Energetics of Brannerite-Type Solid Solutions: The System MnV_2O_6–$LiMoVO_6$–Mo_2O_6

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Brannerite-type solid solutions in the system MnV_2O_6–$LiMoVO_6$–Mo_2O_6 ($MnLi\phi$) were studied by high-temperature drop-solution calorimetry and X-ray diffraction. Enthalpies of mixing, referred to brannerite standard states, are $\Delta H_{mix} = y(1 - y)(24.8 - 51.7y)$ kJ/mole for $(1 - y)MnV_2O_6 - yLiMnVO_6$ (MnLi) and $\Delta H_{mix} = 23.4x(1 - x)$ for $(1 - x)MnV_2O_6 - xMo_2O_6$ ($Mn\phi$). A fit to all the data simultaneously (the two joins above, three ternary points, and one point along $Li\phi$) gives values similar to those above for ΔH_{mix}(MnLi) and ΔH_{mix}($Mn\phi$) while suggesting a negative heat of mixing along the $Li\phi$ binary and negligible ternary excess terms. Parameters for the transformation of Mo_2O_6 from the MoO_3 structure to the hypothetical brannerite structure are estimated to be: $\Delta H = 10.0$ kJ/mole Mo_2O_6, $\Delta V° = 7.65$ cm³/mole. Both the MnV_2O_6–$LiMoVO_6$ system studied here and the MgV_2O_6–$LiMoVO_6$ system studied previously show positive heats of mixing at MnV_2O_6- or MgV_2O_6-rich compositions and negative heats of mixing at $LiMoVO_6$-rich compositions. In each case, a linear correlation of the enthalpy interaction parameter, λ_H, and the volume interaction parameter, λ_V, is observed. Both systems show that positive heats of mixing correlate with negative volumes of mixing and negative heats of mixing correlate with positive volumes of mixing, but the MgLi correlation has a steeper slope than that for MnLi. This rather unusual but systematic behavior thus persists in several systems with brannerite structure. © 1989 Academic Press, Inc.

Introduction

Recently we presented a paper about energetics of brannerite-type solid solutions in AV_2O_6–$LiVMoO_6$ (A = Zn, Mg) systems (*1*). Now we bring attention to the systems with divalent Mn. It is known that MnV_2O_6 forms solid solutions with the general formula $Mn_{1-x-y}\phi_xLi_yV_{2-2x-y}Mo_{2x+y}O_6$ ($MnLi\phi$) (*2*), where ϕ represents a vacancy in the "A" site. Mn^{2+}, Li^+, and ϕ substitute randomly on one sublattice and V^{5+} and

Mo^{6+} substitute randomly on the other (*3, 4*). Detailed descriptions of brannerite-type structure can be found in (*1, 3–5*). The extreme cases of $MnLi\phi$ are $Mn\phi = Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$ (at $y = 0$), $MnLi = Mn_{1-y}Li_yV_{2-y}Mo_yO_6$ at ($x = 0$), and $Li\phi = Li_{1-x}\phi_xV_{1-x}Mo_{1+x}O_6$ (at $x + y = 1$) (*2*). The first represents solid solutions between MnV_2O_6 and MoO_3 (or Mo_2O_6), the second between MnV_2O_6 and $LiVMoO_6$ (also a compound with the brannerite structure) and the last between $LiVMoO_6$ and MoO_3. Only MnLi solid solutions exist over the full range of compositions (*2*). $Mn\phi$ phases are known to $x = 0.53$ (*3, 4*) and $Li\phi$ phases exist to $x = 0.16$ (*3, 6, 7*).

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The purpose of the present study is to obtain thermodynamic data for MnLi and Mnϕ solid solutions. In particular, we find how the high concentration of vacancies influences the thermodynamics of solid solutions and if these solid solutions are in fact thermodynamically stable. High-temperature calorimetric techniques have been used to obtain enthalpies of mixing in the MnV$_2$O$_6$–LiVMoO$_6$ and MnV$_2$O$_6$–MoO$_3$ solid solution series.

Experimental

Sample Preparation

Samples were prepared by two methods: the amorphous citrate precursor method (2) and solid-state synthesis from MnCO$_3$, V$_2$O$_5$, and MoO$_3$ at 823–923 K for 100 hr. Samples obtained by the precursor method were annealed in oxygen at 773–823 K for 17 hr and afterward again annealed in air at this same temperature for 20 hr. Annealing in oxygen was performed in order to remove any remaining carbon deposit from the samples. Several of the MnLi solid solutions prepared by the precusor method were the same samples used in the previous study (2). The sample of Mnϕ with $x = 0.53$ was that investigated by Kozlowski and Stadnicka (4), and was ground from single crystals. Elemental analysis, atomic absorption spectroscopy, and classical flame photometry for Li of some selected samples proved stoichiometry within $+1\%$ in the absolute weight of the metals. The samples were dried at 423 K for 24 hr and were stored in a desiccator before calorimetry.

X-Ray Measurements

X-ray measurements were performed on a Scintag Pad V automatic diffractometer using Cu$K\alpha$ radiation and a solid-state detector. The detailed procedure was the same as in our previous study (1).

Calorimetric Measurements

Preliminary experiments showed that the Mn-containing brannerites dissolved readily in molten sodium molybdate, 3Na$_2$O · 4MoO$_3$, near 973 K. This solvent has been used previously for drop solution calorimetry of Mg and Zn containing brannerites (1). Mn-containing brannerites cannot be maintained at 973 K because of phase transitions to high-temperature polymorphs and/or melting reactions, so, similarly to the Mg and Zn systems studied previously (1), drop solution calorimetry was used instead of solution calorimetry because the latter requires several hours of preequilibration at calorimetric temperature.

