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NOVEL PHOTONIC MATERIALS MADE FROM IONIC EUTECTIC COMPOUNDS[1]

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Directionally solidified binary eutectics are multiphase composites with lamellae or rods of one phase embedded in a matrix of the other phase. Coupled growth from binary liquid produces periodic patterns consisting of well-aligned microstructures. The existence of steep and well defined interfaces make these materials promising candidates for photonic devices such as planar and fibre waveguides or luminescent materials. Here we review some of these applications. We also describe the production of some binary eutectic fluorides with well aligned fibrous microstructures which have been used as precursor materials to obtain centimetre-long alkaline and alkaline-earth fluoride single crystal fibres (SCF), with diameters of the order of light wavelength to find application as optical fibres.

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1 Introduction

Directionally solidified eutectics (DSE) are multiphase materials, which contain huge amounts of minority phases distributed as lamellae or fibres within a matrix phase. The single crystalline phases grow along well-defined crystallographic directions and orientation relationships are generally established between the component phases to minimise the interfacial energy. The basic microstructure of a simple regular eutectic consists of either single crystal rods or lamellae embedded in a single crystal matrix. In the simplest case of isotropic surface energy, fibres rather than lamellae are found below 28% volume fraction of the minority phase. Non-faceted, regular eutectics are favoured when both phases have a low non-dimensional melting entropy; $\alpha = \triangle S/R < 2$ ($\triangle S$ is the melting entropy and R is the gas constant) [1].

The microstructure of the multiphase composite can be controlled to some extent by deliberated selection of the composition and processing parameters. In fact, the microstructure size, and consequently the fibre radius, depends on the growth rate being finer at higher solidification

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rates. In the simple regular binary eutectics, the interphase spacing λ depends on the solidification rate V as $\lambda^2 \cdot V$ = Constant [1]. Interphase spacing is typically in the 0.5 to 10-micron range. In most favourable cases, the eutectic consists of well aligned microstructures with periodic arrays of clean and steep interfaces between micron size crystalline phases. For homogeneous growth, high values of the axial thermal gradients ($\triangle G$) to growth rate ratio $\triangle G/V$ are usually needed to maintain micro- and macroscopically flat solid-liquid interfaces, thus preventing cellular growth [2].

These well-aligned eutectics are promising candidates for photonic devices [3]. For example, fibrous eutectics with transparent components are suitable for 2D photonic crystal applications whereas reflection anomalies in some lamellar eutectics were tentatively assigned to surface polaritons localised at the interfaces [4]. Plates of the MgO/CaF_2 eutectic containing 0.7 μm radius MgO fibres can be used as mechanically resistant optical faceplates of about 40.000 pixel/mm^2 where the light is guided by the higher refractive index MgO fibres. The MgO fibres are embedded in the lower refractive index CaF_2 matrix and perpendicular to the plate face [5]. Also, CaSZ (Calcia Stabilised Zirconia)- $CaZrO_3$ or LiF-CaF_2 binary lamellar eutectics are stacks of single crystalline planar waveguides [6]. Optically active ions can be introduced into the transparent phases by just doping with these ions the eutectic melt. Foreign ions enter the different phases according to their corresponding partition coefficients. For example, Er^{3+} ions only enter the zirconia fibres of the Al_2O_3-ZrO_2 eutectic. In the fine microstructure of this binary eutectic the luminescence probability of this ion is modified by the close presence of the alumina phase [7]. When the substituting ion enters in both phases their optical properties sum up to give a material with combined properties. This is the case of the LiF-CaF_2 DSE doped with MnF_2 that combines LiF and CaF_2 thermo-luminescence properties to give a very efficient dosimeter material for both low and high radiation doses [8].

Aligned eutectics can also be used to obtain shaped single crystals [9]. In this paper we describe a new procedure to produce single crystal optical fibres (SCF). Compared with the glass fibres [10], SCF offer a wider transparency window, greater resistance to radiation damage, better mechanical, chemical and thermal stability, non-linear effects and narrower emission bands. Applications of SCF include pressure and temperature sensors, optical amplifiers, microlasers and non-linear optical devices. The smallest diameter available for single crystalline fibres (SCF) is around 50–100 μm a severe restriction for applications of SCF as single mode optical guides and miniature photonic devices. Reason is that SCF are grown from melt and the minimum melt volume necessary to obtain the stable conditions of melt meniscus and solid-liquid interface for homogeneous crystallisation underlies this limitation [11].

