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Syntheses and structures of Li_3ScF_6 and high pressure $LiScF_{4-}$, luminescence properties of $LiScF_4$, a new phase in the system $LiF–ScF_3$

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Abstract

Colorless single crystals of Li_3ScF_6 have been prepared by reacting the binary components LiF and ScF_3 at 820 °C for 16 h in argon atmosphere. This complex fluoride is the only stable phase in the system $LiF–ScF_3$ under ambient pressure. According to a structure refinement based on single crystal X-ray diffraction data it crystallizes in the centrosymmetric space group $P\bar{3}c1$ with $a = 8.78.3(1)$ Å and $c = 9.518(1)$ Å. The new structure of Li_3ScF_6 is a filled variant of the Na_2GeF_6 type structure and can be described in terms of a hexagonal close packing of fluorine in which 2/3 of the octahedral holes are occupied by Sc and Li.

High pressure/high temperature studies of the system $LiF–ScF_3$ show that the new phase $LiScF_4$ is formed at around 5.5 GPa and 575 °C. According to Rietveld refinements of powder X-ray diffraction data $LiScF_4$ adopts the Scheelite type structure (space group $I4_1/a$) with $a = 4.980(1)$ Å and $c = 10.074(1)$ Å. A sample of $LiScF_4$ doped with 1% Er exhibits an intense luminescence in the far IR region.

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Keywords: Fluoride; Scandium; Structure; Luminescence; High pressure synthesis

1. Introduction

Fluorides are excellent host materials for luminescent ions because of their wide transmission wavelength range and their low refractive index. In particular $LiYF_4$ is widely used as host for trivalent rare-earth ions [1–5]. It is astonishing that not much is known about complex lithium fluorides with the lighter homologue scandium. In systems $LiF–MF_3$ with large ions $M = $ Y, Eu–Lu ($r_M^{3+} > 0.80$ Å) only thermodynamically stable phases with the composition $LiMF_4$ exist at ambient pressure. These fluorides crystallize all in the scheelite type structure [6] in which the M^{3+} ions exhibit the coordination number 8. For smaller ions with $r_M^{3+} < 0.8$ Å only the 3:1 phases with composition Li_3MF_6 ($M = $ Al, Ga, Ti–Ni) [7–13] are found in which the M^{3+} ions are six-fold coordinated by F^- ions. Exceptions are the systems LiF/MF_3 with $M = $ Mn, Co or In, in which also phases with the composition $LiMF_4$ or Li_2MF_5 exist [14–16]. The Sc^{3+} ion is significantly smaller than Y^{3+} or the trivalent lanthanide ions and in agreement with the above-mentioned criteria Li_3ScF_6 is the only stable phase in the system $LiF–ScF_3$ under ambient conditions [17]. According to X-ray powder diffraction (XRD) studies the structure of Li_3ScF_6 is not isotopic to any known hexafluorometallate (III) and only a similarity to the Na_2GeF_6 type structure has been proposed [18]. Here we report on the synthesis, structure determination and refinement of Li_3ScF_6 based on single crystal X-ray diffraction data. Furthermore, we have explored the possible existence of phases in the system

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LiF/ScF_3 under high pressure–high temperature conditions as structural changes under high static pressure are often accompanied by an increase of the coordination number of the constituent ions. Under such conditions we have synthesized $LiScF_4$, and studied its suitability as host material for luminescent rare earth ions.

2. Experimental section

2.1. Li_3ScF_6

Starting materials were LiF (Alfa, 99.9%) and ScF_3 (Alfa, 99.9%) which were dried at 250 °C in a dynamic vacuum of 10^{-5} Torr. LiF and ScF_3 in a 3:1 M ratio were well ground in an argon filled dry box, pressed into a pellet and then placed in a platinum tube, which was transferred to an argon filled sealed quartz glass tube. The ampoule was heated to 820 °C with a heating rate of 5 °C/min, held for 16 h and then cooled to room temperature with a rate of 2 °C/min. A white powder sample of the complex fluoride Li_3ScF_6 was obtained which contained also tiny transparent crystals. The powder XRD pattern of Li_3ScF_6 matched nearly perfectly with the reported XRD pattern [18] which has led to a trigonal unit cell with $a = 8.773(3)$ Å and $c = 4.750(1)$ Å. However, a small reflection around 52° was observed which required a doubling of the c-axis for a complete indexing. The refinement of the trigonal unit cell of Li_3ScF_6 resulted in $a = 8.783(1)$ and $c = 9.518(1)$ Å.

