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Defect Structures in the Brannerite-Type Vanadates

VIII. Synthesis of the $Mg_{1-y}Li_yV_{2-y}Mo_yO_6$ and $Mg_{1-x-y}\varnothing_xLi_yV_{2-2x-y}Mo_{2x+y}O_6$ Solid Solutions: Effect of Strengthening the Crystal Lattice by Substitution of Monovalent Ion for Bivalent Ion

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It is shown that MgV_2O_6 and $LiVMoO_6$, both of the brannerite-type structure, exhibit miscibility in the entire composition range resulting in the formation of MgLi = $Mg_{1-y}Li_yV_{2-y}Mo_yO_6$ solid solutions. For $y > 0.5$ significant capacity of the MgLi matrix to the excess Mo^{6+} cations compensated by cation vacancies $\varnothing$ appears and MgLi$\varnothing$ = $Mg_{1-x-y}\varnothing_xLi_yV_{2-2x-y}Mo_{2x+y}O_6$ solutions become stable. Pronounced negative deviations from Vegard's law are simultaneously observed for MgLi solid solutions. An unusual phenomenon is thus observed: monovalent cation (Li^+) substituted for bivalent cation (Mg^{2+}) strengthens the brannerite-type lattice and increases its toleration to cation vacancies. A similar effect has recently been observed for ZnLi and ZnLi$\varnothing$ solid solutions (K. Mocała and J. Ziółkowski, *J. Solid State Chem.* **71,** 426 (1987)); the effect is absent, however, in the case of MnLi and MnLi$\varnothing$ (J. Ziółkowski, K. Krupa, and K. Mocała, *J. Solid State Chem.* **48,** 376 (1983)). Some speculations concerning this effect and some predictions are offered. X-ray data are listed for MgLi solid solutions of various compositions. © 1987 Academic Press, Inc.

Introduction: Outline of the Idea

A number of bivalent metal vanadates MeV_2O_6 (Me = Mg, Mn, Co, Cu, Zn, Cd) crystallize in the monoclinic brannerite-type structure or at least one of the polymorphs exhibits this structure (*1*). In the brannerite-type structure VO_6 octahedra sharing edges and corners form the anionic sheets parallel to (001) plane and Me^{2+} cations situated also in octahedra link the anionic layers along [001]. The same structure is adapted also by $LVMoO_6$ (L = Li, Na, Ag) compounds (*2, 3*). In former works (*4–10*) we have shown that some of the above-mentioned MeV_2O_6 compounds form solid solutions with MoO_3 and Li_2O of the general formula $Me_{1-x-y}\varnothing_xLi_yV_{2-2x-y}Mo_{2x+y}O_6$ (labeled MeLi$\varnothing$) in which Mo^{6+} ions are substituted randomly for V^{5+} and similarly Li^+ and cation vacancies $\varnothing$ for Me^{2+}. As $Me_{1-x-y}\varnothing_xLi_yV_{2-2x-y}Mo_{2x+y}O_6$ = $(1 - x - y)$ MeV_2O_6 + y $LiVMoO_6$ + $2x$ MoO_3, it is convenient to represent the range of existence of MeLi$\varnothing$ using the equilateral composition-triangle MeV_2O_6–$LiVMoO_6$–MoO_3 (Fig. 1), where composition variables $X = 100x$ and $Y = 100y$ are marked along the MeV_2O_6–MoO_3 and

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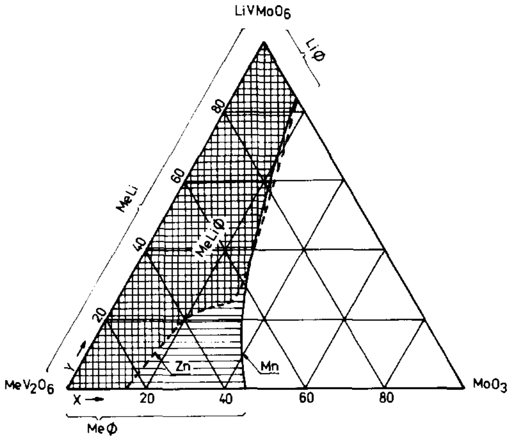

