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An assessment of some melt-grown halide and chalcogenide cubic compounds as passive 8 to 12 μm optical materials

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On the basis of literature data, certain halide compounds were considered liable to be less water soluble than KCl and were grown to assess their physical properties. Data are presented for $CsCdCl_3$, $Cs_2SnPbCl_6$, $Cs_2Sn_2Cl_3Br_3$, K_2PtCl_6, Rb_2PtCl_6 and Cs_2PtCl_6. Two chalcogenide compounds, Ga_2Se_3 and Ga_2Te_3, were also grown and assessed in relation to existing 8 to 12 μm optical materials. Suggestions for future materials work are made.

1. Introduction

There are a limited number of optical component materials available for 8 to 12 μm applications. Germanium and chalcogenide glass are used in thermal imaging systems while germanium, gallium arsenide or zinc sulphide are used in low-power CO_2 laser systems. Zinc selenide or potassium chloride have been used in high-power CO_2 laser systems. These materials may be regarded as possessing satisfactory but not ideal physical properties in relation to environmental requirements. Any proposed new window materials would be required to possess mechanical properties equal to or better than those of germanium while retaining low absorption between 8 and 12 μm and ideally exhibiting good transmission capability in the visible part of the spectrum. New lens materials would be required to possess improved optical properties in terms of multispectral capability and preferably a smaller n and dn/dt than germanium. New materials should be capable of being synthesized in sizes of at least 30 cm diameter by 3 cm thick to a refractive index homogeneity of $\geqslant 0.0001$ preferably by current technology in order to ensure low production costs. It is the aim of the present work to define the possibilities for new materials accessible by melt-growth techniques and to determine whether any of them would be suitable for development.

2. Materials selection

The development of cholcogenide glasses for 8 to 12 μm applications is well advanced [1, 2] and it is perhaps unlikely that any major new glass systems will emerge from which a material with the required improved physical properties might be obtained. However, there are a great many cubic and hence isotropic crystalline compounds amongst which it might be possible to find new infra-red transmitting materials. Elements and compounds have been classified according to crystal structure and lattice parameter in standard works [3, 4]. This literature was surveyed to identify potentially useful materials upon which experimental assessment work could be done. Materials, obviously unsuitable for the present requirement such as metals, metallic alloys or compounds containing O, OH, H_2O or NH_3 were eliminated. Of the remainder, halides and chalcogenides were assessed as being readily synthesized by current technology, while arsenides, phosphides, silicides, nitrides, borides and carbides were assessed as presenting synthesis problems bearing in mind the size and quality requirements and were not considered further in the present work. Non-cubic compounds were not considered since these are optically anisotropic [5].

2.1. Halides

The aim was to find new halide compounds potentially useful as lens or laser window materials possessing water solubilities less than that of KCl. Amongst the halides, the fluorides offer the highest strength and lowest water solubility but

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there are obvious limitations to their infra-red transparency between 8 and 12 μm. There are of the order of 100 fluoride compounds mostly ternaries which possess NaCl, CsCl, CaF_2 or perovskite crystal structures. About 60% of these are of the formula X_2YF_6 and QYF_6*. One of these Cs_2GeF_6 is reported to show lattice absorptions at 600 and 349 cm^{-1} [6] in a thin film spectrum indicating that in bulk the transmission is unlikely to be useful over the whole of the 8 to 12 μm range. The transmission of one of the perovskites, $KNiF_3$ is reported [7] to cut-off at about 10 μm for a thickness of ~2 mm. Hence fluorides of this general formula XQF_3 numbering ~10% of those listed are unlikely to be useful candidate materials. It was considered that fluorides would be unlikely to offer sufficient transmission between 8 and 12 μm to be useful for current applications.

There are of the order of 50 ternary or quaternary chloride compounds listed under cubic, perovskite or antifluorite structures and a similar number of ternaries, whose structures are in doubt, are known from phase-diagram studies. These compounds can be classified as $XQCl_3$, X_2YCl_6, X_2QCl_4 or X_4QCl_6. There are of the order of 50 bromide and iodide compounds listed of similar structures to those of the chlorides. These, however, are likely to be much more soluble than the chlorides and hence are not of major interest. On the basis of literature data, chemical bonding criteria and anology with known compounds, certain chloride and chlorobromide materials were considered liable to be less soluble than KCl and were grown in order to assess their physical properties. These were $CsCdCl_3$ of perovskite structure, $Cs_2SnPbCl_6$ and $Cs_2Sn_2Cl_3Br_3$ solid solutions of perovskite structure and the antifluorite materials K_2PtCl_6, Rb_2PtCl_6, Cs_2PtCl_6 and Tl_2PtCl_6.

