Russian Chemical Reviews **69** (8) 705 – 716 (2000) © 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n08ABEH000582

Fluoroindate glasses

P P Fedorov, R M Zakalyukin, L N Ignat'eva, V M Bouznik

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Abstract. The compositions, properties and concepts of the structure of fluoroindate glasses are considered. These glasses are characterised by low phonon energies and hence very low theoretical optical losses in the IR region. According to the vibrational spectroscopic data, the degree of polymerisation of octahedra in fluoroindate glasses is lower than in fluorogallate and fluoroaluminate glasses. The compositions of fluoroindate glasses containing up to nine components cannot be regarded as being completely optimised. Comparative analysis of the chemical and thermal stability of fluoroindate and fluorozirconate glasses was performed. It is shown that the high susceptibility of indium fluoride to hydrolysis accounts for the instability of glasses and optical losses. The prospects for the use of fluoroindate glasses in lasers, fibre optics and scintillation instruments are discussed. The bibliography includes 157 references.

I. Introduction

Intensive studies of fluoride glasses began in the mid-1970s. At that time, fluoroberyllate and fluoroaluminate glasses were well known. An unexpected discovery of fluorozirconate glasses with high values of coordination numbers (c.n.) of glass-forming atoms (c.n. 6 – 8) stimulated the development of studies of glass formation in multicomponent fluoride systems and revealed other fluorides as 'progenitors of glass'. Fluoride glasses are promising optical materials, including their prospective use in telecommunication systems, because they are characterised by a much wider transmission region in the IR range compared to silicate glasses. Various experimental and computational methods are employed in the studies of the structure of fluoride glasses. Experimental results are described using different models of glassy state (crystal, disordered network, stressed mixed clusters, chemical twinning, ionic glass, polymeric, colloidal, *etc*.). A number of criteria of glass formation have been proposed.[1 – 11]

At present, the best studied glasses are based on zirconium fluoride of the type ZBLAN ($53\,ZrF_4 \cdot 20\,BaF_2 \cdot 4\,LaF_3 \cdot 3\,AlF_3 \cdot 20\,NaF$).† In order to prevent reduction of Zr^{4+} to Zr^{3+}, the fluorozirconate glasses of ZBLAN type are doped with small amounts of indium fluoride (0.015 mol.% – 0.25 mol.%).[12, 13] In this case, no reduction occurs because the couple In^{3+}/In^{+} (like, *e.g*., Sn^{4+}/Sn^{2+} but not Ga^{3+}/Ga^{+}) has a larger electrochemical potential than the couple Zr^{4+}/Zr^{3+} (see Refs 14 and 15). The following redox reaction takes place

$$2Zr^{3+} + In^{3+} \longrightarrow 2Zr^{4+} + In^{+}.$$

An analogous role seems to be played by the additive InF_3 to fluorohafnate glasses: they prevent reduction of Hf^{4+} to Hf^{3+}.[16 – 18] The presence of univalent indium in the glass leads to the appearance of a double absorption peak in the UV region.[14]

Upon addition of up to 4 mol.% of InF_3 to ZBLAN, the resistance of this glass to crystallisation is slightly increased. The refractive index is also increased but less essentially than upon addition of PbF_2.[19] Upon addition of up to 3 mol.% of InF_3 to the fluorozirconate glass of ZBLALi type with a high ($\sim$ 8 mol.%) content of PbF_2, no stabilisation effect was achieved.[20] The increase in the InF_3 concentration in the fluorohafnate glass containing 5 mol.% of CeF_3 induced a decrease in the integral yield of Ce^{3+} luminescence.[18] Attempts to stabilise the glass with composition $24\,CdF_2 \cdot 29\,CdCl_2 \cdot 11\,BaF_2 \cdot 36\,NaF$ by adding up to 8 mol.% of InF_3 were unsuccessful.[21]

In recent years, investigators have shown an appreciable interest in glasses with high content of indium fluoride, the so-called fluoroindate glasses. These glasses are characterised by lower mean values of the energy of phonons ($\sim$ 510 cm^{-1}) than conventional fluorozirconate glasses ($\sim$ 580 cm^{-1}).[22] Thus, fluoroindate glasses absorb in a farther IR region. The range of transparency extends from the UV region to $\sim$ 7 – 8 μm in the IR region (for fluorozirconate and fluoroaluminate glasses, this extends from the UV region to $\sim$ 5.5 μm).‡ Consequently, the

† Hereinafter, the compositions of glasses are given in mol.%.

‡ The edges of transparency are determined approximately, since they depend not only on the sample composition, but also on its thickness.

P P Fedorov A V Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninsky prosp. 59, 117333 Moscow, Russian Federation. Fax (7-095) 135 10 11. E-mail: ppf@newmail.ru
R M Zakalyukin Research Centre 'Kosmicheskoe Materialovedenie' of A V Shubnikov Institute of Crystallography, Russian Academy of Sciences, ul. Akademicheskaya 2, 248033 Kaluga, Russian Federation. Fax (7-084) 224 86 14. E-mail: ruslan@ns.cry.ras.ru
L N Ignat'eva Institute of Chemistry, Far East Branch of the Russian Academy of Sciences, prosp. 100-letia Vladivostoka 159, 690022 Vladivostok, Russian Federation. Fax (7-423) 231 18 89.
E-mail: chemi@online.ru
V M Bouznik Khabarovsk Research Centre, Far East Branch of the Russian Academy of Sciences, ul. Shevchenko 9, 680000 Khabarovsk, Russian Federation. Fax (7-421) 233 74 95.
E-mail: bouznic@khsc.khv.ru

Received 13 March 2000
Uspekhi Khimii **69** (8) 767 – 779 (2000); translated by V D Gorokhov

calculated values of minimum optical losses determined by the sum of the Rayleigh scattering and the multiphonon absorption are substantially smaller in fluoroindate glasses than in fluorozirconate glasses. For example, for the glass BIZYbT ($30\,BaF_2\cdot 30\,InF_3\cdot 20\,ZnF_2\cdot 10\,YbF_3\cdot 10\,ThF_4$) such losses reach ~ 0.002 dB km^{-1} at a wavelength of 3 μm,[23] while for ZBLAN they are ~ 0.044 dB km^{-1} at a wavelength of 2.55 μm.[24] Therefore, fluoroindate glasses may be regarded as promising materials for the IR instrumentation, in particular in systems of optical fibre communication for the transmission of information in the IR region. However, because of technological difficulties the real optical losses are far from the calculated values: they are larger than in the ZBLAN-based fibres and still larger than in the silicate optical fibres (see below). We are still far from the time when it will be possible to use the calculated characteristics of fluoroindate glasses for the development of many-kilometre fibre optical systems for the transmission of information in the range of 2.5–3.7 μm. Characteristically, the impurities of 3*d* elements which affect the transmittance in fluoride glasses in the 0.7–1.5 μm range, even if present in negligible amounts, have virtually no effect on the transmission in the 2.5–3.2-μm range. In the latter range, an essential contribution to the absorption is made by the OH groups (the band at 2.9 μm),[24–26] which creates technological difficulties because of easy hydrolysis of indium fluoride. Other anionic impurities, in particular SO_4^{2-}, also influence essentially optical characteristics of fluoroindate glasses in this range.[27]

The prospects for the use of fluoroindate glasses in the communication optical fibre systems is related to specific features of real silicate fibre-based systems with losses below 1 dB km^{-1}. In the first-generation systems known since 1976, use is made of multi-mode fibres (the operating wavelength is 0.8 μm). Systems of the next generation developed in 1983 are based on the use of both single- and multi-mode fibres (the operating wavelength is 1.3 μm, the second telecommunication window). Modern third-generation systems operate at the wavelength 1.5 μm (the third communication window), which corresponds to the minimum optical losses of the silicate fibre.[28] The systems of all the three generations require installation of laser amplifiers of the signal at intervals of a few tens of kilometres.

The fluoride glasses and especially the fluoroindate glasses are characterised by low energies of phonons; therefore, they can be used as a base for the design of efficient lasers with high quantum yield (up to 6%–7%).[29] For different operating wavelengths, glasses are doped with ions of rare-earth elements, *viz*., with Tm^{3+}, 0.8 μm; Pr^{3+} or Nd^{3+}, 1.3 μm; Er^{3+}, 1.5 μm (Ref. 30). Doping of fluoroindate glasses with ions of rare-earth elements is easier than that of fluorozirconate glasses.[31] In recent years, the subject of most active development is the fluoride fibre doped with Pr^{3+} ions, which is required for the design of optical amplifiers used in telecommunication systems.[17, 32, 33]

The active element of fibre communication is the optical fibre composed of the core and the cladding. A number of requirements are set for the respective materials. The refractive index of the core (n_1) should be larger than that of the cladding (n_2), while the coefficients of thermal expansion and the temperatures of glass transition and crystallisation of the core and the cladding should be close. In order to achieve the maximum operation efficiency of laser amplifiers, it is necessary to use single-mode optical fibres (*i.e*., fibres with a small diameter of the core ranging from 3 to 5 μm) with a large (0.35–0.4) aperture.[20, 34]

$$N_A = (n_1^2 - n_2^2)^{1/2}$$

or the quantity

$$\Delta n = \frac{n_1 - n_2}{n_1}.$$

It is possible that fluoroindate glasses will also find application as optical waveguides (in particular in medicine) for the transmission of laser radiation in the IR region from Er : YAG solid (2.94 μm) and CO gas (4.8–5.5 μm) lasers. The limiting factor is the threshold of glass damage.[29]

Chalcogenide (of the As_2S_3 type) and chalcohalide glasses [*e.g*., formed in the Ge–As–Te–I and Hg–Pb–SI systems,[35] as well as halide (*e.g*., bromide[36] and mixed chloride-fluoride[21])] glasses are characterised by lower mean energies of phonons than fluoroindate glasses. Chalcogenide glasses are transparent much farther into the IR region; however, their transmission in the visible spectral region is limited. Mixed halide glasses are unstable in the ordinary atmosphere and undergo easy hydrolysis.

