Solidification of NaCl-LiF-CaF₂ ternary composites

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Accepted: January 17th, 2017

Abstract The purpose of this work is to refine the microstructure of eutectic halides, candidates to polaritonic metamaterials, through the directional solidification of ternary compositions. NaCl–LiF–CaF₂ ternary composites have been solidified using Bridgman and micro-pulling down (μ PD) techniques at pulling rates from 3 to 300 mm/h for the first time. The interparticle spacing is 12 % smaller for this composition than for the binary fibrous NaCl-LiF eutectic. Conditions for solidification and growth in order to generate ternary aligned microstructures are discussed. The very small amount of melt remaining in the mixtures until 580 °C is probably the consequence of solid solubility of LiCl in NaCl and the formation of the reciprocal salt pairs, as in NaCl-LiF. However, it does not prevent the solidification of homogenous ternary microstructures.

Keywords Halide Eutectics · Directional Solidification · Ternary Composites · Self-assembled microstructures

1 Introduction

Ceramic materials and composites with tailored microstructures are essential in many technology fields. Microstructure (shape and size) has a strong influence in the mechanical properties of ceramics [1–4], and controls also functional properties [5] such as optical properties (as in light guiding [6, 7], in thermal

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and selective emission [8] or in metamaterials [9, 10]). In the latter area in particular there is need to develop materials that can harness light in the THz range [11], where the Quantum Cascade Laser, a new generation and flexible THz source has recently emerged and opened opportunities in applications such as biological tissue imaging, manufacturing quality control, defense and security or sensing [12–15].

Metamaterials are artificially structured media with unit cells much smaller than the optical wavelength. The unit cell is composed of engineered structures with resonances in the appropriate spectral range. For THz metamaterials the structures need to be in the micron range. Appropriate materials to build them are polaritonic materials, that is, polar crystals where an incident electromagnetic wave can couple with lattice vibrations (optical phonons) in the crystal. This occurs specifically in the THz range (several THz), due to the coupling of the electromagnetic radiation with the transverse optical phonons [16]. It has been theoretically proven that polaritonic materials could achieve metamaterial-like properties [17, 18]. In particular, a hyperbolic dispersion relation was later proposed, leading to subwavelength imaging applications [19, 20]. In consequence, by properly structuring such polaritonic materials, one can manipulate the dispersion of THz waves in unique ways, exploiting the interplay between material and microstructure (geometrical) resonances. Recently such hyperbolic dispersion relation behaviour has been experimentally demonstrated in self-assembled polaritonic metamaterials consisting in NaCl-LiF and KCl-LiF composites obtained by directional solidification of eutectics (DSE) [9, 10, 21, 22].

DSE allows the fabrication of fine homogeneous microstructures of two or more crystalline phases from the melt [23–25]. Using this approach one can obtain self-organized systems of 1D, 2D structures [26]. These processes can be used with a wide variety of materials (e.g. metals, magnetic materials, semiconductors...), providing that they have an eutectic point in their phase diagram. The fabrication of metamaterial microstructures with a rich variety of shapes and configurations is then possible [22, 27–33]. Regular coupled growth of binary eutectics result in fibrous or lamellar arrangements [25, 29, 34]. A larger variety of regular microstructural arrangements can be found in ternary eutectics [24, 35–37]. The volumetric fraction is fixed at the eutectic composition for each system. It is known that in a directional solidification process and under conditions for a coupled eutectic growth, the interspacing a and the solidification velocity v follow the Jackson-Hunt (JH) law [38]:

$$a^2v = K_1 \quad (1)$$

An equivalent relationship applies also for ternary eutectics for the appropriate microstructural spacing [39]. According to this equation, by increasing the pulling rate, a smaller interphase spacing, and a smaller size of the dispersed phases, is obtained. At present we are interested in DSE that follow a well aligned, coupled growth, composed of polaritonic materials with as small microstructure size as possible. The reason is that the smaller the microstructure, the shorter the wavelength at which one can describe the electromagnetic

properties of the composite using effective medium theories [19] and the larger the resolution of image transfer devices based on them [21]. In addition, the variability in the shape of the dispersed particles in each sample has less influence in the optical properties as particle size diminishes, which means better accuracy in a possible photonic device.

