# FLUORIDE EUTECTIC COMPOSITES: PREPARATION, MICROSTRUCTURE, FAST IONIC CONDUCTION AND CALCULATION OF THERMAL RESIDUAL STRESSES

VLADIMÍR LABAŠ, VIERA TRNOVCOVÁ, PAVEL P. FEDOROV\*, STANISLAV MINÁRIK

Department of Physics, Faculty of Materials Science and Technology, Slovak University of Technology, Pavlínska 16,91 724 Trnava, Slovak republic E-mail: labas@mtf.stuba.sk

\* Shubnikov's Institute of Crystallography, Russian Academy of Sciences, Moscow 117333, Russia

Submitted October 10, 1997, accepted January 15, 1999.

Phase composition, microstructure, fast ionic conductivity, cracking process, and thermal residual stresses in LiF-RF<sub>3</sub> (R = rare earth element) eutectic composites, prepared by using horizontal directional solidification, are presented. A special emphasis is put on the relationships between the fast fluoride ion conduction, phase composition and microstructure of the composites, and between the mutual crystallographic orientation of phases, microstructure and thermal residual stresses. The temperature dependence of the ionic conductivity of the eutectic composites is compared with that of the corresponding single crystals. In the composite, which contains the tysonite-structured  $RF_3$  phase, conductivity is significantly lower than that in the corresponding  $RF_3$  single crystal. A pronounced conductivity enhancement occurs only in the LiF-LiGdF<sub>4</sub> eutectic composite. The influence of phase composition, microstructure, and mutual crystallographic orientation of both phases on the residual stresses distribution is modeled using the finite element method. The simulation of the thermal residual stresses, which appear due to the thermal expansion mismatch and the anisotropy of the thermomechanical properties of both phases, is performed for the fibrous LiF-TbF<sub>3</sub> (orthorhombic) directionally solidified eutectic composite.

## INTRODUCTION

Superionic conductors (SIC) are solids with a fast ionic conductivity comparable to that of liquid electrolytes or melts of inorganic salts. The SIC are used as solid electrolytes in primary and secondary batteries, fuel cells, gas pumps and in gas or melt sensors. According to the dominant charge carriers, the SIC are divided into cationic (Na<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup>, Li<sup>+</sup>, rarely K<sup>+</sup>, Pb<sup>2+</sup> as charge carriers), anionic (F<sup>-</sup>, O<sup>2-</sup>, Cl<sup>-</sup>, rarely Br<sup>-</sup> as charge carriers) and protonic (H<sup>+</sup> as a charge carrier) conductors. Ionic conductor is classified as the SIC if the ionic conductivity,  $\gamma_i$ , at the operating temperature is higher than 10<sup>-7</sup> or 10<sup>-5</sup> S cm<sup>-1</sup> for sensor or for power (batteries and fuel cells) applications, respectively and the electron conductivity,  $\gamma_e$ , is negligible ( $\gamma_e/\gamma_i << 10^{-2}$ ).

The optimized (considering the fast ionic conductivity) inorganic fluoride solid electrolytes represent the best anionic SIC due to the small ionic radius and the low valence of mobile fluoride ions. Several criteria must be fulfilled to optimize the fast anionic conductivity: 1. high polarizability of cations, 2. proper crystallographic structure and 3. high concentration of defects in the anionic substructure.

High polarizability of cations takes place in fluoride systems with large cations (Ba<sup>2+</sup>, La<sup>3+</sup>, etc.) and/or cations with "lone pair" electrons (Pb<sup>2+</sup>, Sn<sup>2+</sup>, Bi<sup>3+</sup>, etc.). For the fast ionic mobility of fluoride ions, the tysonite  $(LaF_3)$ , fluorite (CaF<sub>2</sub>), hexagonal yttrium fluoride ( $\alpha$ -YF<sub>3</sub>), orthorhombic yttrium fluoride ( $\beta$ -YF<sub>3</sub>), and UF<sub>4</sub> structures are the proper structural types. They are characterized by a high coordination number of cations  $(\geq 8)$  and by a low coordination number of anions  $(\leq 4)$ . An elevated defect concentration can be created thermally at high temperatures. Heterovalent doping can increase defect content at moderate temperatures. Large clusters of defects containing heterovalent impurity cations, anion vacancies and several types of interstitial fluoride ions are present in the concentrated heterovalent solid solutions. The interstitial and/or vacancy migration mechanisms of fluoride ions are usually supposed in fluoride superionics.

