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The Disordered Spinel $NaAgMoO_4$ and Its High-Temperature, Ordered Orthorhombic Polymorph

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Four polymorphs of $NaAgMoO_4$ have been discovered by differential thermal analysis. The well-known spinel phase ($NaAgMoO_4$-I) is stable between room temperature and 455°C. It is cubic, a = 9.220 Å, with a disordered distribution of the Na and Ag cations. One of the high-temperature polymorphs ($NaAgMoO_4$-II) is quenchable and has been investigated by Raman spectroscopy and X-ray diffractometry. It is orthorhombic, space group *Pnma*, with a = 10.384(1), b = 7.1220(8), and c = 5.5933(6) Å; Z = 4. Its structure has been deduced from the diffraction peak intensities: it is isotypic with Ag_2CrO_4, with an essentially ordered distribution of the cations; it is thus a rare example of cation ordering with increasing temperature. Some of the unexpected aspects of the I–II transformation are briefly discussed. © 1988 Academic Press, Inc.

Introduction

The spinels Na_2MoO_4 and Ag_2MoO_4 exhibit polymorphism, with four polymorphs for Na_2MoO_4 (*1*) and three for Ag_2MoO_4 (*2*). In each case, the spinel phase is the stable one at room temperature, and the high-temperature polymorphs cannot be quenched. Since no similar study has been carried out for the solid solutions $(Na_{2-x}Ag_x)MoO_4$, we investigated the composition $NaAgMoO_4$.

Experimental

$NaAgMoO_4$ is easily obtained by heating a carefully ground mixture of the stoichiometric quantities of either Na_2MoO_4 + Ag_2MoO_4 or $NaHCO_3$ + Ag_2CO_3 + MoO_3. The temperature is slowly raised to 550°C; the mixture is then reground and maintained at 550°C for 1 day. Air quenching from this temperature gives the orthorhombic phase; by annealing at about

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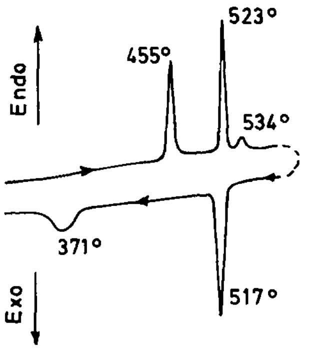

FIG. 1. DTA curve of $NaAgMoO_4$. Heating and cooling rate, 300°C hr^{-1}.

350°C, or slow cooling, the spinel phase is obtained.

If exposed to normal light when hot, the compound turns immediately brown–black; thus, all operations must be carried out in subdued red light. At room temperature, however, the sensitivity to light is much reduced.

X-ray powder patterns for lattice parameter determinations were obtained with Co*Kα* radiation. Intensities were measured from diffractograms recorded on a Philips goniometer using Fe*Kα* radiation. In order to avoid orientational effects, the powder was dispersed in a two-component glue and the solidified sample was polished.

The Raman spectra were obtained with a CODERG PHO double monochromator, equipped with a 50-mW He–Ne laser. No modification of the samples was observed after recording the spectra, as indicated by the lack of modifications in the X-ray diffraction pattern.

DTA curves were obtained at a heating rate of either 600 or 300°C hr^{-1} with Fisher DTA equipment.

Results

Differential Thermal Analysis

The heating curve of the spinel phase exhibits three sharp endothermic peaks at 455, 523, and 534°C (Fig. 1) before melting at 625°C. During the cooling stage, a sharp exothermic peak appears at 517°C, followed by a broad exothermic peak at about 371°C. The spinel phase is recovered after a full cycle. Thus, between room temperature and its melting point, $NaAgMoO_4$ has at least four polymorphs. Since no consistent labeling has been proposed for the pure end members (the spinel phase is labeled γ for Na_2MoO_4 and Na_2WO_4 (*1*), but β for Ag_2MoO_4 (*2*)), these four polymorphs will be labeled I, II, III, IV in the order of increasing temperature stability. The high-temperature, nonquenchable polymorphs III and IV will not be discussed in this paper, which is dealing with a comparative study of $NaAgMoO_4$-I (spinel) and $NaAgMoO_4$-II, for which small quantities (about 1 g) may be metastably obtained at room temperature by air quenching from about 500°C.