Decreasing the interphase spacing below around 1 μm by increasing pulling rate expressed by Eq. 1 has limitations. First, a constant value of K_1 applies at small Péclet numbers (Pe) [23], (diffusion distance in the liquid larger than the interphase spacing in the solidified eutectic). In most directional crystal growth procedures, before reaching that limit one has to take care of staying in the coupled growth regime, avoiding constitutional supercooling. This requires large enough solidification gradients, which limits the size of the grown crystal [29]. Another way of decreasing the interphase spacing while keeping the solidification conditions within the coupled growth regime is to find systems with smaller K_1 values. The parameters that determine K_1 are described in previous works for binary [25, 40] or ternary eutectics [39]. Deep eutectics would possess smaller K_1 . However, often it is not permitted by the intended application (and required material properties) to change drastically the composition of the composite. A stepwise change in composition would be, if feasible, a better solution. In the literature there exists some examples in which the addition of a third component that generates a ternary eutectic has led to smaller interphase spacing with respect to a near binary composition, as for example in some oxide eutectics [41–45]. This is the approach that we explore here.

In this work we will investigate the NaCl–LiF–CaF₂ ternary composition field in order to generate ternary microstructures that might reduce the microstructure size if compared with close binary systems, namely the eutectic NaCl–LiF, for further optical applications at THz frequencies. This is the first time that the directional solidification of this system is reported. The microstructure is shown and conditions for the solidification and growth are discussed.

2 Experimental Procedure

Eutectic NaCl–LiF–CaF₂ ingots of 14 mm diameter and around 50 mm length have been grown using directional solidification by the Bridgman method in a three zone furnace with an approximate thermal gradient of up to 40 K/cm (see Fig. 1).

The starting powder composition was prepared covering the range between (55.5–43.8) mol% NaCl - (41.3–50.4) mol% LiF - (3.2–5.8) mol% CaF₂. Powders of 99.99 % purity (Alfa Aesar) were used and previously dried at 400 °C. The mechanically mixed powder was introduced -typically a 14 g charge- in a graphite crucible and was melted. A vacuum of 10^{-2} mbar was reached in the chamber. An Ar (99.95% purity) atmosphere was used in the experiments. Pulling rates from 3 to 40 mm/h were used.

Fig. 1 Photograph of a Bridgman grown ingot (longitudinal cut) (upper); and of a μ PD grown rod (lower) of NaCl–LiF–CaF₂ eutectic.

For higher pulling rates, the micro-pulling down (μ PD) method was used to grow eutectic rods of NaCl–LiF–CaF₂ typically around 1 mm in diameter. A higher gradient of approximately 100 K/cm [46] in the equipment permits higher rates on cost of smaller sample sizes because of the increased thermal stresses [28]. The μ PD setup allowed a vacuum of 10^{-5} mbar in a 35 liter vacuum-tight steel chamber, avoiding moisture. LiF (Alfa Aesar, 99.99 %), CaF₂ and NaCl powders were mixed at 46.5 mol% NaCl - 45.5 mol% LiF - 8.0 mol% CaF₂. A platinum wire seed and an Ar atmosphere (1 bar, 99.999 % purity, <1 ppm water) were used to grow samples at pulling rates from 15 to 300 mm/h.

Both series, Bridgman and μ PD together, cover the pulling rate range from 3 to 300 mm/h. X-ray diffraction diagrams were acquired at room temperature on powdered samples prepared by both procedures at the Servicio de Difracción de Rayos X y Análisis por Fluorescencia del Servicio General de Apoyo a la Investigación de la Universidad de Zaragoza. A diffractometer RIGAKU, D/max 2500 equipped with rotating Cu anode, graphite monochromator and working at 40 kV, 80 mA was used. Transverse and longitudinal cross-sections of the samples were polished (usually dry polished or using oil based diamond paste) and analyzed in a Merlin Field Emission Scanning Electron Microscope (FESEM) from Carl Zeiss (Germany). Phase interspacing of the phases were obtained from SEM images by using the software Digital Micrograph from Gatan Inc.