It is possible that Mn^{2+} in Mn-containing solid solutions could oxidize to higher valence states during the dissolution in molten sodium molybdate. This point was investigated carefully by weight analyses. About 0.5 g of MnV$_2$O$_6$ was dissolved at about 1.5 g of sodium molybdate at 973 K in air. A very small increase in weight was seen after dissolution. If this were all due to oxidation of Mn^{2+} to Mn^{3+}, then no more than 0.97% of all Mn^{2+} ions could oxidize to Mn^{3+}. However this increase may very likely result, instead, from the high hygroscopicity of the solvent rather than from oxidation. All analyses were performed in closed crucibles but one could not avoid a few seconds of contact of flux with air during transferring and weighing samples. A control experiment performed with flux alone showed a similar increase in weight. The solvent with dissolved MnV$_2$O$_6$ and that resulting from calorimetry of all samples were light in color with none of the dark brown to black coloration characteristic of manganese in higher oxidation states. We conclude that Mn–brannerite solid solutions dissolve in 3Na$_2$O · 4MoO$_3$ without change of oxidation state.

In drop solution calorimetry the sample

is dropped from room temperature into the solvent in the calorimeter at high temperature (976 K). The heat effect measured is the sum of a heat content ($H_{976} - H_{295}$) and heat of solution. As before, a twin Calvet-type microcalorimeter (8), calibrated by the Pt drop method (9) was used. Detailed procedure was described previously (1). Series of experiments were done on the MnLi, Mnφ, MnLiφ solid solutions, one sample of Liφ solid solution, and MoO_3. The molar enthalpies observed (sum of heat content and heat of solution) were in the range 149–197 kJ/mole with errors (two standard deviations of the mean) of 0.35 to 1.93 kJ/mole (0.19 to 1.05%). $LiVMoO_6$ was measured during the previous investigation (1) giving 194.8 ± 1.0 kJ/mole from 28 experiments. This study gave 195.6 ± 1.5 kJ/mole from 7 experiments. A final average of 194.9 ± 0.8 kJ/mole from all experiments was used.

Because enthalpies of mixing (see below) are derived from the difference in observed enthalpies of the solid solutions and the weighted average of the end-members, it is necessary to make certain that the observed enthalpies are indeed independent of the concentration of dissolved components in the solvent (10). To check that this infinitely dilute or Henry's law limit was applicable, a number of experiments were done in which, in a series of three samples dissolved in the same solvent, the composition of each subsequent sample was varied. Within the uncertainities given above, there was no difference in the enthalpy of, for example, MnV_2O_6 dissolved as the first sample in the solvent, as a second or third sample in a solvent containing MnV_2O_6, or in a flux containing MnV_2O_6 or MoO_3. In addition, mechanical mixture of the two end-members (MnV_2O_6 and MoO_3) with composition $x = 0.40$ and $x = 0.53$ was investigated. They gave values which fit on the straight line between MnV_2O_6 and Mo_2O_6 (see Fig. 2b). This confirms that the observed enthalpies are indeed independent of the concentrations of dissolved component in the solvent.

Two solid solutions (Mnφ, $x = 0.40$, and Liφ, $x = 0.16$) and two mechanical mixtures (MnV_2O_6 and MoO_3 and $LiVMoO_6$ and MoO_3 with the same compositions as the solid solutions) were investigated by drop solution calorimetry from 824 to 978 K. In this case samples were equilibrated at 824 K in the furnace gradient above the calorimeter and then dropped into the solvent at 976 K. Temperature was measured by two thermocouples, one at the top and one at the bottom of the sample. The difference was <2 K.

Data Analysis

All model fittings were performed using the program Statgraphics (version 2.6) and weighting each point inversely to the variance. Uncertainities in composition were not considered. The models were accepted at a 95% confidence level.

Results

X-Ray Investigation

Our X-ray patterns for MnLiφ solid solutions show that all the samples are single phases with brannerite-type structures. Calculated lattice parameters for Mnφ and MnLi solid solutions are given in Table I. The results obtained agree very well with previously published data for MnV_2O_6 and Mnφ (see Table I for comparison). Figure 1 presents the dependence of molar volume on composition for MnLi and Mnφ solid solutions, including results published previously.

The observed molar volume for MnLi series was fitted by least squares to a third-order polynomial giving the expression,

$$V(\text{cm}^3/\text{mole}) = 63.24(\pm 0.02)y$$
$$+ 61.82(\pm 0.05)(1 - y)$$
$$+ y(1 - y)[-0.69(\pm 0.34)$$
$$+ 1.82(\pm 0.53)y], \quad (1)$$

