature and the mixture of sodium and potassium nitrates was subjected to extraction by liquid ammonia[1] at -60°C in a modified Soxhlet extractor.

Powder X-ray patterns were recorded using the Debye–Scherrer method on a Mikrometa 2 instrument, as were the diffractograms using radiation with a wavelength of 154·178 pm.

Infrared molecular spectra were recorded using a Perkin–Elmer 684 instrument with a data bank using the KBr pellet method, in the region 350—4 000 cm^{-1}.

RESULTS AND DISCUSSION

Attempts to prepare and isolate fluorooxogermanates indicated potentiometrically[2] were based both on direct fusing of germanates and fluorogermanates as well as on formation by solvolysis and neutralization of fluorogermanates in nitrate melts.

An attempt to prepare fluorooxogermanates by tempering a mixture of the solid components (Na_2GeF_6 and Na_2GeO_3) was not successful. Na_2GeF_6 sublimes from an open platinum crucible at a temperature lower than that of reaction with Na_2GeO_3. In a closed quartz ampoule, fluorogermanate reacts with SiO_2, leading to very strong corrosion of the ampoule. In a closed autoclave, fluorooxogermanate is most probably formed which, however, apparently escapes as a gas through the seals, leaving only nonvolatile NaF. If Na_2GeO_3 did not react with Na_2GeF_6, then it would remain in the closed autoclave, as Na_2GeO_3 is not volatile at a temperature of 650°C, to which the autoclave was heated.

A solution of Na_2GeF_6 in an alkali metal nitrate melt or lead nitrate melt yielded both a solidified solution filtrate (samples designated as F) and a filtered precipitate that was insoluble in the nitrate melt (samples designated as X), except for compound X-4, obtained from the solidified melt at a temperature of $340°C$, while compound F-4 was obtained from the liquid melt at this temperature. The following samples were obtained under the conditions listed in Table I: X-1, F-1, X-2, X-3, X-4, F-4. After removal of nitrates from these samples by washing with liquid ammonia, methanol or dimethylsulphoxide, their compositions were determined by chemical analysis, measuring powder X-ray patterns, infrared molecular spectra and, in some cases, thermal decomposition.

For example, evaluation of the diffractogram of compound X-1 indicated that the main component of the mixture is the tetragonal modification of GeO_2; in addition, all the lines of $K_4[Ge_3F_{10}O]$ were found with suitable intensity, as well as the most intense lines of KNO_3 and NaF. However, the latter two compounds are present in the mixture in far smaller amounts than GeO_2, as is reflected in the low intensity of their otherwise very strong lines. Of the 28 observed lines, only two could not be assigned.

Chemical analysis yielded the molar ratios of Na, K, F, NO_3^-, and O (from the difference):

$$Na \ : \ K \ : \ Ge \ : \ F \ : NO_3^- : \ O$$
$$0·40 \ : \ 0·28 \ : \ 1·00 \ : \ 0·79 \ : \ 0·12 \ : \ 1·89$$

As nitrate anions are present in the mixture as KNO_3 and sodium cations as NaF (from the diffractogram), subtraction of 0·12 moles of KNO_3 and 0·40 moles of NaF leaves:

$$K \ : \ Ge \ : \ F \ : \ O$$
$$0·16 \ : \ 1·00 \ : \ 0·39 \ : \ 1·89$$

The remaining potassium cations belong to 0·04 moles of $K_4[Ge_2F_{10}O]$ and thus 0·92 moles of GeO_2 remains. Recalculation to molar percent yields the composition: 62% GeO_2, 3% $K_4[Ge_2F_{10}O]$, 27% NaF, and 8% KNO_3. The same procedure was employed in the analysis of the other samples. Chemical analysis and X-ray studies were complemented by study of the infrared spectra for those compounds expected to contain both a Ge—F and Ge—O bond. Table II gives a survey of the compositions of the individual samples.

It follows from the compositions of products F-1 and X-1 that the reaction of Na_2GeF_6 with a fused equimolar mixture of $NaNO_3 + KNO_3$ at a temperature of $250-300°C$ yields $K_4[Ge_2F_{10}O]$, which is soluble in this melt and decomposes only very slightly to form tetragonal GeO_2, which begins to precipitate from the melt after several hours. $K_4[Ge_2F_{10}O]$ together with a small amount of the nitrate melt

entered the product as a contaminant as a result of retention of a solid substance on the glass frit. The amount of NaF in products X and F is affected by its solubility in the

TABLE I
Conditions for preparation of the substances in a nitrate melt medium

| Exp. No	Melt solvent	Initial Comp.	Temper. °C	Phase	Wash liquid	Product mass[a], g
1	400 g NaNO$_3$ + KNO$_3$	4·00 g Na$_2$GeF$_6$	250—300	X	NH$_3$	0·38
				F	DMSO, CH$_3$OH	0·85
2	120 g NaNO$_3$ + KNO$_3$	1·32 g Na$_2$GeF$_6$ + 1·21 g Na$_2$CO$_3$	260	X	DMSO, CH$_3$OH	0·91
				F	DMSO, CH$_3$OH	0·17
3	200 g NaNO$_3$ + LiNO$_3$	2·00 g Na$_2$GeF$_6$	250—300	X	CH$_3$OH	1·14
4	150 g NaNO$_3$ + Pb(NO$_3$)$_2$	14·30 g Na$_2$GeF$_6$	340	X	DMSO, CH$_3$OH	4·09
				F	DMSO, CH$_3$OH	10·37

[a] This column indicates the mass distribution of the product between the precipitate (X) and the melt solution (F). Samples in series F were obtained from 100 g of melt filtrate.