Compared to the fluorozirconate glasses, the fluoroindate glasses possess enhanced thermal stability judging from the difference in glass transition temperatures (T_g) and the onset of exothermic of crystallisation (T_x) on the heating curves

$$\Delta T = T_x - T_g$$

or from the Hruby criterion[37]

$$H = \frac{T_x - T_g}{T_m - T_x},$$

where T_m is the melting temperature.§

In the opinion of some investigators (see, *e.g*., Ref. 39), the fluoroindate glasses are more stable than the fluorozirconate ones. The preparation of bulk castings of fluoroindate glasses requires lower cooling rates of glass-forming melts.[40] Apparently, this characteristic depends strongly on the technology of preparation of glasses (oxygen-containing impurities induce their crystallisation).[41]

The critical cooling rates (R_c) of glass-forming melts can be determined experimentally (*e.g*., by the method proposed by Barandiaran and Colmenero[42]), *viz*., from the dependences of the observed supercooling ΔT_1 (the difference between the temperatures of liquidus and the beginning of crystallisation) on the cooling rate R (linear extrapolation to the infinite supercooling using $\ln R - 1/\Delta T_1^2$ coordinates). Yet another method consists in calculations using the data derived from the TTT (temperature–time–transformation) curves.[43, 44] Both methods require laborious experiments. The values of R_c reported from different studies show strong discrepancies. Thus the R_c values measured by the former method for the five-component glass ($30\,BaF_2\cdot 30\,InF_3\cdot 20\,ZnF_2\cdot 10\,YbF_3\cdot 10\,ThF_4$) differ by nearly two orders of magnitude: 1.7 K min^{-1} (Ref. 45) and 120 K min^{-1} (Ref. 44) (for ZBLAN, these values were 0.7 and 3 K min^{-1}, respectively). Measurements by the last-mentioned method gave $R_c =$ 102 K min^{-1} (for ZBLAN, this value was 8 K min^{-1}).[23] Such a difference is possibly explained by different conditions of preparation of the samples.

II. Physicochemical properties of indium fluoride

At normal pressure, indium fluoride has the high-temperature cubic polymorph of the ReO_3 type.[46] As the temperature decreases, it passes into the trigonal polymorph of the VF_3 type, space group $R\bar{3}c$ (Fig. 1). The melting temperature of InF_3 is 1320 °C.[48, 49] Indium fluoride is characterised by high vapour pressure,[50] it vaporises strongly upon heating above 900 °C, undergoes easy hydrolysis upon slight heating and absorbs moisture when stored in air. Its hydrate $InF_3\cdot 3H_2O$ can hardly be dehydrated because its hydrolysis with water of crystallisation occurs even at room temperature[51]

$$InF_3\cdot 3\,H_2O \longrightarrow InOHF_2 + HF + 2\,H_2O\,.$$

The ionic radius of In^{3+} is substantially smaller than those of lanthanide cations, it is close to the radius of scandium ion and is

§ In the original paper,[37] the temperature of the beginning of melting (solidus) is used in this formula; in a number of other papers (see, *e.g*., Ref. 38) the temperature of liquidus is used. The difference between them may be substantial.

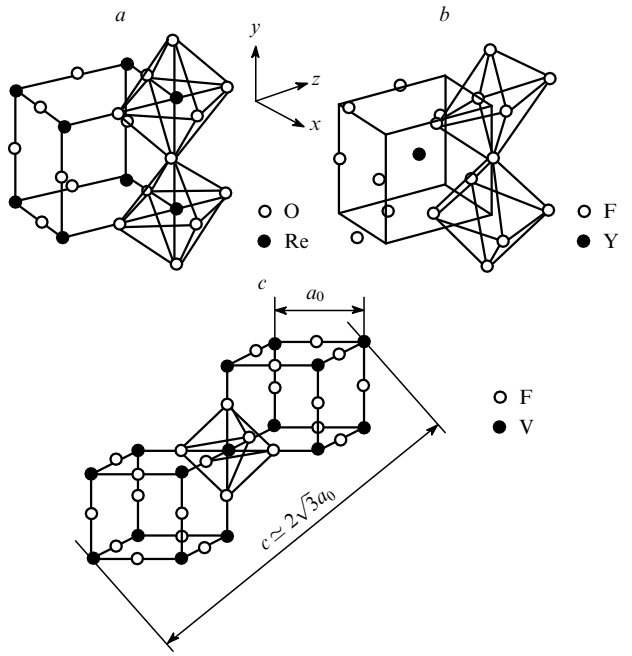


Figure 1. Structural types ReO_3 (*a*), β-YF_3 (*b*)[47] and VF_3 (*c*).

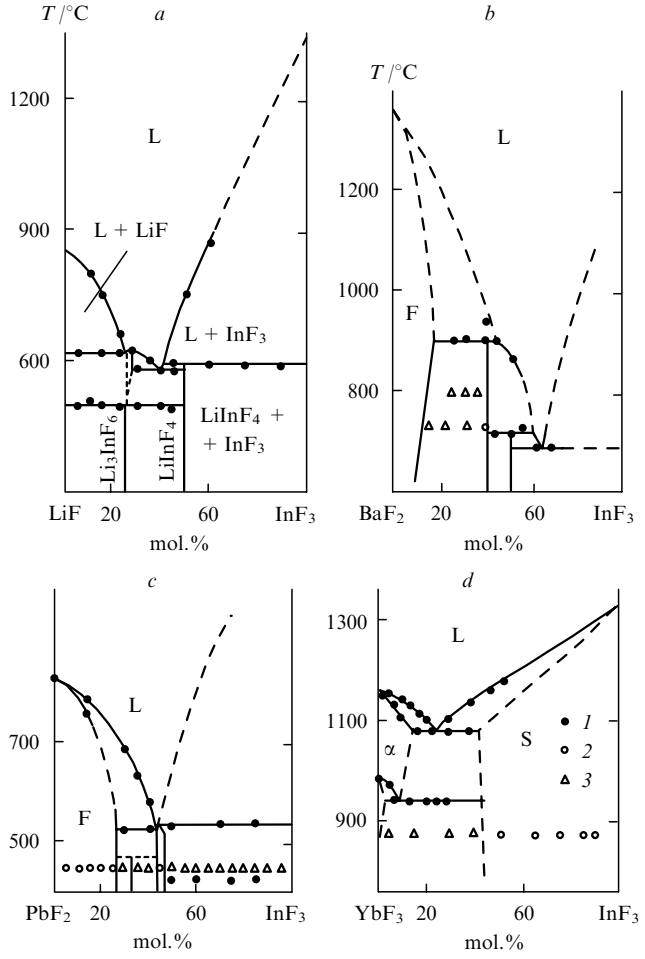


Figure 2. Phase diagrams of the systems $LiF-InF_3$ (*a*), BaF_2-InF_3 (*b*), PbF_2-InF_3 (*c*) and YbF_3-InF_3 (*d*).[48,53] (*1*) DTA data; (*2*) single-phase samples; (*3*) two-phase samples from X-ray powder diffraction data; L, melt; F, solid solution with the fluorite structure; S, solid solution with the ReO_3 structure; α, solid solution with the α-YF_3 structure.

substantially larger than the radii of gallium and aluminium ions.[52]

Ion	La^{3+}	Y^{3+}	Lu^{3+}	In^{3+}	Sc^{3+}
r /Å (c.n. 8)	1.30	1.159	1.117	1.06	1.01

A morphotropic transition occurs on going from InF_3 to trifluorides of heavy rare-earth elements (Lu–Er, Y). Indium fluoride is partially dissolved in high- and low-temperature RF_3 polymorphs corresponding to the structural types α-YF_3 and β-YF_3, respectively.[53]

Being a strong Lewis acid, indium fluoride forms numerous compounds with fluorides of uni- and divalent metals (Fig. 2).[46,54]

III. Optimisation of glass compositions

Undoped indium fluoride is not vitrified. However, like other Lewis acids, such as AlF_3, ZrF_4, GaF_3, ZnF_2 (Fig. 3), it is the 'progenitor' of glass. According to the proposed classification,[11] indium fluoride is classed as a glass former of second degree, since at ordinary quenching rates ($\sim 10^3$ K s^{-1}) glasses are formed in some binary systems, namely, InF_3-BaF_2,[55,56] InF_3-PbF_2[57] and InF_3-SrF_2.[58] The regions of glass formation in the first two systems are in the vicinity of eutectic points; the phase diagram of the third system has not been studied.

First reports on the synthesis of fluoroindate glasses appeared in the early 1980s.[55,59] A double glass-forming system BaF_2-InF_3 was found;[55] however, the glass formed in this system was not sufficiently stable. Numerous stabilising components, *viz*., YF_3, UF_4,[55] FeF_3,[60] ZnF_2, ThF_4,[61] YbF_3,[23,55,62] ScF_3, GaF_3, CdF_2,[63] SrF_2,[58] MgF_2,[57,64] BiF_3[65] and $In(PO_3)_3$,[66] were proposed. A second glass-forming system PbF_2-InF_3 was found almost simultaneously which was doped with CdF_2, ZnF_2, MnF_2 and SnF_2 as stabilising ingredients.

