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Solid Solutions and Phase Transitions in Langbeinites. II. $M^{I}_{2}M^{II}_{2}(XO_4)_3$ (M^{I} = NH_4, K, Tl), (M^{II} = Cd, Mn), (X = S, Se)

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Solid solutions of general formulas $(NH_4)_2Cd_2(SO_4)_x(SeO_4)_{3-x}$, $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$, $Tl_2Cd_2(SO_4)_x(SeO_4)_{3-x}$ $(3 \geq x \geq 2.75)$, and $(NH_4)_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ $(3 \geq x \geq 2.50)$ have been prepared. All the phases within the composition range studied have been established, and their cubic symmetry at room temperature has been confirmed. The cell parameters for each member of the solid solutions have been determined. The substitution has been found to be homogeneous. DSC experiments on solid solutions $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ with x = 0.19 and 0.23 have been carried out in order to study the phase transition mechanism for the langbeinites. The mixed crystals of $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ show phase transition with a decrease in both T_c and ΔH with respect to the langbeinite sulfate. In the mechanism proposed, the size of the monopositive cation is more important than that of the anion.

Introduction

Sulfates with langbeinite structure $M^{I}_{2}M^{II}_{2}(SO_4)_3$ have attracted much interest in recent years because of their ferroelastic and ferroelectric behavior and their structural phase transitions. The crystal structure of the natural mineral $K_2Mg_2(SO_4)_3$ was first solved by Zemann and Zemann (*1*), and the chemical stability of other isostructural double sulfates was investigated by Gatow and Zeeman (*2*).

The study of phase transition mechanisms in langbeinite crystals has attracted much attention in the recent past (*3*, *4*). So far, quite a few attempts, with different physical methods, have been made to understand the physical mechanism involved in this phase transition. Furthermore, it is not known whether the phase transition is mainly of the displacive or of the order–disorder type. Kreske and Devarajan (*4*) studied the hard mode corresponding to the SO_4 stretching vibrations in langbeinites like $K_2Mn_2(SO_4)_3$, $(NH_4)_2Cd_2(SO_4)_3$, and $Tl_2Cd_2(SO_4)_3$ and concluded that the phase transition is mainly of the order–disorder type. However, Speer and Salje (*5*) suggest that the phase transition mechanism in langbeinites can be attributed to instability in the atomic packing around M^{2+} ions near T_c, the large distortion of the octahedra around M^{2+} making structures unstable.

In a previous paper (*6*), we studied the solid solutions of general formulas $K_x(NH_4)_{2-x}Mn_2(SO_4)_3$ $(0 < x < 2)$ and $K_yTl_{2-y}Mn_2(SO_4)_3$ $(0 < y < 2)$ in order to study the transition mechanism in the fer-

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roelastic langbeinite $K_2Mn_2(SO_4)_3$, and we concluded that the size of the M^{I} ion plays an important role in the phase transition. Accordingly, we have studied solid solutions of langbeinites with general formula $M^{I}_2M^{II}_2(SO_4)_x(SeO_4)_{3-x}$ in order to examine the influence of the anion in the temperature of the phase transition, which, together with the results obtained for the substitution of the monovalent cation, will lead us to a proposed mechanism.

Experimental

The systems investigated are: $(NH_4)_2Cd_2(SO_4)_x(SeO_4)_{3-x}$ (ACSSe), $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ (KMSSe), $Tl_2Cd_2(SO_4)_x(SeO_4)_{3-x}$ (TCSSe) ($3 \geq x \geq 2.75$), and $(NH_4)_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ (AMSSe) ($3 \geq x \geq 2.50$). The starting langbeinites $(NH_4)_2Cd_2(SO_4)_3$ (ACS), $(NH_4)_2Mn_2(SO_4)_3$ (AMS), $K_2Mn_2(SO_4)_3$ (KMS), and $Tl_2Cd_2(SO_4)_3$ (TCS) were obtained by evaporation of the 1:2 molar ratio aqueous solution of $(NH_4)_2SO_4$, $CdSO_4 \cdot \frac{8}{3}H_2O$, $MnSO_4 \cdot H_2O$, K_2SO_4, and Tl_2SO_4, at 120°C (2) (thermostated bath with ethylene glycol).

