Synthesis and study of the magnetic properties of micro- and nanosize powders $LiTbF_4$ and TbF_3

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Introduction

Due to their unique physical and chemical properties nanosized particles have attracted increasing interest [1]. The complex fluorides $LiReF_4$ (Re = rare earth ion) present a class of crystal materials as model objects in physics of dipolar magnets. Nanocrystals of rare-earth tetrafluorides compounds with a controlled size, shape, composition and surface have specific optical, electronic, magnetic and catalytic properties that fundamentally important for industrial use [2]. Trifluoride exhibit distinct magnetic properties at low temperatures and interested as model for the theoretical study of magnetic ordering in competition dipole-dipole and exchange interactions [3].

For the first time the transition to the ferromagnetic state in $LiTbF_4$ crystal along easy magnetic axis was found in [4] from the temperature dependence of the longitudinal magnetic susceptibility. The $LiTbF_4$ is dipole Ising dielectric ferromagnet below the T_c (2.89K) temperature [5].

The compound TbF_3 is a dielectric ferromagnet. The phase transition TbF_3 single crystal from the paramagnetic to the ferromagnetic state occurs when the temperature is lowered to T_C=3.95 K [5]. At low temperatures ($T<T_C$) magnetic moments of ions Tb^{3+} (~9 μ_B) in TbF_3 single crystal ordered in two magnetically nonequivalent sublattices due classical dipole-dipole interaction between the ions of terbium, which dominates in the system above the magnetic exchange interaction.

Syntesis of micro- and nanoparticles powders

The samples of $LiTbF_4$ and TbF_3 were synthesized using following technologies [2,6-10].

Sample 1:

$$LiNO_3 + Tb(NO_3)_3 + 4NH_4F \xrightarrow{400^oC,4ч} LiTbF_4 + 4NH_4NO_3.$$

Sample 2:

$$LiOH \cdot 3H_2O + Tb(NO_3)_3 \cdot 5H_2O + 4NH_4F \xrightarrow{300^oC,3ч,CF_4} LiTbF_4 + 4NH_4NO_3 + 8H_2O.$$

Sample 3:

$$Tb(NO_3)_3 \cdot 5H_2O + 3NaF \longrightarrow TbF_3 + 3NaNO_3.$$

The X-ray analysis of synthesized samples is shown in Fig.1.

Phase ratio of $LiTbF_4$ и TbF_3 in samples 1-2 was refined using X-ray diffraction.

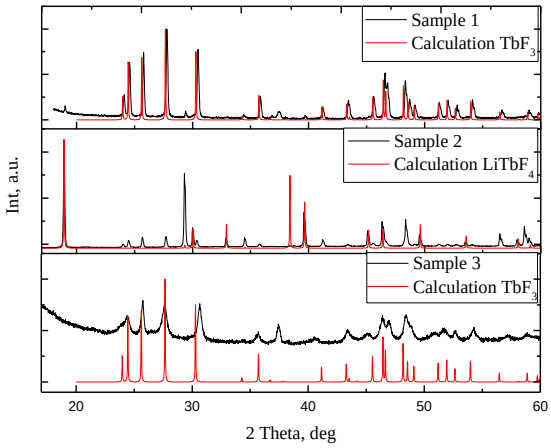
The chemical compositions of the synthesized samples are:

Sample 1 - TbF_3 (81.2±0.4%)+$LiTbF_4$ (6.9±0.1%)+$LiNO_3 \cdot H_2O$(11.9±1.1%),

Sample 2 - $LiTbF_4$ (79.9±0.7%)+TbF_3 (20.0±0.5%),

Sample 3 – TbF_3(99±1%).

Dimensions of powders particles were determined using the dynamic and static light scattering spectrometer for registration nanoparticles size and composition Photocor Complex (table 1).



Sample	Characteristic size (diameter)
$LiTbF_4$(79.9%)+TbF_3(20 %)	20 mkm
$LiTbF_4$(6.9%)+TbF_3(81.2 %)	1,5 mkm
TbF_3	585 nm

Fig.1. X-ray analysis of samples 1-3 **Table 1.** Characteristic size of samples 1-3

Study of magnetic properties, discussion and results

The temperature dependencies of magnetic susceptibility of the all synthesized samples was measured on PPMS in magnetic fields with a strength of 100 Oe and 1 T, at temperatures of 2-300 K.