FIG. 1. Composition triangle MeV_2O_6–$LiVMoO_6$–MoO_3 in which the areas of stability of solid solutions $Me\mathrm{Li}\varnothing$ = $Me_{1-x-y}\varnothing_x\mathrm{Li}_y\mathrm{V}_{2-2x-y}\mathrm{Mo}_{2x+y}\mathrm{O}_6$ are marked for Me = Mn, Zn. Composition variables $X = 100x$ and $Y = 100y$ are marked along the arms MeV_2O_6–MoO_3 and MeV_2O_6–$LiVMoO_6$, respectively. The extreme cases of $Me\mathrm{Li}\varnothing$ are: $Me\varnothing$ (at $y = 0$), $Me\mathrm{Li}$ (at $x = 0$), and $\mathrm{Li}\varnothing$ (at $x + y = 1$).

MeV_2O_6–$LiVMoO_6$ arms, respectively. The extreme cases of $Me\mathrm{Li}\varnothing$ are:

$$Me\varnothing = Me_{1-x}\varnothing_x\mathrm{V}_{2-2x}\mathrm{Mo}_{2x}\mathrm{O}_6 \quad (\text{at } y = 0),$$

$$Me\mathrm{Li} = Me_{1-y}\mathrm{Li}_y\mathrm{V}_{2-y}\mathrm{Mo}_y\mathrm{O}_6 \quad (\text{at } x = 0),$$

$$\mathrm{Li}\varnothing = \mathrm{Li}_{1-x}\varnothing_x\mathrm{V}_{1-x}\mathrm{Mo}_{1+x}\mathrm{O}_6 \quad (\text{at } x + y = 1).$$

$\mathrm{Li}\varnothing$ exists in the range $0 \leq X \leq 16$ (*2*). $Me\varnothing$ are known for Me = Mn, $0 \leq X \leq 45$ (*4*), Me = Co, $0 \leq X \leq 22$ (*9*), Me = Zn, $0 \leq X \leq 15$ (*10*).[1] $Me\mathrm{Li}$ solid solutions have been found (*8, 10*) for Me = Mn, Zn (CoLi has not been studied yet) and exist in the whole composition ranges, i.e., between MeV_2O_6 and $LiVMoO_6$. $Me\mathrm{Li}\varnothing$ exist also for Me = Mn, Zn (*8, 10*) and their stability ranges are marked in Fig. 1. Behind the border of saturated $Me\mathrm{Li}\varnothing$ solutions we deal with a mixture of saturated $\mathrm{MnLi}\varnothing$ + MoO_3 in the first of the discussed systems. In the second one there are several fields in which such phases coexist[2] as saturated $\mathrm{ZnLi}\varnothing$, $ZnMoO_4$, V_2MoO_8, MoO_3, and solid solution of MoO_3 in V_2O_5.

Solid solution highly analogous to $Me\mathrm{Li}\varnothing$ is also known for Me = Cu with Li^+ replaced with Cu^+, however, in this case X and Y may change in a very limited range (*6*). The quoted papers (*4–10*) contain detailed data concerning the preparation of the above-mentioned solid solutions, X-ray studies, and phase diagrams of the systems to which the solutions belong. Moreover, it has been pointed out (*4*) that $Me\varnothing$ solutions are not formed for Me = Mg, Cd.

Comparative analysis of the data gathered for all systems studied so far (*10*) has led us to the following conclusions. The MeV_2O_6 matrix is amenable to substitution of Mo^{6+} for V^{5+} in a quantity exceeding 50%, especially when charge compensation is accomplished by substitution of Li^+ for Me^{2+}. On the contrary, the "solubility" of cation vacancies $\varnothing$ is strongly dependent on the kind of Me, both in $Me\varnothing$ and $Me\mathrm{Li}\varnothing$. For $Me\varnothing$ it changes from the nought (Me = Mg, Cd) to $X = 45$ (Me = Mn). An interesting phenomenon has been observed for MnLi–$\mathrm{MnLi}\varnothing$ and ZnLi–$\mathrm{ZnLi}\varnothing$ pairs of systems. In the first case the lattice parameters of MnLi (as a function of