TABLE I

LATTICE PARAMETERS, UNIT CELL VOLUME, AND MOLAR VOLUME FOR MnLi AND Mnϕ SOLID SOLUTIONS

	a (Å)	b (Å)	c (Å)	β (Å)	V (Å³)	V (cm³/mole)
MnV_2O_6	9.3131(14)[a]	3.5352(11)	6.7543(15)	112.582(15)	205.322(73)	61.829(22)
MnLi $y = 0.10$	9.3116(12)	3.5479(8)	6.7398(8)	112.560(8)	205.619(40)	61.918(12)
$y = 0.20$	9.3155(5)	3.5577(5)	6.7287(3)	112.521(5)	205.995(27)	62.031(8)
$y = 0.30$	9.3274(17)	3.5705(5)	6.7209(8)	112.451(10)	206.823(39)	62.281(12)
$y = 0.40$	9.3254(11)	3.5821(5)	6.7080(6)	112.356(8)	207.235(31)	62.405(10)
$y = 0.50$	9.3303(9)	3.5926(3)	6.6963(6)	112.220(7)	207.789(23)	62.572(12)
$y = 0.60$	9.3349(10)	3.6037(6)	6.6829(6)	112.107(8)	208.288(38)	62.722(12)
$y = 0.70$	9.3404(14)	3.6143(14)	6.6765(11)	112.027(12)	208.943(73)	62.919(22)
$y = 0.80$	9.3431(17)	3.6260(11)	6.6676(12)	111.897(16)	209.571(55)	63.108(17)
$y = 0.90$	9.3443(15)	3.6383(4)	6.6486(6)	111.765(8)	209.921(33)	63.213(10)
$LiVMoO_6$	9.3418(5)	3.6449(3)	6.6342(5)	111.636(6)	209.980(20)	63.231(6)
MnV_2O_6	9.3131(14)	3.5352(11)	6.7543(15)	112.582(15)	205.322(73)	61.829(22)
	9.315(3)[c]	3.5361(1)[c]	6.754(2)[c]	112.66(2)[c]	205.29[c]	61.818[c]
Mnϕ $x = 0.05$	9.3159(20)	3.5443(6)	6.7521(8)	112.575(11)	205.861(51)	61.991(15)
$x = 0.10$	9.3317(17)	3.5603(6)	6.7483(9)	112.610(14)	206.972(45)	62.325(14)
$x = 0.15$	9.3419(14)	3.5664(6)	6.7487(9)	112.570(10)	207.626(42)	62.522(12)
$x = 0.20$	9.3431(19)	3.5733(7)	6.7474(9)	112.536(14)	208.066(50)	62.654(15)
$x = 0.25$	9.3625(13)	3.5855(6)	6.7536(11)	112.424(11)	209.568(42)	63.107(12)
$x = 0.30$	9.3655(14)	3.5951(6)	6.7548(8)	112.352(9)	210.345(40)	63.341(12)
$x = 0.35$	9.3743(11)	3.6041(4)	6.7574(6)	112.239(7)	211.325(26)	63.636(8)
$x = 0.38$	9.3809(26)	3.6094(7)	6.7609(17)	112.152(20)	212.025(63)	63.847(19)
$x = 0.40$	9.3848(10)	3.6146(3)	6.7625(5)	112.104(6)	212.538(24)	64.001(7)
	9.378(3)[c]	3.613(1)[c]	6.761(2)[c]	112.18(2)[c]	212.13[c]	63.880[c]
$x = 0.53$	9.4118(14)	3.6377(16)	6.7734(12)	112.034(13)	214.964(88)	64.732(27)
	9.412(5)[c]	3.643(1)[c]	6.767(3)[c]	112.00(4)[c]	215.13[c]	64.781[c]
Mo_2O_6 (br)[b]						68.765(592)[b]

[a] Values in parentheses are standard deviations of the calculated lattice parameter.
[b] Value calculated from extrapolation of Eq. (4) to $x = 1$ (Mo_2O_6).
[c] From Refs. (2, 3).

with y = mole fraction of $LiVMoO_6$ and r^2 = 0.999. The volume of mixing is then given by

$$\Delta V_{mix}^{MnLi} = y(1 - y)\lambda_V \qquad (2)$$

$$\lambda_V = -0.69(\pm 0.34) + 1.82(\pm 0.53)y. \qquad (3)$$

The observed molar volume for Mnϕ was fitted by least squares to a second-order polynomial giving the expression,

$$V(\text{cm}^3/\text{mole}) = 68.77(\pm 0.59)x$$
$$+ 61.80(\pm 0.06)(1 - x)$$
$$- 2.55(\pm 1.05)x(1 - x), \qquad (4)$$

with r^2 = 0.999 and x = mole fraction of Mo_2O_6. The volume of mixing is

$$\Delta V_{mix}^{Mn\phi} = x(1 - x)\lambda_V$$

with $\lambda_V = -2.55(\pm 1.05)$ cm³/mole. (5)

Figures 3a and 3b present the calculated volume of mixing, ΔV_{mix}, for MnLi and Mnϕ solid solutions according to the equations

$$\Delta V_{mix}^{MnLi} = V_{MnLi} - yV_{LiVMoO_6}$$
$$- (1 - y)V_{MnV_2O_6} \qquad (6)$$

$$\Delta V_{mix}^{Mn\phi} = V_{Mn\phi} - xV_{\phi Mo_2O_6}$$
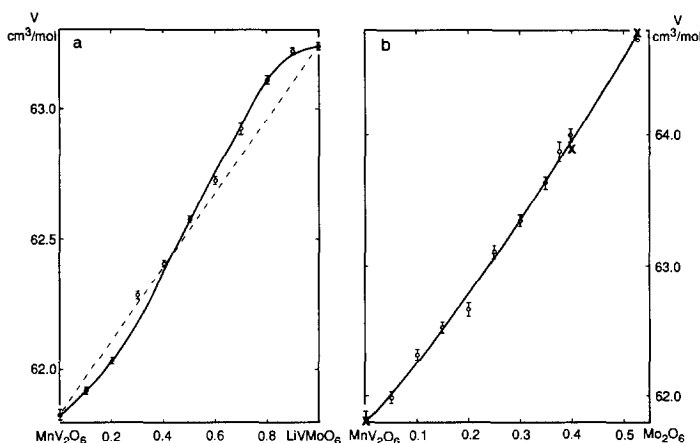$$- (1 - x)V_{MnV_2O_6}, \qquad (7)$$