The temperature dependence of the derivative of magnetic susceptibility of the sample 1 is shown on Fig.2. There are two phase transitions at temperatures T=2.8 K and T=3.76 K, which correspond to the Curie temperature of the transitions to a ferromagnetic state for $LiTbF_4$ and TbF_3 single crystals. The red curve on Fig.2 presents the dependence of the derivative of magnetic susceptibility of single crystal $LiTbF_4$ in a magnetic field B||*c*. In the measurement of the magnetization of the powder all possible directions of arrangement of the particles along the direction of the external magnetic field can be equivalent, which would reduce the total magnetization.

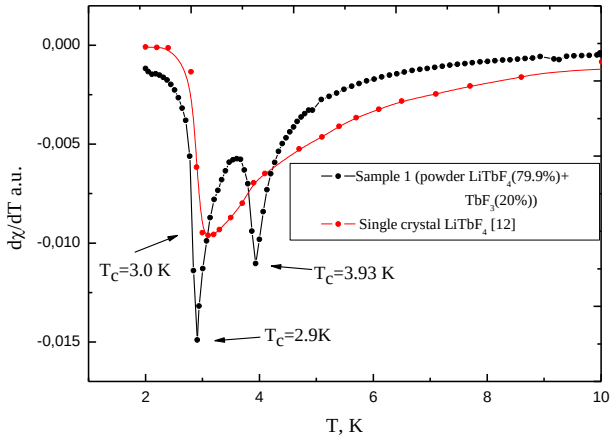


Fig.2. Dependence of the derivatives of magnetic susceptibility of temperature in $LiTbF_4$ (79.9±0.7%)+TbF_3 (20.0±0.5%) powder and $LiTbF_4$ single crystal, B=100 Oe.

The temperature dependence susceptibility of the sample 2 is shown on Fig.3 (black points). There is only one transition to a magnetically ordered state at T = 3.78 K, referring to the ferromagnet TbF_3. Content $LiTbF_4$ of the sample is too low to obtain the temperature transition to a magnetically ordered state of $LiTbF_4$.

Fig.4 shows the measured temperature dependence of the susceptibility of nanosized powder TbF_3 and data from [3] - the temperature dependence of the susceptibility of the powder TbF_3 and single crystal TbF_3 in different directions of crystal lattice – $\chi||a$, $\chi||b$, $\chi||c$. Also for comparison with nanosized powder TbF_3, there is given data on the temperature dependence of the magnetic susceptibility in the micropowder in external magnetic field induction B_0 = 0.01 T (blue points).

The magnetic susceptibility of the powder is described as $\chi_p = (\chi_a + \chi_b + \chi_c)/3$, where χ_a, χ_b, χ_c - magnetic susceptibilities along the axes *a*, *b*, *c* [3]. This calculation is in approximately agreement with the experimental results, because it does not take into account the size and shape of the particles, as well as the parameters of the crystal field and the local magnetic fields on the Tb^{3+} ions.

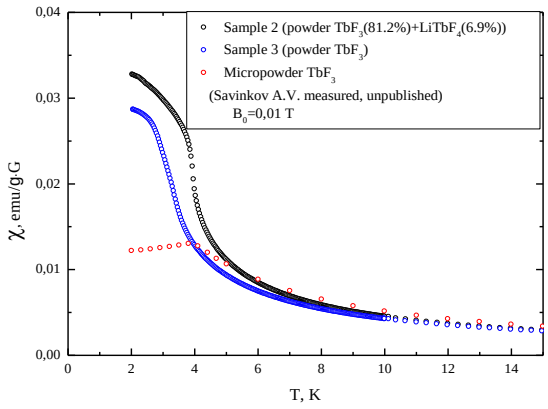


Fig.3 Temperature dependencies of magnetic susceptibility in TbF_3 and TbF_3(81.2±0.4%)+$LiTbF_4$ (6.9±0.1%).

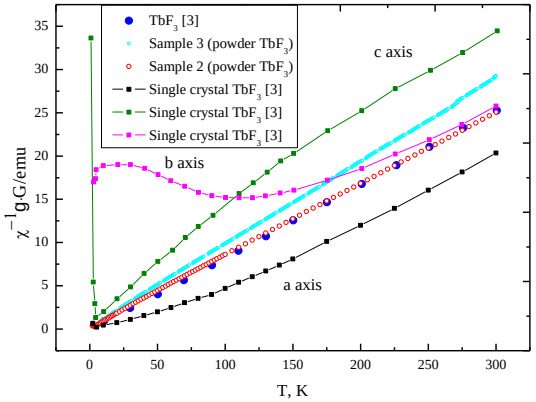


Fig.4. Temperature dependencies of magnetic susceptibility in TbF_3.