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[1] It will be useful to mention that the $\mathrm{Mn}\varnothing$ solution is also formed in the matrix of the high temperature MnV_2O_6 modification of the pseudobrannerite-type structure but only in the range $0 \leq X \leq 4$ (*4*) (the same applies to MnLi, $0 \leq Y \leq 4$ (*8*)). The main difference between brannerite (*B*) and pseudobrannerite (*P*) structures consists in higher distortion of VO_6 octahedra in the latter structure, so that coordination of vanadium is reduced to five and (001) anionic layers are replaced by isolated chains of trigonal bipyramids VO_5, paralleling the [010] direction.

[2] These phases belong to the quaternary ZnO–V_2O_5–MoO_3–Li_2O system, ZnV_2O_6–$LiVMoO_6$–MoO_3 being only its pseudo-ternary part. Therefore the composition of the observed phases is not necessarily expressed on the scale of the latter subsystem. A detailed explanation of this problem is given elsewhere (*9, 10*). It will be seen below (Fig. 4) that in the case of the Mg-containing system we deal with an analogous situation.

composition) closely follow Vegard's law and simultaneously the border of saturated MnLi∅ solution extends almost linearly between saturated Mn∅ and Li∅ (cf. Ref. (*8*) and Figs. 1 and 3). In the second case (Ref. (*10*) and Figs. 1 and 3) marked negative deviations from Vegard's law are observed for the ZnLi matrix suggesting that the synergistic effect linked with the simultaneous presence of Zn^{2+} and Li^+ increases the stability of the matrix. Simultaneously the capacity of the ZnLi matrix to vacancies increases strongly to about $X = 30$ at $Y = 25$ (being only 15 and 16 for the end members Zn∅ and Li∅, respectively). It is unusual that a monovalent ion substituted for a bivalent one may increase the stability of the lattice,[3] but the experimental evidence leaves no doubt.

It also seems worth recalling that the lattice parameters of all studied solid solutions depend in a characteristic manner on the sizes of dopant ions and on the compactness of the brannerite-type matrix in various directions. In particular, parameter *b* (direction of the tight package of the lattice) is strongly dependent and parameter *a* (moderate package) is temperately dependent on the Mo/V ratio in the anionic sheets, while both are practically insensitive to the occupation of the original *Me* position. On the contrary, parameter *c* (or $c \sin \beta$) is almost solely sensitive to the size of $Me^{2+}/Li^+/\varnothing$ in the cationic sublattice (it has been found that vacancies behave as ions of a size smaller by about 0.06 Å than the exhausted cations (*10*)).

In view of the above facts two problems may be raised concerning MgV_2O_6. The first is why an Mg∅ solid solution does not exist. A partial answer results from the data shown in Fig. 2 where the unit cell volume V is drawn vs cubed *Me*–O distance $R,^3$ calculated as a sum of the ionic radii (*11, 12*). It can be seen that the points for all MeV_2O_6 compounds forming the ∅-containing solid solutions (including Me = Cd, whose case will be discussed at the end of this work) lie exactly on the straight line while V of MgV_2O_6 is relatively larger, proving that in this case the lattice is looser and weaker.

