====================== **DIELECTRICS** ======================

Effect of Cation Substitution in Fluorine−Oxygen Molybdates $(NH_4)_{2-x}A_xMoO_2F_4$
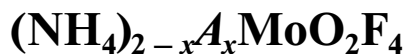
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Abstract—Thermophysical and structural studies of $(NH_4)_{2-x}A_xMoO_2F_4$ (A = Cs, Rb, K) solid solutions of oxyfluorides have been performed. The character of the influence of cation substitutions on the stability of the initial phase (space group *Cmcm*) and on the mechanism of phase transitions has been elucidated.

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1. INTRODUCTION

Earlier, it was shown that the substitution of Mo for the central W cation in $(NH_4)_2MeO_2F_4$ crystals with the orthorhombic structure (space group *Cmcm*) brings about a significant change in the phase transition temperatures and their susceptibility to external pressures but, however, does not practically influence the corresponding changes in the entropy [1, 2]. Such a behavior of the thermodynamic properties is due to different mechanisms of structural distortions: in $(NH_4)_2WO_2F_4$ (*Cmcm* ⟶ *P*-1 ⟶ ?), complete ordering of ligands and partial ordering of the ammonium groups occur; in $(NH_4)_2MoO_2F_4$ (*Cmcm* ⟶ *Pnma* ⟶ ?), complete ordering of the ammonium groups is accompanied by partial ordering of ligands [3, 4]. As a result, the nature of the phase transition is changed from ferroelastic to antiferroelectric.

The active role of the ammonium group in the mechanism of changing the structure was established when studying $(ND_4)_2WO_2F_4$ [5]. The deuteration does not practically influence the phase transition temperatures and the sequence of changes in the structure but leads to a substantial decrease in the entropy of the high-temperature transition due to more retarded vibrations of the deuterium group and also to a significant increase in the pressure coefficient of the low-temperature transformation.
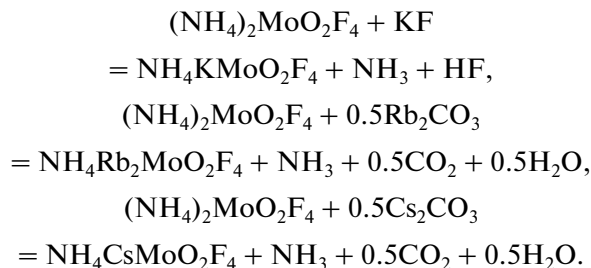
There are no data available in the literature on the existence of phase transitions in $A_2MoO_2F_4$ compounds with atomic cations Cs, K, and Rb. It was shown in [6] that $Rb_2MoO_2F_4$ has an orthorhombic symmetry at room temperature (space group *Amam*, $Z = 4$, which is equivalent to space group *Cmcm* at

other choice of axes) with partially disordering of fluorine and oxygen atoms. Electron diffraction studies show that the initial structure of $K_2MoO_2F_4$ is tetragonal (space group $P4/nmm$, $Z = 4$) with complete ordering of F and O atoms [7]. Thus, only $Rb_2MoO_2F_4$ can demonstrate a phase transition related, in particular, with ordering of the ligands.

For a more detailed elucidation of the role of the ammonium groups in mechanisms of phase transitions, we study the thermodynamic properties and the structure of a number of solid solutions $(NH_4)_{2-x}A_xMoO_2F_4$ (A = Cs, Rb, K) and $Rb_2MoO_2F_4$.

2. SYNTHESIS AND GROWTH OF CRYSTALS AND THEIR STRUCTURE

The solid solutions $(NH_4)_{2-x}A_xMoO_2F_4$ (A = Cs, Rb, K) were synthesized using, as the initial components, $(NH_4)_2MoO_2F_4$ compound and corresponding alkali metal fluoride or carbonate taken in the stoichiometric proportions according to the reactions

$$(NH_4)_2MoO_2F_4 + KF$$
$$= NH_4KMoO_2F_4 + NH_3 + HF,$$
$$(NH_4)_2MoO_2F_4 + 0.5Rb_2CO_3$$
$$= NH_4Rb_2MoO_2F_4 + NH_3 + 0.5CO_2 + 0.5H_2O,$$
$$(NH_4)_2MoO_2F_4 + 0.5Cs_2CO_3$$
$$= NH_4CsMoO_2F_4 + NH_3 + 0.5CO_2 + 0.5H_2O.$$