For chemical analysis of the NaCl majority phase of solidified samples, pieces of Bridgman ingots solidified at 10 mm/h with homogeneous ternary composition were dissolved in water or methanol for short times (1/2 h in H₂O; 3 h in CH₄O). The liquid was filtered and then cation analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) in a Perkin Elmer Elan DRC-e equipment. Water and methanol are selective solvents that dissolve preferentially NaCl and much less efficiently LiF [47]. The result of the cation analysis gives a ratio (weight fraction) of Li to Na of $(Li/Na)_{H_2O}=0.0176$ for the water solution and $(Li/Na)_{CH_4O}=0.0051$ for the methanol solution. For the analysis reported in Table 2, the samples were fully dissolved in HCl.

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) experiments have been performed in grown samples and powder

mixtures. The equipment used was a model STA 449C (NETZSCH, Germany). Graphite DTA crucibles with lid were used to measure eutectic powder samples (see Fig. 3, typically 50-70 mg) with a heating/cooling rate of 10 K/min. Additionally, pieces of the eutectic fibers (Fig. 8, ca. 10 mg) were measured in a more sensitive DSC mode in lidded Pt crucibles with heating rates ranging from 2 to 20 K/min.

3 Results and Discussion

3.1 Solidification of eutectic microstructures

Fig. 2 Liquidus surfaces of the NaCl–LiF–CaF₂ sections. FactSage [48] calculations; Gibbs triangle NaCl–LiF–CaF₂ (projection onto liquidus, 20 K isotherms, first components doubled to have identical anion numbers. ‘Rocksalt’ crystallizes as solid solution, the other phases have fixed stoichiometry).

Gladushchenko et al. [49] report an invariant point in the section NaCl-LiF-CaF₂ of the Ca, Li, Na || Cl, F system with melting temperature 650 °C and composition 56.2 mol% NaCl, 40.7 mol% LiF and 3.1 mol% CaF₂. Solidification of this mixture in the Bridgman furnace gives rise to a rather inhomogeneous microstructure with abundant NaCl primary phase and areas of ternary eutectic microstructure. The starting composition was then varied stepwise until we reached the starting composition 45.7 mol% NaCl - 50.2 mol% LiF - 4.05 mol% CaF₂, that generated homogeneous ingots with eutectic microstructure at pulling rates of 3, 5 and 10 mm/h. Larger pulling rates did not achieve fully homogeneous ingots, as segregated phases or pores and colonies tend to form. Large enough areas with ternary microstructure could be obtained by diminishing a bit the amount of NaCl to 43.8 mol% NaCl - 50.4 mol% LiF - 5.8 mol% CaF₂ at 20 mm/h (this corresponds to sample LCN13, Table 1).

Table 1 Composition details of several ternary mixtures and sample NLC04.025 grown at 15 mm/h measured in DTA and DSC experiments. Proportions are presented as NaCl/LiF/CaF₂ in wt% and mol%.

Sample	Nominal (wt%)	Nominal (mol%)	Powder (Y/N)
C1	58.38/27.25/14.37	44.72/47.03/8.24	Y
C1+LiF	55.87/30.37/13.76	41.51/50.84/7.65	Y
C1+NaCl	59.65/25.85/13.64	46.56/45.47/7.97	Y
C1+CaF ₂	56.04/26.15/18.20	43.58/45.83/10.60	Y
C1+NaCl+CaF ₂	57.80/25.11/17.47	45.34/44.40/10.26	Y
C _{LCN13}	59.3/30.3/10.4	43.81/50.44/5.75	Y
NLC04.025	60.14/26.12/13.7	46.53/45.53/7.93	N

Fig. 3 An overview of second heating/cooling DTA curves of the analyzed compositions described in Table 1. Powders of ~ 65 mg were cooled and heated at 10 K/min rate in argon atmosphere. Inset highlights a zoom from DTA experiments and shows the subsolidus-effect near 580°C in heating curves: it is similar for all samples.