Raman Spectra

(*1*) *Spinel phase.* Four bands are observed in the Raman spectrum of the spinel phase. The spectrum is similar to that of the pure end member Na_2MoO_4 (Fig. 2), the main differences being a significant broadening of the bands (especially the 772-cm^{-1} band) and a general shift toward lower fre-

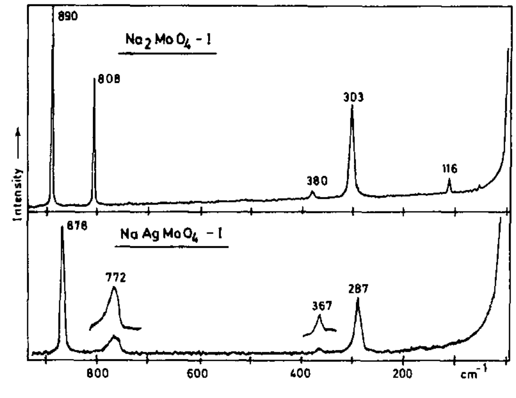

FIG. 2. Raman spectrum of Na_2MoO_4-I and $NaAgMoO_4$-I (spinel phase).

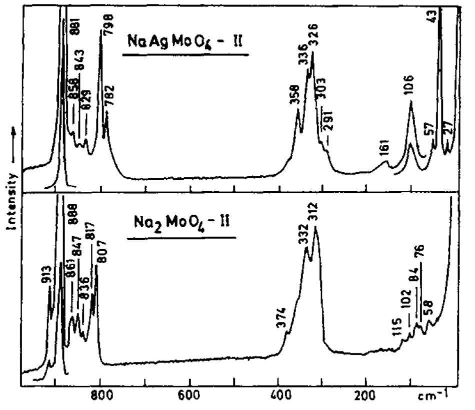

FIG. 3. Raman spectrum of NaAgMoO$_4$-II and Na$_2$ MoO$_4$-II (orthorhombic phases).

quencies. These four bands have been assigned to the four expected internal modes of the MoO$_4$ anion with T_d symmetry, namely, ν_1, ν_3, ν_4, and ν_2 (*3*). This is the spectroscopic behavior expected for a spinel solid solution with a disordered distribution of the Na and Ag cations over the octahedral sites. This is in agreement with the lack of superstructure lines in the X-ray powder diagram (see below).

The weak lowest frequency band (116 cm^{-1} in the spectrum of Na$_2$MoO$_4$) is missing in the spectrum of NaAgMoO$_4$: this is a lattice mode, and it is probably too broad and too weak to be observed in a solid solution.

(*2*) *High-temperature phase NaAgMoO$_4$-II.* The Raman spectrum (at room temperature) of this phase is characterized by the fairly large number of bands and by their sharpness (Fig. 3). The Mo–O bands remain located in the regions 900–700 and 400–300 cm^{-1}, showing that the tetrahedral coordination of Mo is preserved in this structure. But the multiplicity of the bands points to an important lowering of the crystal symmetry (and also probably of the local symmetry of the MoO$_4$ anion). Moreover, the sharpness of the bands (and especially of the lattice modes below 100 cm^{-1}) is not compatible with a disordered distribution of the Na and Ag cations.

To check this point, we tried to prepare the high-temperature phase of solid solutions Na$_{2-x}$Ag$_x$MoO$_4$ with different x values. Both Raman spectroscopy and X-ray diffractometry show that a single phase is obtained only for $x = 1$ (or nearly so). Any significant departure from this composition leads to mixtures containing NaAgMoO$_4$-II and a spinel solid solution Na$_{2-x}$Ag$_x$MoO$_4$. This shows that Na and Ag cannot replace each other and, very probably, play different structural roles in the structure. This has been of prime importance in the search for a possible structure.

X-Ray Diffraction

Phase I gives a typical spinel X-ray powder diagram leading to a cubic cell with $a_0 = 9.220(2)$ Å, which is near the average value deduced from the unit cell dimensions of the end members Na$_2$MoO$_4$ (9.110 Å) and Ag$_2$MoO$_4$ (9.316 Å). Neither tetragonal distortion nor superstructure lines (which would result from the Na–Ag ordering on the octahedral sites) were observed. The lack of ordering is in agreement with the existence of a continuous series of solid solutions Na$_{2-x}$Ag$_x$MoO$_4$, as indicated by the study of 12 compositions in the range $0.1 \leq x \leq 1.8$: we found a practically linear relationship between x and the value of the cubic unit cell parameter a_0.