A mixture of the reagents was dissolved in HF during heating. From the solution obtained, during its
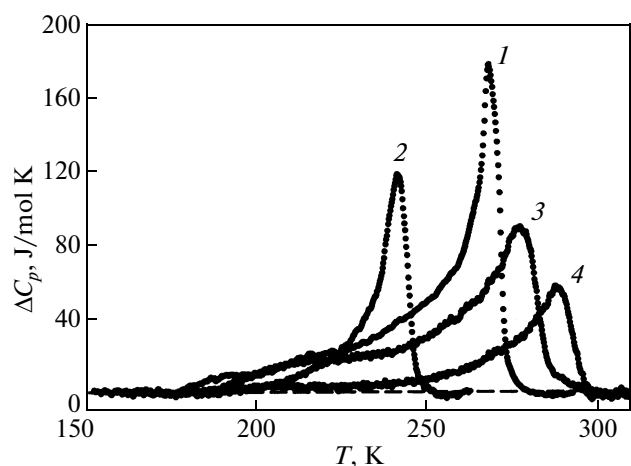
Fig. 1. Temperature dependences of the excess heat capacity of (*1*) $(NH_4)_2MoO_2F_4$, (*2*) NHC, (*3*) $NHR_{0.5}$, and (*4*) NHK.

slow evaporation in air, $(NH_4)_{2-x}A_xMoO_2F_4$ crystals were grown. The compositions of the complexes formed were controlled using the ammonium content determined by the Kjeldahl method and IR spectroscopy and they were as follows: $(NH_4)_{1.8}Cs_{0.2}MoO_2F_4$ (NHC), $(NH_4)_{1.7}K_{0.3}MoO_2F_4$ (NHK), and $(NH_4)_{2-x}Rb_xMoO_2F_4$ with $x = 0.5$, 0.8, and 1.0 (NHR_x).

The $Rb_2MoO_2F_4$ crystals were synthesized using two methods. First, the above described method was used at a certain proportion of the initial components. Second, molybdic acid containing to 5 at. % ammonium was mixed with rubidium carbonate in a platinum cup and was held at 300–400°C to complete removal of ammonia. The Rb_2MoO_4 obtained was wetted with water and processed by an HF solution on heating. The $Rb_5Mo_3O_6F_{11}$ crystalline precipitate was filtered, and, as the mother solution was slowly evaporated in air, $Rb_2MoO_2F_4$ prismatic crystals formed.

The X-ray diffraction studies performed on a Smart Apex II single-crystal diffractometer show that, at room temperature, all the samples are characterized by the orthorhombic symmetry with space group *Cmcm*. The real composition of the solid solutions determined in the process of refining the structures was, exception for the potassium-containing compound, very close to the compositions obtained by a chemical analysis. The refined concentrations of the substituting cations were: $x = 0.19$ in NHC, $x = 0.43$ in NHK, and $x = 0.52$, 0.83, and 1.01 in NHR.

3. INFLUENCE OF SUBSTITUTION FOR UNIVALENT CATIONS ON THE INSTABILITY OF THE ORTHORHOMBIC STRUCTURE

To obtain information on the presence of phase transitions, their temperatures and energetic characteristics, the studies of a series of $(NH_4)_{2-x}A_xMoO_2F_4$ ($A = Cs$, Rb, K) solid solutions synthesized were performed using a DSM-10 differential scanning microcalorimeter. The measurements were performed on the samples with a mass of 0.1–0.2 g in the temperature range 120–400 K at a rate of 8 K/min on heating and cooling.

At the first stage, the measurements were performed on the NHC, $NHR_{0.5}$, and NHK solid solutions. The observed anomalous behavior of the heat capacity $\Delta C_p(T)$ shown in Fig. 1 where, for comparison, the $\Delta C_p(T)$ curve is shown for $(NH_4)_2MoO_2F_4$ is indicative of the existence of phase transition in all the samples. According to the data of X-ray diffraction studies, the first distorted phase of the solid solutions under study is orthorhombic (space group *Pnma*), as well as in $(NH_4)_2MoO_2F_4$.