Enhancement of the ionic conductivity (in comparison with the conductivity of the individual phases) is often observed in dispersed ionic composites containing dispersed insulating (usually  $Al_2O_3$ ) nanosized second-phase particles in an ionic conducting matrix [1]. This effect is applied when using composite solid electrolytes (e.g. LiI- $Al_2O_3$ ) for preparation of miniature

batteries for heart pacemakers. Space charge effects, adsorption effects, percolation effects and formation of new phases are supposed to be responsible for this conductivity enhancement [1].

In eutectic systems, maximum conductivity is usually observed at the eutectic composition [2]. Eutectic composites prepared from melt have relatively low melting temperatures, large areas of interfaces, finegraded (0.5 - 5  $\mu$ m) and highly ordered microstructures, coherent phase boundaries, well-defined orientation relations of both phases and good thermal stability of the eutectic structure [3]. In addition, good mechanical strength, thermal-shock resistance and fracture toughness enhancement often take place in the composite solid electrolytes [4]. Lamellar microstructure usually appears when the volume fractions of both coexisting phases are comparable. If the volume fraction of one of the phases is lower than 0.29, fibrous microstructure usually appears. The interlamellar and/or interfibral spacing decreases with increasing growth velocity and/or temperature gradient at the crystallization front [5].

In the LiF-RF<sub>3</sub> system, the simple eutectic phase diagrams are found for R = La - Nd. The LiRF<sub>4</sub> compounds are formed for R = Eu - Lu, Y (it is supposed that also R = Sm forms the same compound [6]). The thermal stability of these compounds increases with decreasing ionic radius of the R<sup>3+</sup> ion, and incongruent melting (for R = Eu - Ho) is replaced with congruent one (for R = Tm - Lu) [6]. Rare-earth trifluorides (for R = La - Nd) with tysonite (LaF<sub>3</sub>) structure are well known superionic conductors with fast fluoride ion conduction. Therefore, the eutectic composites containing these phases are prospective solid electrolytes having relatively low melting temperatures  $(\leq 700 \ ^{\circ}C)$ . The LiRF<sub>4</sub> compounds are well known matrices for solid state lasers [7], but their electrical properties are not yet known. The information on the electrical properties of the orthorhombic SmF<sub>3</sub> crystal is also lacking.

The important properties determining the lifetime of the solid electrolyte both in sensor and power applications are fracture toughness and thermal-shock resistance. It is known that the composite can exhibit enhanced fracture toughness [5] but till now no evidence of this enhancement has been proved for the fluoride superionic composites.

The aim of this paper is to study the fast ionic conduction and the cracking process in the LiF-RF<sub>3</sub> eutectic composites. Phase composition, microstructure, ionic conductivity and resistance against the cracking of the composites are determined. Conductivity and cracking process in the composite are compared with those in the single crystals of both phases forming the composite. The influence of the thermal residual stresses on the cracking process is discussed. The finite element method (FEM)

is used to predict the thermal residual strains and stresses arising during the preparation of the eutectic composite.

# EXPERIMENTAL PROCEDURE

The eutectic composites of the LiF-RF<sub>3</sub> system were prepared from the melt by using the Bagdasarov method of the horizontal directional crystallization. The preparation was performed for the R = La with graphite boats having width 28 or 8 mm in argon atmosphere. The growth velocities were 80 and 16 mm h<sup>-1</sup>. For R = Pr, Nd, Sm and Gd, large slabs of the composite, with a thickness of 3 mm, were prepared in a broad, flat Ni boats under helium atmosphere. The growth velocity 8 mm h<sup>-1</sup> was used. Pieces of optical LiF single crystals and pure (99.9 wt.%) RF<sub>3</sub> powder (premelted in graphite crucible under fluorinating atmosphere) were used as starting reactants.

The phase composition of the eutectic composites was determined using Philips X-ray PW 1710 powder diffractometer, and/or HZG-4 diffractometer, and CuK<sub> $\alpha$ </sub> radiation. Measurements were performed both for bulk samples and powders. The atomic composition of the eutectic composites was analyzed with help of the EDX. The micromorphology of the composites was examined in polished surfaces of samples by both optical microscopy and scanning electron microscopy (SEM), using the JSM-US, Jeol, 25 kV and back scattered electrons.

