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A NEW FAMILY OF VITREOUS MATERIALS : THE CESIUM ALUMINUM OR GALLIUM THIOHALIDE GLASSES

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ABSTRACT

A new class of non-oxide glasses with the general composition $CsAXY_2$ (A = Al, Ga ; X = S, Se ; Y = Cl, Br) has been isolated and characterized. Raman spectroscopy, investigations of the I.R. multiphonon edge, Differential Thermal Analysis measurements show that these glasses contain a giant polymeric tetrahedra-based anion and have a good stability towards devitrification. Their chemical durability in normal atmosphere is very poor and affects severely their optical properties, specially in the I.R. multiphonon region.

MATERIALS INDEX: thiohalide, gallium, cesium, aluminum

Introduction

Halide and chalcogenide glasses have received special attention as potential candidate for infrared transmission (1, 2). Glass formation in mixed chalcohalide systems has been essentially investigated in adding metal halides or halogens such as Br_2 or I_2 to wellknown glass forming materials like As_2S_3, GeS_2 and so on (3). Very recently, new original glasses have been discovered in the binary system Te-Cl (4). These new vitreous materials containing polymeric chains have modified compositions if Cl is replaced by Br or I and Te partly by Se and exhibit interesting I.R. transmission properties due to the shift of the multiphonon edge.

One of us, R.W. Berg (5), when investigating the solubilities of sulfur and sulfides in chloroaluminate melts remarked the formation of a polymeric material of the composition $CsAlSCl_2$.

This glass compound was assumed to contain the polymeric tetrahedra based anion $|AlSCl_2|_n^{n-}$. The same phenomenon was observed when Al was replaced by Ga (6). In both cases, the melt formed a stable fully transparent glass when cooled at room temperature. It was also observed that these vitreous materials were highly corroded by atmospheric moisture.

In this contribution, we describe new glassy materials of the same family, extended to Se and Br, and we give some complementary features on their thermal and spectroscopical properties.

Method of preparation and new glass compositions

The glass $CsAlSCl_2$ selected as a prototype composition is prepared according to the equation :

$$CsCl + 2/3\ Al + S + 1/3\ AlCl_3 \rightarrow CsAlSCl_2$$

The starting materials are :

- $CsCl$ 99.5 % suprapur MERCK, dehydrated under a HCl gas stream at 200° C for two hours
- Al 99.999 % gold label ALDRICH, treated in a 8M NaOH aqueous solution, then in a mixture 12:10:3 v/v/v of 98 % H_3PO_4, concentrated H_2SO_4 and HNO_3 and finally conserved in CCl_4
- Sulfur is a sublimated MERCK product.
- $AlCl_3$ was prepared from aluminium metal and HCl gas and then purified twice by distillation in a closed glass ampoule.

Because of the extreme moisture sensitivity, weighings and transfer operations of the stoichiometric mixture were done in a N_2 containing dry box having less than 10 ppm of moisture. The mixture is introduced in a silica tube which is evacuated, sealed and then heated to 600° C in a rocking furnace. The melt initially yellow, becomes dark, green, blue, light green and then colourless and viscous after 24 hours. The sequence of the reaction is considered as the following :

$$2/3\ Al + S \rightarrow 1/3\ Al_2S_3$$

Then $1/3\ Al_2S_3 + 1/3\ AlCl_3 + CsCl \rightarrow CsAlSCl_2$

The glassy transparent material is obtained by cooling to room temperature. The relatively high tendency to vitrification is explained by the strong polymerization process of the melt giving a highly viscous liquid. Sometimes, the glass contains some black particles whose origin could come from a partial reduction of SiO_2 by a small amount of Al (see Ref. 28 of (5)).

Other glass compositions

As previously mentioned (6), the glass $CsGaSCl_2$ has also been prepared in the same conditions as the aluminium derivative, and also shows a very poor chemical durability in normal atmosphere.

In order to extend the series of glasses belonging to this family and to try to improve their resistance to corrosion by moisture, many other compositions have been tried, in replacing aluminium by indium, sulfur by selenium, chlorine by bromine or iodine, and cesium by thallium or potassium.

The same procedure as previously described is used for glass preparation. In the case of the bromine derivatives, for instance for the $CsAlSeBr_2$ glass, the method of preparation has been slightly modified in using Br_2 as starting material instead of $AlBr_3$ and following the equation :

$$CsBr + Al + Se + 1/2\ Br_2 \rightarrow CsAlSeBr_2$$

The sealed tube, after being evacuated at N_2 liquid temperature is heated in boiling water in order first to react Al and Br_2 until the brown vapors of Br_2 have disappeared ; then the tube is introduced in the furnace and heated to 600° C. A total of six new compositions have been proved to lead to vitreous materials in just cooling the sealed silica tube at room temperature. The Table I gives the different attempts with the results leading either to vitreous materials or to crystalline compounds.