A further decrease in the amount of NaCl was successful in achieving almost ternary eutectic areas at 40 mm/h, although with some LiF and NaCl primary crystals, and ternary colony formation at the end of the ingot. Some NaF crystallites could also be observed at intercolonial regions.

It is not unusual that the increase in pulling rate requires a shift of the starting composition when the component crystals have very different melting temperatures (as here) that hints towards a skewed zone for coupled growth.

But, still, 40 mm/h seems to be a too high pulling rate for coupled growth here. Larger solid-liquid thermal gradients are required.

Consequently, solidification at larger pulling rates was done using the μ PD method, using the composition determined in the following section (see Sect. 3.2): 46.5 mol% NaCl - 45.5 mol% LiF - 8.0 mol% CaF₂. The microstructure of those samples is homogeneous, with three phases (except for a thin rim rich in NaCl in the outer shell) at all pulling rates, from 15 to 300 mm/h. In the μ PD growth, the main liquid/solid interface is in contact with the atmosphere and leads to Marangoni convection. This additional driving force generates segregation to the external shell of the sample, being the microstructure of the external part of the rod as shown in Fig. 4. Some scattered NaCl primary crystals are found at large pulling rates. XRD of powdered samples growth at 10 mm/h (Bridgman) and 15 mm/h (μ PD) showed that the samples contained rock-salt NaCl, LiF and CaF₂ in their expected crystallographic structures (ICDD PDF 00-005-0628, PDF 00-045-1460 and PDF 00-035-0816 powder diffraction files respectively [50]), and no other phase.

Fig. 4 SEM micrograph of transverse cross-section of NaCl-LiF-CaF₂ grown at 15 mm/h by μ PD method. Image shows a detail of the outer rim of the sample (in contact to the growth atmosphere during the μ PD process). Inset: dark phase correspond to LiF and brighter phase correspond to CaF₂, the majority phase (matrix) corresponds to NaCl.

3.2 The eutectic composition

The fact that we need to decrease the amount of NaCl relative to the invariant point reported by Gladushchenko [49] to solidify a eutectic microstructure coincides with the FACT-Sage calculation results of the liquidus projection of the NaCl-LiF-CaF₂ composition triangle reproduced in figure Fig. 2. A composition near to this minimum was used as starting point (composition C1 in Table 1). Five different mixtures were prepared, C1 and four others shifting

C1 by a small amount (see Table 1). The enthalpy change during heating and cooling was measured using either Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC).

Measured DTA heating and cooling curves are presented in Fig. 3 for the powder mixtures. As expected the main endothermic peak (in heating curves) or exothermic in cooling runs, appears at around 665 °C. This corresponds to the melting event predicted in the calculations.

We find that adding a small amount of NaCl or NaCl+CaF₂ to the first C1 composition led to a sharper peak around the eutectic temperature. On the contrary, when adding circa 1-2 mol% of LiF, an extra shoulder appears in front of the eutectic crystallization peak, which means a stronger deviation in composition from the minimum melting temperature (Fig. 3). All curves in Fig. 3 present a small endothermic on heating (exothermic on cooling) band at around 580 °C, that is, at more than 80 K below the expected melting temperature, with a much smaller enthalpy change. That indicates the begin of melt formation on heating. This area is expanded in an inset in Fig. 3.

This event is reproducible and appears also in cooling curves in exothermal direction (Fig. 3). In ‘true’ eutectics any melting events below the eutectic temperature are ruled out. The current experiments indicate that the minimum of the liquidus surface in the NaCl–LiF–CaF₂ system is not simply ternary: small amounts of liquid phase are present below the ternary minimum melting temperature. It is similar for all samples, meaning that it does not depend on stoichiometry deviations (inset in Fig. 3).

We chose composition C1+NaCl given in Table 1 as the starting composition for the samples grown by μ PD, as this gives one of the sharpest DTA melting peaks on heating in DTA experiments.