The indexed X-ray powder diagram of NaAgMoO$_4$-II (obtained by quenching from 500°C) is given in Table I. All the observed diffraction peaks are satisfactorily accounted for by an orthorhombic cell with $a = 10.384(1)$, $b = 7.1220(8)$, $c = 5.5933(6)$ Å (values obtained after refinement). If we assume $Z = 4$, the calculated density is $\rho = 4.669$ g · cm^{-3}, a quite reasonable value with respect to that of the cubic spinel phase, namely, $\rho_{\text{calc}} = 4.928$ g · cm^{-3}.

According to the observed ($h\ k\ l$) values, the reflection conditions are as follows:

hkl and *h*0*l*, no condition;
*hk*0, $h = 2n$; 0*kl*, $k + l = 2n$;
*h*00, $h = 2n$; 0*k*0, $k = 2n$; 00*l*, $l = 2n$.

Additional conditions derived from the existing sites and their multiplicity lead to *Pnma* as the most probable space group. This has been used as a working hypothesis for the search for the true structure. In view of the well-known spinel–olivine polymorphism, the olivine structure was considered as a first possible candidate. However, it appeared (Table A-12 in Ref. (*4*)) that the $a:b:c$ axis ratio remained remarkably constant ($1:0.59 \pm 0.01:0.46 \pm 0.01$) among olivines of various compositions and was significantly different from that given by $NaAgMoO_4$ ($1:0.686:0.539$).

Finally, we found a close analogy with Ag_2CrO_4, space group *Pnma*, $Z = 4$, $a = 10.063$, $b = 7.029$, $c = 5.540$ Å, $a:b:c = 1:0.698:0.551$. The structure (*5*) is rather peculiar, the Ag^+ cations being located on two very different crystallographic sites. Ag(1) is coordinated to six oxygen atoms forming a tetragonal bipyramid with approximate D_{4h} symmetry; this may be also very roughly described as octahedral coordination. Ag(2) is coordinated to four oxy-

TABLE I

$NaAgMoO_4$ HT: INDEXATION OF d_{hkl}; OBSERVED AND CALCULATED INTENSITIES FROM ATOMIC COORDINATES OF TABLE II

h k l	d_{obs}	d_{calc}	I_{obs}	I_{calc}
2 0 0	5.1968	5.1918	9.22	9.60
1 0 1	4.9240	4.924	29.60	29.16
2 1 0	4.1917	4.1955	1.0	1.74
1 1 1	4.0568	4.0503	3.33	2.13
0 2 0	3.5629	3.5613	26.61	29.09
3 0 1	2.9437	2.9432	64.66	64.27
2 2 0		2.9369		
1 2 1	2.8860	2.8857	25.78	24.03
0 0 2	2.7960	2.7964	26.46	24.40
3 1 1	2.7200	2.7201	12.95	12.06
1 0 2	~2.704	2.7002		
2 2 1		2.600	11.84	12.20
4 0 0	2.596	2.5959		
2 0 2	2.4620	2.4620	5.15	3.7
4 1 0	2.4390	2.4390		
2 1 2	2.3263	2.3269	3.28	3.68
3 2 1	2.268	2.2687	15.31	14.10
0 2 2	2.1990	2.1994	13.42	12.92
2 3 0	2.1601	2.1592	0.76	1.58
1 2 2		2.1517		
4 2 0	2.0976	2.0978	5.35	7.0
2 2 2	2.0245	2.0252	7.79	8.76
2 3 1		2.0144		
4 0 2	1.9010	1.9025	1.48	1.50
3 2 2		1.8564	7.24	7.09
3 3 1	1.8479	1.8480		
4 1 2	1.8381	1.8376		
1 0 3		1.8350		
1 3 2		1.7831	7.30	8.31
0 4 0	1.7805	1.7807		
1 1 3		1.777		
2 0 3		1.7546	1.62	0.71
4 3 0	1.7512	1.7520		
6 0 0	1.7304	1.7306	3.35	3.19
2 3 2		1.7091	2.98	3.85
5 2 1	1.7082	1.7083		
2 1 3		1.7037		
2 4 0		1.6844	11.80	12.35
6 1 0		1.6817		
4 2 2	1.6788	1.6781		
1 4 1		1.6746		
4 3 1		1.6719		
5 0 2		1.6673		
6 0 1		1.6533	14.78	14.07
3 0 3	1.6417	1.6413		
1 2 3	1.6312	1.6311		
5 1 2		1.6234		
3 3 2		1.6039	3.42	3.66
3 1 3	1.5995	1.5994		
6 2 0	1.5565	1.5566		
3 4 1	1.5236	1.5235	8.07	10.27
5 2 2		1.5100	6.39	7.25
5 3 1		1.5055		
0 4 2	1.5016	1.5020		
6 2 1		1.4996		
3 2 3	1.4908	1.4906	8.19	7.98
1 4 2		1.4866		
4 3 2		1.4847		
4 1 3		1.4812		
6 0 2	1.4720	1.4716		
6 1 2	1.4410	1.4411		