2.2. Chalcogenides

There are of the order of 180 binary and ternary sulphide, selenide and telluride compounds possessing NaCl, zinc blend, spinel, fluorite, pyrite and thorium phosphide structures. About 50% of these are high melting point rare-earth compounds such as CeS_2, EuS, La_2Se_3 and YbTe the majority of which change structure on cooling from the melting point. However, the binary chalcogenide compounds of Sm and Eu do not suffer this phase change being cubic at room temperature, and are thus worthy of further consideration as potential window materials. Some of the remainder of the compounds are relatively low-melting binaries or ternaries such as $CuCrS_4$ or Zn_2GeS_4, some of which might be difficult to synthesize and others may have too low an energy gap for the present requirement. However, two of these Ga_2Se_3 and Ga_2Te_3 are worthy of consideration since they should be readily grown from the melt. The cubic Sm and Eu chalcogenide compounds possess melting points $>2000°$ C and thus would only be accessible in the size and quality required by utilization of the large-scale vapour growth technology recently developed for ZnS and ZnSe. Since this would be a major crystal growth project it was decided to investigate it separately and it is not reported on here.

3. Experimental techniques

3.1. Crystal synthesis

The halide, Ga_2Se_3 and Ga_2Te_3 compound raw materials were obtained from BDH Chemicals and Johnson Matthey Chemicals. Crystals of 20 or 100 g were grown in normal wall silica Bridgeman tubes 18 or 28 mm i.d. as shown in Fig. 1 or where higher pressures were involved 3 mm walled silica tubes were employed. Each tube was rinsed in 50% vol/vol HCl then thoroughly washed with distilled water prior to drying in an air oven and then evacuated to 10^{-5} Torr and outgassed by a prolonged heating of the exterior of the tube with an oxyhydrogen torch. After cooling under vacuum each tube was filled to atmospheric pressure with argon gas, removed from the vacuum system and charged with the previously weighed compound raw material of particle size $\leqslant 7$ mm. Each tube was repumped to 10^{-5} Torr and held at this pressure for $1\frac{1}{2}$ h before sealing with an oxyhydrogen torch. The hexachloroplatinates were only available in powder form and it was necessary to remove water vapour and gases from the powder by vacuum-baking using a resistance heater at 200° C for 3 h before finally sealing the melt tubes. Each growth tube was mounted by its stem in a chuck inside a wire-wound resistance furnace whose temperature profile is indicated in Fig. 1. The furnace temperature was ramped up and down by a motor-driven potentiometer backing-off unit

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*X = monovalent, Q = divalent, Z = trivalent, Y = tetravalent, throughout.

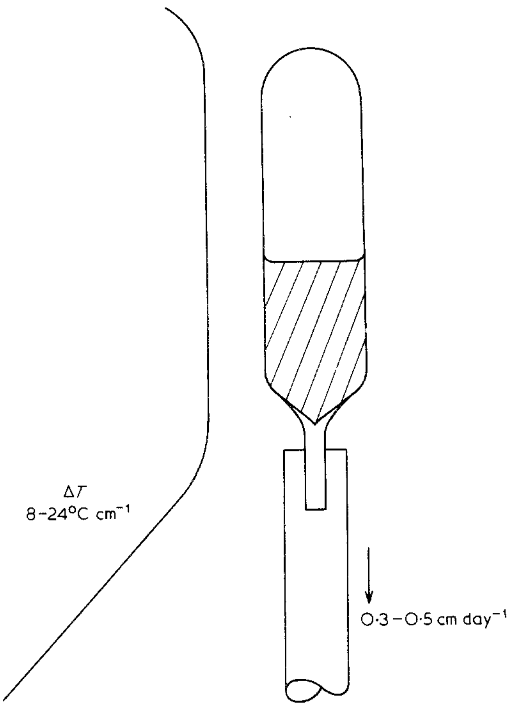

Figure 1 Schematic representation of Bridgeman growth showing the position of a growth tube with respect to the furnace temperature gradient.

