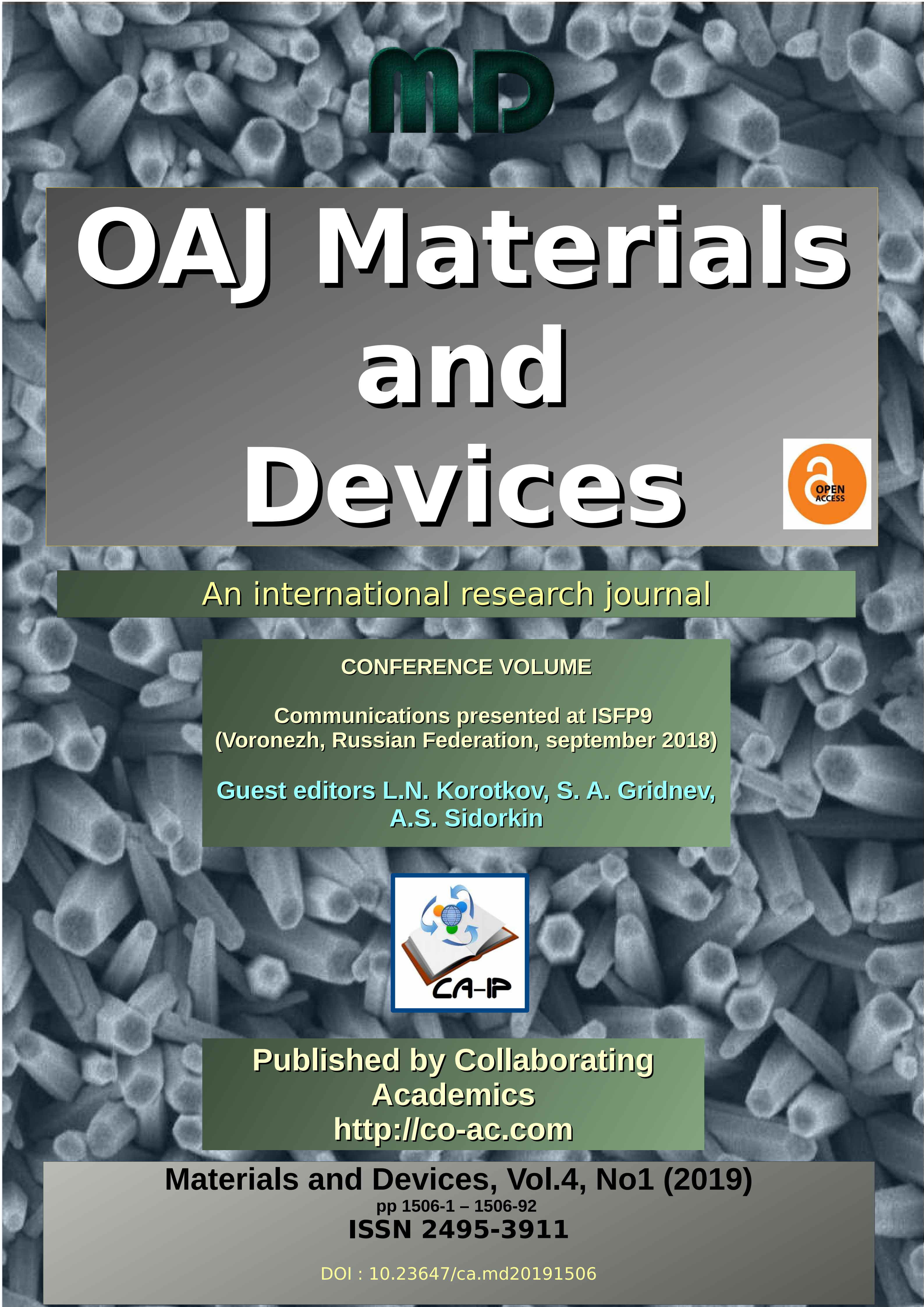


OAJ Materials and Devices

An international research journal

CONFERENCE VOLUME

Communications presented at ISFP9
(Voronezh, Russian Federation, september 2018)

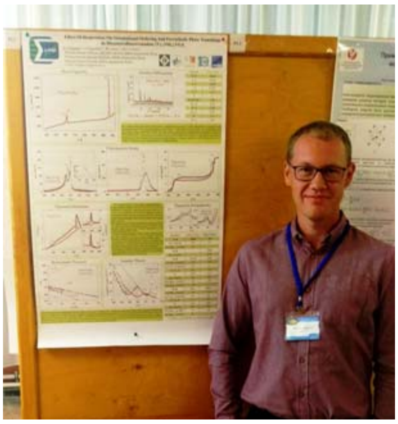
Guest editors L.N. Korotkov, S. A. Gridnev, A.S. Sidorkin