The NHC solid solution demonstrates only one anomaly of the heat capacity at T_1 (table) that is characterized by the value of the ΔC_p maximum lower as compared to $(NH_4)_2MoO_2F_4$ (Fig. 1). By the integration of the $\Delta C_p(T)$ function, we determined the

Temperatures and entropies of phase transitions in $(NH_4)_{2-x}A_xMoO_2F_4$ according to differential scanning microcalorimetry and the unit cell volume V in the *Cmcm* phase

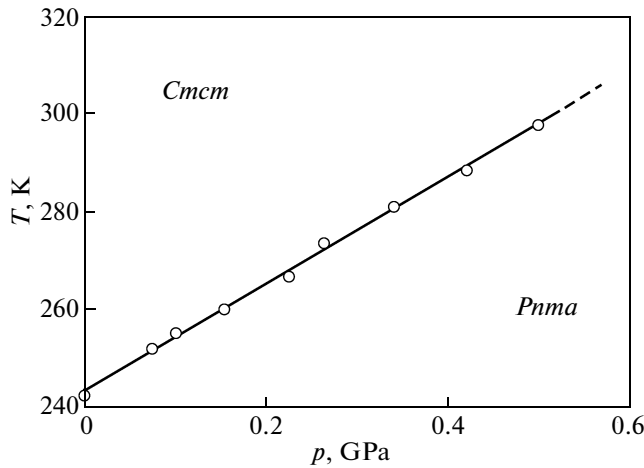| Compound	V, Å^3	T_1, K	δT_1, K	ΔS_1, J/mol K	T_2, K	ΔS_2, J/mol K
$(NH_4)_2MoO_2F_4$	612.05	268	2.8	10.8 (18.2* [2])	191	2.5
NHC	626.24	242	4.8	6.9	–	–
NHK	605.65	288	3.9	4.7	204	0.5
$NHR_{0.5}$	611.76	277	3.2	9.1	210	1.7
$NHR_{0.8}$	609.36	281	2.3	8.4	220.0	1.4
$NHR_{1.0}$	610.76	283	3.3	7.4	219.6	1.7
$Rb_2MoO_2F_4$	606.79	257		9.2*	210	1.2*

* Data obtained using adiabatic calorimetry.

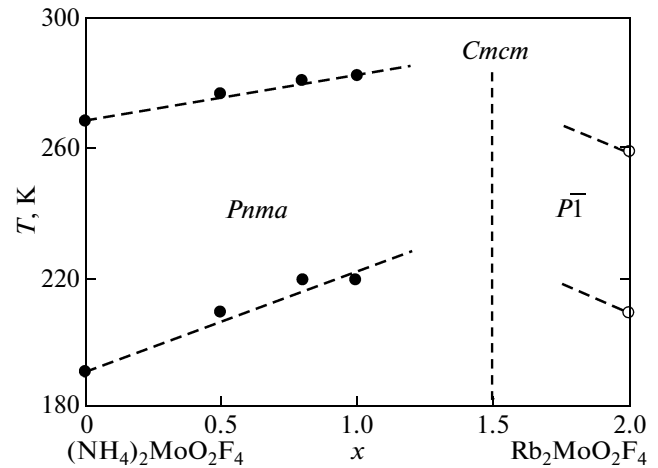**Fig. 2.** Experimental T–p phase diagram of $(NH_4)_{1.8}Cs_{0.2}MoO_2F_4$.

Fig. 3. Temperature–concentration phase diagram of $(NH_4)_{2-x}Rb_xMoO_2F_4$.

enthalpy change $\Delta H_1 = 1600$ J/mol that also decreases with respect to the initial crystal enthalpy $\Delta H_\Sigma = 3200$ J/mol.

Substitutions K $\longrightarrow$ NH$_4$ and Rb$_{0.5}$ $\longrightarrow$ NH$_4$ do not influence the number of the heat capacity anomalies in $(NH_4)_2MoO_2F_4$: both samples have two ΔC_p peaks (Fig. 1 and table). The summary enthalpies were $\Delta H_\Sigma = 1600$ J/mol (NHK) and 2700 J/mol (NHR$_{0.5}$). Thus, at all types of substituting, the phase transition enthalpies decrease as compared to the initial $(NH_4)_2MoO_2F_4$.

The DTA studies of the effect of hydrostatic pressure on the phase transition temperatures performed using the technique described in [8] were successful only for NHC. In the range 0–0.5 GPa, the pressure dependence of the phase transition temperature is described by the relationship $T(p) = 242 + 110.5p$ (Fig. 2). Thus, the substitution Cs $\longrightarrow$ (NH$_4$) leads to not only a decrease in the temperature T_1 but also to a significant increase in the pressure coefficient $dT_1/dp = 110.5 \pm 0.5$ K GPa^{-1} as compared to the ammonium molybdenum compound $dT_1/dp \approx 98$ K GPa^{-1} [2]).