3.3 Microstructure

SEM images of several samples of NaCl–LiF–CaF₂ polished transverse cross-sections grown by Bridgman method are in Fig. 5 (a) to (c). As shown in Fig. 5(a), the microstructure is a coupled, fibrous one with rather isotropic cross-sections. It consists of LiF (darker phase) and CaF₂ (brighter phase) cylinders with irregular cross-section embedded in a NaCl matrix. The CaF₂ phase is typically found adjacent to the LiF phase as can be observed in Fig. 5, at several different growth rates. As expected, the microstructure size gets smaller, as the pulling rate increases.

Homogeneous samples with eutectic microstructure are successfully obtained with growth rates between 3 to 20 mm/h. However, the resulting microstructure starts to deviate from the well ordered eutectic one at 40 mm/h, although large eutectic regions are still found. Severe segregation occurs and cells and primary LiF phase appear at 70 mm/h pulling rate.

In Fig. 6 we show images of longitudinal and transversal cross-sections after a water etching process, where one can appreciate the continuity of the

Fig. 5 SEM micrographs of transverse cross-sections of NaCl-LiF-CaF₂ grown by the Bridgman method at 3 (a); 20 (b) and 40 mm/h (c) and grown by μ PD method at 30 (d), 120 (e) and 300 mm/h (f). Dark phases correspond to LiF and brighter phases correspond to CaF₂, the majority phase (matrix) corresponds to NaCl.

Fig. 6 SEM micrographs of longitudinal (a) and transversal (b) cross-sections of NaCl-LiF-CaF₂ grown at 3 mm/h by the Bridgman method after a water etching process.

LiF and CaF_2 phases along the growth direction in a lateral surface of the macroscopic disc.

Samples were also prepared by μPD at pulling rates from 15 to 300 mm/h. The microstructure of the samples was found to be fully coupled and quasi fibrous ordered as it is observed in SEM micrographs in Fig. 5 (d), (e) and (f).

Fig. 7 Interspacing as a function of the square root of the pulling rate for the eutectic system NaCl-LiF-CaF_2 by Bridgman (red circles) and μPD methods (blue triangles).

Interphase spacing (or LiF phase center-to-distance) was estimated from SEM images of transverse cross-section through FFT analysis. Spacing values from 8.17 to 0.79 μm were obtained (Fig. 7). Bridgman as well as μPD samples can be fitted to the same JH relationship (see Eq. 1) with $K_1 = (56 \pm 3) \mu\text{m}^3/\text{s}$.

The phase diagram sets the volume fraction of LiF and CaF_2 in the NaCl matrix. The microstructure size is forced to be reduced when the interphase spacing decreases in order to keep the volume proportion. The dispersed particle transverse size can be scaled down below 0.5 μm (supposed average circular section) by increasing the pulling rate to the maximum accessible value of 300 mm/h, as observed in the SEM images (Fig. 5).

We have compared interphase spacings with to ones observed in the nearby NaCl-LiF studied by Orera et. al [28]. For that purpose we have grown NaCl-LiF eutectic samples by the Bridgman method and quantified the interphase spacing using the same procedure (FFT), so that quantitative comparison is meaningful. One obtains a somewhat smaller K_1 value for the ternary, which implies approximately 12 % smaller for the ternary composition at the same pulling rate.

3.4 Solidification path

Table 2 NaCl–LiF–CaF₂ sample compositions. Proportions are given as NaCl/LiF/CaF₂ in mol%. Nominal compositions of some solidified samples (determined by ICP analysis) are shown. *Chemical analysis of the cation content was done by ICP. The halide content reported was calculated assuming that only stoichiometric NaCl, LiF and CaF₂ were present and neglecting solid solubility. Samples grown by Bridgman are listed first, starting with L. A tabular line separates μ PD samples, starting with N.

Sample acronym	Nominal (mol%)	ICP* (mol%)	Pulling rate (mm/h)
LCN6F	45.74/50.21/4.05	46.65/49.58/3.77	3
LCN9F	45.74/50.21/4.05		5
LCN15F	46.53/45.51/7.96		5
LCN4F	45.74/50.21/4.05		10
LCN8F	45.74/50.21/4.05		20
LCN13F	43.81/50.44/5.75		20
LCN10F	39.24/54.12/6.64		40
NLC04.025	46.53/45.53/7.93	48.02/46.01/5.97	15
NLC04.1	46.53/45.53/7.93		60
NLC04.5	46.53/45.53/7.93		300

It was discussed already in Sect. 3.2 that the definition of the eutectic composition x_{eut} in the ternary system was somewhat ambiguous; and especially it was found that the melting of minor parts of the sample mass started already ca. 80 K below the ‘normal’ eutectic temperature T_{eut} where the main part of the melt crystallizes. This contradicts the behavior of a simple eutectic. It should be noted again that no variation of the sample composition around x_{eut} determined by the liquidus surface in the concentration triangle (Fig. 2) resulted in a significant diminution of the pre-eutectic peak.