Electrical properties were measured in a sandwich arrangement. Rectangular samples with the thickness of 1 - 2 mm were used. Painted graphite (alcoholdag 450) and/or silver (Leitsilber) contacts were applied. The samples were placed between spring-loaded Pt electrodes in a furnace heated by dc current. Measurements were performed under argon atmosphere in the frequency range from 1Hz to 10 MHz at the temperature interval 20 - 550 °C. The samples were measured both during the heating, with a heating rate of 2 K min<sup>-1</sup>, and under isothermal conditions, after one hour annealing at the given temperature. The bulk ionic conductivity  $\gamma$  was determined by an impedance analysis.

The cracks were initiated using the Vickers diamond indentor (Zeiss Neophot 21), loaded with 0.56 N. The crack paths were studied on polished samples using the Zeiss Jenatech Inspection optical microscope and/or the Tesla BS-340 scanning electron microscope.

The influence of the microstructure. phase composition and mutual crystallographic orientation of both phases on the residual stresses distribution of the composite was modeled using the FEM. The simulation of the microstructure was performed by the SYSTUS program.

#### MODEL DETAILS

The thermal residual stress and strain fields arise when cooling the eutectic composite from melting to the room temperature. The fields resulting from the mismatch of the temperature dependence of the thermomechanical properties (the elasticity tensors and thermal expansion coefficients) of both phases and from the anisotropy of these properties can be determined using a numerical simulation of the cooling process.

The general computational model for the determination of the stress and strain fields in eutectic composites is based on the microstructural level. The fibrous LiF-TbF<sub>3</sub> eutectic composite is chosen for the simulation, as demanded thermomechanical properties of both phases are known for the whole temperature range from the melting point down to room temperature [8,9,10]. The interplanar distance of the crystallographic planes (200),  $d_{200} = 0.201$  nm, for the cubic LiF, is close to that of the (221) planes,  $d_{221} = 0.209$  nm, for the orthorhombic TbF<sub>3</sub>. Thus, the fiber-matrix phase boundaries are quasi-coherent, when the normal of the (200) planes in fibers is parallel to the normal of the (221) planes in the matrix. This kind of orientation of both phases is assumed in the simulation. For simplicity, both normals are supposed to be perpendicular to the upper surface of the sample. The rotation of the cubic phase around the normal of the (200) plane by an  $\omega_1$ angle, or the rotation of the orthorhombic phase around the normal to the (221) plane by an  $\omega_2$  angle do not disturb the quasi-coherency of the phase boundaries. For the simulation, the values  $\omega_1 = 30^\circ$ ,  $60^\circ$ ,  $90^\circ$  and  $\omega_2 = 0^\circ$ are used. Both the tensors of elasticity and the thermal expansion coefficients are transformed into the model coordinate system [11]. The arrangement of fibers in the matrix is supposed to be regular and the fibers are modeled as cylinders with a radius of either 0.5 or 1  $\mu$ m. Fully constrained (strongly bonded) interfaces between the fibers and the matrix are assumed.

The calculation of the thermal residual stresses is performed in two steps, by using the FEM and the SYSTUS program. In the first step the whole sample of the LiF - TbF<sub>3</sub> (32 - 68 vol.%) eutectic composite with the size of  $50 \times 20 \times 5 \text{ mm}^3$  is cooled from the eutectic (670 °C) to room (20 °C) temperature. With respect to the thermal expansion coefficient of the boats we suppose that all surfaces of the sample are free during the cooling phase. For the simulation, the sample is built up of 8-node cubic hexahedral elements, which are stress-free at the eutectic temperature. The initial distance of the nodes is equal to 1 mm. The simulation brings a shift of the nodes during cooling. The displacements of the nodes obtained from this model are used to determine the displacements of the bounded surfaces of the unit cell.

In the second step, a representative unit cell of the size  $3 \times 3 \times 1 \ \mu m^3$  is selected from the subsurface layer of the sample. (This layer is important for the indentation method.) The upper surface of the unit cell is free. The boundary conditions of the other surfaces consider the properties of the surrounding material. By using interpolation of the shift of the hexahedral elements nodes, the initial displacement of the unit cell nodes is obtained. In this modeling, the nodes in the fiber-matrix boundary are common for both phases to ensure the continuity of strains. It is also supposed that the sample can be treated as an in-parts homogeneous elastic body, and that the generalized Hooke's law is valid.

$$\sigma_{ij} = c_{ijkl} \cdot \varepsilon_{kl} \tag{1},$$

Here  $\sigma_{ij}$  and  $\varepsilon_{kl}$  are the components of the stress and strain, respectively, and  $c_{ijkl}$  is the elastic coefficient).