Single crystals of Li_3ScF_6 were picked up by physical fragmentation from a sample under an optical microscope. Their suitability for intensity data collection was ascertained by recording a Laue photograph. Out of 5 one was found to have acceptable quality. The single-crystal X-ray investigation was performed on a four-circle diffractometer using Mo$K\alpha$ radiation (graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction was applied on the basis of ψ-scans. Table 1 contains the crystallographic data and the experimental conditions of the data collection and refinement. The structure was solved in the space group $P\bar{3}c1$ by direct methods and refined against the F^2 data (SHELX program [19,20]) to residuals $wR_2 = 9.96\%$ and $R_1 = 8.09\%$ for all 652 independent reflections, respectively, and $wR_2 = 8.41\%$ and $R_1 = 3.75\%$ for 359 reflections with $I > 2\sigma(I)$, see Table 1. The displacement factors of the atoms were taken into account in the anisotropic harmonic approximation. Atomic scattering factors and anomalous dispersion corrections were taken from the 'International Tables for X-ray Crystallography' [21]. The atomic position parameters and the isotropic displacement factors for Li_3ScF_6 are given in Table 2. Listings of the observed and calculated structure factors are available.

Table 1
Crystallographic data[a] and experimental conditions for Li_3ScF_6

Name	Lithiumhexafluoroscandate
Formula	Li_3ScF_6
Formula weight	179.78
Space group; Z	$P\bar{3}c1$ (No. 165), 6
Temperature	293 K
Unit cell dimensions:	$a = 8.783(1)$ and $c = 9.518(1)$ Å $V = 635.8(1)$ Å^3
Density (calculated)	2.817 g/cm^3
Crystal size (mm)	$0.01 \times 0.03 \times 0.03$
μ(Mo$K\alpha$), λ (Mo$K\alpha$)	1.77 mm^{-1}, 0.71073 Å
Diffractometer, scan mode	Enraf-Nonius, ϖ-scan Graphite-Monochromator, Scintillation counter
Limiting indices	$4° < 2\theta < 61°$, $-12 < h < 12$, $-12 < k < 12$, $-13 < l < 13$
Scan speed	Variable depending on I
Scan-width	1.1°
Reflections collected	9487
Absorption correction	ψ-scan with 10 reflections
Refinement	Full-matrix least square method SHELX-97 [20]
$F(000)$	504
Number of free parameters	47
Goodness-of-fit on F^2	0.925
Independent reflections	652 $F_o(hkl)$ 359 $F_o(hkl)$ with $I\| > 2.0\sigma(I)$
wR_2 (359 indep.refl.)	8.41%
R_1 (359 indep.refl.)	3.75%

[a] Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-415135, the names of the authors, and the journal citation.

2.2. $LiScF_4$

High pressure and high temperature (HP–HT) experiments have been performed up to 12 GPa and 900 °C, using a multianvil press (Voggenreiter GmbH, Germany) and a belt uniaxial press (Dieffenbacher GmbH, Germany). The multianvil press is equipped with a Walker module, employing 32 mm edge size WC cubes, with 11 and 8 mm truncation edge length, respectively. Both presses have been previously pressure–temperature calibrated. Temperature was controlled by Eurotherm units, and was measured using NiCr/Ni and W5Re/W26Re thermocouples, no correction being made for the pressure effect on thermocouple wires. Thermal gradient in the high pressure cell was minimized by using stepped cylindrical heaters.

Starting materials LiF (Merck, 99.9%), ScF_3 (Chempur, 99.9%), ErF_3 (REacton, Johnson Matthey, 99.99%), were dried at 250 °C in dynamic vacuum for overnight. Intimate mixtures of the reactants in an appropriate ratio were placed in tightly sealed Pt

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^4$) for Li_3ScF_6

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	*B* (is/eq)
Li1	6*f*	0	0.7000(9)	1/4	0.0207(17)
Li2	12*g*	0.6372(8)	0.6574(8)	0.4629(6)	0.0205(13)
Sc1	2*b*	0	0	0	0.0117(3)
Sc2	4*d*	2/3	1/3	0.2639(1)	0.0108(2)
F1	12*g*	0.7846(3)	0.5535(2)	0.1450(2)	0.0152(4)
F2	12*g*	0.5417(3)	0.4298(3)	0.3817(2)	0.0156(4)
F3	12*g*	0.1179(3)	0.2267(2)	0.1076(2)	0.0156(4)

capsules in order to avoid contamination. The experimental duration varied between 4 and 18 h at different temperatures (550–900 °C). The desired product $LiScF_4$ free from any byproduct was obtained at 575 °C, 5.5 GPa and 4.5 h. After the experiment the Pt capsules were extracted from the high pressure modules, and the sample material was retrieved under controlled atmosphere conditions. All samples resulting from experiments in which the Pt capsule was found broken, were eliminated from the final analysis.