in conjunction with an SCR temperature controller capable of maintaining a steady-state furnace temperature within 1° C. After a growth tube had been positioned in the uniform temperature section of the furnace and the temperature had been maintained for 2 h to allow thermal equilibrium to be established, the growth-tube support rod was gradually withdrawn from the furnace by means of a rack and pinion driven by a motorized gear box. By this means the growth tube was lowered pointed-end first through a temperature gradient of 8 to 24° C cm^{-1} depending upon the temperature of the hot zone at a rate of 0.3 to 0.5 cm day^{-1}. When all of the melt had been crystallized the furnace temperature was ramped down to room temperature. Specimens for physical property measurements were cut from the boules with a slow-speed diamond saw and polished as necessary by conventional techniques.

3.2. Physical measurements

A Du Pont 900 thermal analyser console, a differential scanning calorimeter cell, a standard DTA cell and a thermomechanical analyser were employed in making thermal measurements. General visual examination of materials was carried out on a visible and infra-red microscope (1 μm) and the transmittance was measured on a Unicam SP1200 spectrophotometer in the 2.5 to 24.0 μm range. Density measurements were made by the Archimedes method and hardness was determined by the Vickers diamond indentation method [2].

Water solubilities were determined by dissolving the material in a minimum quantity of water at 100° C allowing the solution to cool and the excess solute to precipitate over a 3 day period and then evaporating an aliquot of this saturated solution to dryness and determining the weight of dissolved material. X-ray determinations were carried out in some cases on the raw materials and on the grown crystals by the powder method and the Läue technique. Refractive indices were calculated from the transmission curves.

4. Experimental results

4.1. $CsCdCl_3$

Lump $CsCdCl_3$ was obtained from BDH Chemicals and the melting point was determined by DTA. A crystal was then grown in a normal wall evacuated and sealed silica Bridgeman tube as described in Section 3.1. The resulting single crystal was pale straw coloured, visually transparent and slightly cracked. Sufficiently large pieces were available for cutting into specimens for the measurement of physical properties. These properties are listed in Table I and a transmission curve for the 8 to 20 μm spectral region is shown in Fig. 2. Additional growth runs were completed employing slower ramp cooling and/or annealing at 450° C in an attempt to avoid the crystals cracking. This was unsuccessful and all of the crystals contained moderate to minor cracks. The direction of growth of all of these crystals was found to be ~ 3 1 1.

4.2. $Cs_2SnPbCl_6$ and $Cs_2Sn_2Cl_3Br_3$ solid solutions

KCl and KBr are low absorption but also low strength and soft materials. A 0.67/0.33 KCl/KBr solid solution was researched [8] in an attempt to retain the low absorption properties while improving the mechanical properties by a process of solid-solution hardening. This was successful in producing a relatively uniform crystalline material possessing improved physical properties. The literature suggests that single-phase solid solutions of perovskite cubic structure [9] at room temperature are obtainable from several mixed chlorides or chlorobromides. Two typical solid solutions from

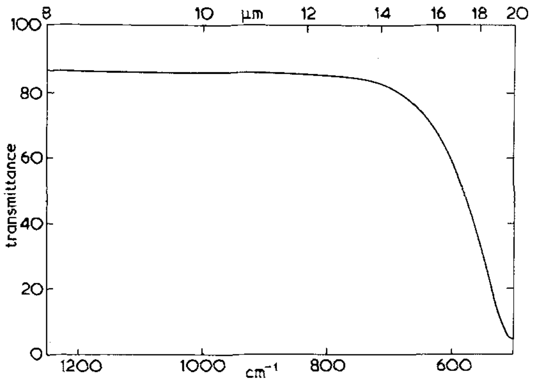

Figure 2 Infra-red transmission of a 3.5 mm thick slice of $CsCdCl_3$.

this group were grown in order to assess the prospects of improved chemical and mechanical properties over those of KCl/KBr. Lump $Cs_2SnPbCl_6$ and $Cs_2Sn_2Cl_3Br_3$ were obtained from BDH Chemicals and grown as described in Section 3.1. The resulting $Cs_2SnPbCl_6$ was mid-yellow in colour, transparent near the growth-initiating tip of the Bridgeman tube and opaque at the end of the boule, which was the last to freeze, indicating major compositional segregation during the growth. Measurements were made on the transparent section of the boule and physical property data are listed in Table I. The $Cs_2Sn_2Cl_3Br_3$ boule after growth was dark red in colour, transparent near the growth tip, and opaque at the end which was last to freeze. Again the data listed in Table I were measured on material from the transparent end of the boule.