Theoretical calculation of the susceptibility $\chi=M/B$, shown in Fig.5 (red line). It was made taking into account all possible orientations of the external magnetic field along the crystallographic c-axis of the nanoparticle. Assuming that the angle between the *c*-axis of the lattice and the external magnetic field of α, the projection of the magnetic field on the direction of the *c*-axis lattice $B_z=B_0 cos\alpha$. The shape of the nanoparticles assumed spherical, the summation carried on sphere 360^0. The calculation was performed using the Matlab software:

$$M_z = B_z\left[\lambda\left(\frac{th(\delta/2k_BT_C)}{th(\delta/2k_BT)}-1\right)+N\right]^{-1}, \qquad (1)$$

where M_z – magnetization along *c*-axis, λ – molecular field constant (λ=5.23±0.56), δ - initial splitting quasidoublet (δ = 1 cm^{-1}), N – demagnetization factor (N=4π/3), B_z – external magnetic field, k_B – Boltzmann's constant, T - temperature magnetic ordering [2].

The measured temperature dependences of the magnetization in sample 1 and single crystal $LiTbF_4$ at $B_0||a$ and $B_0||c$ in external magnetic field (B_0 = 1 T) are presented on the Fig.5.

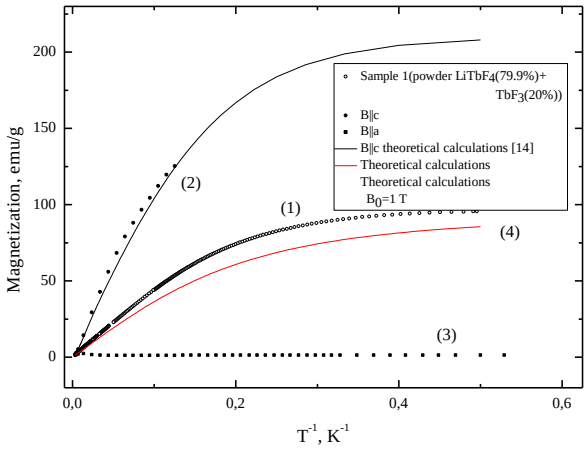


Fig.5. Temperature dependence of the magnetization in $LiTbF_4$ (79.9±0.7%)+TbF_3 (20.0±0.5%) and $LiTbF_4$ single crystal, B=1T.

Curve 4 in Fig.5 shows the calculations taking into account all possible orientations of the external magnetic field along the crystallographic c-axis of the nanoparticle. The discrepancy between the theoretical calculations in this case can also be explained by the fact that the calculation has not been considered TbF_3 particle content of a sample, and particle shape.

The fact that the values of magnetization were calculated without taking into account the content of TbF_3 in the compounds and particles shapes, can explain the difference between experimental results and theoretical description. This approximation describes the temperature dependence of the susceptibility for samples in the paramagnetic phase, above the transition temperature to magnetic ordered state.

The unusual behavior of the magnetization and magnetic susceptibilities in micro- and nanosized powders $LiTbF_4$ and TbF_3 should be considered in detail.

Acknowledgments

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References

[1]. Kuznetsov S. V. et al. Russian chemical reviews.V.75. №.12. P.1065-1082 (2006).
[2]. Du, Y. P., Zhang, Y. W., Sun, L. D., & Yan, C. H. Dalton Transactions, (40), 8574-8581 (2009) .
[3]. L.M. Holmes, H.J. Guggenheim. Journal de Physique. V.32. P. 501-502 (1971).
[4]. L.M. Holmes, T. Johansson. Solid State Commun. V.12. I.10. P.993-997 (1973).
[5]. J. Als-Nielsen, L.M. Holmes, F.K. Larsen, H.J. Guggenheim. Phys. Rev. B, 12,191 (1975).
[6]. Fedorov, P.P., Kuznetsov, S.V., Voronov, V.V. et al. Russ. J. Inorg. Chem. 53(11), 1681 (2008).
[7]. Chunhua Lu, et al. Materials Research Bulletin. 46(2), 216-222 (2011).
[8]. Shi Chen, Shiwei Wang, Jian Zhang, Liqiong An. Journal of Nanoscience and Nanotechnology.V.9.P.1942–1946 (2009).
[9]. Chunxia Li, Jun Lin. J. Mater. Chem. V.20. P. 6831-6847 (2010).
[10]. M.F. Joubert, B. Jacquier, R. Moncorge. Phys. Rev. B. V.28. P.3725 (1983).
[11]. I.V. Romanova, B.Z. Malkin, I.R. Mukhamedshin, H. Suzuki & M.S. Tagirov. Physics of the Solid State, 44(8), 1544-1549 (2002).