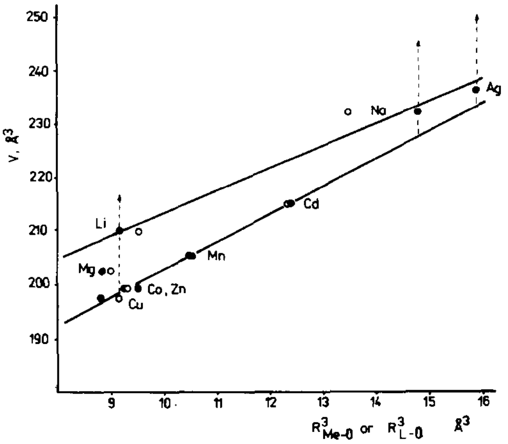

FIG. 2. Volume of the unit cell V drawn vs the cubed cation-oxygen distance R^3 for a number of MeV_2O_6 and $LVMoO_6$ compounds (Me = Mg, Cu, Co, Zn, Mn, Cd; L = Li, Na, Ag) of the brannerite-type structure. R is calculated as a sum of the ionic radii taken from (*11*) (black points) or (*12*) (open points). The points of arrows mark the expected values of V for $LVMoO_6$ compounds resulting from the extrapolation (see text). The radius of Ag^+ in six-fold coordination is assumed to be 1.15 Å (*12*) because that (*11*) resulting from the structure of Ag_2O (which probably has not been well resolved) has an irrational value.

Thus it is no wonder that the MgV_2O_6 matrix does not tolerate vacancies in Mg^{2+} sites since removing Mg^{2+} would further weaken the structure and lead to its destruction. It seems worth noting that the V–R^3 dependence for $LVMoO_6$ brannerites which also form ∅-containing solid solutions of L∅ type is also practically linear (Fig. 2), though, due to some ambiguities concerning the values of ionic radii, this line is determined with lower precision.

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[3] Let us stress that Zn^{2+}/Li^+ in the brannerite-type structure are not trapped in the network of O–V–O–Mo–O bonds but make the necessary bridges linking the lattice in the [001] direction.

Theoretically the two lines should be parallel and should reflect the difference of impacts of $(VO_6)_n$ and $(V_{0.5}Mo_{0.5}O_6)_n$ sheets in the unit cell volume of MeV_2O_6 and $LVMoO_6$ compounds, respectively. The expected distance of the discussed two lines may be determined by their extrapolation to the point at which the radius of cation is equal to nought i.e., to $R^3 = R^3_{\text{oxygen}}$ and it is equal to 17.5 Å^3 (extrapolation is done with the least-squares method). The expected values of V for the $LVMoO_6$ compounds are marked in Fig. 2 by arrows. The conclusion is that the $LVMoO_6$ structures are more compact as compared to MeV_2O_6. This may be the reason for the curious effect observed for ZnLi∅ (increased capacity to vacancies in the presence of Li). It seems very probable that the described effect of the monovalent dopant may have more general significance provided that L^+ and Me^{2+} are of comparable size. Namely, no significant effect of Li^+ was observed when it was introduced to MnV_2O_6 containing Mn^{2+} ions of much larger size.

The above considerations encourage us to raise the second question of whether MgV_2O_6 matrix—in analogy to ZnV_2O_6—could be strengthened by doping with lithium. We intend to clear up this problem experimentally in this work by attempting to synthesize MgLi and MgLi∅ solid solutions.

Experimental and Results

The X-ray diffraction patterns of the studied samples were obtained with the DRON-2 diffractometer using Cu$K\alpha$ radiation. Phase identification was based on published patterns of MgV_2O_6 (*1*), $LiVMoO_6$ (*2*), $MgMoO_4$ (*13*), and V_2O_5 (*14*). Determination of the lattice parameters was carried out in the same way as described in Ref. (*4*). Anticipating the data described below we would like to mention that we have managed to prepare some MgLi and MgLi∅ solid solutions. The X-ray patterns of all these samples could be easily indexed in a monoclinic system with systemic extinctions for $h + k = 2n + 1$. The determined lattice parameters of MgLi samples are presented in Table I and compared in Fig. 3 with those for ZnLi and MnLi.