XRD data for the Rietveld refinement were collected on a STOE STADI-P powder diffractometer equipped with a mini-PSD detector, with a rotating sample in symmetric transmission mode (Ge monochromator, CuKα radiation). For $LiScF_4$, the atomic parameters from $LiYF_4$ were used as starting parameters and the positional and thermal parameters were refined by full powder profile method using the CSD software [22]. The background scale, zero-shift and asymmetry parameters were refined, together with the profile parameters. The profile line shape was simulated by using a pseudo-Voigt function. The calculated pattern of $LiScF_4$ shows a good agreement with the observed one, Fig. 1. The details of the final Rietveld refinement for $LiScF_4$ are given in Table 3. The atomic parameters are listed in Table 4.

Photoluminescence spectra of powder samples of $LiScF_4$ and $LiScF_4$:Er (1%) were recorded at room temperature using the 488-nm line of an Ar ion laser with a laser power of 50 mW/cm^2. The photoluminescence was analyzed with a grating monochromator and detected by a cooled Ge diode. The spectral resolution of the monochromator was 1 nm.

3. Discussion

Systems LiF–MF$_3$ with small ions *M* = Al, Ga, Ti, V, Cr, Fe ($r_M^{3+} < 0.8$ Å) are characterized at ambient conditions by the existence of phases Li_3MF_6, which all crystallize in the monoclinic β-Li_3VF_6 type structure [9]. With the larger rare earth elements (*RE* = La–Lu, Y) only compounds of the type $LiREF_4$ are found in the systems LiF–REF_3, but with the smallest rare earth ion

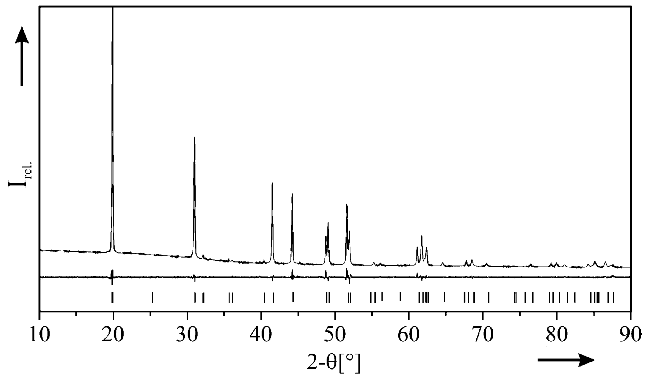

Fig. 1. Rietveld refinement of the crystal structure of $LiScF_4$. Observed diffraction pattern (upper curve), difference between calculated and observed intensities (lower curve). The tick marks show the positions of the allowed Bragg reflections.

Table 3
Crystallographic data[a] and experimental conditions for $LiScF_4$

Name	Lithiumtetrafluoroscandate
Formula	$LiScF_4$
Formula weight (g/mol)	127.9
Space group (Nr.), Z	$I4_1/a$ (Nr. 88), 4
Lattice constants (Å)	$a = 4.980(1)$, $c = 10.074(1)$
Cell volume (Å^3)	249.92(2)
F(000) (electrons)	240
Number of atoms in cell	36
Calculated density (g/cm^3)	3.399(1)
Absorption coefficient (cm^{-1})	25.31
Radiation and wavelength	Cu*K*α, 1.54051 Å
Diffractometer, monochromator	Stoe Stadi P, Ge
Mode of refinement, program	Full profile, CSD [22]
Number of atom sites	3
Number of free parameters	7
2Δ and sin θ/l (max)	96.4, 0.484
Reflections used in refinement	55
R_I, wR_p	0.037, 0.081
Goodness of fit	0.33
Scale factor	1.79(2)

[a] Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-412050, the names of the authors, and the journal citation.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^4$) for $LiScF_4$

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	*B* (is/eq)
Li	4*b*	0	1/4	1/8	0.01[a]
Sc	4*a*	1/2	3/4	1/8	0.039(5)
F	16*f*	0.2894(3)	0.0760(2)	0.0430(2)	0.099(7)

[a] Fixed during refinement.