Note. $F_N = 33.5$ (0.013; 83); $M_{20} = 35.8$; $a_0 = 10.384(1)$, $b_0 = 7.1220(8)$, $c_0 = 5.5933(6)$; $R_I = 0.079$, $R_F = 0.059$.

gen atoms forming a badly distorted tetrahedron. The chromate ion is tetrahedral.

Structure Calculations

It is now possible to make, for NaAg MoO_4-II, an approximate calculation of the diffraction peak intensities by considering three types of cation distribution:

(1) Na on Ag(1) and Ag on Ag(2) of the Ag_2CrO_4 structure;
(2) Ag on Ag(1) and Na on Ag(2);
(3) statistical distribution.

The two last distributions led to unacceptable discrepancies between observed and calculated intensities, and the structure was thus refined according to the first distribution.

Despite the poor determination of the structure calculations—18 parameters for 29 observed reflections—refinements of atomic and thermal parameters were performed. The intensities were corrected for Lorentz-polarization effects but no absorption has been taken into account. The X-ray scattering factors of the ions were taken from the "International Tables for Crystallography" (*8*) including the real and imaginary parts of the anomalous dispersion. For the unresolved peaks, only the total intensity of the multiplet was refined.

As discussed previously, we took, as starting point of the refinement procedure, the positions and B isotropic thermal factors calculated for Ag_2CrO_4 (*5*). The calculation of the interatomic distances based on the published data showed that there is a typing error in Ref. (*5*):

$$z_{O(3)} = -0.9353 \text{ instead of } 0.9353$$

(the distance Ag–O(3) was abnormally short (1.54 Å) while the distance Cr–O(3) was too long (2.42 Å)).

With all the sodium atoms on the octahedral sites (4a) and all the silver atoms on the tetrahedral sites (4c), refinement calculations led to a good value for $R_I = \Sigma|I_o - I_c|/\Sigma I_o = 0.08$, but there was serious trouble with the values of the B factors:

—B_{Na} and $B_{O(3)}$ fall to zero
—$B_{O(2)}$ was too large (≈8 $Å^2$).

Because the value of the B_{Na} was too small, we hypothesized that the structure might not be completely ordered: we found in fact a significant decrease in the value of R_I (0.073) when the octahedral sites are occupied by 94% of sodium and 6% of silver. This is not too surprising as, in Ag_2CrO_4, the silver atoms occupy the octahedral and the tetrahedral sites. This also implies that 6% of the Na^+ ions are located on the tetrahedral sites. This is unexpected, but recall that Na^+ is tetrahedrally coordinated in compounds such as β-$NaFeO_2$ (Table 44 in Ref. (*4*)).

Under these conditions, except for the B thermal factor of O(2) which always shows a large value, all the atomic parameters are correctly refined. Tables I and II give the final values of these parameters and the corresponding calculated intensities (R_I = 0.079). We tried to take into account the large value of $B_{O(2)}$ by splitting their 4(c) position in the general positions 8(d) with an occupancy factor equal to 0.5. A significant decrease of R_I is observed (R_I = 0.055 with $B_{O(2)}$ = 0.92 $Å^2$). But, a significant deviation of the *y* value of O(2), 0.18 instead of 0.25, leads to some discrepancies in interatomic distances, particularly for the NaO_6 octahedron. An anisotropic thermal motion of O(2) is very likely; one must conclude that this point cannot be satisfactorily solved from powder structure calculations.