The regions of glass formation in some ternary systems are shown in Fig. 4. Note that the boundaries of the regions of glass formation are tentative. These depend on the experimental conditions and are in particular very strongly dependent on the cooling rate. The data from different studies on the regions of glass formation correlate but do not coincide. For example, glass formation was observed in the binary system BaF_2-InF_3,[55,61] whereas according to the results of another study,[63] only three-component systems $BaF_2-InF_3-MF_n$ did undergo vitrification. The results of studies on the system $BaF_2-InF_3-YF_3$ (*cf*. Refs 57 and 61) are at variance [two regions of glass formation were revealed (*cf*. Ref. 57, Fig. 4 *b*)]. It was stated that the system $BaF_2-InF_3-GaF_3$ has an isolated region of glass formation,[63] while Boutarfaia *et al*.[57] revealed a 'belt' region between the systems BaF_2-InF_3 and BaF_2-GaF_3 (see Fig. 4 *d*). Some discrepancies are found even within the framework of a single study. In particular, in a study,[60] of all the studied systems $PbF_2-InF_3-MF_n$ the glass formation in a binary system PbF_2-InF_3 was revealed only in a single case (see Fig. 4 *g*), while in other cases the glass formation was observed only in three-component systems (Fig. 4 *h*,*i*).

In three-component systems, the rate of devitrification is great. Only in the system $PbF_2-BaF_2-InF_3$ was a glass which has prospects for practical application found. Videau *et al*.[55] have described the four-component glass $40\,InF_3 \cdot 32\,BaF_2 \cdot 17\,YF_3 \cdot 11\,PbF_2$. A 2 mm-thick sample of this glass had the optical transmission edge of 13 μm. Auriault *et al*.[60] obtained a bulk casting for the glass $30\,PbF_2 \cdot 20\,BaF_2 \cdot 50\,InF_3$, the transmission edge in the IR region being ~ 8.2 μm for a 3 mm-thick sample. Attempts were undertaken to vary the composition of this glass by doping it with ZnF_2, SrF_2, AlF_3, YF_3, CdF_2 and PbF_2 to enhance stabilisation. Optical characteristics of some 5–8-component glasses (the refractive indices being in the range from 1.549 to 1.566, the edges of IR transmission varying from 7.7 to 8.9 μm) were determined. The possibility of replacement of InF_3 by GaF_3 as well as doping of glasses with rare-earth fluorides were also

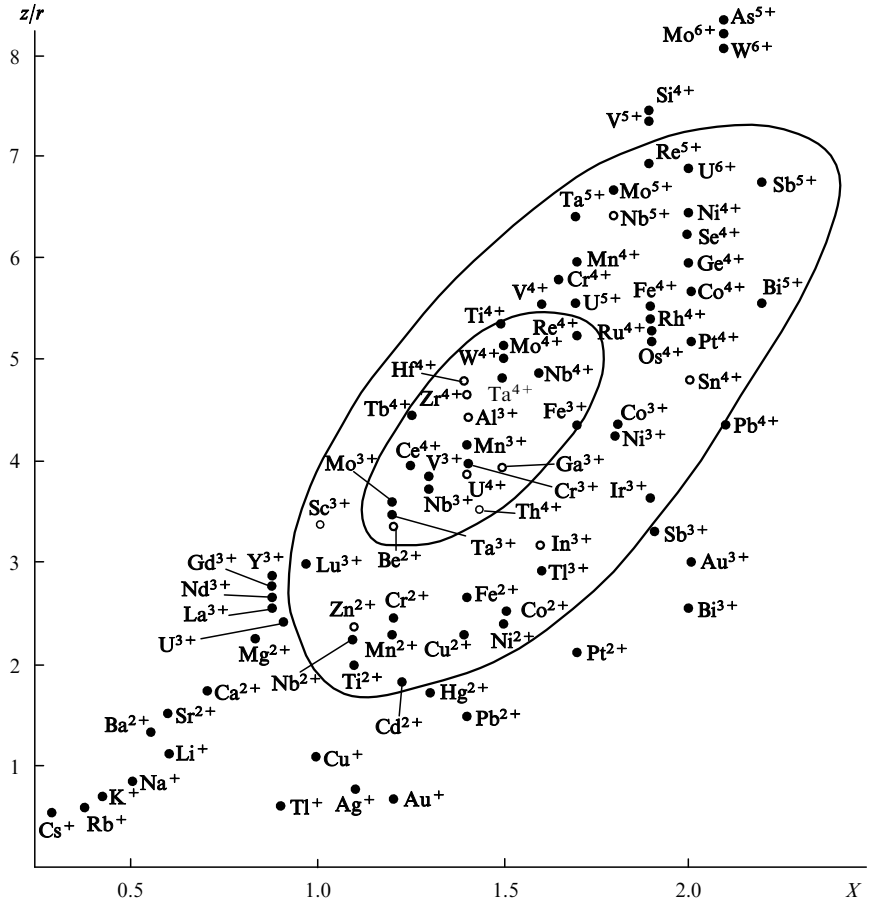


Figure 3. The positions of glass formers in the plot of electronegativity (X) *vs.* generalised moment of cation (z/r),[10] where z is the oxidation state and r is the ionic radius; the open circles refer to the glass-forming cations in fluoride systems.

noted. Of the glasses of this type, some prospects for practical uses have $19\,PbF_2 \cdot 23.8\,BaF_2 \cdot 47.6\,InF_3 \cdot 1.9\,AlF_3 \cdot 4.9\,SrF_2 \cdot 2.8\,YF_3$[67] and $48\,InF_3 \cdot 24\,PbF_2 \cdot 24\,BaF_2 \cdot 3\,LaF_3 \cdot 1\,LuF_3$.[68]

Further search for optimum compositions was conducted for the Pb-free glasses (apparently, this was related to the idea of an increase in T_g and enhancement of the thermal stability of glasses). Gradual increase in the stability was achieved by increasing the number of components. For example, Bouaggad *et al.*[23] found a glass with composition $30\,BaF_2 \cdot 30\,InF_3 \cdot 30\,ZnF_2 \cdot 10\,ThF_4$ in a four-component system (1 cm-thick samples were prepared) and a glass $30\,BaF_2 \cdot 30\,InF_3 \cdot 20\,ZnF_2 \cdot 10\,YbF_3 \cdot 10\,ThF_4$ was found in a five-component system. Chiaruttini *et al.*[43] used the latter glass (the sample with $R_c = 120$ K min^{-1}) as the initial system in the experiments aimed at the increase in the number of glass components. Partial replacement of InF_3 by GaF_3 decreased R_c; the minimum values (20–25 K min^{-1}) were observed for a glass containing 8 mol.%–14 mol.% of GaF_3. Synthesis of several stable glasses was carried out by increasing the number of components of the system. These include $30\,BaF_2 \cdot 18\,InF_3 \cdot 12\,GaF_3 \cdot 20\,ZnF_2 \cdot 10\,YbF_3 \cdot 6\,ThF_4 \cdot 4\,ZrF_4$ (glass BIGaZYbTZr, $R_c = 6$ K min^{-1}) and $30\,BaF_2 \cdot 18\,InF_3 \cdot 12\,GaF_3 \cdot 16\,ZnF_2 \cdot 10\,YbF_3 \cdot 10\,ThF_4 \cdot 4\,MnF_4$ (glass BIGaZYbTMn, $R_c = 6$ K min^{-1}).[43, 69]

These glasses may be regarded as the known glasses $15\,BaF_2 \cdot 28.3\,ZnF_2 \cdot 28.3\,YbF_3 \cdot 28.3\,ThF_4$[70] and $12.5\,BaF_2 \cdot 26.25\,YbF_3 \cdot 35\,ThF_4 \cdot 26.25\,MnF_2$[71] modified in order to increase their stability and decrease the content of radioactive thorium.

A rather stable composition $40\,InF_3 \cdot 20\,ZnF_2 \cdot 20\,BaF_2 \cdot 20\,SrF_2$ (glass IZBS) has become the 'parent' of a separate family of glasses.[58] Messaddeq *et al.*[39] varied this composition by adding PbF_2, CdF_2, CaF_2, NaF and GdF_3. Taking into account the ΔT values, these authors have selected the most stable composition, *viz.*, $40\,InF_3 \cdot 20\,ZnF_2 \cdot 20\,SrF_2 \cdot 16\,BaF_2 \cdot 2\,GdF_3 \cdot 2\,NaF$, with the refractive index n equal to 1.4930. Isomorphic replacement of InF_3 by GaF_3 was carried out in a wide range (up to 30 mol.% of GaF_3, with an optimum of 6 mol.% of GaF_3) in order to decrease n.[72]

Further variations of compositions were undertaken with the aim of enhancement of the resistance of glasses to crystallisation, changes of physical properties (in particular, for selecting the appropriate core/cladding combinations in optical fibres), incorporation of corresponding activators for the appearance of special properties of glasses which allow their use in generators of stimulated radiation and scintillation instruments.

In order to remove optically active Yb^{3+} and Mn^{2+} ions, Adam *et al.*[26] selected an eight-component composition $27BaF_2 \cdot 18InF_3 \cdot 12GaF_3 \cdot 20ZnF_2 \cdot 10LuF_3 \cdot 6ThF_4 \cdot 4ZrF_4 \cdot 3PbF_2$, which possessed however a somewhat higher critical cooling rate (16 K min^{-1}). It is of note that for some practical applications the presence of ytterbium is desirable (see, *e.g.*, Ref. 16).