Conversely, in the binary eutectics the size of the phases is limited by their interactions and very fine phases can be obtained from the melt. Following these ideas we have developed a different strategy to obtain micron diameter and oriented single crystal fibres which is based on the production of aligned fibrous eutectic microstructures. The component matrix is then chemically removed to leave bunches of micron sized SCF's. Conversely, removing one of the phases in a lamellar eutectic leaves a highly porous SC matrix with micron size pores. However, one of the main problems to get large SCF's is the ubiquitous presence of eutectic grains of sub-millimetre size, which interrupt fibre orientation and continuity. These grains are the consequence of instabilities in the solidification front. In order to minimise that problem we used the Bridgman method to grow binary eutectics. The large melt volumes involved in this growth method promote large eutectic grain sizes. In particular we have explored several halide eutectics to obtain

Tab. 1. Component phases, melting point, eutectic composition, and microstructure for some fluoride eutectics.

Components	Melting point [K]	Composition (%wt)	%volume minor phase	Microstructure
$NaF/NaMgF_3$	1105	29 NaF + 71 MgF_2	44 $NaMgF_3$	Lamellae
LiF/NaCl	955	29 LiF + 71 NaCl	25 LiF	Fibre
MgF_2/NaCl	1060	5 MgF_2 + 0.95 NaCl	4 MgF_2	Fibre
NaF/NaCl	950	28NaF + 72 NaCl	25 NaF	Fibre
NaF/CaF_2	1085	50 NaF + 50 CaF_2	45 CaF_2	Lamellae
NaF/BaF_2	1085	28.2 NaF + 71.8 BaF_2	43 BaF_2	Lamellae

both SCF and single crystal porous materials.

2 Experimental Details

The method we used is a two step procedure. First, we grew by the Bridgman method a large eutectic ingot of a composition such that the desired phase is in the right volume fraction to ensure an ordered fibrous or lamellar microstructure. The matrix is chemically removed in a second step. An additional advantage of this method is that before matrix removal, the composite can be easily handled, cut, polished, etc.

The starting eutectic compositions and melting points are given in Table 1. The powders were dried, mechanically mixed and placed into a vitreous graphite crucible of about 1 cm^2 section. Typically, charges of 10–15 g were grown in a vertical Bridgman apparatus with conventional resistance heating elements in a dry Ar atmosphere. Powders were melted at temperatures slightly above the eutectic temperatures. Solidification thermal gradient was ≈ 5000 K/m. X-ray diffraction experiments (XRD) patterns of the solids were recorded on a Siemens D501 X-ray diffractometer. SEM and TEM experiments were carried out with a Jeol 6400 and Jeol 2000 FXII microscope respectively.

3 Experimental results

3.1 LiF Single crystal fibres

In particular, we have explored several fibrous NaCl based binary eutectics. The NaF fibres in the NaF/NaCl crystallised eutectics grow perpendicular to the growth direction and consequently their length is limited by the short grain wideness. Besides, NaF tend to form ribbons instead of fibres [4]. Best results were obtained on the production of LiF and MgF_2 SCF's. The optical transparency window of these fluoride crystals is outstanding: 50.000–1.700 cm^{-1} for LiF and 45.000–1.500 cm^{-1} for MgF_2 (absorption coefficient $<$0.2 cm^{-1}) [12]. LiF is a cubic (rocksalt structure) halide with a low refractive index (n = 1.3943 at 0.5 μm). With respect to possible applications LiF is commonly used as a radiation dosimeter. Low-threshold tuneable colour

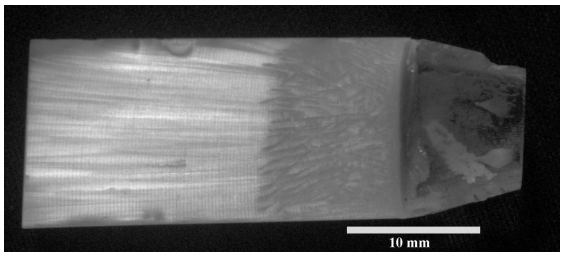


Fig. 1. Longitudinal section of an as-grown LiF/NaCl ingot showing the seed and hypoeutectic transition regions.