Sc^{3+} the 3:1 phase Li_3ScF_6 is found which crystallizes in a new structure type, Fig. 2. The motifs of the mutual adjunction [23] and interatomic distances are given in Table 5. The crystal structure of Li_3ScF_6 is according to $Li(1)_3Li(2)_6$ $Sc(1)_1Sc(2)_2F(1)_6F(2)_6F(3)_6$ based on the treble of the formula. It can be described in terms of a close packing of puckered layers of F which are stacked along [001] according to the motif …ABAB… Sc(1) occupies 1/18th and Sc(2) occupies 2/18th of the octahedral holes within neighboring *F* layers, i.e., a total of 1/6th of the octahedral holes are occupied by Sc, Fig. 2. Both, the $Sc(1)F_6$ and $Sc(2)F_6$ octahedra are nearly regular ($d_{Sc-F} = 2.00$–2.03 Å). Within the anion layers additional the Li occupy octahedral holes in such a way that layers of 1 Sc(1) and 6 Li(2) alternate with 2 Sc(2) and 3 Li(1). However, it should be mentioned that the polyhedra around the Li are rather distorted and only for Li(1) the coordination number 6 is assigned unambiguously. For Li(2) the assumption of the coordination 6 is only a rough approximation as the Li(2)–F distances range from 1.944 to 2.495 Å, see Table 5. Accordingly the coordination number of *F*(1) is 3 + 1 whereas *F*(2) and *F*(3) are surrounded by only 3 next nearest cations.

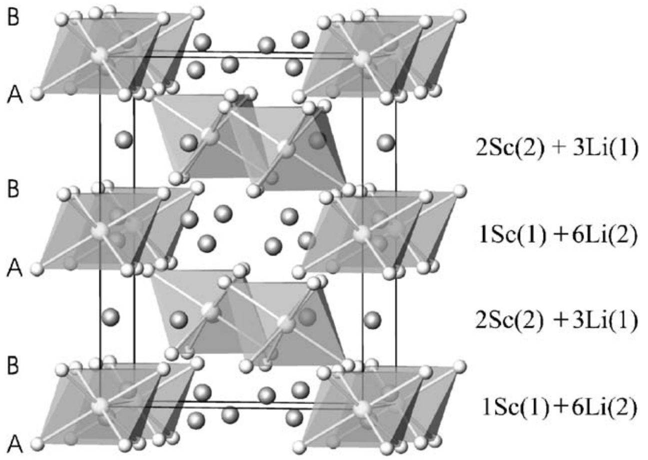

Fig. 2. Perspective view of the crystal structure of Li_3ScF_6. Small light circles represent *F*, small gray circles Li and large gray circles Sc. The ScF_6 octahedra are graphically emphasized.

Table 5
Motifs of the mutual adjunction [23] together with interatomic distances (Å), and coordination numbers (C.N.) for Li_3ScF_6

Atoms	12 F1	12 F2	12 F3	C.N.
6 Li1	2/1 1.944 (2 ×)	2/1 1.949 (2 ×)	2/1 2.226 (2 ×)	6
12 Li2	2/2 1.915 + 2.495	2/1 1.902 + 2.010	2/1 2.047 + 2.206	6
2 Sc1	—	—	6/1 2.006(6 ×)	6
4 Sc2	3/1 2.022 (3 ×)	3/1 2.027 (3 ×)	—	6
C.N.	4	3	3	

As mentioned above the structure of Li_3ScF_6 is closely related to the well-known structure of Li_2GeF_6 [24] which crystallizes in the Na_2GeF_6 type structure and exhibits also a hexagonal packing of anion layers, Fig. 3. In both structures the arrangements of the ScF_6 and GeF_6 octahedra are nearly identical and the main difference arises from the occupation of the Li sites. As the scattering power of Li is rather small it is not surprising that the XRD patterns of both structures are very similar, see Section 2. However, an essential difference is found for the charges of the metal atom layers (along [001]) which in the structure of Li_2GeF_6 are + 7 for Ge(1) + 3 Li(2) and + 11 for 2 Ge(2) + 3 Li(1), see Fig. 3, whereas the structure of Li_3ScF_6 exhibits a much more balanced the charge distribution, i.e. both Sc/Li layers have the charge + 9, see Fig. 2. Nevertheless, due to the similarity of the unit cell dimensions it is possible to synthesize members of the mixed series $Li_{3-x}(Ge_xSc_{1-x}F_6)$ which might be promising candidates for Li ionic conductivity.