Among $A_2MoO_2F_4$ compounds with atomic cations, the existence of phase transitions due to ordering of ligands with decreasing temperature can be suggested only in Rb$_2MoO_2F_4$ having a disordered orthorhombic structure [6]. That is why the DSM studies were continued on a series of solid solutions NHR$_x$, and the heat capacity anomalies related to structural transformations were detected in all the samples. The results are presented in Fig. 3 and the table.

An increase in the rubidium concentration brings about a change in the phase transition temperatures in comparatively narrow temperature ranges (table) but it is accompanied by a significant spreading of the heat capacity anomalies. One of important results of the calorimetric measurements is a possibility of detecting the phase transitions at T_1 and T_2 even in the NHR$_x$ samples with a high Rb concentration. The $\Delta C_p(T)$ temperature dependence of NHR$_{1.0}$ has one more heat capacity anomaly between temperatures T_1 and T_2, nature of which is still unknown.

The unit cell volumes in the *Cmcm* phase of all the solid solutions under study are given in the table. In all the compositions, the low-temperature phase remains orthorhombic (*Pnma*) as is the case in the $(NH_4)_2MoO_2F_4$ compound.

The DSM experiments do not detect an anomalous behavior of the heat capacity of Rb$_2MoO_2F_4$. However, a comparison of the X-ray diffraction data of the crystal at room (space group *Cmcm*) and low temperatures shows that the symmetry is changed near ~260 K. The preliminary results testify that the distorted phase is not orthorhombic (space group *Pnma*) as in $(NH_4)_2MoO_2F_4$ and in all $(NH_4)_{2-x}A_xMoO_2F_4$ solid solutions under study; it is the triclinic phase (space group $P\bar{1}$) which was determined for oxyfluoride $(NH_4)_2WO_2F_4$ [3]. Based on a set of the calorimetric and structural data, one can be suggested that Rb$_2MoO_2F_4$ undergoes a second-order phase transition that is not always detected by the DSM method. At the next stage, the heat capacity of this oxyfluoride was measured on an adiabatic calorimeter that has a significantly higher sensitivity.

4. STUDIES OF THE HEAT CAPACITY OF Rb$_2$MoO$_2$F$_4$

The measured temperature dependence of the molar heat capacity of the Rb$_2MoO_2F_4$ crystal is depicted in Fig. 4. An anomaly in the heat capacity behavior is detected in the range from 200 to 310 K
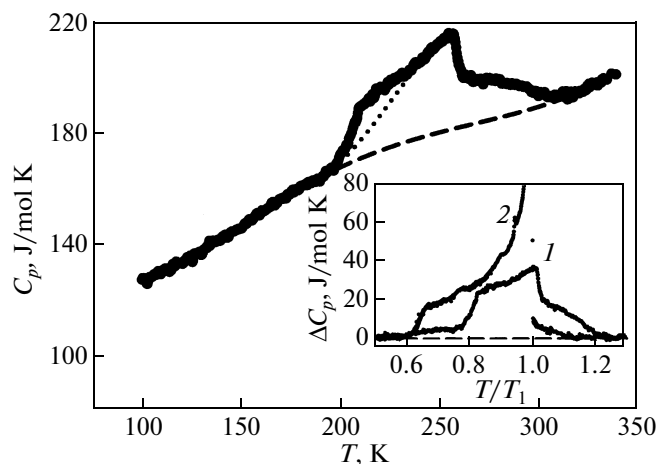
Fig. 4. Temperature dependence of the molar heat capacity of $Rb_2MoO_2F_4$. The dashed line indicates the lattice heat capacity. The inset shows the relationships between the anomalous heat capacities of (1) $Rb_2MoO_2F_4$ and (2) $(NH_4)_2MoO_2F_4$.

with a local maximum at the temperatures $T_1 = 256.50 \pm 0.5$ K and $T_2 = 210 \pm 2$ K. The temperature T_1 agrees satisfactorily with the temperature at which the crystal symmetry is changed. The heat capacity temperature dependence shows that $Rb_2MoO_2F_4$ really undergoes the second-order phase transition at T_1.