Fig. 1. Molar volumes in (a) MnV_2O_6–$LiMoVO_6$ and MnV_2O_6–Mo_2O_6 solid solutions. Curves are from Eqs. (1) and (4). Circles with error bars represent this work, crosses represent data in Ref. (2).

where $V_{\phi Mo_2O_6} = 68.77 \pm 0.59$ cm^3/mole is extrapolated from the existing Mnϕ solid solutions to $x = 1$ (this represents the volume of the hypothetical ϕMo_2O_6 compound with brannerite-type structure). Error bars represent the standard deviation of the mean for ΔV_{mix} calculated from the propagation of errors for the molar volumes of MnV_2O_6, $LiVMoO_6$, ϕMo_2O_6, and Mnϕ solid solutions. A third-order polynomial for the MnLi series and a second-order polynomial for the Mnϕ series are statistically warranted. The second-order polynomial for the Mnϕ series results in negative volumes of mixing and a negative regular interaction parameter over the entire composition range. For the MnLi series, ΔV_{mix} is negative for $y < 0.40$ and positive for $y > 0.40$.

Calorimetric Results

Results of drop solution calorimetry are given in Table II. The difference between the drop solution enthalpy of a mechanical mixture of the end-members (or, as discussed above, the weighted average of the two end-member drop solution enthalpies) and the observed drop solution enthalpy of the solid solution gives the enthalpy of mix-

ing at room temperature of the solid solution having a structural state characteristic either of the preparation temperature (823–923 K) or of a somewhat lower temperature where any reequilibration of cation and vacancy distribution during quench has ceased. The X-ray work refers to the same samples, also measured at room temperature. Thus, rigorously, both heats and volumes of mixing refer to those parameters at room temperature for samples having a structural state characteristic of high temperature. The possible effect of temperature on heats of mixing is discussed below.

The observed drop solution enthalpy and the enthalpy of mixing for the MnLi solid solutions are shown in Figs. 2a and 3c. The MnLi system shows definite deviation from ideal enthalpy behavior. There are positive heats of mixing for $y < \sim0.4$ and negative heats of mixing for $y > \sim0.4$. The observed enthalpy was fitted by least squares to a third-order polynomial giving the expression,

$$H_{obs}^{MnLi} \text{ (kJ/mole)} = 194.98(\pm0.40)y$$
$$+ 191.07(\pm0.47)(1 - y)$$
$$- y(1 - y)[24.80(\pm3.32)$$
$$- 51.66(\pm5.65)y], \quad (8)$$

TABLE II

RESULTS OF DROP SOLUTION CALORIMETRY (295 TO 976 K) FOR MnLi, Mnϕ, MnLiϕ, AND Liϕ SOLID SOLUTIONS

Composition		H_{obs} (kJ/mole)
MnV$_2$O$_6$		191.22 ± 0.97(13)[a]
MnLi	$y = 0.10$	189.15 ± 1.51(13)
	$y = 0.20$	189.64 ± 1.09(11)
	$y = 0.30$	190.06 ± 0.61(10)
	$y = 0.40$	192.84 ± 1.14(15)
	$y = 0.50$	193.49 ± 1.23(5)
	$y = 0.60$	194.57 ± 1.00(6)
	$y = 0.70$	195.52 ± 1.21(6)
	$y = 0.80$	196.97 ± 0.65(19)
	$y = 0.90$	196.84 ± 1.69(6)
LiVMoO$_6$		194.93 ± 0.80(35)
MnV$_2$O$_6$		191.22 ± 0.97(13)
Mnϕ	$x = 0.05$	186.54 ± 0.35(6)
	$x = 0.10$	181.75 ± 1.53(4)
	$x = 0.15$	179.19 ± 1.55(6)
	$x = 0.20$	175.71 ± 1.45(6)
	$x = 0.25$	173.05 ± 1.24(4)
	$x = 0.30$	170.57 ± 1.16(17)
	$x = 0.35$	167.05 ± 0.89(4)
	$x = 0.38$	166.07 ± 1.12(6)
	$x = 0.40$	164.34 ± 1.45(10)
	$x = 0.40^b$	173.08 ± 1.43(4)
	$x = 0.53$	156.76 ± 1.12(8)
	$x = 0.53^b$	168.01 ± 1.92(5)
Mo$_2$O$_6$ (MoO$_3$ str.)		149.02 ± 1.32(10)
MnLiϕ		
$x = 0.10$	$y = 0.60$	189.70 ± 1.39(6)
$x = 0.20$	$y = 0.40$	182.43 ± 1.93(6)
$x = 0.30$	$y = 0.20$	173.12 ± 1.69(6)
Liϕ		
	$x = 0.16$	189.19 ± 1.11(5)
	$x = 0.16^b$	189.46 ± 0.83(5)

[a] Error is two standard deviations of the mean; number in parentheses is number of experiments performed.

[b] Mechanical mixture of end-members.

where y = mole fraction LiVMoO$_6$, with r^2 = 0.972. The curves representing the enthalpy of mixing, ΔH_{mix}, and the enthalpy interaction parameter, λ_H, plotted in Figs. 3c and 3e, are given by the expressions:

$$\Delta H_{mix} = y(1 - y)\lambda_H \qquad (9)$$

$$\lambda_H = 24.80(\pm 3.32) - 51.66(\pm 5.65)y. \qquad (10)$$

Figure 3e shows a linear relationship between the enthalpy interaction parameter λ_H and composition. Extrapolation of Eq. (10) shows that the enthalpy interaction parameter changes from 24.80 ± 3.32 kJ/mole for LiVMoO$_6$ dissolving at infinite dilution in MnV$_2$O$_6$ to -26.56 ± 6.54 kJ/mole for MnV$_2$O$_6$ dissolving in LiVMoO$_6$.