The reaction of LiF with ScF_3 under a pressure of 5.5 GPa at 575 °C for 4.5 h leads to white powder samples and colorless transparent crystallites of $LiScF_4$, see Section 2. $LiScF_4$ crystallizes in the scheelite type structure, like $LiYF_4$, in accordance with the so-called pressure homologue rule. Characteristic building units are ScF_8 bisdisphenoids with four short Sc–F distances of 2.101 Å and four longer ones of 2.179 Å, Fig. 3. Despite the fact that $LiScF_4$ has been synthesized under high pressure it is remarkable that it is the first compound which contains eight-fold coordinated Sc. The Li–F distances within the LiF_4 tetrahedra are 1.874 Å and slightly shorter than the corresponding distances in $LiYF_4$ (1.899 Å). As it can be seen from Fig. 4 the LiF_4 tetrahedra in $LiScF_4$ are highly squeezed along the *c*-axis with four long edges (3.36 Å) and two short ones (2.89 Å). This squeezing becomes even more

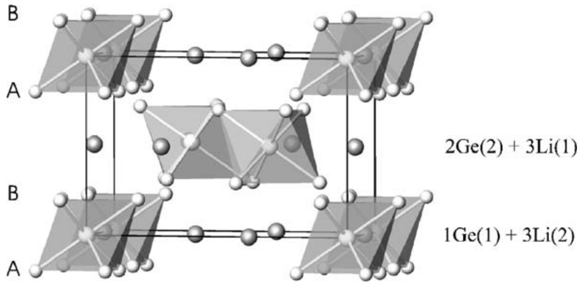

Fig. 3. Perspective view of the crystal structure of Na_2GeF_6. Small light circles represent *F* and large gray circles Na. The GeF_6 octahedra are graphically emphasized.

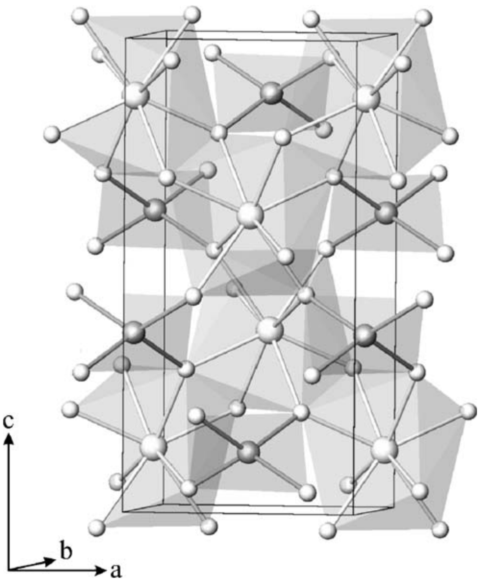

Fig. 4. Perspective view of the crystal structure of $LiScF_4$. Small black circles represent *F*, large dark gray circles Li and large gray circles Sc. The ScF_8 polyhedra and the LiF_4 tetrahedra are graphically emphasized.

evident from the F–Li–F angles, which are 101.2° and 127.8°, respectively.

$LiScF_4$ is a stable phase at room temperature as could be seen from an XRD pattern recorded more than three months after the synthesis. However, $LiScF_4$ decomposes into ScF_3 and Li_3ScF_6 on heating at 250 °C. This observation clearly indicates that though it is thermodynamically metastable it is a kinetically stable phase, like most of the recovered high pressure phases. Li_3ScF_6, on the other hand, is not stable under high pressure–high temperature conditions and decomposes into LiF and $LiScF_4$, as shown in a separate experiment (5.5 GPa, 400 °C). This appears reasonable as the molar volume $V(Li_3ScF_6) = 63.8\,cm^3/mol$ is approximately 10% larger than the sum of the molar volume $V(LiScF_4) + 2 \times V(LiF) = 37.6\,cm^3/mol + 2 \times 9.76\,cm^3/mol = 57.12\,cm^3/mol$. One can also conclude that there is no pressure/temperature range where both phases, Li_3ScF_6 and $LiScF_4$, coexist. It is worth mentioning that Li_3ScF_6 does not get converted to $LiScF_4$ and LiF on applying high pressures up to 10 GPa for 50 h at ambient temperature. Therefore, it can be inferred that the decomposition mechanism of Li_3ScF_6 into $LiScF_4$ and LiF is reconstructive rather than displacive.