The thermal expansion coefficients of both phases are temperature dependent over the temperature range of cooling. The thermoelastic cooling effect appears as an initial thermal strain vectors  $\{\overline{e}_0^{th}\}$  in the program Systus. For the three-dimensional case with anisotropic thermomechanical properties, the initial thermal strain vector is given by the equation:

$$\overline{\mathbf{\epsilon}}_{0}^{t} = \begin{cases} \overline{\mathbf{\epsilon}}_{0x}^{th} \\ \overline{\mathbf{\epsilon}}_{0y}^{th} \\ \overline{\mathbf{\epsilon}}_{0y}^{th} \\ \overline{\mathbf{\epsilon}}_{0z}^{th} \end{cases} = \int_{T}^{T} \begin{cases} \alpha_{x} \\ \alpha_{y} \\ \alpha_{z} \end{cases} dT , \qquad (2)$$

where  $\alpha_x$ ,  $\alpha_y$  and  $\alpha_z$  are the thermal expansion coefficients to the directions of the axis of the model coordinate system. The loading of the unit cell is then determined.



Figure 1. The shape of a unit cell, which is used in simulations, finite element mesh, orientations of the fibers and of the coordinate system, and definition of the angle  $\alpha$ .

The FEM solution for the unit cell created in this manner enables us to determine the node displacement of the elements of the unit cell. The partition of the unit cell into the elements, macroscopic orientation of fibers in the matrix and the deformed form of the unit cell (the strains are 19-times enlarged) during cooling is presented in figure 1.

# RESULTS

The phase composition of the eutectic composites, as determined from the eutectic composition and X-ray diffraction data, is given in table 1. Two phases are found for all investigated samples, except of the LiF-LiGdF<sub>4</sub> composite. This composite contains a small amount of orthorhombic  $\beta$ -GdF<sub>3</sub> phase, in addition to the LiGdF<sub>4</sub> phase. The EDX analysis shows traces of carbon in the composites coming probably from the premelting process in carbon crucibles.

Table 1. Description of composites.

| Material                | Туре               | Eutectic<br>(vol.%) | Composition (mol.%) |
|-------------------------|--------------------|---------------------|---------------------|
| LaF <sub>3</sub> -LiF   | Tysonite-cubic     | 42 + 58             | 18 + 82             |
| PrF <sub>3</sub> -LiF   | Tysonite-cubic     | 44.5 + 55.5         | 20 + 80             |
| NdF <sub>3</sub> -LiF   | Tysonite-cubic     | 44 + 56             | 20 + 80             |
| SmF <sub>3</sub> -LiF   | Orthorhombic-cubic | 51.4 + 48.6         | 25 + 75             |
| LiGdF <sub>4</sub> -LiF | Scheelite-cubic    | 67 + 33             | 31 + 69             |

The diffraction data confirm a well-defined crystallographic texture of the composites as only very few reflections (in comparison with powders) are observed (figure 2). An almost-complete set of diffraction lines was developed only in some samples of the LiF-SmF<sub>3</sub> composite (figure 3). This fact confirms the orthorhombic structure of the SmF<sub>3</sub> phase of the composite. All composites contain the cubic LiF phase. The structural type of the second phase depends on the ionic radius of the rare earth element. The composites comprise the RF<sub>3</sub> phase with the tysonite (LaF<sub>3</sub>) structure (R = La - Nd), the scheelite-like LiRF<sub>4</sub> phase (R = Eu - Lu, Y) and the orthorhombic  $\beta$ -SmF<sub>3</sub> phase is negligible in all the composites.

Figure 4 shows the eutectic microstructure of directionally solidified composites (the LiF phase is dark, the cross section is perpendicular to the growth direction). A fine-graded, regular, highly ordered lamellar, fibrous, or mixed microstructure appears in all composites. The interphase spacings of about 3 - 5  $\mu$ m are observed at growth velocities 8 - 16 mm h<sup>-1</sup>. The microstructure is purely lamellar in the LiF-LaF<sub>3</sub> eutectic composite (figure 4*a*). In the LiF-PrF<sub>3</sub> and LiF-NdF<sub>3</sub>

composites, a disordering of the lamellar microstructure is observed (figures 4b, c). The orthorhombic  $SmF_3$ matrix exhibits mixed lamellar-fibrous microstructure (figure 4d). The scheelite-like LiRF<sub>4</sub> matrices show regular fibrous microstructure (figure 4e). The fibers are almost parallel to the growth direction having the diameter about 4 mm.