Fig. 8 compares DSC heating curves for a powder mixture LCN13 with a piece of the fiber NCL04.025 that was grown from the starting material (for chemical compositions see Table 2). Two observations are remarkable: the composition of the ‘eutectic fiber’ differs from that of the ‘eutectic powder’, and the pre-eutectic peak is not found for the fiber. It will be shown in the following that these peculiarities result from two circumstances, and these circumstances can be discussed already in terms of the LiF–NaCl rim system of the concentration triangle Fig. 2.:

(1) One has not only two cations, but also two anions in the system. Consequently, the equilibrium

must be considered. Such systems are ‘reciprocal salt pairs’, and here Li⁺, Na⁺, Cl[−], and F[−] rather than the four salts from equation (2) should be used as components. It is important to note, that the four components are not

Fig. 8 Second heating curves of fiber NCL04.025 (blue dashed curve) and mixture C_{LCN13} (brown solid curve) in a DSC experiment. Inset: additional tiny effect around 580°C is only present in the mixture not in the fiber.

independent, because the sum of the cations $[Li^+] + [Na^+]$ equals the sum of the anions $[Cl^-] + [F^-]$.

(2) Sodium chloride, in contrast to lithium fluoride, is not a stoichiometric compound. This is taken into account in Fig. 2 by the label ‘rocksalt(ss)’ for its primary crystallization field. Besides NaCl, this rocksalt phase may contain LiCl.

Gibbs phase rule [51] simplifies with these conditions to

$$P + F = C \equiv 4 \quad (3)$$

in contrast to the usual expression $P + F = C + 2$. This is a result of the first constraint $p = 1$ bar (constant pressure), and of the second constraint that is expressed by reaction (2). P , F , and C are the number of phases, degrees of freedom, or components, respectively. From (3) one obtains that at an invariant point $F = 0$ one has as much as 4 phases in equilibrium, which is in contrast to $P = 3$ which holds for the eutectic point of a normal binary eutectic system. Vice versa, if only 3 phases (1 melt + 2 solids) are in equilibrium, one degree of freedom remains.

Fig. 9 shows the phase equilibria that apply on the left NaCl–LiF rim of the concentration triangle Fig. 2. First, it is remarkable that the liquidus curves are bend downwards, which is untypical for ‘normal’ eutectics. Actually this results from the larger number of species that grows according to the

Fig. 9 Left: Phase equilibria for NaCl-LiF mixtures show no simple eutectic behavior, as below the ‘eutectic temperature’ $T_{\text{eut}} \approx 680^\circ\text{C}$ some melt remains. Right: Magnification of the part close to NaCl; phase compositions at the filled and empty points near 600°C given in the text. Calculated with FactSage [48].

equilibrium (2) faster than indicated on the concentration scale. Second, at the ‘eutectic point’ near 680°C indeed one has $P = 3$ (melt, rocksalt, LiF), but still $F = 1$ because the composition x of the rocksalt phase remains a free parameter and depending on x the lower boundary of the ‘melt+rocksalt(ss)’ phase field bends downwards for large x .