The observed enthalpy and the enthalpy of mixing for the Mnϕ solid solutions are shown in Figs. 2b and 3d and in Table II. The observed enthalpies for MnV$_2$O$_6$ and 10 solid solution compositions were fit by

$$H_{obs}^{Mn\phi} \text{ (kJ/mole)} = 139.04(\pm 4.47)x$$
$$+ 190.29(\pm 0.29)(1 - x)$$
$$- 23.44(\pm 8.05)x(1 - x), \qquad (11)$$

where x = mole fraction of Mo$_2$O$_6$ and r^2 = 0.998. Statistical analysis shows that the second-order polynomial is appropriate. The dashed line in Fig. 2b represents ideal enthalpy behavior between MnV$_2$O$_6$ and Mo$_2$O$_6$. On this line are also two points for mechanical mixtures between MnV$_2$O$_6$ and Mo$_2$O$_6$ = 2MoO$_3$ with compositions x = 0.40 and x = 0.53. Figure 2b shows clearly that all Mnϕ solid solutions are less stable in terms of enthalpy than a mechanical mixture of MnV$_2$O$_6$ and MoO$_3$.

Extrapolation of Eq. (11) to x = 1 (e.g., Mo$_2$O$_6$) gives value for $H_{obs}(\phi$Mo$_2$O$_6$ (brannerite structure)) = 139.04(± 4.57) kJ/mole. This is the drop solution enthalpy for the hypothetical ϕMo$_2$O$_6$ compound with brannerite-type structure.

The enthalpy of mixing between end-member with brannerite-structure standard states is given by

$$H_{mix}^{Mn\phi} = x(1 - x)\lambda_H, \qquad (12)$$

where $\lambda_H = +23.44(\pm 8.05)$ kJ/mole.

Because data could only be obtained for the attainable range of solid solutions, x < 0.53, and the value for ϕMn$_2$O$_6$ had to be extrapolated from Eq. (11), a higher order polynomial (asymmetric heat of mixing) is

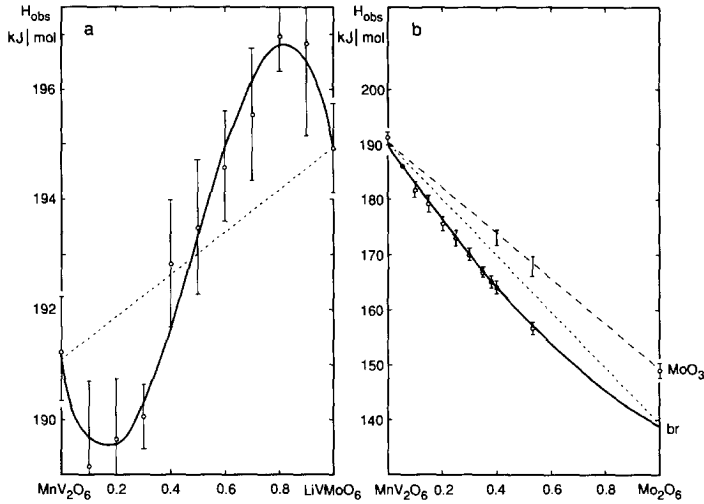FIG. 2. Measured enthalpies (kJ/mole) for sample (brannerite structure, 295 K) → sample (dissolved in 3Na$_2$O · 4MoO$_3$, 976 K) for (a) MnV$_2$O$_6$–LiVMoO$_6$ (MnLi) and (b) MnV$_2$O$_6$–Mo$_2$O$_6$ (Mnϕ). Circles represent data for solid solutions; bars represent data for mechanical mixtures of MnV$_2$O$_6$ and Mo$_2$O$_6$ (MoO$_3$ structure). Solid curves represent best fit of data by Eqs. (8) and (11). Dotted lines represent ideal mixing between brannerite end-members. Dashed line shows enthalpy for a mechanical mixture of MnV$_2$O$_6$ (br) and Mo$_2$O$_6$ (MoO$_3$).

not warranted. Once Eq. (11) is used to fix the enthalpy of ϕMn$_2$O$_6$, the observed heats of mixing (calculated as the difference in drop solution enthalpies of a mixture of brannerite end-members and the solid solution) appear to lie above the calculated values (though not outside the errors) for $x <$ 0.3 (see Fig. 3d). This may suggest some asymmetry in the enthalpy of mixing, with $\lambda^{Mn\phi}$ greater near $x = 0$ than near $x = 1$. However this conclusion depends on the choice of enthalpy for ϕMn$_2$O$_6$ (brannerite) and trying to extract three rather than two parameters from the Mnϕ data, with all parameters interdependent, is not useful. Similar caution applies to the volume data.

Three samples of MnLiϕ and one of Liϕ, $x = 0.16$, were investigated. The composition Liϕ, $x = 0.16$, represents the saturated solid solution at 823–923 K of MoO$_3$ in LiV MoO$_6$ along the LiVMoO$_6$–Mo$_2$O$_6$ join of the pseudoternary MnV$_2$O$_6$–LiVMoO$_6$– Mo$_2$O$_6$ system (2, 6, 7). The enthalpy of formation of Liϕ, $x = 0.16$, from LiVMoO$_6$

and Mo$_2$O$_6$ is +0.3 ± 1.4 kJ/mole at room temperature.