TABLE I

Experiments on glass formation

Formula	Glass formation
Cs Al S Cl_2 (5)	yes
Cs Al S Cl Br	yes
Cs Al S Br_2 (5)	yes
Cs Al Se Cl_2 (5)	yes
Cs Al Se Cl Br	yes
Cs Al Se Br_2	yes
Cs Al S I_2	no*
Cs Al Se I_2	no*
Cs Al Te Cl_2	no
Cs Al Te Br_2	no
Cs In Te Cl_2	no
K Al S Cl_2	no*
K Al S Br_2	no*
K In S Cl_2	no*
Tl Al S Br_2	no*
Cs $Al_{0,8}$ Se Br_2	no
Cs Al S $Cl_{2,5}$	no
Cs $Al_{1/2}$ $In_{1/2}$ Se Cl_2	no*
Cs $Al_{1/2}$ $In_{1/2}$ S Br_2	no
Cs Al $S_{1/2}$ $Te_{1/2}$ Cl_2	no
Cs Al $S_{1/2}$ $Te_{1/2}$ Br_2	no
Cs $Al_{1/2}$ $In_{1/2}$ $S_{1/2}$ $Te_{1/2}$ Cl_2	no
Cs Ga S Cl_2 (6)	yes

* Sample quenched in cold water.

The Fig. 1 represents some samples of aluminium thiohalide glasses which must be kept in silica sealed tube because of a very fast corrosion by atmospheric humidity with HCl and H_2S vapor formation.

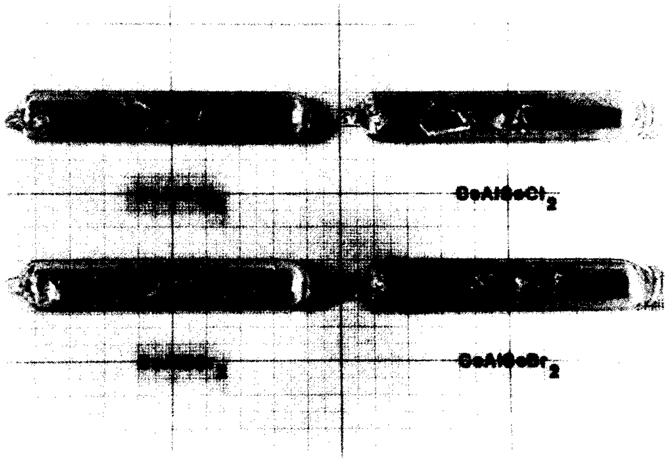

FIG. 1

Samples of $CsAXY_2$ type glasses kept in vacuo.

Thermal properties - Characteristic temperatures

Due to their very poor chemical durability in air and corrosive properties of the melt, these glasses have not been analysed by Differential Scanning Calorimetry using sealed anodized aluminium capsules. The best results have been obtained in sealing small pieces of glass in thin cooled platinum tubes and examined then by D.T.A. The Table II gives the results for six glass compositions, including also the density of the different glasses measured by the hydrostatic method using dry CCl_4.

Table II

Table II

Characteristic temperatures : Tg, Tc, Tl respectively glass, crystallization, liquidus temperatures (melting points) for some aluminium thiohalide glasses. Also the density is given.

Glass composition	Tg (°C)	Tc (°C)	Tl (°C)	Density (gcm^{-3})
$CsAlSCl_2$	193			2.34
CsAlSClBr	174			2.89
$CsAlSBr_2$	167			3.31
$CsAlSeCl_2$	208	262	400	2.88
CsAlSeClBr	192	266	380	3.26
$CsAlSeBr_2$	180	265	370	3.59

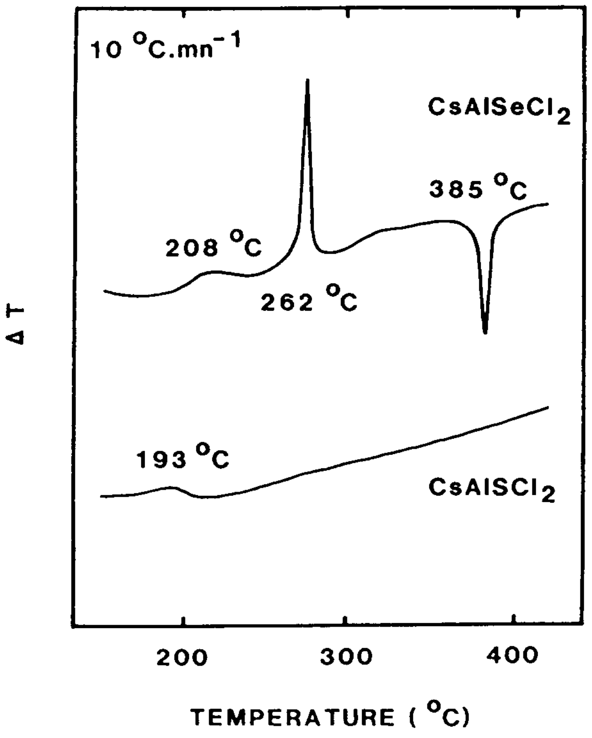

FIG. 2

D.T.A. curves for $CsAlSeCl_2$ and $CsAlSCl_2$. Heating rate is 10° C/min.