The mixed crystals of general formula ACSSe, KMSSe, TCSSe, and AMSSe were obtained by mixing aqueous solutions of: $(NH_4)_2SeO_4$, $CdSeO_4 \cdot H_2O$, $(NH_4)_2SO_4$, and $CdSO_4 \cdot \frac{8}{3}H_2O$; K_2SO_4, K_2SeO_4, $MnSO_4 \cdot H_2O$, and $MnSeO_4 \cdot H_2O$; Tl_2SO_4, Tl_2SeO_4, $CdSO_4 \cdot \frac{8}{3}H_2O$, and $CdSeO_4 \cdot H_2O$; $(NH_4)_2SO_4$, $(NH_4)_2SeO_4$, $MnSO_4 \cdot H_2O$, and $MnSeO_4 \cdot H_2O$, in varying proportions. All chemicals used were analytical grade.

The cubic symmetry at room temperature of these crystals was confirmed by X-ray powder diffraction. Values of x different from those given lead, in all cases studied, to mixtures of solid solutions sometimes contaminated with reagents or to species which are not langbeinites.

The samples were mounted on a Siemens automatic diffractometer, D500-DACOMP. Ni-filtered Cu$K\alpha$ radiation was used with scan speed equal to $\frac{1}{2}\theta$ min^{-1} and θ range of 5–30°.

Indexing of the powder diffraction patterns of $(NH_4)_2Cd_2(SO_4)_{2.91}(SeO_4)_{0.18}$ (ACSSe-1) and $(NH_4)_2Cd_2(SO_4)_{2.74}(SeO_4)_{0.25}$ (ACSSe-2) was carried out from the values of $(NH_4)_2Cd_2(SO_4)_3$ (PDF 21-279). Cell parameters are $a_0 = 10.358(1)$ and $10.370(1)$ Å, respectively. These parameters were refined by a full matrix least-squares method from the cell parameters of $(NH_4)_2Cd_2(SO_4)_3$.

Indexing of the powder diffraction patterns of $K_2Mn_2(SO_4)_{2.80}(SeO_4)_{0.19}$ (KMSSe-1) and $K_2Mn_2(SO_4)_{2.76}(SeO_4)_{0.23}$ (KMSSe-2) was carried out from the values of $K_2Mn_2(SO_4)_3$ (PDF 20-909). Cell parameters are $a_0 = 10.132(2)$ and $10.143(2)$ Å, respectively. These parameters were refined by a full matrix least-squares method from the cell parameters of $K_2Mn_2(SO_4)_3$.

Indexing of the powder diffraction patterns of $Tl_2Cd_2(SO_4)_{2.88}(SeO_4)_{0.11}$ (TCSSe-1) and $Tl_2Cd_2(SO_4)_{2.73}(SeO_4)_{0.26}$ (TCSSe-2) was carried out from the values of $Tl_2Cd_2(SO_4)_3$ (PDF 22-1645). Cell parameters are $a_0 = 10.391(1)$ and $10.451(1)$ Å, respectively. These parameters were refined by a full matrix least-squares method from the cell parameters of $Tl_2Cd_2(SO_4)_3$.

Indexing of the powder diffraction patterns of $(NH_4)_2Mn_2(SO_4)_{2.78}(SeO_4)_{0.21}$ (AMSSe-1) and $(NH_4)_2Mn_2(SO_4)_{2.49}(SeO_4)_{0.50}$ (AMSSe-2) was carried out from the values of $(NH_4)_2Mn_2(SO_4)_3$ (PDF 20-96). Cell parameters are $a_0 = 10.211(1)$ and $10.242(2)$ Å, respectively. These parameters were refined by a full matrix least-squares method from the cell parameters of $(NH_4)_2Mn_2(SO_4)_3$.

The computer program used was AFFMAIL (7). Elemental analyses of N and S were carried out in a Perkin–Elmer 240 microanalyzer. Atomic absorption spectroscopy of Mn, K, and Cd was carried out in a

TABLE I

ANALYSES AND COMPOSITION OF SOLID SOLUTIONS $(NH_4)_2Cd_2(SO_4)_x(SeO_4)_{3-x}$

System	%S	%Se	Formula
ACS	17.60	—	$(NH_4)_2Cd_2(SO_4)_3$
ACSSe-1	16.45	2.51	$(NH_4)_2Cd_2(SO_4)_{2.91}(SeO_4)_{0.18}$
ACSSe-2	15.67	3.53	$(NH_4)_2Cd_2(SO_4)_{2.74}(SeO_4)_{0.25}$

TABLE III

ANALYSES AND COMPOSITION OF SOLID SOLUTIONS $Tl_2Cd_2(SO_4)_x(SeO_4)_{3-x}$

System	%S	%Se	Formula
TCS	10.50	—	$Tl_2Cd_2(SO_4)_3$
TCSSe-1	9.95	0.94	$Tl_2Cd_2(SO_4)_{2.88}(SeO_4)_{0.11}$
TCSSe-2	9.36	2.20	$Tl_2Cd_2(SO_4)_{2.73}(SeO_4)_{0.26}$

PYE UNICAN SP 1900. ICP of Tl and Se was carried out on a JOBIN YBON analyzer. Infrared spectra were recorded on a Perkin–Elmer 1330 spectrophotometer; samples prepared as KBr pellets or Nujol mulls gave the same spectra.