4.3. Hexachloroplatinates

Work on the gel growth of small single crystals of this family of materials has been reported [10] but the present authors are not aware of any attempts to grow reasonably large crystals from the melt. Since this was thought to be feasible, K_2PtCl_6 powder was obtained from BDH Chemicals for initial DTA assessment. This indicated that a bake-out to remove water vapour would be necessary and clearly showed that the material decomposes on heating in an open capsule forming a residue of bright platinum metal. The powder was baked as described in Section 3.1 before growth in thick-walled Bridgeman tubes to avoid any possible problems due to pressure generated as a result of any decomposition. A transparent, dark orange, cracked crystal containing inclusions of metallic platinum was obtained. The metallic inclusions were mainly attributed to the decomposition of free H_2PtCl_6 thought to be present in the raw material. BDH then boiled the powder in aqua regia to remove free H_2PtCl_6 before washing and filtering in an attempt to improve the material. The crystals grown from this powder were improved but still contained some platinum inclusions. At this stage rubidium, caesium and thallium hexachloroplatinates were grown in order to assess their water solubilities which are listed in Table I. From this point of view, Tl_2PtCl_6 and Cs_2PtCl_6 are to be preferred, but since thallium compounds are poisonous and expensive it was decided to concentrate upon improving the quality of Cs_2PtCl_6. When grown from BDH material the crystals contained some platinum inclusions and were dark red in colour. Since an alternative material was available from Johnson Matthey Chemicals, this was grown and resulted in a much improved crystalline material, slightly cracked, mid-orange in colour, and containing no visible platinum inclusions. A transmission curve of a slice of this material is shown in Fig. 3 and other properties are listed in Table I.

4.4. Ga_2Se_3 and Ga_2Te_3

Phase diagrams [11] indicate that Ga_2Se_3 and Ga_2Te_3 are congruently melting compounds of cubic sphalerite structure whose melting points are 1022° C and 791° C respectively. These compounds should be readily grown by the Bridgeman technique. The compound raw materials were grown as described in Section 3.1. The resulting polycrystalline boule of Ga_2Se_3 was uncracked, of brown colour, and was opaque to visible light. However, sufficient red light was transmitted through a thin section to allow microscopic examination which showed a number of opaque inclusions within the sample. An infra-red transmission of the Ga_2Se_3 is shown in Fig 4 and some

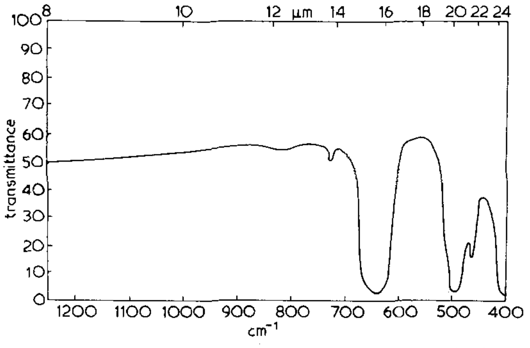

Figure 3 Infra-red transmission of a 5 mm thick slice of Cs_2PtCl_6.