It is clear that the sulfur containing compounds are the best glass forming materials and no crystallization has been detected with a heating rate of 10° C/minute. As also indicated on Table II, the Se derivatives have a poor resistance towards crystallization which occurs around 265° C. The Fig. 2 represents a typical D.T.A. curve for the glasses $CsAlSeCl_2$ and $CsAlSCl_2$: for $CsAlSeCl_2$, distinct peaks of crystallization and melting are seen.

Spectroscopical investigations

Previous Raman studies of the glass $CsAlSCl_2$ by Berg (5, 6) showed, as indicated in Fig. 3, a strong band at 325 cm^{-1} attributed to the vibrational mode of the elementary "AlS_2Cl_2" tetrahedra or at 315 cm^{-1} for GaS_2Cl_2. The polymerization of these tetrahedra by sharing the corners occupied by S atoms leads to a polymeric anion $(AlSCl_2)_n^n$ responsible of the high viscosity of the melt and consequently the easy vitrification. These infinite chains represented in Fig. 4 can loose very easily their periodicity by rotation and bending along the Al-S-Al-S bond ; this giant anion is counter-balanced by large Cs^+ cations which keep these chains separated from each other. It must be noted that the size of the alkali cation is critical and that it has not been possible to synthesize the equivalent K^+ or Na^+containing glasses ; however, the chain anions $(AlSCl_2)_n^n$ are formed in melts diluted with $KAlCl_4$ or $NaAlCl_4$ and such melts when not too diluted also tend to form glasses.

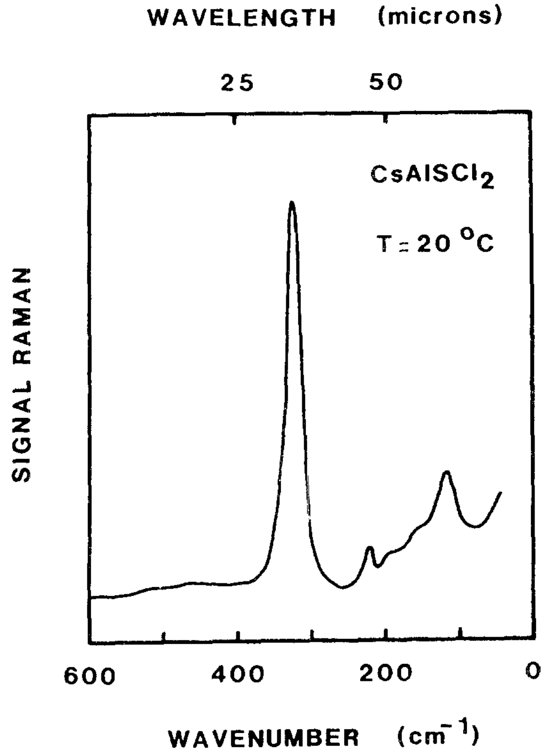

FIG. 3

Raman spectra of $CsAlSCl_2$ at 20° C.