Heat flows of the samples were measured on a Perkin–Elmer differential scanning calorimetric DSC 7 in the temperature range from +30 to −170°C and with a rate of 10.0°C/min.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) studies were carried out on a JSM 840, Model JEOL, Ltd. The measurements were made on polycrystalline samples which were metallized with gold by sputtering.

Results

The results of the solid solution analyses and the composition of the different phases have been established (Tables I, II, III, and IV). The results of X-ray diffraction are shown in Table V. The IR spectra clearly shows the internal vibrational modes ν_1, ν_2, ν_3, and ν_4 of the tetrahedral SO_4 group in all the crystals: ν_1, above 1000 cm^{-1}; ν_2 at 470 cm^{-1}; ν_3 between 1170 and 1080 cm^{-1}; ν_4 between 640 and 605 cm^{-1}. Also, the crystals show the internal vibrational modes ν_3 and ν_4 of the tetrahedral SeO_4 group, ν_3 between 800 and 900 cm^{-1}; and ν_4 ca. 400 cm^{-1}. All the samples with NH_4^+ show the ν_3 and ν_4 vibrations of the ammonium ion in the region 1410–3200 cm^{-1}.

The results of SEM show that small amounts of selenate in the samples do not change the langbeinite morphology. EDAX confirms the presence of Se in the new compounds.

Figure 1 shows the heat flow (mW)/temperature (°C) of $K_2Mn_2(SO_4)_3$. Sample weight = 56.430 mg, $T_c = -75.9$°C, and $\Delta H = 1.626$ J/g. Figure 2 shows the heat flow (mW)/temperature (°C) of $K_2Mn_2(SO_4)_{2.80}(SeO_4)_{0.19}$. Sample weight is 35.690 mg, $T_c = -85.986$°C and $\Delta H = 1.5576$ J/g. Figure 3 shows the heat flow (mW)/temperature (°C) of $K_2Mn_2(SO_4)_{2.76}(SeO_4)_{0.23}$. Sample

TABLE II

ANALYSES AND COMPOSITION OF SOLID SOLUTIONS $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$

System	%S	%Se	Formula
KMS	20.03	—	$K_2Mn_2(SO_4)_3$
KMSSe-1	18.51	3.10	$K_2Mn_2(SO_4)_{2.80}(SeO_4)_{0.19}$
KMSSe-2	18.18	3.74	$K_2Mn_2(SO_4)_{2.76}(SeO_4)_{0.23}$

TABLE IV

ANALYSES AND COMPOSITION OF SOLID SOLUTIONS $(NH_4)_2Mn_2(SO_4)_x(SeO_4)_{3-x}$

System	%S	%Se	Formula
AMS	22.20	—	$(NH_4)_2Mn_2(SO_4)_3$
AMSSe-1	20.09	3.74	$(NH_4)_2Mn_2(SO_4)_{2.78}(SeO_4)_{0.21}$
AMSSe-2	17.46	8.65	$(NH_4)_2Mn_2(SO_4)_{2.49}(SeO_4)_{0.50}$

TABLE V

Cell Parameters and Volume for Each Member of the Solid Solutions

	a_0 (Å)	V (Å^3)	ε	NP
ACS	10.350(2)	1108.7(6)	1.74	25
ACSSe-1	10.358(1)	1111.1(3)	0.95	25
ACSSe-2	10.370(1)	1115.2(3)	1.30	25
KMS	10.119(1)	1036.2(3)	1.07	26
KMSSe-1	10.139(2)	1042.3(6)	2.12	25
KMSSe-2	10.143(2)	1043.6(6)	1.83	24
TCS	10.376(1)	1117.0(3)	1.38	22
TCSSe-1	10.391(1)	1122.3(3)	0.91	25
TCSSe-2	10.415(1)	1129.8(3)	1.44	26
AMS	10.1908(6)	1058.3(1)	0.71	26
AMSSe-1	10.211(1)	1064.6(3)	1.16	26
AMSSe-2	10.242(2)	1074.3(6)	1.95	25

weight is 39.180 mg, $T_c = -89.918°C$, $\Delta H = 1.094$ J/g.