In order to determine the integral characteristics of the phase transition, the molar heat capacity of $Rb_2MoO_2F_4$ was separated into the regular component and an anomalous contribution due to phase transitions. The experimental $C_p(T)$ data at temperatures significantly higher than T_1 and lower than T_2 were approximated by a polynomial function with interpolation in the region of anomalous behavior of the heat capacity (dashed line in Fig. 4). Integration of the $\Delta C_p(T)$ over temperature over entire range of existence of the anomalous heat capacity (190–320 K) allows the determination of the summary change in the enthalpy $\Sigma \Delta H_i = 2400 \pm 60$ J/mol. Approximate separation of the contributions to the enthalpy of two transitions (Fig. 4, dotted line) gives $\Delta H_i \approx 2100$ J/mol and $\Delta H_2 \approx 270$ J/mol. Corresponding changes in the entropy are $\Delta S_1 = 9.2$ J/mol K and $\Delta S_2 = 1.2$ J/mol K.

The temperature dependence of the anomalous heat capacity is shown in the inset of Fig. 4 where the data for $(NH_4)_2MoO_2F_4$ [2] for comparison are presented. It is of interest that details of both the dependences are identical: the existence of the anomalous heat capacity above T_1 and their behavior in the range T_1–T_2. However, the Rb $\longrightarrow$ NH$_4$ substitution narrows this range, changes the first-order transition at T_1 to the second-order one, and substantially decreases the entropy related to the sequence of the transitions (table).

The temperature dependence of the permittivity of $Rb_2MoO_2F_4$ has no any marked anomalies in the temperature range 100–350 K under study.

5. COMPARISON OF THE EFFECTS OF THE CHEMICAL AND HYDROSTATIC PRESSURES IN MOLYBDENUM OXYFLUORIDES

Unlike an external (hydrostatic and uniaxial) pressure, the chemical pressure (varied by all kinds of substitutions for structural elements) can both decrease and increase the crystal unit cell volume. The latter case can be considered as the effect related to a decrease in the internal pressure when the sign of change in phase transition temperature is opposite to the sign of the pressure coefficient dT/dp.

For the solid solutions under study at $x \leq 1$, the sign of the shift of the phase transition temperature from the *Cmcm* dT_1/dx phase corresponds to the sign expected from the T–p phase diagram.

A partial substitution for the ammonium group NH$_4$ of Cs cations with larger ionic radius is accompanied by a significant increase in the unit cell volume V (~2.3%) (Fig. 5 and table) which can be considered as a result of applying an internal negative pressure. Using the experimental pressure coefficient of $(NH_4)_2MoO_2F_4$ ($dT_1/dp \approx 98$ K GPa^{-1} [2]), we can estimate the pressure required to decrease the temperature T_1 from 268 K in $(NH_4)_2MoO_2F_4$ to 242 K at which the transition in NHC occurs at the atmospheric pressure. This pressure can be $p \sim (-0.3)$ GPa. However, if the same pressure to is applied to NHC for which $dT_1/dp \approx 110.5$ K/GPa, we obtain $T_1 \approx 280$ K which exceeds the phase transition temperature in $(NH_4)_2MoO_2F_4$. There are at least two reasons of this disagreement. First, it is a nonlinearity of the boundary between the *Cmcm* and *Pnma* phases. Second, and most likely, the difference in the pressure coefficients of $(NH_4)_2MoO_2F_4$ and NHC is, to a great extent, due to the fact that the Cs $\longrightarrow$ NH$_4$ substitution changes not only the size of the effective univalent cation but also its shape. According to the T–p phase diagram of $(NH_4)_2MoO_2F_4$, the area of existence of an intermediate phase is narrowed at negative pressures. At $p \approx (-0.3)$ GPa, the temperature T_2 must be very close to the lower limit of the temperature range of the DSM studies. Most likely, it is exactly the reason why the low-temperature anomaly is not observed in NHC.

The ionic radius of potassium atom is smaller than that of the ammonium group; because of this, the K $\longrightarrow$ NH$_4$ substitution leads to the expected decrease in the unit cell volume V by ~1% (Fig. 5 and table). The above reasoning for NHC allows the statement that the increase in the temperature T_1 by ~20 K in

NHK is due to a change in the excess internal pressure within the limits of $p \sim 0.2$ GPa.