Charron *et al.*[73] studied the replacement of BaF_2 by lithium, sodium and potassium fluorides in the glass $30\,BaF_2 \cdot 18\,InF_3 \cdot 12\,GaF_3 \cdot 20\,ZnF_2 \cdot 10\,YbF_3 \cdot 10\,ThF_4$ (BIGaZYbT). The incorporation of alkali metals decreased the refractive index; T_g was decreased upon addition of LiF and NaF and remained virtually unaltered upon introduction of KF. The critical cooling rates remained approximately at the same level (18 K min^{-1} for the initial glass and 12, 7 and 24 K min^{-1} for the glasses doped with 5 mol.% of LiF, 12.5 mol.% of NaF and 5 mol.% of KF, respectively). A family of glasses $30\,BaF_2 \cdot 30\,InF_3 \cdot 10\,ThF_4 \cdot 9\,ZnF_2 \cdot 20\,MF \cdot 1\,RF_3$ (M = Li, Na, K; R = Pr, Nd, Tb) with high contents of alkali metal fluorides has been described.[74]

In order to reduce the energy of phonons (and thus shift the absorption edge to the far IR region), Adam *et al.*[75] attempted to decrease the content of InF_3 (and fluorides of other trivalent

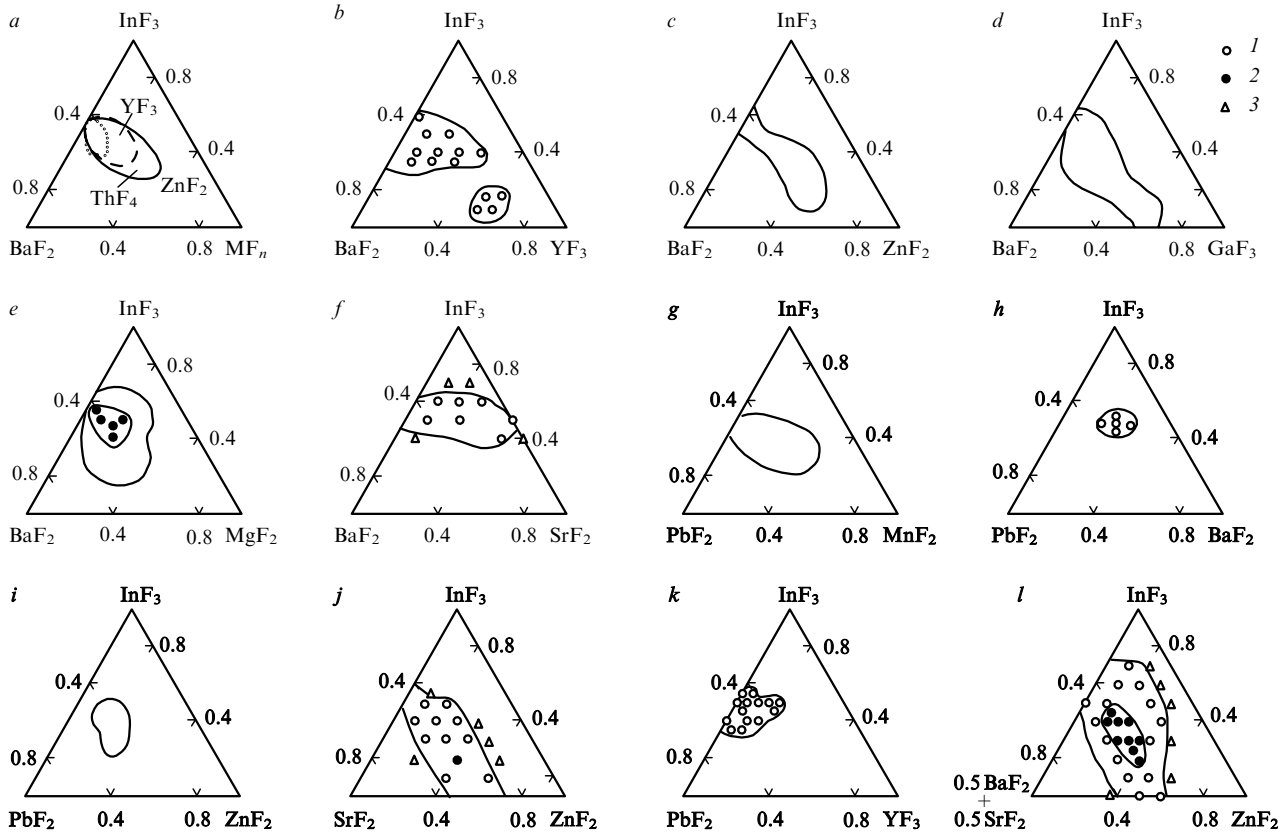


Figure 4. Regions of glass formation in systems involving InF_3: (*a*) $BaF_2-InF_3-MF_n$ (M = Y, Th, Zn);[61] (*b*) $BaF_2-InF_3-YF_3$;[57] (*c*) $BaF_2-InF_3-ZnF_2$;[58] (*d*) $BaF_2-InF_3-GaF_3$;[57] (*e*) $BaF_2-InF_3-MgF_2$;[57] (*f*) $BaF_2-InF_3-SrF_2$;[58] (*g*) $PbF_2-InF_3-MnF_2$;[59,60] (*h*) $PbF_2-InF_3-BaF_2$;[60] (*i*) $PbF_2-InF_3-ZnF_2$;[60] (*j*) $SrF_2-InF_3-ZnF_2$;[58] (*k*) $PbF_2-InF_3-YF_3$;[57] (*l*) $(0.5\,BaF_2 + 0.5\,SrF_2)-InF_3-ZnF_2$;[58] (*1*) quenched glasses; (*2*) cast glasses; (*3*) glass-ceramic.

metals) below 10 mol.%. The modified glass IZBS with composition $12.5\,BaF_2 \cdot 30\,InF_3 \cdot 30\,ZnF_2 \cdot 12.5\,SrF_2 \cdot 8\,NaF \cdot 5\,CdF_2 \cdot 2\,LaF_3$ [58] was taken as the base. It turned out that upon substitution of zinc for indium the stability of the glass is decreased. The problem of stability was solved in part by replacement of certain portion of InF_3 by GaF_3 and optimisation of the content of modifiers.

Qui *et al.*[76] studied the possibility of incorporation of SnF_2 into a glass of the IZBS type with composition $15\,BaF_2 \cdot 40\,InF_3 \cdot 20\,ZnF_2 \cdot 20\,SrF_2 \cdot 2\,NaF \cdot 3GdF_3$. It was found that it is possible to replace BaF_2, ZnF_2 or SrF_2 by SnF_2 (up to 15 mol.% – 20 mol.%); however, in all the cases T_g and the difference $T_x - T_g$ decreased. With the SnF_2 content above 20 mol.%, crystal phases appear, including that of InF_3. Upon variation of the BaF_2 to SrF_2 ratio, a glass with intermediate composition was selected which exhibited maximum stability (judging from the ΔT value).

Zhang and Poulain [31] studied the effect of additions of rare-earth fluorides on the properties of the glass with composition $30\,PbF_2 \cdot 20\,GaF_3 \cdot 15\,InF_3 \cdot 20\,GdF_2 \cdot 15\,ZnF_2$; up to 10 mol.% of RF_3 (R = La, Ce, Pr, Nd, Gd, Er, Yb and Lu) was introduced. It was established that the stability of the glass first increased and then diminished passing through a maximum with 1 mol.% – 2 mol.% of RF_3. On the whole, rare-earth fluorides act as modifiers. Up to 20 mol.% of GdF_3 may be incorporated into the glass-forming system $BaF_2 \cdot InF_3 \cdot ZnF_2$;[77] however, the compositions including 10 mol.% of GdF_3 and 10 mol.% of SrF_2 are the most stable.

Akella *et al.*[78] studied the possibility of variation of the composition of the nine-component glass $28\,InF_3 \cdot 20ZnF_2 \cdot 16.5BaF_2 \cdot 12GaF_3 \cdot 9PbF_2 \cdot 6NaCl \cdot 5SrF_2 \cdot 3CaF_2 \cdot 0.5PrF_3$, which has the optical transmission edge at 10 μm. Sodium chloride was introduced to increase the cross-section of absorption at *f–f* transitions of rare-earth elements. It was found that 10 mol.% of GaF_3 can be replaced by InF_3, 4 mol.% of GaF_3 can be replaced by YF_3, whereas PbF_2 can be totally replaced by CaF_2 or partially replaced by SrF_2 or BaF_2 without crystallisation.

Delben *et al.*[79] studied a glass of the type IZBS doped with 5 mol.% of NaCl or LiCl. Complex temperature dependence of viscosity was established and bifurcation of temperature T_g was noted. Taking this into account, a two-phase model of glass was proposed.

Compositions and properties of some fluoroindate glasses are listed in Table 1, while the evolution of their compositions is reflected by Scheme 1.

The stabilities of glasses could be enhanced upon increase in the number of components of the system. This method is known as 'the confusion principle'.[70] The efficacy of this approach is explained by the fact that it is difficult to attain an ordered structure (the obstruction effect) [76,86] with great diversity of types of local ordering, *i.e.*, polymorphism of clusters. It is of note that the glasses BIGaZYbTZr and BIGaZYbTMn [69] contain each six (!) glass formers per one modifier. In many cases, the increase in the number of components and isomorphous replacements of one glass component by another result in the appearance of a stabilising 'polycationic effect', which consists in the enhancement of glass stability reaching a maximum for some intermediate composition.[87] For fluoroindate glasses of different compositions, this effect is observed upon partial isovalent substitution of GaF_3 for InF_3 [43,57,75,88] and heterovalent substitution of ZnF_2 for InF_3 [75] (isomorphism of glass formers) as well as strontium for barium [75] (isomorphism of modifiers). Destabilisation observed upon substitution of ZnF_2 for InF_3 is apparently explained by the fact that the initial glass has already been stabilised (the optimum

Table 1. Some properties of fluoroindate glasses: temperatures (°C) of glass transition T_g, onset of the exothermic crystallisation T_x, maximum peak of the exothermic crystallisation T_c and onset of melting (solidus) T_m, refractive index for white radiation or at a wavelength of 584.9 nm (n), density (d /g cm^{-3}) and coefficient of thermal expansion (α /10^7 K^{-1}).