TABLE II
Survey of the compositions of the individual samples

Sample	GeO$_2$ (tetr.)	GeO$_2$ (hex.)	GeO$_2$ (amorph.)	K$_4$[Ge$_2$F$_{10}$O]	Na$_2$[GeF$_4$O]	NaF	LiF	PbF$_2$	KNO$_3$
X-1	62/66[a]			3/14		27/12			8/8
F-1				36/87		64/13			
X-2			20/38			80/62			
F-2				3/28		97/72			
X-3		28/61				72/39			
X-4					9/17	64/24		27/59	
F-4					8/9	33/8	59/83		

[a] The number prior to the vertical line indicates the mole %, that after the line is the wt. % of the compound in the mixture.

nitrate melt[6]. The dissolution and reaction of solid Na_2GeF_6 with the $KNO_3 +$ $NaNO_3$ melt thus occurs according to the reaction

$$2\,[GeF_6]^{2-} + 2\,NO_3^- = [Ge_2F_{10}O]^{4-} + 2\,F^- + 2\,NO_2 + 1/2\,O_2 \quad (A)$$
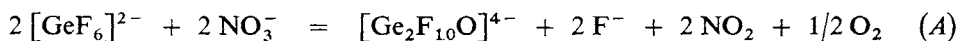
Under these conditions, compound $K_4[Ge_2F_{10}O]$ partly and very slowly decomposes to form the tetragonal modification of GeO_2 (rutile structural type[7]). The decomposition to form GeO_2 increases with increasing temperature. At a temperature of 400°C in a melt of pure $NaNO_3$ (in the absence of K^+ cations), the decomposition of Na_2GeF_6 to GeO_2 and NaF is complete, and GeO_2 is precipitated in the hexagonal modification (quartz structural type[8]) even though the tetragonal modification is stable below a temperature of 1 000°C. It can thus be assumed that the formation of various modifications of GeO_2 occurs as a result of the formation of different intermediates in the solvolysis of Na_2GeF_6, depending on whether potassium ions are present in the nitrate melt.

Product X-2 obtained from Na_2GeF_6 in a $KNO_3 + NaNO_3$ melt alkalized by sodium carbonate (with potentiometric control up to the equivalence point) contains both NaF and an X-ray amorphous germanium compound. In the absence of an infrared spectrum, it is not clear whether this is a mixture of NaF and GeO_2 or NaF and $(Na, K)_2[GeF_2O_2]$, as assumed on the basis of potentiometric measurements[2]. However, the infrared spectrum indicated that no Ge—F bonds are present and thus that this is a mixture of NaF and GeO_2 (amorph.). The small amount of $K_4[Ge_2F_{10}O]$ in product F-2 corresponds to unreacted substance remaining after alkalization of the melt by sodium carbonate dissolved in the melt; it is present in a negligibly small amount. Thus, except for the already known compound, $K_4[Ge_2F_{10}O]$, no new fluorooxogermanate could be obtained from a nitrate melt containing potassium and sodium ions.

All the germanium present in product X-3 was in the form of hexagonal GeO_2, indicating that this modification of GeO_2 can be formed at a lower temperature which decreases with decreasing cation size in the nitrate melt. The melt filtrate (corresponding to the sample designated F-3) did not contain any germanium compound. The solvolytic reaction of Na_2GeF_6 with the nitrate melt occurred in the presence of $LiNO_3$ at a much faster rate, with a quantitative yield of GeO_2, so that the formation of fluorooxogermanates could not be observed. Thus, fluorooxogermanate could be obtained only from a melt containing potassium cations. However, in the presence of potassium ions, primarily the known compound, $K_4[Ge_2F_{10}O]$, is formed.