Discussion

X-ray diffraction patterns of the solid solutions with general formulas $(NH_4)_2Cd_2(SO_4)_x(SeO_4)_{3-x}$, $K_2Mn_2(SO_4)_x(SeO_4)_{3-x}$, $Tl_2Cd_2(SO_4)_x(SeO_4)_{3-x}$ ($3 \geq x \geq 2.75$), and $(NH_4)_2Mn_2(SO_4)_x(SeO_4)_{3-x}$ ($3 \geq x \geq 2.50$) indicated reflections attributable only to the pure phases. In order to determine the homogeneity of the substitution between the SO_4^{2-} and SeO_4^{2-} ions, a linear regression of cell parameters and cell volume has been carried out. The largest deviations from linearity are within three times the highest standard deviation, assuming the substitution to be homogeneous.

An increase in the amount of selenate in all the solid solutions studied (x less than the values above) leads to phases other than cubic; i.e., either langbeinites are not obtained or cubic species are not obtained, although some replacement of sulfate by selenate may take place.

The infrared spectra are typical of the SO_4^{2-} ion, and the selection rules for C_1 symmetry are approximately adhered to. The ν_1 and ν_2 regions (symmetric vibrations) are relatively weak. ν_2 invariably appears as only one component. The stronger absorption in the ν_3 and ν_4 (asymmetric vibrations) regions and the fact that they are triply degenerate agrees with the symmetry decrease in the SO_4^{2-} groups in the langbeinites.

The atomic arrangement proposed by Zemann (*1*) implies the SO_4 groups to be practically ideal tetrahedra in $K_2Mg_2(SO_4)_3$, which is isostructural with $K_2Mn_2(SO_4)_3$.

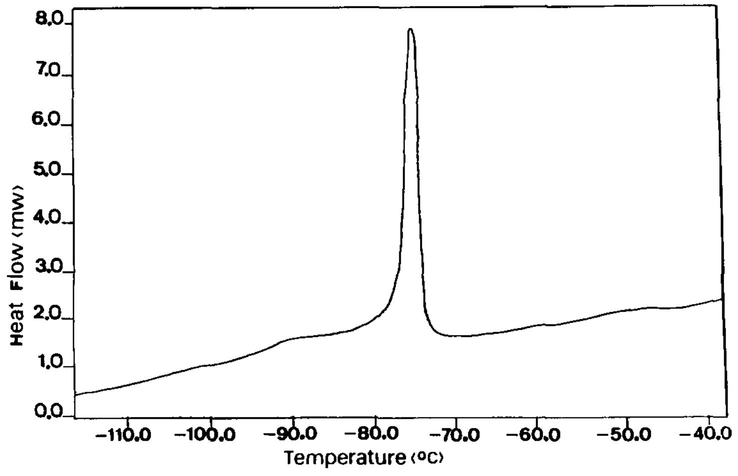

Fig. 1. Heat flow of $K_2Mn_2(SO_4)_3$.

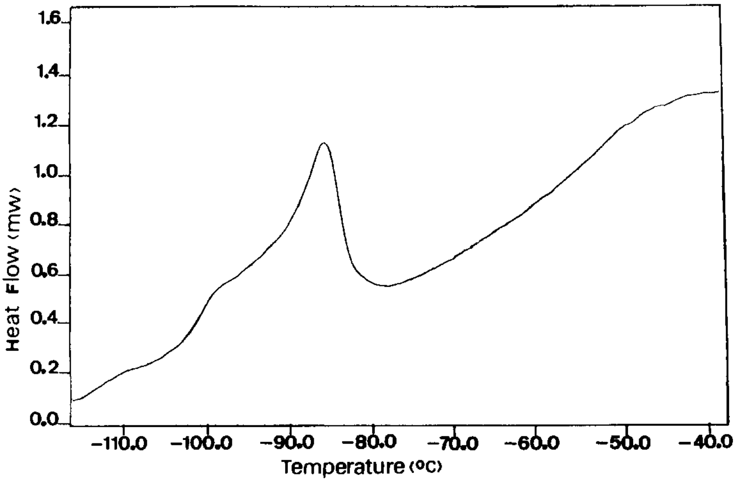

FIG. 2. Heat flow of $K_2Mn_2(SO_4)_{2.80}(SeO_4)_{0.19}$.

This observation was confirmed by Speer and Salje (*5*).

The presence of small amounts of selenate in the samples precludes study of the degeneration of ν_3 and ν_4 vibrations.