This drop of the ‘eutectic temperature’ for $x \lesssim 1$ was found already in the experiments of Haendler [52] who measured for T_{eut} always 680 or 681 for $0.6 \leq x \leq 0.8$, 679 for $x = 0.85$ and $x = 0.9$, but only 676 for $x = 0.95$ (all temperatures in centigrades). The right panel of Fig. 9 gives a magnified view on the last 3 per cent of the system, close to NaCl. There it becomes obvious that the ‘melt+rocksalt(ss)’ phase field ends in an invariant point with $P = 4$ (melt, rocksalt, LiF, NaF); again fulfilling the phase rule (3). It is interesting to calculate two phase equilibria close to that invariant point near 600°C and $x = 0.995$. From 100 mol substance one obtains:

- 1) at the filled point: 99.3 mol rocksalt(ss), (consisting of 99.75% NaCl + 0.25% LiCl) + 0.7 mol melt (63% Na⁺, 37% Li⁺, 73% F⁻, 27% Cl⁻).
- 2) at the empty point: 99.8 mol rocksalt(ss), (consisting of 99.8% NaCl + 0.2% LiCl) + 0.2 mol NaF).

The diagrams in Fig. 9 demonstrate, that the equilibrium reaction (2) produces from the starting materials NaCl and LiF also sodium fluoride as a stable solid phase. LiCl is not found as a separate solid phase, because it forms a continuous series of solid solutions with NaCl [53]. The calculation of minor amounts NaF as an equilibrium phase, however, is in agreement with experimental findings in intercolony regions of Bridgman grown ingots growth with $v = 40 \text{ mm/h}$, as reported above.

The above results suggest the way in which the solidification of the NaCl-LiF-CaF₂ might take place, even when the presence of less than 8 % mol CaF₂ will modify at least temperatures, compositions and volume ratio of the phases. At around the minimum in the liquidus surface in composition and temperature (Fig. 2), CaF₂, LiF and rock-salt grow coupled while the liquid is enriched in NaF (to compensate for the rock-salt solid-solution). Volume ratio of

the phases and rock-salt composition can be dependent on growth conditions (total undercooling, or solid-liquid composition re-equilibration processes). If diffusion and convection mix the rejected liquid with the liquid reservoir, as in Bridgman solidification at sufficiently low growth rate, the coupled growth continues along a relevant length of the solidified ingots. Finally, all remnant liquid solidifies and NaF particles are actually observed at intercolony areas. As the Li/Na ratio in rock-salt is below 0.0051 (see Sect. 2), only minor amounts of NaF need to precipitate. In micro-pulling down convection transports the rejected liquid, rich in NaCl according to Fig. 9, towards the outer rim (see Fig. 4), and coupled growth of the inner part of the rod is then possible.

4 Conclusions

We have obtained solidified aligned ternary NaCl–LiF–CaF₂ composites with compositions close to NaCl/LiF/CaF₂=46.65/49.58/3.77 mol% (Bridgman) or NaCl/LiF/CaF₂=48.02/46.01/5.97 mol% (μ PD) in a pulling rate ranging from 3 to 300 mm/h. The solidification has generated homogenous regular ternary microstructures with approximately a 30 vol% of LiF and 6 vol% CaF₂ in NaCl matrix. The average distance between LiF phases in transverse cross-sections is a 12 % smaller in this ternary than in the closest binary, NaCl–LiF.

Although all mixtures were obtained from the three substances NaCl + LiF + CaF₂, the system cannot be described as simple ternary. This peculiarity results from reciprocal salt pair interactions which lead potentially to the combination of all anions with all cations in the system. Especially, NaF is formed as a separate solid phase in minor amounts, and LiCl forms a rocksalt type solid solution with NaCl. This extra degree of freedom means that below the minimum of the liquidus surface in Fig. 2 there is still melt. In fact, in the NaCl–LiF system there are lower melting points for mixtures either towards higher content of NaF or towards higher content of LiCl [54]. Between 680 °C and 600 °C solid phases and remaining melt are in contact, but equilibration between these phases can be limited by kinetic restrictions. Consequently, the phase state after cooling to room temperature is not only a question of the initial composition, but depends also on the rate of solidification.

Acknowledgements Authors would like to acknowledge the financial support by EU under the project NMP4-SL-2008-213669-ENSEMBLE and MAT2013-41045R. MFA acknowledges Ministerio de Educación, Cultura y Deporte (Spain) for the FPU scholarship. R. Gotor from ICMA is acknowledged for his assistance in sample preparations. MFA and RIM would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza.

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