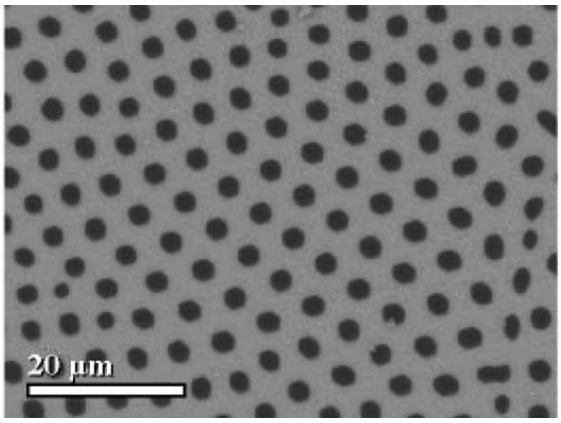


Fig. 2. SEM image of a transverse section of a NaCl/LiF ingot grown at 3 mm/h. Dark fibers correspond to LiF phase.

centre lasers have also been developed with LiF crystals [13]. The crystal structure of MgF_2 is tetragonal and consequently optically anisotropic (rutile structure, $n_o = 1.3795$ and $n_e = 1.3914$ at 0.5086 μm). It has a relatively high melting entropy value ($\alpha = 4.6$) and a tendency to form ribbons instead of cylindrical fibres. From the point of view of applications MgF_2: Co^{2+} is a continuous-wave 1.63–2.08 μm laser material [14].

In the case of NaCl/LiF eutectic, LiF has low melting entropy ($\alpha = 2.9$) similar to that of NaCl ($\alpha = 3.15$), which favours a broad eutectic coupling region. Then, unidirectional solidification yields large eutectic grains along the growth direction (several mm^2 section, centimeter long). In Figure 1 we show a LiF/NaCl ingot cut longitudinally along the grow direction. The growth was seeded with a LiF single crystal and the hypoeutectic zone is easily observed between the seed and the eutectic. Opal iridescence in the aligned eutectic zone is also observed indicating a good alignment of the LiF fibres. SEM observations reveal the high hexagonal order of the LiF fibres in the NaCl/LiF ingots. Figure 2 shows a typical SEM image of a transverse

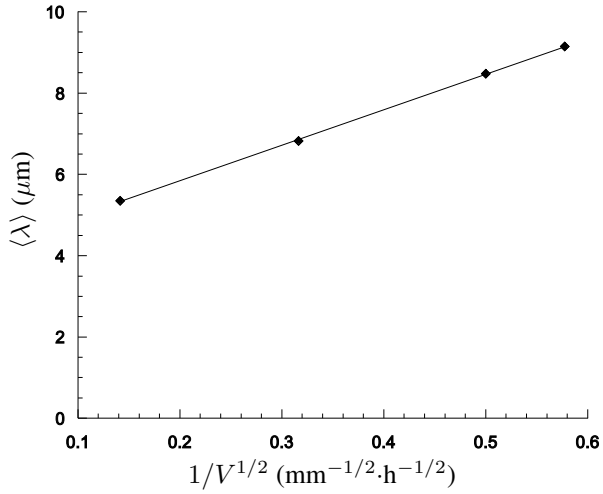


Fig. 3. Fiber interspacing as a function of the growth rate for NaCl/LiF eutectics grown at different growth rates.

(perpendicular to the growth direction) eutectic cross-section. The fibre spacing was measured by applying a Fourier Transform (FT) analysis to these SEM images. In Figure 3 we plot the fibre spacing λ as a function of the growth rate V. The equation

$$(\lambda - 4.1\ \mu m)^2 \times \mathrm{V} = 21.3\ \mu m^3 s^{-1}$$

fits the experimental data which indicates that the fibre size can be controlled by the growth rate. However, two factors limiting the useful fibre size are found. First, LiF fibres with diameters above 4 μm obtained at low growth rates tend to develop $\{110\}$ facets. In addition, the high growth rates needed for narrow fibres produce instabilities on the solidification front resulting in a dramatic decrease of the eutectic grain size and hence of the SCF length. In consequence, our procedure only gives long (10 mm length range) cylindrical LiF fibres with diameters from 1 to 5 μm.

The NaCl matrix is removed by soaking in distilled water, leaving behind long single crystalline LiF fibres. LiF fibres present a high homogeneity in section as it is shown in the optical microscope image of one of these long fibres given in Figure 4. A representative TEM image and the corresponding electron diffraction pattern of a LiF SCF are given in Figure 5. These experiments indicate that single crystal LiF fibres grow in the NaCl matrix along the [111] direction. The NaCl matrix phase grows in the [100] direction as indicated by XRD.