The divalent metals in the langbeinites are always coordinated by six oxygen atoms forming a distorted octahedron. For the $P2_13$–$P2_12_12_1$ phase transition, there is a correlation between the critical temperature and the octahedral distortions; when the octahedron becomes sufficiently distorted the structural phase transition takes place. The high symmetry coordination of $M^{2+}O_6$ is only possible at the expense of larger M^+–O distances and a rather poor packing around M^+. With decreasing temperatures, the coordination of M^{2+} becomes less symmetric, and the structural phase transition is expected to take place. In the orthorhombic phase, the MO_6 octahedra are heavily distorted, the average M^{2+}–O distances become larger, and the M^+–O distances become shorter. There-

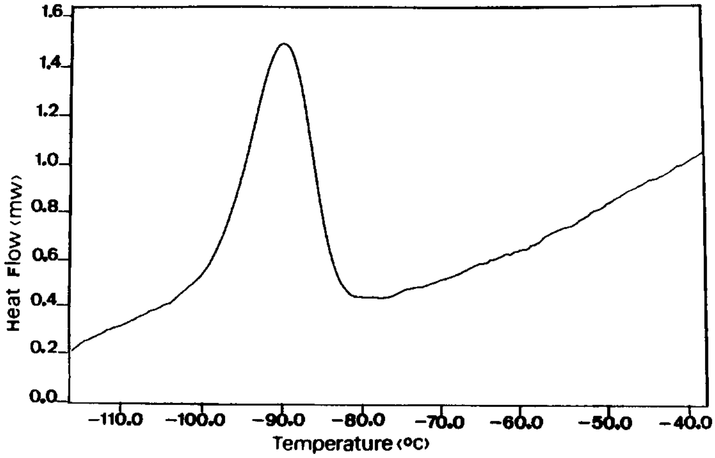

FIG. 3. Heat flow of $K_2Mn_2(SO_4)_{2.76}(SeO_4)_{0.23}$.

TABLE VI

EFFECT OF THE REPLACEMENT OF THE MONOVALENT METAL OR THE ANION IN T_c AND ΔH FOR THE LANGBEINITE $K_2Mn_2(SO_4)_3$

	T_c (°C)	ΔH(J/g)	Ref.
$K_2Mn_2(SO_4)_3$	−75.9	1.626	*6*
$K_{1.81}(NH_4)_{0.17}Mn_2(SO_4)_3$	−110.9	0.235	*6*
$K_2Mn_2(SO_4)_{2.80}(SeO_4)_{0.19}$	−86.0	1.576	This work

fore, the M^+O_n polyhedra show a closer packing at the expense of the wider $M^{2+}O_6$ packing.

It is known that the SO_4 tetrahedra shift and rotate during the phase transition to achieve better packing of the M^+O_n polyhedron.

The mechanism by which the phase transition occurs can be explained as the result of a cooperative effect among the SO_4^{2-} tetrahedra, the M^+–O distance, and the distortion of the $M^{2+}O_6$ octahedra. These three factors contribute to the phase transition.

If the mechanism proposed involves the shift and rotation of the SO_4 groups, then the random substitution of SO_4 tetrahedra for SeO_4 tetrahedra must affect both the transition temperature and the enthalpy variation. The results obtained for the KMSSe series show the decrease in T_c and ΔH on increasing the substitution of SO_4 for SeO_4. In a previous work (*6*), we observed that the substitution of potassium for ammonium in KMS langbeinite caused, likewise, a decrease in T_c and ΔH. The values of T_c and ΔH are more similar to those observed for the unsubstituted langbeinite when sulfate is substituted for selenate (ca. 10% substitution); on the contrary, the values are more dissimilar when, at the same degree of substitution, potassium is substituted for ammonium (Table VI).

These results suggest that in the mechanism proposed, the packing of the polyhedra MO_n is more important than the shift and rotation of the tetrahedra XO_4. The larger radius of SeO_4 compared to that of SO_4 makes the packing of K–O polyhedra difficult, thereby requiring lower temperatures for the phase transition (paraelastic–ferroelastic) to occur.

The results disagree with those of Yamada *et al.* (*8*), as stated correctly, but agree well with the Speer–Salje model (*5*) in explaining the cubic–orthorhombic phase transition of the langbeinite KMS on the basis of the ordering of the sulfate groups.

We have not been able to observe any phase transition for the two series ACSSe and TCSSe down to liquid nitrogen since ACS and TCS show very low T_c; however, we believe that the mechanism proposed can be generalized to include these cases under appropriate temperature conditions.

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