Figure 5 presents the temperature dependence of the ionic conductivity (parallel to the growth direction) of the directionally solidified composites.



Figure 2. X-ray diffraction patterns of the LiF-NdF<sub>3</sub> powder (of the eutectic composition) and of the LiF-NdF<sub>3</sub> eutectic composite (CuK<sub> $\alpha$ </sub> radiation).



Figure 3. X-ray diffraction pattern of the LiF-SmF<sub>3</sub> eutectic composite (CuK<sub> $\alpha$ </sub> radiation).

In the directionally solidified eutectic composites, an enhanced resistance against cracking is observed, in comparison with that in the corresponding single crystals. In the LaF<sub>3</sub>, NdF<sub>3</sub> and LiF single crystals, the crack lengths, initiated by the Vicker's indentor loaded with 0.56 N, range from 6 to 46  $\mu$ m (table 2). The crack length sometimes exceeds the value 50  $\mu$ m, and some single crystalline samples break apart already at the load of 1N. In the eutectic composites, the cracks are either not observed or they are deflected by the reinforcing phase (figures 6a, b). The cracks are deflected around the



Figure 4. The SEM micrographs of directionally solidified eutectic composites of the LiF-RF<sub>3</sub> system. *a*) R = La, b) R = Pr, c) R = Nd, d) R = Sm, e) R = Gd. (The LiF phase looks dark. The cross section is perpendicular to the growth direction. Eutectic composition.)

fibres in the fibrous composites and into the planar phase-to-phase boundaries in the lamellar composites. Generally, the crack deflection near the phase-to-phase interface is related to the thermal residual stresses and to the mismatch of the thermomechanical properties of both phases.

The residual thermal stresses  $\sigma_{ij}$  was obtained by solving the FEM. The critical stress state of the material (initiation of the crack, permanent deformations, etc.) can be described by the von Mises stress. Figure 7 shows the dependence of the normalized value of the von Mises stress,  $\sigma_N$ , on the distance from the centre of the fiber for the angle  $\alpha = 45^{\circ}$  ( $\alpha$  is defined in figure 1). Figure 8 presents the dependence of the von Mises stress (in the fiber-matrix interface) on the direction  $\alpha$  for distinguished radii of the fibres (figure 8*a*) and for various mutual crystallographic orientations of both phases (figure 8*b*).

# DISCUSSION

All directionally crystallized eutectic composites, except the LiF-SmF<sub>3</sub> one, show a high degree of both crystallographic (figure 2), and microstructural ordering (figure 4). The crystallographic disordering of the LiF-SmF<sub>3</sub> composite (figure 3) probably results from the  $\alpha \rightarrow \beta$  SmF<sub>3</sub> (tysonite→orthorhombic) phase transition when cooling the composite from the eutectic tempe-



Figure 5. The temperature dependences of the bulk ionic conductivity of directionally solidified eutectic composites of the LiF-RF<sub>3</sub> system.

O - R = La,  $\Delta$  - Pr,  $\Box$  - Nd,  $\blacktriangle$  - Gd,  $\times$  - Y,  $\blacksquare$  - Sm. The temperature dependences of the bulk ionic conductivity of the LiF (<sub>6</sub>), LiYF<sub>4</sub> ( $\nabla$ ), LaF<sub>3</sub> (n) and NdF<sub>3</sub> (+) single crystals are given for comparison purposes.

Table 2. The crack lengths of single crystals

| Load<br>(N) | Crack lengths<br>(µm) |                  |     |  |
|-------------|-----------------------|------------------|-----|--|
|             | LaF <sub>3</sub>      | NdF <sub>3</sub> | LiF |  |
| 0.56        | 13                    | 11               | 14  |  |
| 0.56        | 23                    | 34               | 20  |  |
| 0.56        | 30                    | 9                | 15  |  |
| 0.56        | 46                    | 31               | 10  |  |
| 0.56        | 27                    | 33               | 6   |  |

rature. The phase diagram indicates that the primary crystallization of the eutectics results in the cubic LiF and the tysonite-structured  $\alpha$ -SmF<sub>3</sub>. However, the scheelite-like LiSmF<sub>4</sub> phase (according to the phase diagram, the phase transition LiF+ $\alpha$ -SmF<sub>3</sub>  $\leftrightarrow$  LiSmF<sub>4</sub> takes place at 470 °C [6]) is not observed in the composite at room temperature, probably due to the quick cooling. The diffraction data show that the orthorhombic  $\beta$ -SmF<sub>3</sub> phase is the only Sm-containing phase in the composite at room temperature.