In order to adjust suitable conditions for the formation of new fluorooxogermanates in the absence of potassium ions, a mixture of $Pb(NO_3)_2$ and $NaNO_3$ was used as a solvent; this mixture also contains sufficiently large Pb^{2+} cations. The compositions of products X-4 and F-4 indicates that a new fluorooxogermanate

is formed in this case, $Na_2[GeF_4O]$, primarily from product X-4. It is thus very poorly soluble in the nitrate melt employed at a temperature of 340°C. The diffraction line that could not be assigned to sodium fluoride or the two modifications of PbF_2, apparently corresponds to compound $Na_2[GeF_4O]$; however, it should be borne in mind that a complete set of lines is not present for this substance as some could be overlapped by the more intense lines of NaF and PbF_2. Unassigned lines $d(I)$: 194·9(7), 183·1(13), 171·3(8), 167·0(9), 150·8(2), 128·1(6) (the interplanar distances are given in pm and the numbers in brackets indicate the intensity). The intensities are related to the most intense line β-PbF_2 340·1(100). This compound has not yet been described in the literature, but the analogous compound K_2SnF_4O is known[3,9]. In addition to this compound and NaF, PbF_2 is also formed in both modifications simultaneously[10], *i.e.* α and β, of which the former is collected exclusively in the insoluble precipitate, while the latter remains primarily in the solution melt. The formation of both modifications of PbF_2 and of GeO_2 indicates that less readily available modifications of some substances can be prepared from nitrate melts.

The fluorooxogermanates $K_4[Ge_2F_{10}O]$ and $Na_2[GeF_4O]$ can be separated from the nitrate melt by decantation with a suitable solvent, but cannot be separated from sodium or lead fluoride in this manner.

The analysis of the infrared spectra of products F-1, X-2, and X-4 was based on comparison of the spectra of compounds Na_2GeO_3, GeO_2 (refs[11,12]), Na_2GeF_6 (refs[13,14]), and $K_4[Ge_2F_{10}O]$ (ref.[15]). The assignment of the vibrational bands of

TABLE III

The infrared spectrum of product X-4

Wavenumber, cm^{-1}		Assignment[b]
calculated	measured[a]	
466	486 w	ν_s(Ge—F)
508	516 w	ν_s(Ge—O—Ge)
558	560 w	ν_{as}(Ge—F)
586	606 s	ν_{as}(Ge—F)
634	667 sh ⎫	ν_s(Ge—F) and ν_s(Ge—O)
783	744 w ⎭	
850	851 sh ⎫	ν_{as}(Ge—O—Ge)
	877 m ⎭	

[a] s strong, m medium, w weak, sh shoulder; [b] ν_s, ν_{as} valence symmetric and valence antisymmetric vibrations.

these compounds was refined where necessary by comparison of the spectra of Na_2GeO_3 with the published spectra of isotypical Na_2SiO_3 (ref.[16]) and $K_2Pb_2Ge_2O_7$ (ref.[17]) and the spectra of $K_4[Ge_2F_{10}O]$ with the published[3,15] spectrum of $K_4[Sn_2F_{10}O]$. It was assumed that the force constants of the bonds of the vibrations of Ge—O and Si—O or Ge—O and Sn—O or Ge—F and Sn—F are roughly identical[18] and that the shift in the vibration can be assigned in terms of the reduced mass μ:

$$\tilde{v}_{Ge-O} = \left(\mu(Si—O)/\mu(Ge—O)\right)^{1/2} \quad \tilde{v}_{Si-O} = 0{\cdot}8818\tilde{v}_{Si-O} \tag{1}$$

$$\tilde{v}_{Ge-O} = \left(\mu(Sn—O)/\mu(Ge—O)\right)^{1/2} \quad \tilde{v}_{Sn-O} = 1{\cdot}0370\tilde{v}_{Sn-O} \tag{2}$$

$$\tilde{v}_{Ge-F} = \left(\mu(Sn—F)/\mu(Ge—F)\right)^{1/2} \quad \tilde{v}_{Sn-F} = 1{\cdot}0429\tilde{v}_{Sn-F}. \tag{3}$$

These observations and assumptions can complement the analytical and X-ray data on the compositions of products F-1, X-2, and X-4.

The main component of product F-1 is the fluorooxogermanate $K_4[Ge_2F_{10}O]$, indicated by the presence of absorption bands at 357 (vs), 489 (w), 606 (vs), 668 (vw), 750 (w), and 840 (w) cm^{-1}, corresponding to the absorption bands of a sample of $K_4[Ge_2F_{10}O]$ with a precision of 3 cm^{-1} and suitable intensity. (Sodium fluoride does not absorb in the measured spectral region. Its spectrum is almost identical with that of the KBr pellets.)

The spectrum of product X-2 does not contain any of the typical intense bands for Ge—F vibration, especially the very intense band of the deformational vibration of F—Ge—F (at $354-358$ cm^{-1}) and the very strong antisymmetric valence vibration of Ge—F (at $603-606$ cm^{-1}). The product thus more probably contains amorphous GeO_2 rather than fluorooxogermanate $Na_2GeF_2O_2$.

The spectrum of product X-4 (Table III), reminiscent of the spectrum of $K_4[Ge_2F_{10}O]$, contains all the bands corresponding to K_2SnF_4O (ref.[15]) shifted to higher wavenumbers according to relationship (2) and (3) that do not differ from the calculated values by more than $10-20$ cm^{-1}. The absorption band of the very intense antisymmetric vibration of Ge—F, typical for all fluorooxogermanates, was observed at a wavenumber of 606 cm^{-1}. Contamination of the mixture by NaF and PbF_2 does not appear in the spectrum, confirming the above assumption that product X-4 contains a fluorooxogermanate.

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