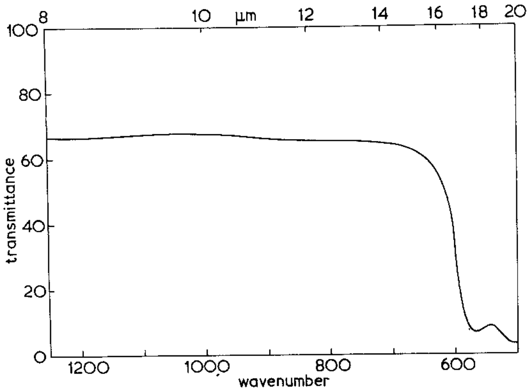

Figure 4 Infra-red transmission of a 2 mm thick slice of Ga_2Se_3.

other physical properties are given in Table I. The gallium telluride grown was polycrystalline, contained inclusions, and a 2 mm slice transmitted to 18 μm finally cutting off at 24 μm. Other physical properties are given in Table I. Wright and Newman [12] have reported that Ga_2Te_3 has a large existence range leading to inclusions being present in the material. It is likely that this phenomenon explains the inclusions present in the Ga_2Te_3 and it may be that Ga_2Se_3 behaves similarly accounting for the inclusions also seen in this material.

5. Discussion

Growth defects of a macroscopic kind were present in all of the materials grown as described in Section 4. No attempts were made to eliminate these since the materials obtained were of sufficient quality for preliminary assessment. If the properties of the chlorides as shown in Table I are examined it is seen that it is possible to find infra-red transmitting materials with much reduced solubilities over that of KCl. However, on the evidence of the present work, the solid-solution materials $Cs_2SnPbCl_6$ and $Cs_2Sn_2Cl_3Br_3$ are unlikely to be grown with sufficient uniformity in large sizes to be useful so that these materials need not be discussed further. Of the family of hexachloroplatinate materials, Tl_2PtCl_6 and Cs_2PtCl_6 are interesting low-solubility materials. Since these decompose on heating to their melting points, with the evolution of chlorine, growth in a closed container is necessary, and this would become increasingly difficult with large-size boules of say 6 in. or greater in diameter. Also the cost of a material containing platinum is likely to be high so that on balance these materials are not likely to offer a significient advantage over KRS5 which is commercially available. Of the chlorides in Table I, $CsCdCl_3$ appears to offer the greatest potential. One would expect to grow the material in open crucibles and one would expect cracking problems to be overcome with normal development. The water solubility is about one sixth that of KCl and the hardness about 16 times that of KCl also implying an increased mechanical strength. Hence the material may be worthy of further development to determine whether significant overall improvement over KCl can be established. However, slight birefringence is to be expected in this material since it is of perovskite structure.

From the limited work of Section 4 it appears that both Ga_2Se_3 and Ga_2Te_3 may have growth problems due to a wide existance range, neither are transparent in the visible in significant thicknesses and thus offer no advantage over the newly developed chemical vapour-deposited ZnS and

TABLE I

Material	Structure	Density ($g\,cm^{-3}$)	Refractive index	Melting point (° C)	Thermal expansion ($\times 10^{-6}\,°C^{-1}$)	Water solubility RT ($g\,l^{-1}$)	Hardness, Vickers
KCl	NaCl	1.99	1.46 (10 μm)	776	36	347	9 (Knoop)
$CsCdCl_3$	Perovskite	3.94	1.7 (10 μm)	557	30.7	53	147
$Cs_2SnPbCl_6$	Perovskite solid solution	3.36	–	601	30.8	44	33
$Cs_2Sn_2Cl_3Br_3$	Perovskite solid solution	3.80	–	410	39.6	100	28
K_2PtCl_6	Antifluorite	3.50	–	812	–	9.3	–
Rb_2PtCl_6	Antifluorite	3.96	–	835	–	1.4	–
Cs_2PtCl_6	Antifluorite	4.20	–	860	47.3	0.7	27
Tl_2PtCl_6	Antifluorite	5.77	–	–	–	0.01	–
Ga_2Se_3	Sphalerite	4.92	–	1022	9.6	Insol.	290
Ga_2Te_3	Sphalerite	5.57	–	791	–	Insol.	222

ZnSe. It would appear that no new bulk infra-red optical materials possessing better mechanical properties than germanium are accessible by the limited growth techniques employed in this work and that one must look at other materials accessible by more complex growth techniques, for example, the rare-earth chalcogenide compounds by a CVD technique as mentioned in Section 2.2. A profitable alternative approach might be to overcoat existing infra-red window materials such as ZnS or KCl utilizing vapour-growth techniques involving energetic ion impact or energetic impact of neutral atoms such as in ion plating [13] or sputtering to provide very adhesive, dense, polycrystalline or amorphous [14], rain-erosion resistant [15] coatings, respectively.

Acknowledgement

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