As the lower volume fraction of the LiF phase (table 1) supports fibrous microstructure, the decrease of the ionic radius of the rare earth element gives rise to a continual change from lamellar to fibrous microstructure (figure 4). The short-range order of LiF fibers in the  $\text{LiGdF}_4$  matrix is characterized by the 6-fold coordination (figure 4e). A long range ordering of the fibers does not occur.

The ionic conductivity of the LiF phase is negligible in comparison to that of the phases containing rare earth elements (figure 5). Therefore, the ionic conductivity of the composites is related to that of the rare-earth element containing phase. The conductivity enhancement (well known in the ceramic composites) is perceivable only for a conductivity lower than  $10^{-6}$  S cm<sup>-1</sup> in directionally solidified composites. Therefore, it is observed only in the LiF-LiRF<sub>4</sub> composites. The LiF-SmF<sub>3</sub> composite exhibits a negligible conductivity enhancement comparing with the conductivity of the other orthorhombic RF, single crystals [12]. The composites with the superionic tysonite-structured phase (for R = La - Nd) do not show the conductivity enhancement. In these composites, the conductivity is always lower than that of the corresponding RF<sub>3</sub> single crystals. This effect probably results from the fact that the phase-to-phase boundary is quasi-coherent and does not form fast diffusion paths for fluoride ions.

The increase of the resistance against crack propagation is observed in the composites, when compared with the cracks in both corresponding single crystalline phases. Both length and form of the cracks in eutectic composites initiated by the Vickers indentor are usually affected by the crack-deflection, crack branching or microcracking (figures 6a, b). Generally, it is supposed that these processes are controlled by the residual stress [13]. The FEM simulation shows that the maximum thermal residual stress is localized near the fiber-matrix interface (figure 7). This result is valid for a variety of fiber radii. The values of the von Mises stresses decrease with the decreasing radius of fibers. Due to the anisotropy of the thermophysical properties of the phases, discrete directions (determined by the specific values of the angle  $\alpha$  appear, along which the value of the normalized von Mises stress,  $\sigma_N$ , reaches a maximum. The maximum values depend both on the fiber diameter (figure 8a) and on the mutual crystallographic orientation of both phases (figure 8b). It means that due to the thermal residual stresses, the eutectic composite is maximally stressed in a close neighborhood of the fiber-matrix boundaries. The microcracks probably arise in this area. The energy necessary for the growth of the main, technologically dangerous crack, dissipates when creating new surfaces of the microcracks. The coalescence of the microcracks can result in a crack-deflection and/or in a crackbranching of the main crack. These processes bring about a shielding of the main crack in the composite. As the mutual fiber-matrix crystallographic orientation influences the distribution of the residual stress field, a proper choice of the radius and of the crystallographic orientation of fibers can improve the stress level, the cracking process and the fracture toughness enhancing processes in the composites.



Figure 6. The crack deflection into the phase-to-phase boundary, in the vicinity of the Vickers indent, in directionally solidified composites.

a) LiF-LiGdF<sub>4</sub> eutectic composite, b) LiF-SmF<sub>3</sub> eutectic composite.

# CONCLUSIONS

High degree of crystallographic ordering both of the lamellar and fibrous microstructure takes place in the directionally solidified eutectic composites of the system LiF-RF<sub>3</sub> (R = rare earth element). The crystallographic disordering in the LiF-SmF<sub>3</sub> eutectic composite results probably from the  $\alpha \rightarrow \beta$  SmF<sub>3</sub> phase transition during cooling from the eutectic temperature. When decreasing the ionic radius of rare earth ions, the microstructure of the composites changes from lamellar (for R = La - Pr)

to lamellar-fibrous microstructure (for R = Sm), and finally to fibrous microstructure (for R = Gd - Y).

The eutectic composite contains the cubic, poorly ionic conducting LiF phase, and a tysonite-structured  $RF_3$ phase being responsible for the fast ionic conductivity of the composite. The conductivity of these eutectic composites is significantly lower than that of the corresponding  $RF_3$  single crystals. The ionic conductivity of the composite (R = Sm) is carried by the orthorhombic  $SmF_3$  phase and is significantly lower than that of the eutectic composites with a tysonite-structured  $RF_3$  phase. The conductivity is comparable to that of the orthorhom-



Figure 7. The dependence of the normalized von Mises stress (for the fibers with a radius of 1  $\mu$ m ( $\blacksquare$ ) and 0,5  $\mu$ m ( $\bigstar$ )) on the distance from the center of the fiber, for  $\alpha = 45^{\circ}$ .

bic RF<sub>3</sub> single crystals. The enhancement of conductivity is significant in LiF-LiRF<sub>4</sub> composites. The conductivity of the composite for R = Gd is comparable to that of the composites containing a tysonite-structured phase.