In order to demonstrate light guiding effect in the SC fibres the following experiments have been performed. First, the He-Ne laser beam was focussed by an optical microscope objective of $\times$ 60 magnification and 0.85 numerical aperture, on one of the ends of a bunch of parallel air bounded LiF fibres obtained from a polished 10 cm long eutectic piece. The laser light is deflected by the fibres and it can be observed to appear at the other bunch end even for large deflection angles according to the LiF refractive index. Secondly, one single LiF was isolated

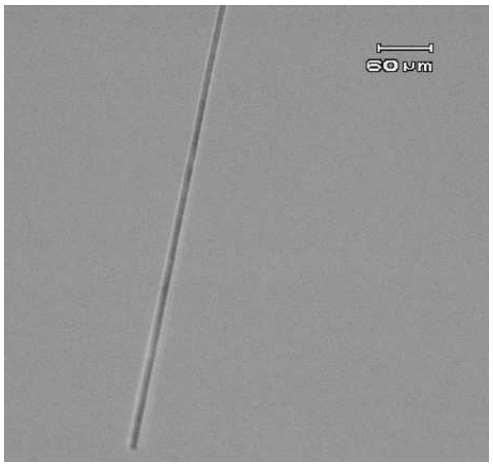


Fig. 4. Optical microscope image of a SC LiF fiber obtained from a NaCl/LiF eutectic grown at 10 mm/h.

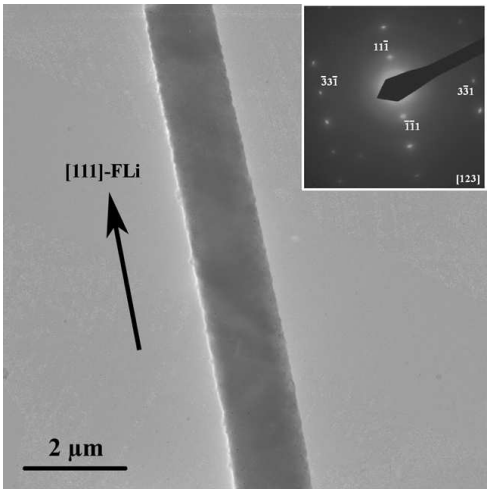


Fig. 5. TEM image of a narrow LiF fiber obtained from a NaCl/LiF eutectic grown at 50 mm/h. Inset is the electron diffraction pattern showing the [111] orientation of the fiber.

and mounted in an optical fibre piece placed in a XYZ micrometer. In this case an aspheric lens of 11 mm focal length and 0.25 numerical aperture was used to obtain a narrow focus spot. In the Figure 6 we show this experiment performed on a 5.5 mm long LiF fibre where the guided light can be seen due to light leaks caused by some defects. The union between the glass fibre supporting the SC fibre also produces light drain. Laser light is coming out the LiF fibre at the output end.

3.2 MgF_2: Co fibres

Due to the high fusion entropy of MgF_2 the NaCl/MgF_2 eutectic is irregular and some ribbons coexist with fibres. Figure 7 shows a typical MgF_2 fibre obtained after removal of the NaCl matrix. In this case the MgF_2 fibres are optically uniaxial with the optical axis along the grow [100] direction. The MgF_2 fibres were done optical active by doping with Co^{2+} ions. Cobalt was incorporated into the starting powders. Since Co^{2+} does not enter the NaCl structure, it enters only into the MgF_2 matrix in substitution for the Mg^{2+} lattice ions. It has been proven by optical absorption spectroscopy experiments performed in the doped eutectic (Figure 8) which only revealed the presence of the $^4T_1 \rightarrow {}^4T_1(^4P)$ ($\approx 15.000\,cm^{-1}$) and $^4T_1 \rightarrow {}^4T_2(^4F)$ (≈ 6.500 cm^{-1}), absorption bands characteristic of substitutional Co^{2+} in MgF_2.

3.3 Porous fluoride single crystal

Entangled 3D binary eutectic structures consist of two interpenetrating single crystalline phases with a micron size microstructure. Chemically removing one of the component phases leaves a

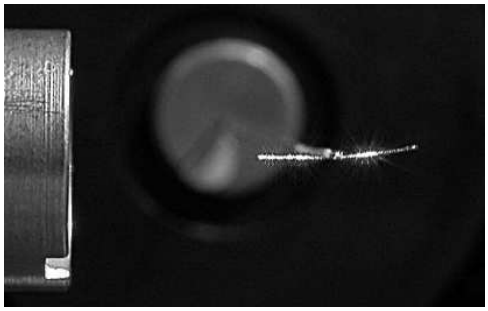


Fig. 6. Demonstration of the light guiding effect in a 5.5 mm long LiF SC fiber. The He-Ne laser spot is focussed on the left fiber end. LiF fiber is glued on a glass fiber.