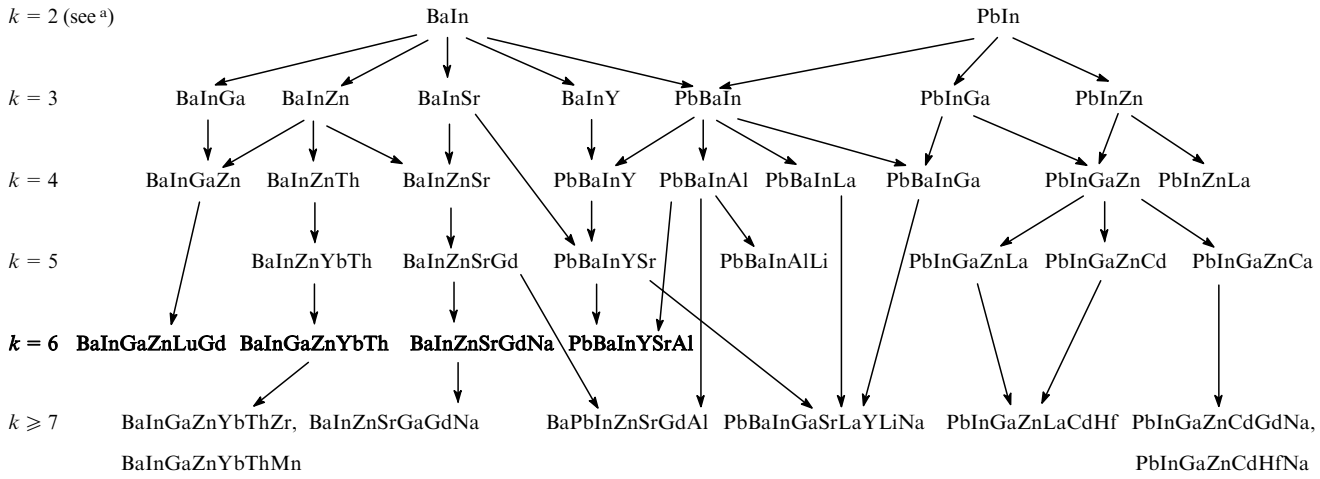
Composition (mol.%)	T_g	T_x	T_c	T_m	n	d	α	Ref.
40 InF_3 · 43 BaF_2 · 17 YF_3	332	400	–	–	–	–	–	55
41 InF_3 · 43 BaF_2 · 16 YbF_3	328	388	–	–	–	–	–	55
40 InF_3 · 44 BaF_2 · 16 UF_4	307	377	–	–	–	–	–	55
40 InF_3 · 23 BaF_2 · 21 CaF_2 · 16 UF_4	298	357	–	–	–	–	–	55
40 InF_3 · 32 BaF_2 · 17 YF_3 · 11 PbF_2	304	372	–	–	–	–	–	55
37 InF_3 · 22 BaF_2 · 21 MnF_2 · 15 YF_3 · 5 LaF_3	306	356	–	591	–	–	–	80
37 InF_3 · 22 BaF_2 · 21 CdF_2 · 15 YF_3 · 5 LaF_3	306	356	–	591	–	–	–	80
20 PbF_2 · 40 CdF_2 · 40 InF_3	222	255	–	–	–	–	–	60
48 PbF_2 · 25 ZnF_2 · 27 InF_3	214	258	–	–	–	–	–	60
40 PbF_2 · 30 MnF_2 · 30 InF_3	209	263	–	–	–	–	–	60
40 PbF_2 · 25 MnF_2 · 35 InF_3	202	238	–	–	–	–	–	60
30 PbF_2 · 20 BaF_2 · 50 InF_3	250	318	–	588	1.5492	–	–	60
20 PbF_2 · 30 BaF_2 · 50 InF_3	283	351	–	–	–	–	–	60
40 BaF_2 · 40 FeF_3 · 20 InF_3	336	409	–	–	–	–	–	60
30 BaF_2 · 30 InF_3 · 20 ZnF_2 · 10 YbF_3 · 10 ThF_4	324	447	–	650	1.517	5.56	171	23
50 CdF_2 · 35 GaF_3 · 15 InF_3	285	367	–	580	–	–	–	63
40 InF_3 · 25 BaF_2 · 20 ZnF_2 · 5 CdF_2 · 10 NaF	283	346	–	537	1.495	5.09	–	63
55 InF_3 · 22.5BaF_2 · 22.5 SrF_2	324.5	381	386	–	–	–	–	58
40 InF_3 · 40 BaF_2 · 20 ZnF_2	287	360	–	–	–	–	–	58
40 InF_3 · 20 BaF_2 · 20 ZnF_2 · 20 SrF_2	300.6	388	396	–	1.5005	5.14	187	58
30 InF_3 · 15 BaF_2 · 30 ZnF_2 · 20 SrF_2 · 5 CdF_2	290.6	393	401	–	1.4990	5.05	–	81
50 InF_3 · 40 YF_3 · 10 BaF_2	333	416	425	–	–	4.96	–	57
50 InF_3 · 3 YF_3 · 33 BaF_2 · 14 SrF_2	323	395	401	–	–	5.09	–	57
50 InF_3 · 5 YF_3 · 31.5 BaF_2 · 13.5 SrF_2	328	412	419	–	–	5.10	–	57
45 InF_3 · 10 YF_3 · 31.5 BaF_2 · 13.5 SrF_2	339	390	394	–	–	5.07	–	57
45 InF_3 · 5 YF_3 · 35 BaF_2 · 15 SrF_2	327	385	394	–	–	5.10	–	57
50 InF_3 · 5 YF_3 · 13.5 BaF_2 · 31.5 SrF_2	332	418	425	–	–	5.02	–	57
40 InF_3 · 20 BaF_2 · 20 ZnF_2 · 20 SrF_2	300.6	388	396	–	1.5005	5.14	187	58
40 InF_3 · 20 ZnF_2 · 20 SrF_2 · 15 BaF_2 · 5 CdF_2	291	383	400	–	1.4980	–	182	39
40 InF_3 · 20 ZnF_2 · 5 SrF_2 · 25 BaF_2 · 10 PbF_2	277	366	372	–	1.5300	–	189	39
40 InF_3 · 20 ZnF_2 · 20 SrF_2 · 15 BaF_2 · 5 CaF_2	295	385	390	–	–	–	186	39
30 InF_3 · 30 ZnF_2 · 20 SrF_2 · 15 BaF_2 · 5 NaF	290	380	389	–	1.4870	–	192	39
40 InF_3 · 20 ZnF_2 · 20 SrF_2 · 17 BaF_2 · 2 GdF_3 · LaF_3	294	390	410	–	1.5080	–	–	39
40 InF_3 · 20 ZnF_2 · 20 SrF_2 · 16 BaF_2 · 2 GdF_3 · 2 NaF	290	390	401	–	1.4930	4.99	–	39, 82
15 InF_3 · 20 GaF_3 · 30 PbF_2 · 20 CdF_2 · 15 ZnF_2	260	354	364	–	–	–	–	83
	243	354	374	–	1.611	6.017	166	31
30 BaF_2 · 18 InF_3 · 12 GaF_3 · 20 ZnF_2 · 10 YbF_3 · 6 ThF_4 · 4 ZrF_4	330	442	–	641	1.5050	5.44	171	43
30 BaF_2 · 18 InF_3 · 12 GaF_3 · 16 ZnF_2 · 10 YbF_3 · 10 ThF_4 · 4 MnF_4	332	442	–	634	1.5090	5.56	–	43
27 BaF_2 · 18 InF_3 · 12 GaF_3 · 20 ZnF_2 · 10 LuF_3 · 6 ThF_4 · 4 ZrF_4 · 3 PbF_4	332	478	–	579	–	–	–	26
29 PbF_2 · 3 $PbCl_2$ · 15 InF_3 · 20 GaF_3 · 13 ZnF_2 · 20 CdF_2	250	370	–	–	1.60	–	170	32
10 BaF_2 · 6I nF$_3$ · 47 ZnF_2 · 26 SrF_2 · 4 GaF_3 · 5 CdF_2 · 2 LaF_3	306	380	–	–	1.498	4.88	209	75
15 BaF_2 · 40 InF_3 · 20 ZnF_2 · 20 SrF_2 · 2 NaF · 3 GdF_3	291	383	–	–	–	5.114	–	76
40 InF_3 · 20 ZnF_2 · 20 BaF_2 · 10 SrF_2 · 10 GdF_3	300	405	424	582	–	–	–	77
30 BaF_2 · 30 InF_3 · 15 ZnF_2 · 25 BiF_3	250	–	350	–	1.578	–	–	65
28 InF_3 · 20 ZnF_2 · 16.5 BaF_2 · 12 GaF_3 · 9 PbF_2 · 6 NaCl · 5 SrF_2 · 3 CaF_2 · 0.5 PrF_3	–	–	–	–	1.5091	5.15	–	78
36 InF_3 · 20 ZnF_2 · 20 SrF_2 · 16 BaF_2 · 6 GaF_3 · 2 NaF	–	–	–	–	1.49	4.8	–	84
30 BaF_2 · 18 InF_3 · 12 GaF_3 · 20 ZnF_2 · 9 YF_3 · 6 ThF_4 · 4 ZrF_4 · NdF_3	320	–	–	–	–	–	–	85
19 ZnF_2 · 17 InF_3 · 17 GaF_3 · 43 PbF_2 · 4 LaF_3	236	327	–	460	1.61135	6.32	–	86
30 PbF_2 · 20 GaF_3 · 15 InF_3 · 15 ZnF_2 · 20 CaF_2	265	345	–	–	1.564	5.55	–	see [a]

[a] The data of R Lebullenger, L A O Nuces and A C Hernandes, in *The XIIth International Symposium on Non-Oxide Glasses and Advanced Materials (Extended Abstracts), Florianópolis, Brazil, 2000* p. 439.

ratio InF_3 : ZnF_2 has been reached). Upon partial substitution of AlF_3 for InF_3,[38,43] the stabilities of glasses did not change. Substitutions of SrF_2 for PbF_2 and of PbF_2 for BaF_2 have not been studied systematically. Substitution of PbF_2 for BaF_2 in the BIZYbT glass leads to its destabilisation.[43]

Considering the isomorphism concept, the substitutions observed are well expected and correspond to the so-called 'geochemical star' of indium.[89] In particular, a wide heterovalent isomorphism of indium and zinc is known among compounds with different ionicities. From the physicochemical viewpoint and in conformity with the Rawson principle, the essence of the 'confusion principle' is reduced to the decrease in the temperatures of eutectics as the number of components in the system is increased.[10] It is of note that Bouaggad *et al.*[23] suggested that the five-component composition of BIZYbT with a melting temperature of 650 °C is close to the eutectic composition; however, the thermogram derived from the same study contradicts this suggestion. The thermogram of the IZSB glass does not correspond to the eutectic either.[90] This discrepancy may be indicative of the potential reserves of the stability enhancement. However, the

Scheme 1



[a] k is the number of components; only cationic composition of glasses is indicated.

studies performed so far show that the stabilities of fluoroindate glasses virtually reach 'saturation' with the number of components equal to 6 or 7. The attainment of saturation corresponds to the Berezhnoi rule[91] for the temperatures of multicomponent eutectics.