All solid solutions and end-members studied (total of 25 samples) were used to fit simultaneously the eight parameters in a model of the form

$$H_{obs}^{MnLi\phi} \text{ (kJ/mole)} = aH_{MnV_2O_6} \text{ (br)}$$
$$+ bH_{Mo_2O_6} \text{ (br)} + cH_{LiVMoO_6} - ab\lambda_H^{Mn\phi}$$
$$- ac\lambda_H^{MnLi} - bc\lambda_H^{Li\phi} - abc\lambda_H^{MnLi\phi}, \quad (13)$$

where $\lambda_H^{MnLi} = (\alpha + \beta c)$ and a, b, c represent the mole fraction of MnV$_2$O$_6$, Mo$_2$O$_6$, and LiVMoO$_6$ in the MnLiϕ solid solutions, respectively. This equation describes the enthalpy of the system as consisting of contributions from three sources: (a) drop solution enthalpies of the pure end-members, $H_{MnV_2O_6}$ (br), $H_{Mo_2O_6}$ (br), H_{LiVMoO_6} (br); (b) regular solution binary mixing terms $\lambda_H^{Mn\phi}$ and $\lambda_H^{Li\phi}$ and a term, λ_H^{MnLi}, linearly dependent on composition; and (c) ternary excess term $\lambda_H^{MnLi\phi}$. This formalism is similar to that used by Navrotsky *et al.* in describing

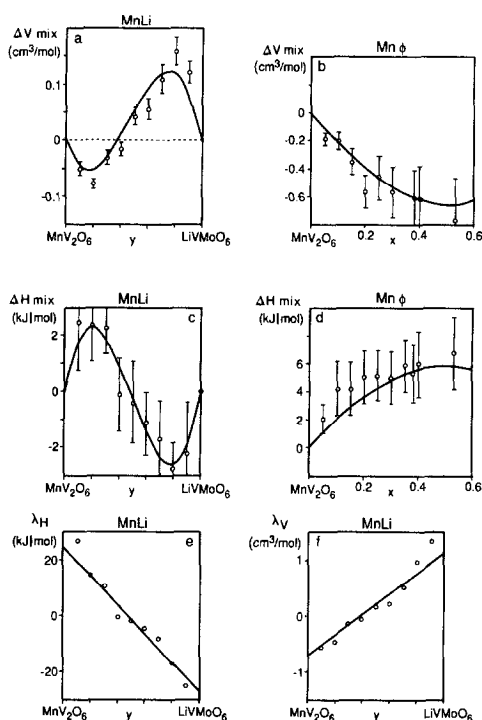FIG. 3. Volumes of mixing in (a) MnV_2O_6–$LiVMoO_6$ (MnLi) and (b) MnV_2O_6–Mo_2O_6 (Mnϕ) (brannerite standard states). Enthalpy of mixing in (c) MnV_2O_6–$LiVMoO_6$ and (d) MnV_2O_6–Mo_2O_6 (brannerite standard states). Enthalpy (e) and volume (f) interaction parameters in MnV_2O_6–$LiVMoO_6$. Errors bars were obtained by propagation of errors in original data. Curves represent best fits to data; see text.

heats of mixing in ternary glass systems (11, 12). It is rigorous for a regular solution and approximate for systems less symmetric than regular. Results show that ternary

excess term is statistically unwarranted. Next we fit the remaining seven parameters to the 25 data points. All terms were statistically significant and the fit gave an excellent description of the observed experimental values. Table III compares these results to the results obtained for individual binary systems separately. The calculated values of parameters using all the data points are very similar to the ones derived separately from MnLi or Mnϕ solid solutions only. This indicates internal consistency of all results for MnLiϕ solid solutions.

To test whether the heats of mixing, especially in vacancy-containing solid solutions, depend on temperature (implying either substantial excess vibrational heat capacities or significant reequilibration of structural state at intermediate temperatures) several drop solution experiments were done in which samples were dropped from 824 K into solvent at 976 K (see Table IV). Two compositions (Mnϕ, $x = 0.40$, and Liϕ, $x = 0.16$) were studied and results for solid solutions and mechanical mixtures were compared at each temperature. In both cases the heat of mixing is the same within experimental error at both 295 and 824 K and the actual values of ΔH_{mix} do not differ by more than 1 kJ/mole at the two temperatures for each composition. Furthermore, the difference between the 295 and 824 K drop solution data give the enthalpy (heat content), $H_{824} - H_{295}$, of the

TABLE III

COMPARISON OF PARAMETERS CALCULATED FROM FITS TO ALL DATA IN MnLiϕ TERNARY WITH
PARAMETERS FROM MnLi AND Mnϕ BINARIES TAKEN SEPARATELY

	$H_{MnV_2O_6}$ (kJ/mole)	H_{LiVMoO_6} (kJ/mole)	$H_{Mo_2O_6}$ (kJ/mole)	λ_H^{MnLi} (kJ/mole)	$\lambda_H^{Mn\phi}$ (kJ/mole)	$\lambda_H^{Li\phi}$ (kJ/mole)
MnLiϕ s.s. (25 data points)	190.26(±0.24)	194.99(±0.39)	138.67(±3.91)	20.28(±2.52) − 46.48(±5.06)y	22.59(±6.82)	−24.59(±5.98)
MnLi s.s. (11 data points)	191.07(±0.47)	194.98(±0.46)	—	24.80(±3.32) − 51.66(±5.64)y	—	—
Mnϕ s.s. (11 data points)	190.29(±0.29)	—	139.04(±4.57)	—	23.44(±8.05)	—
Experimental values	191.22(±0.97)	194.93(±0.80)	—	—	—	—