The crack lengths in the eutectic composites are compared with those of both corresponding single phases. An increase of resistance to crack propagation is observed in the composites. The influence of microstructure, thermo-mechanical properties and crystallographic orientation of both phases on the distribution of the residual stresses is modeled. The following conclusions can be drawn from the results of the numerical simulation. 1. Field of the thermal residual stresses arises when cooling the eutectic composite. 2. The thermal residual stresses depend on the type of microstructure. 3. The thermal residual stresses increase with increasing radius of fibers. 4. The maximum stresses are localized near the fiber-matrix boundaries. 5. The anisotropy of the thermomechanical properties of both phases plays a significant role in the distribution of the stress and thus, can enhance the fracture toughness in the eutectic composites.



Figure 8. The dependence of the normalized von Mises stress, in the fiber-matrix boundary, on the  $\alpha$  angle. a) for a radius of 0.5  $\mu$ m ( $\blacksquare$ ) and of 1  $\mu$ m (\*); b) for different crystallographic orientations of LiF fibers:  $\omega_1 = 0^\circ$  ( $\blacksquare$ ),  $\omega_1 = 30^\circ$  ( $\blacksquare$ ),  $\omega_1 = 60^\circ$  ( $\blacktriangle$ ).

#### Ackowledgement

This work was supported by the grant agency VEGA, Slovak republic, Project no. 2/4184/98 and 95/5305/588.

### References

- Poulsen F.W. In: Transport-Structure Relation in Fast Ion and Mixed Conductors, (F.W.Poulsen, N.Hessel Andersen, K. Clausen, S. Skaarup, O. Toft Sorensen, Eds.), pp. 67-78, Riso National Laboratory, Roskilde 1985.
- Fedorov P.P., Trubitsyn M.Y., Trnovcová V., Sobolev B.P.: Inorg. Mater. 28, 2215 (1992).
- 3. Trnovcová V., Bárta Č., Fedorov P.P., Zibrov I.P.: Mater. Sci. Forum 76, 13 (1991).
- Labaš V., Trnovcová V., Minárik S.: Proc. Akademická Dubnica '96, (J.Turza, I. Jurčo, Eds) pp. 6-13, Dubnica 1996.
- 5. Kurz W., Sahm P.R.:Napravlennaja kristallisacia eutektičeskich materialov, Metalurgia, Moscow 1980.
- 6. Fedorov P.P., Sobolev B.P., Medvedeva L.V., Niterov V.M.: Growth of Crystals, Vol.21, 1999, (to be published).
- 7. Sobolev B.P., Fedorov P.P.: Inorg. Mater. 29, 458 (1993).
- 8. Van Uitert L.G., O'Bryan H.M., Guggenheim H.J., Barns R.L., Zydzik G.: Mat. Res. Bull. 12, 307 (1977).
- 9. Käräjämäki E., Laiho R., Levola T.: Phys. Rev. B 23, 6307 (1981).
- Francevič I.N., Voronov F.F., Bakuta C.A.: Uprugiye postojannyye i moduli uprugosti metallov i nemetallov, Naukova dumka, Kiiv 1982.
- Labaš V., Trnovcová V., Minárik, S. In: Microsim II, Simulation and Desing of Microsystems and Microstructures, (R.A.Adey, Ph.Renaud, Eds.), pp. 3-12, Computational Mechanics Publications, Southampton and Boston 1998.
- Trnovcová V., Fedorov P.P., Sobolev B.P., Seiranyan K.B., Oganesyan S.A., Vaľkovskij M.D.: Crystallography Reports 41, 731 (1996).
- 13. Xia K., Langdon T.G.: J.Am.Ceram.Soc. 29, 5219 (1994).

Submitted in English by the authors.