Two methods were used to synthesize

TABLE I

LATTICE PARAMETERS AND THEIR RELATIVE CHANGES $\Delta p\%$ FOR THE MgLi = $Mg_{1-y}Li_yV_{2-y}Mo_yO_6$ SOLID SOLUTIONS

y	a [Å]	b [Å]	c [Å]	β [deg]	$c \sin \beta$ [Å]	V [Å^3]
0.00	9.284 (1)[a]	3.491 (1)	6.731 (1)	111.74 (1)	6.252 (1)	202.63
0.10	9.278 (4)	3.5115 (16)	6.706 (3)	112.00 (1)	6.218 (3)	202.57
0.20	9.282 (4)	3.5305 (15)	6.687 (3)	112.14 (1)	6.194 (3)	202.97
0.30	9.290 (4)	3.557 (1)	6.669 (3)	112.21 (1)	6.174 (3)	204.02
0.40	9.296 (3)	3.575 (1)	6.654 (2)	112.18 (1)	6.162 (2)	204.80
0.50	9.308 (4)	3.5895 (18)	6.652 (3)	112.15 (1)	6.161 (3)	205.86
0.60	9.311 (4)	3.605 (2)	6.642 (3)	112.09 (1)	6.154 (3)	206.57
0.70	9.316 (4)	3.617 (1)	6.641 (2)	111.98 (1)	6.158 (2)	207.49
0.80	9.322 (4)	3.622 (2)	6.638 (2)	111.92 (1)	6.158 (2)	207.90
0.90	9.332 (4)	3.635 (2)	6.639 (3)	111.76 (1)	6.166 (3)	209.20
1.00	9.338 (5)	3.644 (2)	6.632 (4)	111.63 (2)	6.165 (4)	209.79
$\Delta p\%$	0.65[b]	4.38	−1.49		−1.75	3.55

[a] Estimated standard deviation.

[b] In the case of nonmonotonous dependencies extreme values are taken into account.

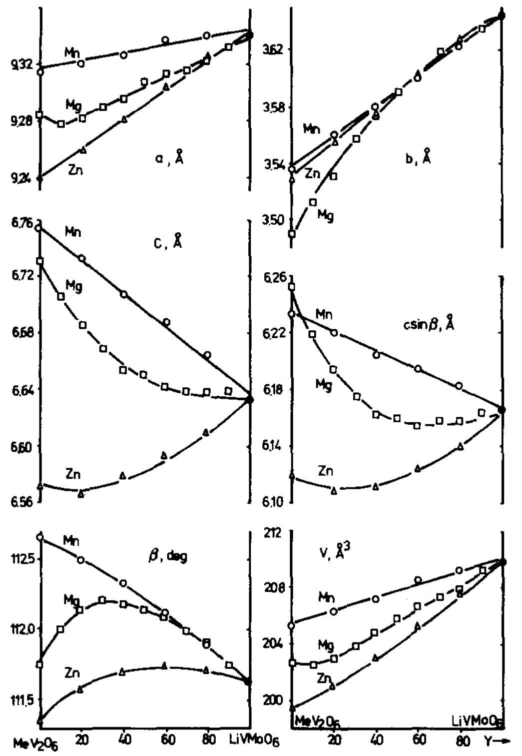

FIG. 3. Lattice parameters of MgLi solid solutions as function of composition. For comparison the data for MnLi and ZnLi are included.

MgLi solid solutions. One of them involved a solid state reaction between MgV_2O_6 and $LiVMoO_6$. Calcination at 550–600°C for 50–100 hr in air was necessary for total consumption of reactants. According to the X-ray phase analysis all mixtures of the composition corresponding to $Y > 20$ transformed to homogenous MgLi solid solutions of univocally indexable patterns. Samples of $Y \leq 20$ were nonhomogeneous mixtures of phases of brannerite-type structure with some reflexions broadened or split into doublets. As MgV_2O_6 transforms at 535°C into the *P*-polymorph (*1*), the latter-mentioned result, highly analogous to that already described for Mn∅ (*4*), suggests that increasing the temperature above 550°C (necessary for completion of the reaction) apparently results in entering such an area of the phase diagram where MgLi solid solutions of *B* and *P* structure and different Li-content coexist, nonhomogenizing on cooling.