IV. The structures of fluoroindate glasses

In order to elucidate the structures of fluoroindate glasses, it is necessary to know the structures of crystalline compounds which are similar in their compositions to those of the glasses under study and to reveal the types of polymers favouring the glass formation (Stenwart's criterion[1]). Relevant measurements showed that the temperature dependences of the viscosities of melts of a number of fluoroindate glasses (like those of fluorozirconate glasses) are substantially non-linear in the coordinates $\log\eta \sim 1/T$. This is the indication of 'fragile' glasses and suggests that the polymerisation processes occur during the cooling of melts. This also points to higher ionicities of fluoride glasses compared, *e.g.*, with 'strong' silicate glasses.[92,93]

The crystal structures of indium fluoride compounds are very diverse and are similar to the structures of ScF_3 compounds. The indium cation can have c.n. 6 or 7 (it is not ruled out that its c.n. is 8 in solid solutions).

The most characteristic polyhedra are octahera, often distorted. The structure of InF_3 is a three-dimensional framework of octahedra connected through their vertices (the octahedra are slightly deformed in the low-temperature polymorph). Successive addition of fluorides of uni- and divalent metals to indium fluoride leads to a typical structural depolymerisation of octahedral structures (Fig. 5) with the following sequence: a framework – a layer ($[InF_4]^-$, compounds $MInF_4$) or a corrugated layer ($LiInF_4$) – a framework ($[In_3F_{14}]^{5-}$, compounds $M_5In_3F_{14}$ of the chiolite type) – a chain ($[InF_5]^{2-}$, $BaInF_5$) – isolated octahedra ($[InF_6]^{3-}$, compounds M_3InF_6). In all the cases, the octahedra are linked by vertices through the bridging fluorine atoms.[54,94,95]

The structure of high-temperature β-$Ba_3In_2F_{12}$ (the structural type $Sr_3Fe_2F_{12}$) comprises chains of octahera, in addition to isolated octahedra. Ternary compounds with octahedral formations are known (*e.g.*, of the type of weberite $Na_2M^{II}InF_7$). Compounds with octahedra $[InF_6]^{3-}$ are isostructural to the corresponding fluoroaluminates and fluorogallates.[94]

Yet another important structural motif, which can give polymeric structures, are seven-vertex pentagonal bipyramids $[InF_7]^{4-}$. In compounds of the KIn_2F_7 type, such bipyramids bind to each other through equatorial edges, form layers which are in turn linked to form a three-dimensional framework through the vertices of bipyramids. In compounds $M_2In_3F_{11}$ and MIn_3F_{10} (M = K, Rb, Cs), junctions of bipyramids with octahedra occur. Crystallochemical analysis showed that the structures containing $[InF_7]^{4-}$ are related to the α-U_3O_8 structure, which in turn is a derivative of the α-UO_3 structure.[96] Thus, the corresponding fluoroindates may be regarded as the products of depolymerisation of the virtual InF_3 polymorph of the α-YF_3 (α-UO_3) type. According to the data of X-ray powder diffraction, the structural type inherent in high-temperature polymorphs of fluorides of heavy rare-earth elements is identical to α-UO_3. It may also be described as anti-Li_3N. The structure of hypothetical RF_3 proposed by Aleonard *et al.*[96] may also be one of the α-YF_3 models. On the basis of the corresponding RF_3 polymorphs, solid solutions with indium fluoride are formed (see Fig. 2). The structures of BaR_2F_8 compounds of the type of ortho-rhombic $BaTm_2F_8$ (R = Dy–Yb) and monoclinic $BaLu_2F_8$, in which isomorphous substitutions of indium for rare-earth elements are possible, are related to the structural type α-YF_3.[97]

Yet another type of seven-vertex polyhedron which is found in fluoroindates may be described as trigonal prisms with one capped lateral face. Slightly distorted polyhedra of this type are present in the structures Sr_2InF_7[98] and Pb_2InF_7, which is isostructural to the former, whereas paired seven-vertex polyhedra linked along the edge are found in the low-temperature polymorph of α-$Ba_3In_2F_{12}$.[99] Judging from the interpretation of KYF_4,[100] which is isostructural to $NaInF_4$, the structure of the latter contains chains of the above-mentioned seven-vertex polyhedra. They may be regarded as the products of polymerisation through collectivisation of the 'caps' of dimeric groups identified in α-$Ba_3In_2F_{12}$. The structure of ortho-rhombic polymorphs of β-YF_3 (see Fig. 1) in which InF_3 can also be dissolved (see Fig. 2) may also be represented as the result of polymerisation of such polyhedra to form a three-dimensional framework due to which they are transformed into eight-vertex polyhedra by acquiring one more 'cap' (trigonal prisms with two centred faces).

Thus, in fluoroindate (like in fluorozirconate) glasses different structural units can be responsible for glass formation. In conformity with the known diagrams,[57,61] the regions of glass formation in the systems BaF_2–InF_3–MF_n adjoin the region of primary crystallisation of compound $BaInF_5$ (see Figs 2, 4), which testifies in favour of the octahedral structures of these glasses.

However, the facts that the system BaF_2–InF_3–YF_n contains, in addition to the region of glass formation adjoining the side BaF_2–InF_3, yet another region similar in composition to that of BaY_2F_8[57] and that two types of glasses exist with considerably different T_g allow one to suggest the presence of two structural motifs in fluoroindate glasses (octahedra and pentagonal bipyramids). However, this may simply be related to the existence of two eutectics (without structural differentiation). Grande *et al.*[101]