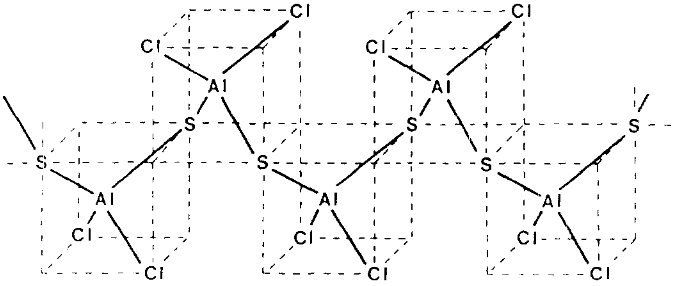

FIG. 4

Representation of the chain $(AlSCl_2)_n^{n-}$

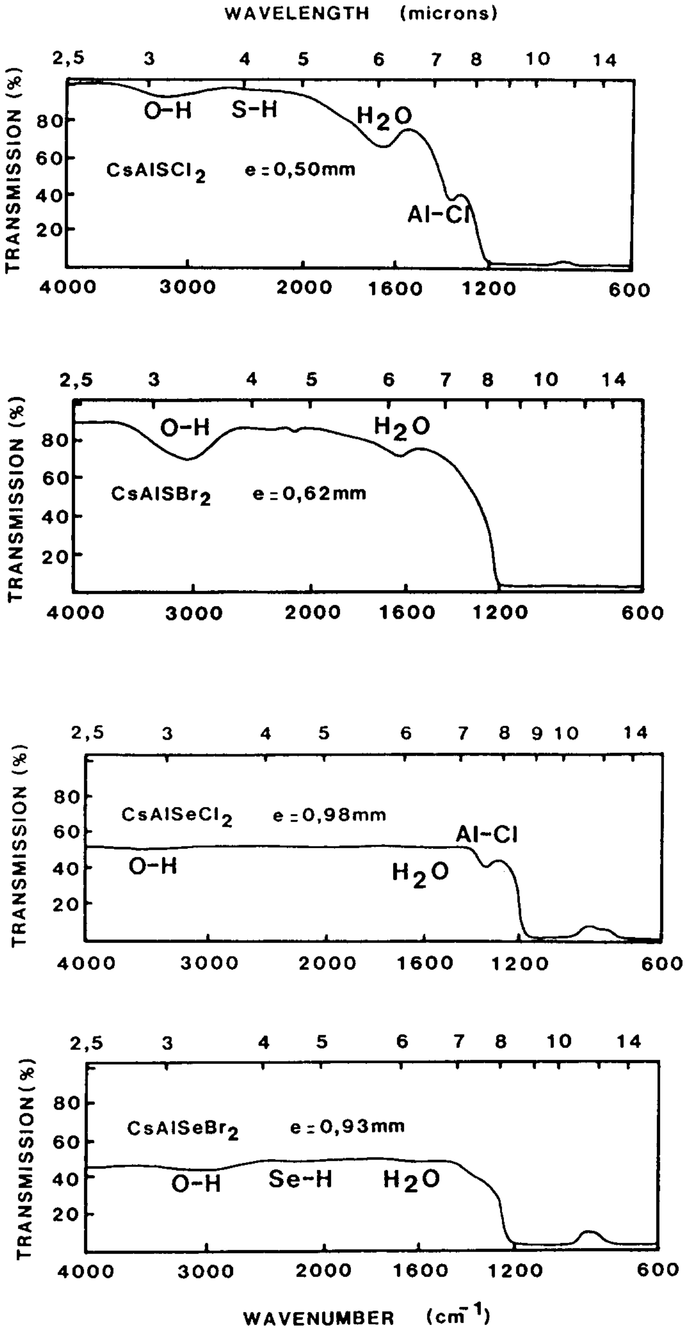

FIG. 5

I.R. transmission spectra for $CsAXY_2$ *type glasses*

With such a prominent Raman frequency at 325 cm^{-1}, the associated vibrational mode of the $CsAlSCl_2$ glass must correspond to a multiphonon absorption edge located in the 10 μm region ; this to be compared to the ZrF_4-based glasses with a frequency ν = 550 cm^{-1} and an I.R. edge at about 7 μm (1) and $ZnCl_2$ glass with ν = 230 cm^{-1} and I.R. edge at 13 μm (2).

The I.R. transmission spectra of several glasses have been recorded in using a special technique because of the very strong corrosive behaviour of these materials in atmospheric conditions.

The pieces of glass roughly polished are handled in a dry box and introduced in a closed sample holder equipped with two KBr windows. This system allows for the recording of the glass spectrum under atmospheric conditions, but a small corrosion of surface is impossible to avoid.

The Fig. 5 represents the I.R. transmission spectra of the four glasses, $CsAlSCl_2$, $CsAlSBr_2$, $CsAlSeCl_2$ and $CsAlSeBr_2$. The examination of these spectra indicates clearly that the samples have been slightly corroded by humidity. The presence of OH peak in the 3 μm region and H_2O vibrations at 6.2 μm shows that some oxygen is present in the glass, leading to the formation of Al-OH or Al-O parasitic bonds which modified strongly the multiphonon absorption region. The I.R. cuttoff in the 7-8 μm region is not corresponding to the Raman frequency of 320 cm^{-1} measured on samples, which have been kept in sealed silica tube and are not corroded.

The ill-defined I.R. edge observed here on the samples examined for I.R. spectra could be attributed to water attack of the samples during the different manipulations.

Conclusion

This new family of non-oxide glasses has been demonstrated to be a new original class of chain libre vitreous materials : the prototype $CsAlSCl_2$ glass with Al-S or Al-Cl bonds was a potential candidate as I.R. transmitting material because of an expected I.R. edge in the 10 μm region and a good stability versus devitrification. Unfortunately because of a poor chemical durability towards humidity, the optical properties of such materials are strongly affected and they will need some special waterproff coating to keep their transparency.

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