	Mnϕ $x = 0.40$	Liϕ $x = 0.16$
ΔH drop solution		
(295 to 976 K)		
Solid solution	164.34 ± 1.45(10)	189.19 ± 1.11(5)
Mechanical mixture	173.08 ± 1.43(4)	189.46 ± 0.83(5)
ΔH drop solution		
(824 to 976 K)		
Solid solution	64.53 ± 3.91(4)	88.52 ± 2.08(6)
Mechanical mixture	72.53 ± 0.57(3)	87.72 ± 0.99(3)
ΔH mixing at 295 K	8.9 ± 2.0	+0.3 ± 1.4
ΔH mixing at 824 K	8.0 ± 3.9	−0.8 ± 2.3
Heat content (H_{824}–H_{295})		
Solid solution	99.8 ± 4.2	100.7 ± 2.4
Mechanical mixture	100.6 ± 1.5	101.7 ± 1.3

crystalline materials. For each composition, $H_{824} - H_{295}$ is the same within experimental error for the solid solution and for the mechanical mixture and the actual values obtained differ by 1 kJ/mole or less. Even when comparing the two different compositions, the heat contents, $H_{824} - H_{295}$, are all within a range of 2 kJ/mole. We conclude, therefore, that the correction to heats of mixing arising from effects of temperature in the range 293–824 K is unlikely to exceed 1.0 kJ/mole and appears to be zero within experimental error. The heats of mixing measured by drop solution calorimetry and referring to room temperature thus also represent, within experimental errors, values at high temperature.

Discussion

The enthalpy and volume of transformation of MoO$_3$ to the hypothetical brannerite-type structure can be calculated. Based on literature data for lattice parameters of MoO$_3$ (13), the unit cell volume of MoO$_3$ is 202.98 Å^3 ($Z = 4$) equal to 61.124 cm^3 per mole Mo$_2$O$_6$. Using this value and our results (Tables I and II) we calculate ΔH and ΔV for transformation

$$\text{Mo}_2\text{O}_6 \rightarrow \phi\text{Mo}_2\text{O}_6 \text{ (br)} \qquad (14)$$
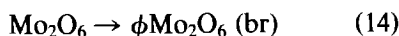
as +10.0 ± 4.7 kJ and +7.65 cm^3 per mole Mo$_2$O$_6$, respectively.

These values depend on the quadratic polynomial used for volumes and to enthalpies in the Mnϕ system (Eqs. (4), (11)). This is the best approximation to use on statistical grounds (see above). Furthermore, although the enthalpy and volume trends are definitely curved (see Figs. 1b, 2b), precluding a linear equation, a cubic equation could introduce uncontrollable, untestable, and unwarranted curvature in the extrapolated region between $x = 0.53$ and $x = 1$.

Our data permit a thermodynamic estimate of the solubility of MoO$_3$ (Mo$_2$O$_6$) in the Mnϕ solid solution as follows. Since the solubility of MnV$_2$O$_6$ in Mo$_2$O$_6$ with the MoO$_3$ structure can be presumed negligible, the chemical potential of Mo$_2$O$_6$ in the two-phase mixture of terminal brannerite solid solution plus MoO$_3$ is essentially identical to that of pure Mo$_2$O$_6$ (MoO$_3$ structure). One can then write

$$\mu(\text{Mo}_2\text{O}_6 \text{ (br)}) = \mu(\text{Mo}_2\text{O}_6(\text{MoO}_3))$$
$$+ \Delta H(\text{Mo}_2\text{O}_6(\text{MoO}_3 \rightarrow \text{br}))$$
$$- T\Delta S(\text{Mo}_2\text{O}_6(\text{MoO}_3 \rightarrow \text{br}))$$
$$+ \Delta \bar{h}(\text{Mo}_2\text{O}_6, \text{br.ss.})$$
$$- T\Delta \bar{s}(\text{Mo}_2\text{O}_6, \text{br.ss}), \qquad (15)$$

where ΔH and ΔS refer to the transformation of Mo$_2$O$_6$ from the MoO$_3$ to the brannerite structure and $\Delta \bar{h}$ and $\Delta \bar{s}$ refer to the partial molar enthalpy and entropy of mixing of Mo$_2$O$_6$, referred to a brannerite standard state. ΔH is 10.0 kJ/mole (see above). ΔS is unknown. For solid-solid transitions ΔS is generally small, and, for lack of a better constraint, we set it to zero for the present calculation. From Eq. (12), $\Delta \bar{h} = 23.44(1 - x)^2$ kJ. We take $\Delta \bar{s}$ as the partial molar configurational entropy of mixing for the system Mn$_{1-x}\phi_x$(V$_{2-2x}$Mo$_{2x}$)O$_6$. Assuming random mixing of manganese and vacancies on one set of sites and, independently, random mixing of V and Mo on

another set of sites, the configurational entropy is given by

$$S_{conf} = -R[X_{Mn} \ln X_{Mn} + X_\phi \ln X_\phi]$$
$$-2R[X_V \ln X_V + X_{Mo} \ln X_{Mo}]$$
$$= -3R[x \ln x + (1 - x)\ln(1 - x)].$$
$$(16)$$

This gives $\Delta \bar{s}(Mo_2O_6) = -R \ln x^3$. Then

$$10,000 + 23,440(1 - x)^2$$
$$+ 8.314T \ln x^3 = 0. \quad (17)$$

For a temperature of 824 K, $x = 0.41$. This compares favorably to reported solubilities of $x = 0.45$ and $x = 0.53$ at that temperature (2–4). In principle an analogous calculation could be done for the whole MnLiϕ system, but we believe the enthalpies of mixing in the ternary are not well enough constrained by only three ternary data points in MnLiϕ and one along Liϕ to make this comparison meaningful.