The second method of preparation consisted in the application of the amorphous citrate precursor method (*15*) as adapted to our systems (*8*). The starting materials were $Mg(NO_3)_2 \cdot 6H_2O$, Li_2CO_3, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and NH_4VO_3, all of p.a. grade. As the final thermal treatment in air at 500–530° for 6 hr was sufficient, the second method turned out to be successful in preparing the *Me*Li solid solutions in the whole range of composition. The same method was applied in an attempt to prepare a number of solid solutions of the MgLi∅ stoichiometry (Fig. 4). The synthesis was successful only for two samples of $X = 10$, $Y = 60$ and $X = 14$, $Y = 80$ (open circles in Fig. 4). The other samples from the MgV_2O_6–$LiVMoO_6$–MoO_3 field (triangles in Fig. 4) contained homogenous brannerite along with $MgMoO_4$ and V_2O_5. The described results clearly demonstrate the entire miscibility of MgV_2O_6 and $LiVMoO_6$ leading to the formation of the MgLi solid solution. On the other hand, incorporation

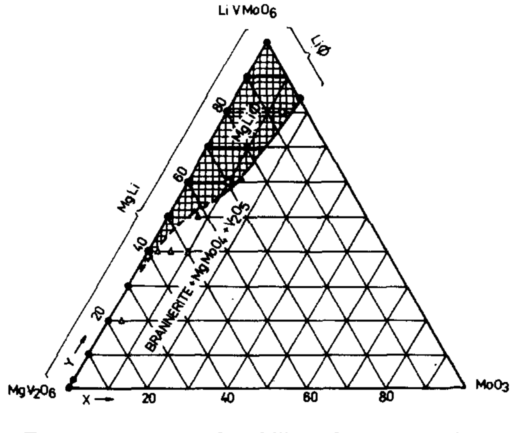

FIG. 4. The area of stability of the MgLi∅ solid solution. MgV_2O_6 and $LiVMoO_6$ show miscibility and form solid solutions in the whole composition range.

of an excess amount of Mo^{6+} to MgLi, compensated by cation vacancies (MgLi∅), may take place in a significant extent only at Y higher than about 50. One cannot exclude (and it even seems highly probable) that the area of existence of MgLi∅ is extended up to MgV_2O_6, however, the experimental methods used so far are insensitive to the presence of ∅ at $X < 2$.

Conclusions

The lattice parameters of MgLi solid solutions shown in Fig. 3 change with the composition in a nonlinear manner. In analogy to ZnLi, evident negative deviations from Vegard's law are observed for c, $c \sin \beta$ and V; moreover, a minor negative deviation is observed for a, while the changes of b show a positive deviation. The resultant deviation corresponding to the changes of V with composition is negative and more pronounced than that for ZnLi. Simultaneously, the MgV_2O_6 matrix does not tolerate the substitution of Mo^{6+} for V^{5+}, compensated solely by cation vacancies in the Mg^{2+} sublattice, while V^{5+} may be exchanged with Mo^{6+} up to 50% provided that Mg^{2+} is simultaneously replaced by Li^+ (MgLi solutions). Moreover, at least at a higher content of Li^+, a part of Mo^{6+} can be compensated by cation vacancies and MgLi∅ solid solutions are formed. Therefore, in analogy to the formerly studied Zn-containing system, and in agreement with the hypothesis set up in the Introduction, the MgV_2O_6 matrix can be strengthened by doping with lithium. This is already the second example of an unexpected effect of increasing the stability of the brannerite-type lattice by the substitution of a monovalent cation for a bivalent one. The elucidation of the nature of interactions responsible for this effect shall require further investigation.

Nevertheless, based on the described empirical observations (and taking into account that L^+ substituted for Me^{2+} should not be too small), one could predict an analogous phenomenon in the brannerite-type matrices containing such pairs of cations as, e.g., $Co^{2+} + Li^+$, $Mn^{2+} + Na^+$, and $Cd^{2+} + Na^+$.

In view of the V–R^3 dependence shown in Fig. 2, CdV_2O_6 should belong to the brannerite-type matrices forming the solution of the *Me*∅ type. Failure in the synthesis of Cd∅ probably results from the fact that it transforms to a pseudo-brannerite-type polymorph (hardly forming *Me*∅ solutions (*4*)) already at 170°C (*1*) while higher temperatures were used to complete the reaction. Cd∅ is expected to be formed by using the method proposed recently by Garcia-Clavel *et al.* (*16, 17*) that is successful in the synthesis of CdV_2O_6 and includes the solid state reaction between oxides carried out at 20–150° in an atmosphere saturated with water vapor. The experimental verification of the above predictions is in progress.

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