# FLUORIDOVÉ EUTEKTICKÉ KOMPOZITY: PRÍPRAVA, MIKROŠTRUKTÚRA, RÝCHLA IÓNOVÁ VODIVOSŤ A VÝPOČET ZVYŠKOVÝCH TERMICKÝCH NAPÄTÍ

## VLADIMÍR LABAŠ, VIERA TRNOVCOVÁ, PAVEL P. FEDOROV\*, STANISLAV MINÁRIK

Katedra fyziky, Materiálovotechnologická fakulta Slovenskej technickej univerzity, Pavlínska 16, 91724 Trnava, Slovenská republika

\*Šubnikovov Ústav kryštalografie, Ruská Akadémia Vied, Moskva 117333, Rusko

Uvádzajú sa výsledky vyšetrovania fázového zloženia, mikroštruktúry, vodivosti a odolnosti voči šíreniu trhlín eutektického kompozitného systému LiF-RF<sub>3</sub> (R = prvok vzácnej zeminy) pripraveného horizontálnym smerovým tuhnutím. Špeciálna pozornosť sa venuje rýchlej iónovej vodivosti a súvislostiam medzi kryštalografickou orientáciou fáz, mikroštruktúrou a zvyškovými termickými napätiami. Vplyv mikroštruktúry, zloženia a vzájomnej kryštalografickej orientácie fáz na rozloženie termických zvyškových napätí sa modeluje metódou konečných prvkov. Porovnáva sa teplotná závislosť iónovej vodivosti kompozitov a monokryštálov odpovedajúcich fáz.

Rontgenová difrakčná analýza potvrdila vysoký stupeň kryštalografického usporiadania lamelárnej aj vláknitej mikroštruktúry a rastrovacia elektrónová mikroskopia ukázala dobre vyvinutú textúru v kompozitných systémoch pripravených smerovým tuhnutím. Kryštalografické rozusporiadanie eutektického kompozitu LiF-SmF<sub>3</sub> pochádza pravdepodobne z fázového prechodu tysonitovej fázy SmF<sub>3</sub> na orthorombickú fázu počas ochladzovania kompozitu z eutektickej teploty na izbovú teplotu. Zmenšovaním iónového polomeru iónov vzácnych zemín sa mikroštruktúra postupne mení z lamelárnej (R = La -Pr) na zmiešanú lamelárno-vláknitú (R = Sm) a nakoniec na vláknitú (R = Gd - Lu, Y).

Pre R=La. Pr, Nd je eutektický kompozit zložený z kubickej fázy LiF, s nízkou iónovou vodivosťou, a z tysonitovej fázy RF<sub>3</sub>, ktorá je zodpovedná za rýchlu iónovú vodivosť kompozitu. Vodivosť týchto kompozitov je nižšia než vodivosť monokryštálov RF<sub>3</sub>. Pre R = Sm, iónová vodivosť kompozitu je určená orthorombickou fázou SmF<sub>3</sub>, je porovnateľná s vodivosť orthorombických RF<sub>3</sub> monokryštálov a je výrazne nižšia ako vodivosť kompozitov s tysonitovou RF<sub>3</sub> fázou. Výrazné zvýšenie iónovej vodivosti oproti vodivosti príslušných fáz pozorujeme iba v kompozitoch typu LiF-LiRF<sub>4</sub> (R = Gd, Y, Lu).

Zvýšenie odolnosti kompozitných systémov LiF-RF, voči poškodeniu lomom, v porovnaní s monokryštalickými fázami vytvárajúcimi kompozit, je zrejmé z merania dĺžok trhlín vyvolaných vpichom Vickersovho tvrdomeru. Mechanizmy vedúce k zvýšeniu tejto odolnosti súvisia s prítomnosťou zvyškových termických napätí. Vplyv mikroštruktúry, zloženia a vzájomnej kryštalografickej orientácie oboch fáz kompozitu na úroveň a distribúciu zvyškových napätí je modelovaný matódou konečných prvkov. Na základe numerickej simulácie možno konštatovať: (i) ochladením eutektického kompozitu z teploty tavenia na izbovú teplotu počas jeho prípravy vytvorí sa pole zvyškových termických napätí a deformácií, (ii) zvyškové napätia závisia od geometrického usporiadania mikroštruktúry, (iii) so vzrastajúcim polomerom vlákien zvyšuje sa namáhanie kompozitu v dôsledku zvyškových napätí, (iv) maximálne hodnoty napätí sú lokalizované v blízkosti rozhrania medzi matricou a vláknom, (v) anizotropia fyzikálnych vlastností významne ovplyvňuje distribúciu zvyškových napätí, (vi) geometrickým tvarom spevňujúcej fázy, rozmermi a vzájomnou kryštalografickou orientáciou fáz v kompozite je možné optimalizovať odolnosť kompozitu voči poškodeniu lomom.