Our previous study (1) showed a complex relation between enthalpies and volumes of mixing in MgV$_2$O$_6$–LiMoVO$_6$ and ZnV$_2$O$_6$–LiMoVO$_6$ solid solutions, where more positive ΔH_{mix} correlated with more negative ΔV_{mix}. The present data for Mn-containing systems show analogous trends. In the MnLi series (MnV$_2$O$_6$–LiMoVO$_6$), for $y < 0.4$, ΔH_{mix} is positive and ΔV_{mix} is negative (see Figs. 3a and 3c). For $Y > 0.4$, when ΔV_{mix} becomes positive, ΔH_{mix} becomes negative. The relation between the volume and the enthalpy interaction parameters is shown in Fig. 4. The slope of λ_V vs λ_H is steeper for the MgLi system than for MnLi. Nevertheless, all systems studied so far (MgLi, ZnLi, MnLi, and Mnϕ) are similar in that they show increasingly negative enthalpies of mixing as the volume of mixing becomes more positive. Figure 4 contains one point for the Mnϕ solid solution. This correlates an average enthalpy interaction parameter ($\lambda_H = 23$ kJ/mole) and an average volume interaction parameter ($\lambda_V = -2.5$ cm^3/mole) obtained for the compositions studied ($0 \leq$ mole fraction Mo$_2$O$_6 \leq$
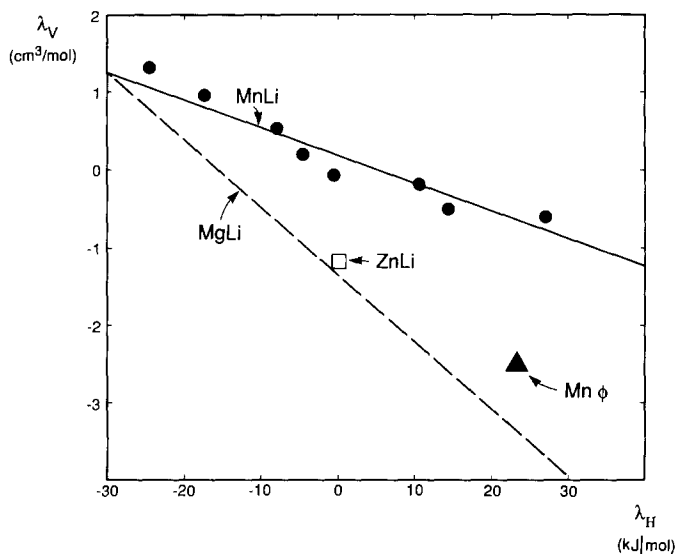

FIG. 4. Correlation between enthalpy and volume interaction parameters. Filled circles and solid line represent data (this work) for MnV$_2$O$_6$–LiVMoO$_6$ (MnLi). Dashed line represents correlation for MgV$_2$O$_6$–LiVMoO$_6$ (MgLi) (1). Square represents average value for ZnV$_2$O$_6$–LiVMoO$_6$ (ZnLi) (1). Triangle represents average value for MnV$_2$O$_6$–Mo$_2$O$_6$ (Mnϕ) (this work). Uncertainties are generally ±5 to ±8 kJ/mole for λ_H, ±0.5 to ±1 cm^3/mole for λ_V, estimated from propagation of errors.

0.4). In this range, λ_H and λ_V show no detectable composition dependence (within uncertainities of about ± 10 kJ/mole and about ± 1 cm^3/mole, respectively).

The introduction of substantial vacancy concentrations (up to 40% of Mn sites empty) in the MnLiϕ system does not appear to lead to any strikingly new energetic behavior compared to MnLi. Referred to a brannerite standard state for Mo$_2$O$_6$, the ternary solid solution shows negative heats of mixing for compositions near the LiV MoO$_6$ corner and positive heats of mixing toward the MnV$_2$O$_6$ corner. The enthalpies of mixing toward Mo$_2$O$_6$ are not well constrained because of the limited range of solid solution but the absence of a strong composition dependence for $\lambda_{\text{Mn}\phi}$ and the apparent absence of significant ternary excess terms argue against any pronounced destabilization within the brannerite structure due to the introduction of vacancies. The rather small enthalpy of transition of MoO$_3$ from the MoO$_3$ to the fictive brannerite structure (10.0 kJ/mole Mo$_2$O$_6$ or 5.0 kJ/mole MoO$_3$) also argues against any large destabilization of the brannerite structure by the coupled substitution of vacancies. Rather, the limits of solid solubility are determined by a balance of slowly varying energy and entropy factors in the solid solutions relative to MoO$_3$. Thus the substitutions Mn + V = Li + Mo, Mn + 2V = ϕ + 2Mo, and Li + V = ϕ + Mo behave energetically and structurally as analogous charge-balanced ionic reactions.

Possible structural reasons for the complex energetic behavior in MV$_2$O$_6$–Li MoVO$_6$ were discussed in our previous paper (1). The similarity in enthalpy behavior between the Mn and Mg systems is striking. The Mg system, on the other hand, shows larger negative volumes of mixing, which may be related, as suggested previously, to relaxation from somewhat anomalously large lattice parameters for MgV$_2$O$_6$. However, local order at Li-rich compositions may also play a role. The lack of structure refinements which would provide bond lengths and polyhedral distortions for intermediate compositions precludes more detailed analysis of the relation between crystal chemical and energetic factors.

Acknowledgments

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