Table III brings together the main interatomic distances and angles. The (NaO_6) octahedron seems to be rather regular, instead of the corresponding (AgO_6) polyhedron in Ag_2CrO_4 which looks like a tetragonal bipyramid (*5*). The molybdate anion (MoO_4) is tetrahedral with two short Mo–O distances, 1.70 and 1.67 Å. Such values have been already observed, as in the mo-

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $NaAgMoO_4$ (HT), WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	% Occup.	Site Wickhoff	X	Y	Z	B_{iso}
Na Ag	94 6	4a	0.5	0.5	0.5	0.9
Ag Na	94 6	4c	0.1384(5)	0.25	0.509(5)	1.00
Mo	100	4c	0.3160(10)	0.25	0.0009(80)	0.8
O(1)	100	4c	0.3559(58)	0.25	0.2965(68)	1.0
O(2)	100	4c	0.1595(44)	0.25	−0.068(11)	1.0[a]
O(3)	100	8d	0.3760(29)	−0.9532(47)	−0.1254(39)	0.7

[a] Arbitrarily fixed.

lybdate $ZrMo_2O_8$ (*6*) where one Mo–O distance is equal to 1.69 Å.

The (AgO_4) polyhedron is a highly distorted tetrahedron with strong angular deviations from the ideal value, as in Ag_2CrO_4 (*5*). The projections of the structure of $NaAgMoO_4$-II onto (001) and (010) are drawn in Figs. 4 and 5, respectively, by using the STRUPLO program (*7*). The characteristic feature is the existence, along [010], of octahedral $(NaO_4)_\infty$ chains by the sharing of opposite edges. These rutile-like chains are connected by molybdenum atoms in tetrahedral coordination. This structure is another example of a 3-D mixed tetrahedral and octahedral framework. One

TABLE III

MAIN INTERATOMIC DISTANCES AND ANGLES IN $NaAgMoO_4$-II

Distances (Å)	Angles (°)
(NaO_6) polyhedron	O(1)–Na–O(2) (×2): 87.7
Na–O(1) (×2): 2.59	O(1)–Na–O(2) (×2): 92.3
Na–O(2) (×2): 2.46	O(1)–Na–O(3) (×2): 88.8
Na–O(3) (×2): 2.48	O(1)–Na–O(3) (×2): 91.2
	O(2)–Na–O(3) (×2): 83.0
	O(2)–Na–O(3) (×2): 97.0
(AgO_4) polyhedron	O(2)–Ag–O(2) (×1): 112.5
Ag–O(1) (×1): 2.55	O(1)–Ag–O(3) (×2): 84.4
Ag–O(2) (×1): 2.38	O(3)–Ag–O(2) (×2): 109.8
Ag–O(3) (×2): 2.25	O(3)–Ag–O(3) (×1): 140.1
(MoO_4) polyhedron	O(1)–Mo–O(2) (×1): 117.4
Mo–O(1) (×1): 1.70	O(1)–Mo–O(3) (×2): 108.0
Mo–O(2) (×1): 1.67	O(3)–Mo–O(2) (×2): 104.9
Mo–O(3) (×2): 1.73	O(3)–Mo–O(3) (×1): 113.9

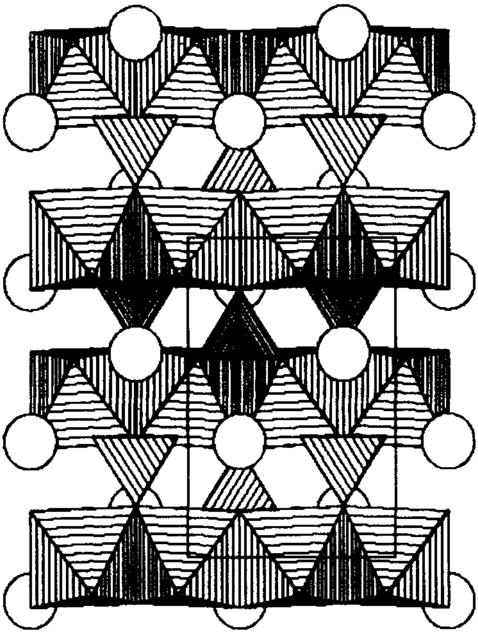

FIG. 4. Projection along the (001) direction, showing chains of edge-sharing NaO_6 octahedra, connected by MoO_4 tetrahedra. The strongly distorted AgO_4 tetrahedron is simply represented by a circle of 1.8 Å diameter.