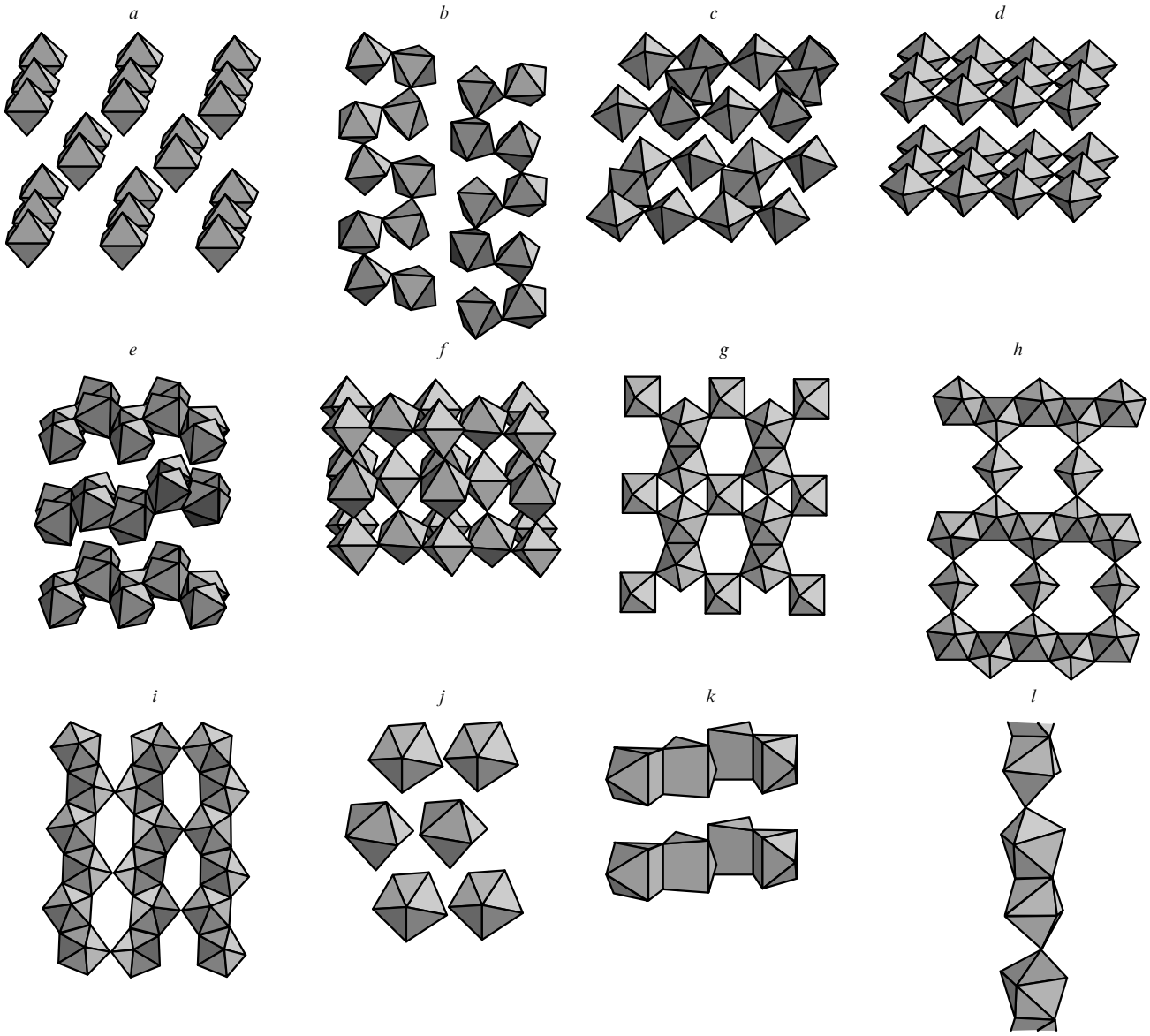


Figure 5. Packings of $[InF_6]^{3-}$ and $[InF_7]^{4-}$ polyhedra in structures of fluoroindates: (*a*) $[InF_6]^{3-}$ in the M_3InF_6 structure; (*b*) $[InF_5]^{2-}$ in the $BaInF_5$ structure; (*c*) $[In_3F_{14}]^{5-}$ in the $M_5In_3F_{14}$ structure; (*d*) $[InF_4]^{-}$ in the $MInF_4$ structure; (*e*) $[InF_4]^{-}$ in the $LiInF_4$ structure; (*f*) InF_3; (*g*) $[In_3F_{10}]^{-}$ in the MIn_3F_{10} structure; (*h*) $[In_3F_{11}]^{2-}$ in the $M_2In_3F_{11}$ structure; (*i*) $[In_2F_7]^{-}$ in the MIn_2F_7 structure; (*j*) $[InF_7]^{4-}$ in the Sr_2InF_7 structure; (*k*) $[In_2F_{12}]^{6-}$ in the structure of low-temperature phase $Ba_3In_2F_{12}$; (*l*) $[In_2F_{11}]^{-}$ in $NaInF_4$.

noted the glass formation on the basis of lithium nitride, which is structurally related to BaY_2F_8.

Wide isomorphism with Ga in fluoride glasses (*cf.*, *e.g.*, Refs 57, 75, 82) suggests the octahedral surrounding of indium. Isomorphism with aluminium is usually restricted;[38] however, complete isomorphism of Al^{3+} and In^{3+} (though, with the conjugated replacement of barium and lead) in both the crystalline and glassy states occurs in the system $PbF_2-BaF_2-AlF_3-InF_3$.[41, 102]

Analysis of binary glasses containing 50 mol.% – 67 mol.% of InF_3 in combination with BaF_2 or SrF_2 by the EXAFS method showed that the nearest surrounding of indium is octahedral, the distance In – F (2.06 – 2.07 Å) being virtually the same as in InF_3 (2.05 Å).[103] According to the data from EXAFS, X-ray radial distribution function and molecular dynamics for the glass $45\,InF_3 \cdot 40\,BaF_3 \cdot 15\,ErF_3$, the mean c.n. values are 7.15, 8.86 and 7.83 for In, Ba and Er, respectively. According to the X-ray photoelectron spectroscopy, the energies of the F_{1s} bond are virtually equal to the arithmetic mean of the energies of the bonds of glass components.[104] Todotoki *et al.*[68] studied the up-conversion luminescence¶ of Er^{3+} in the glass $48\,InF_3 \cdot 24\,PbF_2 \cdot 24\,BaF_2 \cdot 3\,LaF_3 \cdot 1\,ErF_3$ and found that the local frequency of vibrations in the vicinity of Er^{3+} ions (260 ± 10 cm^{-1}) is considerably lower than the mean frequency of the phonon spectrum of the matrix (470 ± 5 cm^{-1}) as determined by Raman scattering. The EPR data on transition metal ions (Cr^{3+}, Ti^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}) in the glass $25.2\,PbF_2 \cdot 22.5\,BaF_2 \cdot 44\,InF_3 \cdot 3.7\,SrF_2 \cdot 3.8\,YF_3 \cdot 0.8\,AlF_3$ provide evidence of their octahedral surrounding.[105]

Important information on the structures of glasses is provided by spectroscopic methods. In the IR and Raman spectra of fluoroindate glasses, there are bands corresponding to the vibrational modes of isolated octahedra $[InF_6]^{3-}$.[106, 107] According to the interpretation of the data from vibrational spectroscopy for the IZBS glass,[106] its structure contains isolated octahedra $[InF_6]^{3-}$. Later, the octahedral coordination of In^{3+} was con-

¶ The up-conversion is the ionic fluorescence at a shorter wavelength than that of the acting laser radiation.

firmed for the series of glasses $60\,InF_3\cdot 40\,BaF_2$, $40\,InF_3\cdot 20\,ZnF_2\cdot 20\,SrF_2\cdot 15\,BaF_2\cdot 5\,CdF_2$ and $20\,InF_3\cdot 40\,ZnF_2\cdot 20\,SrF_2\cdot 15\,BaF_2\cdot 5\,CdF_2$. A suggestion was put forward about the high content of vertex-bound octahedra in the binary glasses and the transition to almost unbound structures in the multicomponent glasses.[108,109] The vibrational modes of the octahedra $[ZnF_6]^{4-}$ and $[InF_6]^{3-}$ lie close to each other. Ignat'eva *et al.*[107] studied glasses in the system $RF_3-PbF_2-MF_2$ (R = Ga, In; M = Zn, Mn, Ba). Analysis by IR and Raman spectroscopy showed that the glasses contain octahedral groups $[InF_6]^{3-}$ and $[GaF_6]^{3-}$, the degree of their polymerisation being higher in the fluorogallate glasses. Based on the analysis of the IR spectra in the system $PbF_2-BaF_2-AlF_3-InF_3-LiF$, Ignat'eva *et al.*[110] suggested that their structures consist of frameworks formed by the octahedra. Upon successive substitution of AlF_3 for InF_3, starting approximately from the ratio 1 : 1 ($\sim$ 15 mol.% of AlF_3), aluminium fluoride forms an independent framework in the glass close to the structural motif in the crystalline $Pb_3Al_2F_{12}$. Incorporation of lithium fluoride disturbs the degree of connectivity of polyhedra in the glass. The fluoroindate glass $15\,BaF_2\cdot 40\,InF_3\cdot 20\,ZnF_2\cdot 20\,SrF_2\cdot 2\,NaF\cdot 3\,GdF_3$ underwent destruction as the degree of polymerisation of octahedra was increased judging from the IR spectra (devitrification upon polymerisation).[76]

Bureau *et al.*[111] used precision ^{19}F NMR spectroscopy to investigate glasses in the system $BaF_2-PbF_2-InF_3$ (PBI) and $48\,PbF_2\cdot 25\,ZnF_2\cdot 27\,InF_3$ (PZI). They found that three types of fluoride ions contribute to the chemical shift: the ions unbound to the glass former, the ions present in isolated octahedra around the glass-forming atom and the bridging fluoride atoms binding the octahedra to each other. The relative contents of these ions are 5%–11%, 62%–68% and 21%–32% for the PBI glasses and 11%, 37% and 52% for the PZI glasses. The dimensionality of octahedral formations for PZI is 2*D*, whereas for PBI it is in the interval between 1*D* and 2*D*.

Thus, according to the classification based on c.n. of the glass-forming cation,[11] the fluoroindate glasses, like the aluminate ones, may be referred to the octahedral glasses. Upon replacement Al → Ga → In, the degree of the glass polymerisation decreased on the whole (it depends strongly on the particular glass composition).

A number of complex fluoroindate glasses include different glass formers. Presumably, these glasses have complex microheterogeneous structures. Azkargorta *et al.*[112] studied properties of the glass $30\,BaF_2\cdot 18\,InF_3\cdot 12\,GaF_3\cdot 20\,ZnF_2\cdot 9\,LuF_3\cdot 6\,ThF_4\cdot 4\,MnF_2\cdot 1\,NdF_3$. Emission of the stimulated radiation at two wavelengths, *viz.*, 1050.2 and 1054.9 nm, was obtained for the laser transition $^4F_{3/2}\rightarrow{}^4I_{11/2}$, which suggests the existence of two spatially separated subsystems with different coordination surroundings of the neodymium ions.

V. Properties and prospects for the application of fluoroindate glasses

Refractive indices of fluoroindate glasses ($n\simeq 1.5$) are somewhat higher than those of the ZBLAN glasses (see Table 1); the values of Abbe numbers ($\nu\simeq 80$), which characterise the dispersion of refractive indices, correspond to the values of this parameter for the fluorozirconate glasses. In the generalised $\nu-n$ diagram, the fluoroindate glasses occupy approximately the same area as the fluorozirconate glasses.[113] The dispersion of refractive indices of glasses of the types BIZYTh and IZBS was measured.[72,114] The refractive indices and dispersions, as well as the theoretical minima of optical losses,[115] can be calculated from the molecular increments.[113] Upon addition of Pb^{2+} and Bi^{3+}, the refractive indices of these glasses increased, while upon substitution of Ga^{3+} for In^{3+} they decreased on the contrary [72] (like upon substitution of Hf^{4+} for Zr^{4+} in the fluorozirconate glasses).

The values of heat and thermal conductivities in fluoroindate glasses are $\sim$ 20% higher than those in ZBLAN, but are approximately the same magnitude lower than those in majority of silicate and phosphate glasses.[116] Studies of the stress relaxations for the glass $40\,InF_3\cdot 20\,SrF_2\cdot 16\,BaF_2\cdot 20\,ZnF_2\cdot 2\,GdF_3\cdot 2\,NaF$ at temperatures below T_g showed that this process is strongly influenced by the atmospheric moisture.[117] Characteristics of some fluoroindate glasses are presented in Table 2.