For an electrostatic analysis and a check the quality of the refinements, especially with respect to the Li positions, we have calculated the Madelung Parts of Lattice Energy, MAPLE [25] for Li_3ScF_6 and $LiScF_4$ and obtained 2312.6 kcal/mol and 1746.6 kcal/mol, respectively. These values have to be compared with the corresponding sum of the MAPLE values of the binary components LiF and ScF_3 [26].

$$\begin{array}{lll}
\mathrm{MAPLE(ScF_3)} + 3-\mathrm{MAPLE(LiF)} & & = \mathrm{MAPLE_{calc.}(Li_3ScF_6)} \\
1476.8 & 3 \times 288.7 & = 2342.9\ \mathrm{kcal/mol} \\
\mathrm{MAPLE(ScF_3)} & \mathrm{MAPLE(LiF)} & = \mathrm{MAPLE_{calc.}(LiScF_4)} \\
1476.8 & +288.7 & = 1765.5\ \mathrm{kcal/mol}
\end{array}$$

The differences are rather small ($<1.3\%$) and indicate that the MAPLE concept holds for highly ionic compounds even when comparing the structures of high pressure and normal pressure phases. In addition, it reflects the excellent quality of the structure refinements.

As mentioned in Section 1 fluorides like $LiYF_4$ are good host materials for luminescent ions such as the lanthanides. Matrix effects are very important for optical transitions and therefore we have made attempts to prepare $LiY_{0.95}Sc_{0.05}F_4$, under high temperature–ambient pressure conditions. However, we found that not even 5 mol% of Y in the lattice of $LiYF_4$ can be substituted by Sc and obviously the size difference of Sc and Y is too large. We have used $LiScF_4$ itself as host material and measured the photoluminescence spectrum of a sample $LiScF_4$ doped with 1 mol% Er, see Fig. 5. Two intense groups of sharp luminescence lines around 1500 nm are observed. This spectrum is similar to what has been found for $LiYF_4$:Er [27], however, due to the smaller sites for Er in $LiScF_4$ the lines are shifted towards shorter wavelengths by approximately 20 nm. Considering the large difference in the molar volumes $V(LiScF_4) = 37.6\,cm^3/mol$ and $V(LiYF_4) = 43.3\,cm^3/mol$ mixed samples with compositions $LiY_{1-x}Sc_xF_4$:*RE* (*RE* = rare earth element) prepared under high pressure appear promising candidates for the access of emission lines in an intermediate spectral range compared to pure doped $LiYF_4$ and $LiScF_4$ samples. Furthermore, the spectra of $LiScF_4$:RE can be also used to estimate pressure effects on the optical properties of $LiYF_4$:*RE* [28].

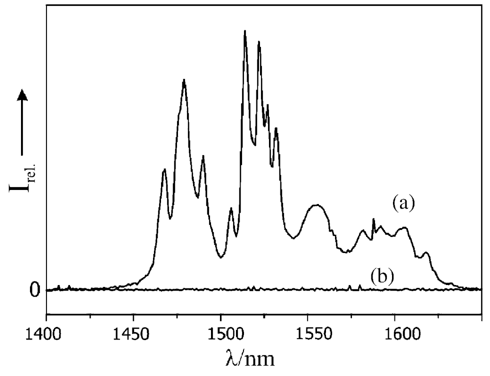

Fig. 5. Photoluminescence spectra of: (a) a sample of $LiScF_4$ doped with 1% Er and (b) an undoped $LiScF_4$ sample.

4. Summary and outlook

The main focus of this contribution lies in the preparative and chemical aspects of phases in the system LiF/ScF_3. However, the new phases in the system LiF/ScF_3 call for studies of structure property relationships, such as Li ionic conductivity of the mixed series $Li_x(Ge_xSc_{1-x}F_6)$, which are in progress. The intense luminescence in the far IR region of a $LiScF_4$ sample doped with 1% Er is given as an example to show the potential of $LiScF_4$ as a host material for studies of optical properties, possibly also for some optical applications. Detailed structural studies of $LiScF_4$ based on high pressure in situ experiments have already been performed and will be reported in the near future [29].

Appendix A. Supplemental Data

The online version of this article contains additional supplementary data. Please visit doi:10.1016/j.jssc.2005.04.038.

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