Both cases of substitutions under consideration are related to comparatively low concentrations of substitutes. A series of NHR_x solid solutions is studied in more details. The unit cell volume V regularly changes as the concentration x increases (Fig. 5 and table). Owing to close values of the NH_4^+ and Rb^+ ionic radii, the unit cell volume of the crystals with $x \leq 1$ is varied within the limits of several tenths of percent. In this case, the temperatures of both phase transitions increase but the rate of varying T_1 is lower and it is maximum at $x = 1$. The complete substitution for the ammonium group leads to the fact that the phase transition temperatures in $Rb_2MoO_2F_4$ decrease. Such a behavior can be explained, e.g., as follows: at the initial stage ($x \leq 1$), the $Rb \longrightarrow NH_4$ substitution occurs only in one of nonequivalent crystallographic positions occupied by the ammonium group; and at $x > 1$, the occupation of another position is accompanied by a significant change in the character of interatomic interactions. As a result, $Rb_2MoO_2F_4$ whose unit cell volume is about 1% smaller than that in $(NH_4)_2MoO_2F_4$ undergoes the phase transition to the phase with symmetry P-1, not $Pnma$ which was found for all compositions of the solid solutions under study. It should be noted that the low-temperature phase P-1 is characteristic of also $(NH_4)_2WO_2F_4$ [1] that also has unit cell volume $V = 608.9$ Å^3 smaller than that of $(NH_4)_2MoO_2F_4$, although the ionic radii of the central atoms in these oxyfluorides are very close: $R_{W^{+6}} = 0.60$ Å and $R_{Mo^{+6}} = 0.59$ Å^3.

When refining the structure using the single-crystal X-ray diffractometer, it was established that the various substituting cations nonuniformly occupy two nonequivalent positions occupied by ammonium groups in the solid solution structure.

It should be emphasized as well that, in all the solid solutions, the transition from the $Cmcm$ phase is accompanied by quite large thermal hysteresis whose magnitude is varied insignificantly as the cation-substitute concentration is changed (table). In both phase transitions, the entropy changes decrease in the solid solutions, but they vary from composition to composition within the limits of error of their determination by the DSM method. The exception is only NHK in which ΔS_1 and ΔS_2 decrease by several times.

It is of indubitable interest to compare the effects of substitution of a spherical cation for a tetrahedral cation on the stability of the initial phases of the orthorhombic $(NH_4)_{2-x}A_xMoO_2F_4$ ($Cmcm$) and cubic $(NH_4)_{3-x}A_xMoO_3F_3$ ($Fm3m$) [9−11] oxyfluorides. In the former type of the structure, the octahedral anions MoO_2F_4 are isolated, and, in the latter type, the MoO_3F_3 and $A_xO_3F_3$ polyhedrons are connected by

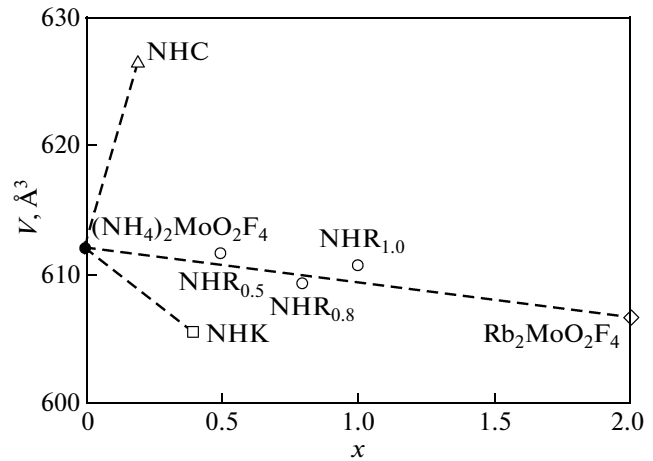**Fig. 5.** Unit-cell volume–concentration phase diagram of $(NH_4)_{2-x}A_xMoO_2F_4$ solid solutions.

the common ligands in their vertices. On the one hand, both the structural types are characterized by significant decrease in the entropy of the transitions from the initial phases as a result of the substitution $A \longrightarrow NH_4$; on the other hand, the transition temperatures in the orthorhombic crystals are changed not very substantially as is the case in the cubic crystals.

6. CONCLUSIONS

A change in the chemical pressure in oxyfluorides $(NH_4)_{2-x}A_xMeO_2F_4$ due to the substitution of a spherical cation for the univalent tetrahedral cation allows the controlling the stability of the $Cmcm$ phase with respect to changes in the transition temperatures and pressures, changes a kind and entropy of the phase transition at T_1, and slightly influences the anomalous behavior of the crystals at T_2. A set of the facts established and also a significant decrease in the transition entropy from the $Cmcm$ phase to $Rb_2MoO_2F_4$ as compared to $(NH_4)_2MoO_2F_4$ allow the conclusion that the ammonium cation plays an important role in the mechanism of this structural transformation.

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