Published by Collaborating Academics
http://co-ac.com

Materials and Devices, Vol.4, No1 (2019)
pp 1506-1 – 1506-92
ISSN 2495-3911

DOI : 10.23647/ca.md20191506

Effect of Deuteration on Orientational Ordering and Ferroelastic Phase Transitions in Dioxotetrafluorovanadate $(NH_4)_3VO_2F_4$



E.V. Bogdanov[1,2], E.I Pogoreltsev[1,3], M.V. Gorev[1,3]
and I.N. Flerov[1,3]

[1] Kirensky Institute of Physics, FRC KSC SB RAS, 660036, Krasnoyarsk, Russia
[2] Krasnoyarsk State Agrarian University, 660049, Krasnoyarsk, Russia
[3] Siberian Federal University, 660074, Krasnoyarsk, Russia
e-mail: evbogdanov@iph.krasn.ru

The crystals of vanadium oxyfluorides (VOF) can form various distorted VOF-octahedra due to the ability of vanadium to adopt different valence. VOF-elements can be used to create crystalline structures with interesting physical properties for designing functional elements in electronics and microelectronics, and can also be considered as materials for creating solid-state cooling devices. Despite the variety of vanadium oxyfluorides, the VOF anion is disordered. In particular, the structure $(NH_4)_3VO_2F_4$ contains two independent OF-anions one of which is orientationally disordered and other is completely ordered [1]. The crystal $(NH_4)_3VO_2F_4$ undergoes four successive phase transitions with with the following symmetry change: $Fm3m \leftrightarrow Immm \leftrightarrow$rhombic $\leftrightarrow P112/m \leftrightarrow P1$ at T_1=448K, T_2=244K, T_3=210K and T_4=205K respectively.

In the present work, the studies of disordering/ordering processes using deuteration of the ammonium group [2] and complex thermophysical and dielectric studies of crystals $(NH_4)_3VO_2F_4$ have been performed. It was found that deuteration has practically no effect on the temperature of the phase transitions T_1=437K, T_3=212K and T_4=208K but led to the disappearance of the transformation *Immm* ↔ *rhombic* at T_2 (Fig. 1*a*). As a result of D→H substitution, the total entropy change (ΔS_Σ=12.3 J/mol·K → 17.0 J/mol·K) but the contribution from low-temperature transformations has changed insignificantly (Fig. 1*b*). The substitution D→H led to large change in the susceptibility to external hydrostatic pressure the of low-temperature transformations (dT_3/dp=-43 K/GPa → -27 K/GPa and dT_4/dp=-79 K/GPa → -25 K/GPa). The phase *P*112/*m* becomes more stable under pressure in spite of the fact that in $(NH_4)_3VO_2F_4$ it was wedged out at low pressure (p_{trp}≈0.3 GPa). The nature of the phase transitions remains ferroelastic. Significant changes in the thermal expansion are observed at the high-temperature transformation at T_1 ($\delta\beta_1$=0.6%), that shows the first order of phase transition is preserved.

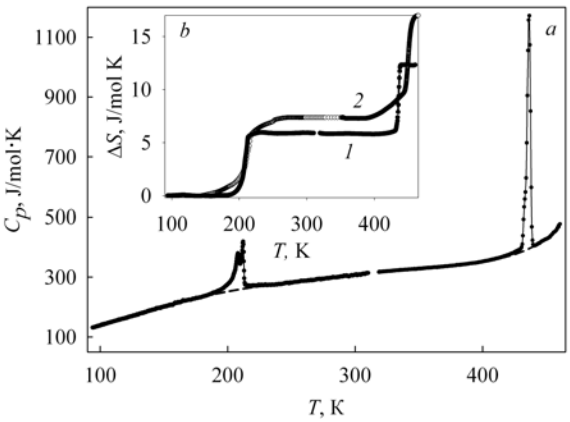


Fig 1. Temperature dependence of the molar heat capacity in a wide temperature range (*a*). Temperature dependence of the total excess entropy change $(ND_4)_3VO_2F_4$ (*1*) and $(NH_4)_3VO_2F_4$ (*2*) (*b*).

Acknowledgment. The reported study was funded by Russian Foundation for Basic Research, Government of Krasnoyarsk Territory, Krasnoyarsk Regional Fund of Science to the research project: «Effect of deuterium on orientational ordering and phase transitions in ammonium fluorine oxygen vanadates» № 18-42-243003

References

1. A.A. Udovenko, E.I. Pogoreltsev, Y.V. Marchenko and N.M. Laptash Acta Cryst. **B73,** 1085 (2017)
2. E.V. Bogdanov, E.I. Pogoreltsev, M.V. Gorev and I.N. Flerov. Inorg. Chem., **56** (11), 6706 (2017).