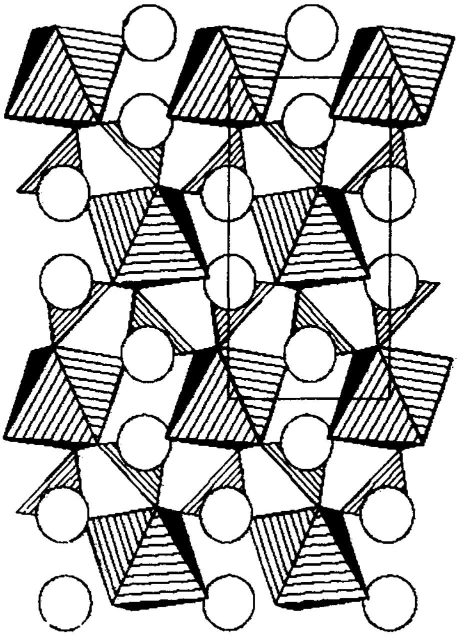

FIG. 5. Projection along the (010) direction.

(MoO_4) tetrahedron is linked to $3(NaO_4)_\infty$ chains. Silver atoms are inserted in big pseudotetrahedral cavities made from oxygen atoms of three chains.

Discussion

Stability of the High-Temperature $NaAgMoO_4$-II and Na_2MoO_4-II

Despite the fact that $NaAgMoO_4$-II may be obtained in a practically pure state by quenching, it does not persist indefinitely at room temperature. Moreover, the decomposition rate is essentially variable from sample to sample. Some have been kept for weeks without any sign of alteration or decomposition; others were more or less altered after a few days. This matter has not been systematically investigated, but it is clear that several factors come into play to explain this instability.

First of all, $NaAgMoO_4$-II is metastable at room temperature. If the quenching procedure is not fast enough, some small regions of the crystal may return to the stable spinel structure and, even though these regions are too small to be detected by X-ray diffraction, they may act as nucleation centers inducing the progressive return of the whole sample to the spinel structure.

Generally speaking, $NaAgMoO_4$-II is not hygroscopic and may be kept for hours in the presence of air. We have noticed, however, that the samples contained for several months in capped (not sealed) vials were decomposed into Ag_2MoO_4 and $Na_2MoO_4 \cdot 2H_2O$.

As are many silver salts, $NaAgMoO_4$ is more or less sensitive to light; this may induce, or favor, either the return to the spinel structure, or a chemical decomposition.

The situation is qualitatively the same for Na_2MoO_4: the first transition occurs with a nonnegligible thermal hysteresis (65°C (*1*), against 84° for $NaAgMoO_4$) and we were able, by fast quenching from 550°C, to recover Na_2MoO_4-II at room temperature. Its Raman spectrum, registered immediately after quenching, exhibits a band multiplicity similar to that of $NaAgMoO_4$-II (Fig. 3), in qualitative agreement with the proposed space group $Pbn2_1$ (*1*). However, peaks of the spinel phase are present in the Raman spectrum after a few hours, indicating a fairly rapid return to the stable phase, even at room temperature. We were unable to obtain a satisfactory diffraction diagram of the quenched sample.

Thermodynamic Aspects

In most cases, the disordering of a structure (or of the cation distribution in a structure) is obtained by increasing the temperature. To the best of our knowledge, this is always the case in the order–disorder transition of spinels. We have here an unexpected example of cation ordering when the temperature is increased; moreover, this transformation is reversible, and the observed structures correspond to the thermodynamically stable phases.

Since the cubic to orthorhombic transition is clearly endothermic (as shown by DTA), it should be characterized by a significant increase of entropy, despite the associated *ordering* of the cations. This is probably correlated to the fact that the orthorhombic phase has a more open structure, as indicated by the increase in molecular volume (103.40 Å^3 against 97.97 Å^3) for the spinel phase).

For Na_2MoO_4 itself, the following data have been published (*1*). Molecular volume: spinel phase, 94.4 Å^3; orthorhombic phase at 563°C, 112.7 Å^3. Molar transition entropy: 7.89 ± 0.16 emu. This transition entropy is rather large with respect to many "classical" cases (e.g., calcite–aragonite, quartz–cristobalite, rutile–anatase, $CaSiO_3$ α–β, . . .), for which the transition entropy rarely exceeds 1 emu. In fact, this transition entropy is greater than the melting entropy (5.12 ± 0.10 emu). If we consider the analogies between Na_2MoO_4 and $NaAgMoO_4$, we can reasonably assume that the overall transition entropy is also high for $NaAgMoO_4$ and largely overcomes the influence of the cation ordering.

Acknowledgment

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