Table 2. Densities (*d*), heat capacities (*C*) and thermal conductivities (λ) of some fluoroindate glasses.[116]

Composition (mol.%)	*d* /g cm^{-3}	*C* /J g^{-1} K^{-1}	$10^3\,\lambda$ /W K^{-1} cm^{-1}
$30\,PbF_2\cdot 15\,InF_3\cdot 15\,ZnF_2\cdot 20\,GaF_3\cdot 20\,CaF_2$	5.359	0.67	10.4 ± 0.9
$34\,InF_3\cdot 20\,ZnF_2\cdot 20\,SrF_2\cdot 16\,BaF_2\cdot 6\,GaF_3\cdot 4\,NaF$	4.761	0.67	9.9 ± 0.8
$40\,InF_3\cdot 20\,ZnF_2\cdot 20\,SrF_2\cdot 16\,BaF_2\cdot 2\,GdF_3\cdot 2\,NaF$	4.753	0.67	10.2 ± 0.8

As it was mentioned above, smooth pyrohydrolysis of indium fluoride complicates the preparation of high-quality glasses, the appearance of oxofluoride phases inducing devitrification. Jha *et al.*[83] studied the influence of the fluorinating atmosphere on the quality and stability of the glass $15\,InF_3\cdot 20\,GaF_3\cdot 30\,PbF_2\cdot 20\,CdF_2\cdot 15\,ZnF_2$ in the course of its casting. The best samples were obtained when SF_6 was added to nitrogen as the carrier gas, whereas the flow of hydrogen fluoride had a somewhat weaker effect. The poorest effect was produced by ammonium hydrogen fluoride.

In studies of the possibility of the use of fluoroindate glasses as the laser matrices, spectroscopic data on the following dopant ions were analysed: UO_2^{2+} (Ref. 118), Er^{3+} (Refs 84, 119–121), Nd^{3+} (Refs 85, 122–125), Pr^{3+} (Refs 126–128), Tm^{3+} (Refs 129–131), Cr^{3+} (Ref. 132), Yb^{3+} (Ref. 133) and Eu^{3+} (Refs 125, 134). The non-linear effects appearing upon the laser radiation in fluoroindate glasses doped with erbium and neodymium were studied.[121,135]

The up-conversion was studied in the glasses activated by Nd^{3+} (Ref. 136), Tm^{3+} (Refs 131, 137), Yb^{3+} (Ref. 138), $Yb^{3+}-Er^{3+}$, $Yb^{3+}-Tm^{3+}$ or $Yb^{3+}-Pr^{3+}$ (Refs 139–141).

In order to increase the pumping efficiency of praseodymium lasers used for the fibre amplifiers at 1.3 μm, it was proposed to coactivate (sensitise) the fluoroindate glasses containing ytterbium with a third rare-earth element, *viz.*, neodymium or erbium.[16,17]

When selecting the cladding for the glass $30\,BaF_2\cdot 18\,InF_3\cdot 12\,GaF_3\cdot 20\,ZnF_2\cdot 10\,YbF_3\cdot 6\,ThF_4\cdot 4\,ZrF_4$, Rigout *et al.*[38] found that the addition of 10 mol.% of KF, 3 mol.% of NaF (instead of a part of BaF_2) and 6 mol.% of AlF_3 (instead of InF_3/GaF_3) led to $\Delta n = 1.53\%$ with virtually the same coefficients of thermal expansion and T_g. The critical cooling rate is somewhat increased (20 instead of 6 K min^{-1}). Soufiane *et al.*[72] selected the compositions of the core and claddings of glasses of the IZIBS type by varying *n* by way of incorporation of GaF_3 and PbF_2: $\Delta n = 0.24\%$ was achieved.

Jiang *et al.*[32] described the selection of the cladding for the fluoroindate fibres. Good results were obtained for fluorophosphate glasses in combination with the GIPCZ glass. The components of the glass fibre, $29\,PbF_2\cdot 3\,PbCl_3\cdot 15\,InF_3\cdot 20\,GaF_3\cdot 13\,ZnF_2$ (the core) and $20\,NaPO_3\cdot 10\,(NH_4)_2HPO_4\cdot 40\,ZnF_2\cdot 15\,PbF_2\cdot 15\,BaF_2$ (the cladding), have close values of T_g and the coefficients of thermal expansion. Both glasses mix in unlimited proportions.

The technology of manufacture of the optical fibres based on the fluoroindate glasses is making good progress. The first fibres based on the BIZYbT glass had the optical losses of $\sim$ 10 000 dB km^{-1}.[142] For the fibres based on the BIGaZYbTMn glass this value was already 500 dB km^{-1}.[26] Soufiane *et al.*[72] reported the fabrication of an optical fibre with

losses of 400 dB km^{-1} at 1.2 μm. Kanamori *et al.*[143] described the technology of preparation of single-mode fibres with a length up to 500 m from fluoride glasses of the system $InF_3-GaF_3-PbF_2-BaF_2-SrF_2-LaF_3-YF_3-LiF-NaF$. Based on the fluoroindate glass doped with Pr^{3+} with $\Delta n = 3.6\%$, the minimum level of optical losses was achieved (114 dB km^{-1} at a wavelength of 1.23 μm). The coefficient of signal amplification at the wavelength 1.3 μm is 0.18 dB mW^{-1}.This is sufficient for these fibres to be used as laser amplifiers, although the level of optical losses is very far from the theoretical level and is fivefold higher than the level achieved for the optical fibre based on ZBLAN. The reason for such a difference seems to be latent crystallisation. In order to decrease the optical losses, it is necessary to enhance the resistance of glasses to crystallisation and to increase the degree of purification from oxygen-containing admixtures.

Itoch *et al.*[144] used a single-mode fibre with the core from the glass $18\,InF_3\cdot 20\,GaF_3\cdot 32\,PbF_2\cdot 10.5\,ZnF_2\cdot 10.5\,CdF_2\cdot 4\,LaF_3\cdot 5\,HfF_4$ doped with Pr^{3+} and the cladding from the ZBLAN glass. The main characteristics of this fibre are: $N_A \simeq 0.55$ at 0.6 μm, the optical losses are 150–250 dB km^{-1}, the coefficient of signal amplification is 0.29 dB mW^{-1} at 1.3 μm. Optical amplifiers based on fluoroindate glasses doped with Nd^{3+} (Ref. 145) and Pr^{3+} (Ref. 146) have been described.

There are prospects for the use of planar and channel waveguides based on the fluoride glasses, including the fluoroindate glasses, as elements of solid lasers. The idea is to create surface structures with high refractive indices. P de Melo *et al.*[147] obtained such a structure by diffusion of silver ions from the AgF film deposited on the surface of fluoroindate glass. Ionic exchange was observed [148] (Na^+ for Li^+ and K^+) in the glass $15\,BaF_2\cdot 18\,InF_3\cdot 12\,GaF_3\cdot 20\,ZnF_2\cdot 10\,YbF_3\cdot 10\,ThF_4\cdot 15\,NaF$ dipped in the melts of salts. An increase in the refractive index was found in both cases, although judging from the bulk samples,[73] the incorporation of potassium instead of sodium should rather decrease the value of *n*. The effect observed was explained by the mechanical stresses. Josse *et al.*[149] used the surface pyrohydrolysis (treatment with the water vapour): the refractive index increased owing to the ionic substitution of OH^- for F^-. The surface structure was applied by the photolithography method. The fluoride films for planar waveguides can be obtained by physical vapour-phase deposition.[80]

Fluoroindate glasses, particularly those enriched in lead fluoride, are characterised by rather high fluorine ion conductivities,[150] which are however smaller than the conductivities of the crystalline phases of analogous compositions. High mobility of fluorine ions was detected in fluoroindate glasses by the ^{19}F NMR spectroscopy.[107, 151, 152] For the glasses of the type IZBS and $40\,RF_3\cdot 40\,BaF_2\cdot 20\,YbF_3$, the ionic conductivity was observed to decrease [82, 153] upon replacement of indium by gallium and then aluminium. Costa *et al.*[154] studied the mechanical properties of fluoroindate glasses.

VI. Conclusion

In contrast to the fluorozirconate glasses, the compositions of fluoroindate glasses cannot be regarded as optimised. Apparently, in the multicomponent systems involving InF_3 there are several concentration-dependent regions of the stabilities of glasses. It was found that the replacement of InF_3 by GaF_3, BaF_2 or SrF_2 induced a stabilising polycationic effect; however, the possibility of isomorphous substitutions of PbF_2 for BaF_2 has not been studied systematically. It should be noted that the following techniques have a potential in a search for the optimum composition of glasses, *viz.*, the multifactorial design of experiment, the addition of a new component until a new crystalline phase appears as described by Mukhin and Gutkina [10, 155] and physicochemical analysis including prognostication of the coordinates of multicomponent eutectics.[156]

The statements about the higher chemical and thermal stabilities of fluoroindate glasses compared to the fluorozirconate glasses are questionable. Great discrepancies (by two orders of magnitude) in the determination of the critical cooling rates of multicomponent fluoroindate glasses suggest non-reproducibility of the technology of their preparation. The proneness of InF_3 to hydrolysis determines the instability of these glasses and optical losses in the range of 2.0–3.2 μm.

According to the data from vibrational spectroscopy, fluoroindate glasses are characterised by lower degrees of polymerisation of octahedra than fluorogallate and fluoroaluminate glasses. The reasons for this phenomenon are unclear.

The fields of possible applications of fluoroindate glasses have been little studied. Optical transparency over a wide spectral range, comparatively high density and the possibility of doping with different activators increase the prospects of the practical applications of fluoroindate glasses. It is expedient to investigate the possibility of the production of scintillation materials (including those doped with cerium) with the short decay time.[157] Owing to high concentration of indium fluoride, fluoroindate glasses may be applied for the creation of scintillation media for the neutrino detection.[96] In order to manufacture highly efficient readjustable lasers, it seems attractive to co-activate fluoroindate glasses with neodymium and chromium ions.

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