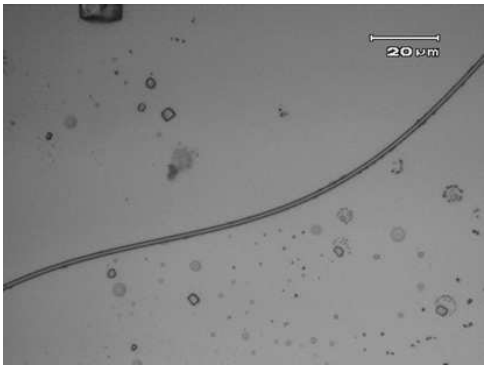


Fig. 7. Optical microscope image of a SC MgF_2 fiber obtained from a NaCl/MgF_2 eutectic grown at 10 mm/h.

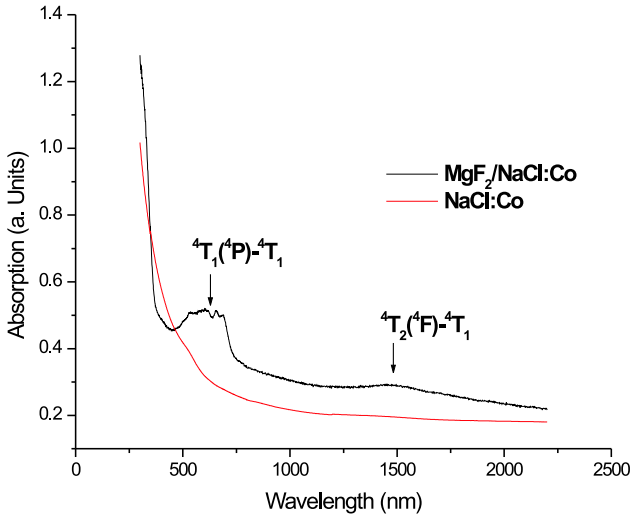
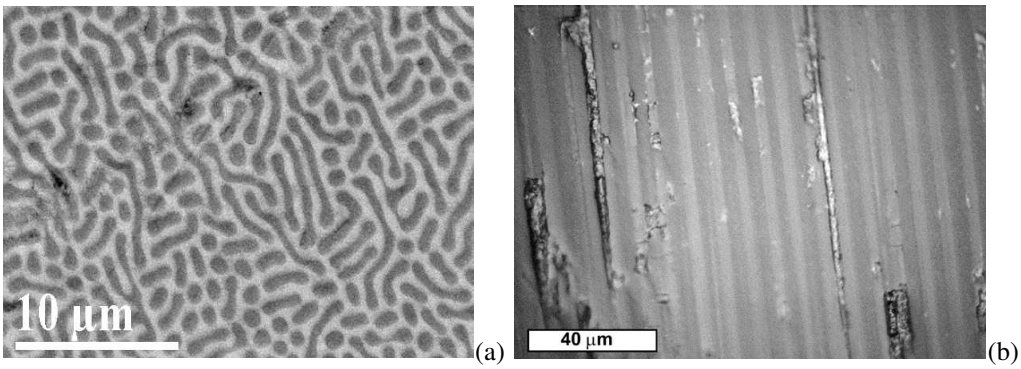


Fig. 8. Optical absorption spectra of a NaCl:Co crystal and a NaCl/MgF_2:Co eutectic showing that Co impurity enters the MgF2 phase.

highly porous single crystal with connected porosity. Micro–cavities can be subsequently filled up with selected compounds to produce, eventually, any desired composite. We have explored NaF based eutectics. In particular we have prepared NaF/$NaMgF_3$, NaF/CaF_2 and NaF/BaF_2 binary fluoride eutectics. These eutectics have primarily a lamellar microstructure but under



(a) (b)

Fig. 9. Optical micrographs of a transverse (a) and longitudinal (b) cross-section of the NaF-$NaMgF_3$ eutectic melt grown at 5 mm/h where the NaF phase has been removed.

certain growth conditions the microstructure is interpenetrating. Removing with distilled water the NaF phase leaves a continuous material with a high density of connected pores. In spite of their high pore volume (see Table 1) the crystals have mechanical integrity. In Figure 9 we show optical micrographs of transverse and longitudinal sections of a porous $NaMgF_3$ crystal.

4 Conclusions

A new set of possible applications for aligned eutectic composites in the field of optical devices is proposed. We proved the feasibility of fabrication of both single crystalline fibres of micron diameter and highly porous crystals. The method is based on the natural capability of eutectic compounds to develop fibrous or lamellar structures and the further elimination of one of the component phases. The procedure has been applied to the production of centimetre–long LiF and MgF_2: Co fibers and of porous $NaMgF_3$, CaF_2 and BaF_2 crystals via a previous growth of their NaCl and NaF binary eutectics. Many different eutectic compositions can be essayed for this purpose which may open a new route for the production of single crystals with new properties.

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