

# IMPURITY PARTITIONING BETWEEN FORSTERITE CRYSTAL AND MELT: CRYSTALLOCHEMICAL AND THERMODYNAMIC CONTROL

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$\text{Me}^+$ ,  $\text{Me}^{2+}$ ,  $\text{Me}^{3+}$ ,  $\text{Me}^{4+}$  impurities partition coefficients between forsterite crystals and melt have been experimentally determined. The forsterite single crystals  $\text{Mg}_2\text{SiO}_4$  were grown from the melt by the Czochralski technique. Impurity concentrations in crystals were determined by various techniques: electron microprobe analysis (EM), neutron activation analysis (NAA), ICP emission spectrometry (ICP), and atom absorption analysis (AA), flame photometry (FP).

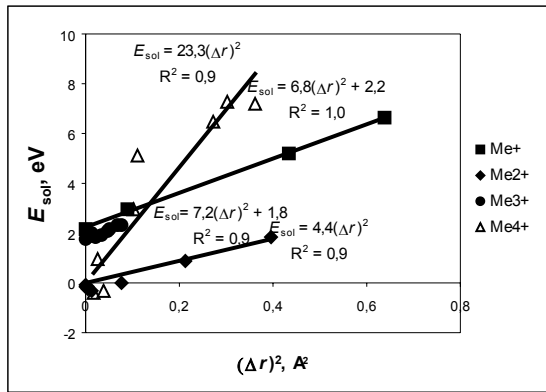
Partition coefficients  $K$  were determined by extrapolation of function  $C_s/C_{Lo} = K = f(g)$  to  $g=0$ , where  $C_s$  is impurity concentration in crystal,  $C_{Lo}$  is an initial impurity concentration in the melt;  $g$  is the crystallized part of the melt. Experimentally determined  $K$  values and corresponding analytical techniques used are shown in Table 1.

**Table 1. Impurity partition coefficients between forsterite crystal and melt ( $K$ ) and their solution energies ( $E_{sol}$ )**

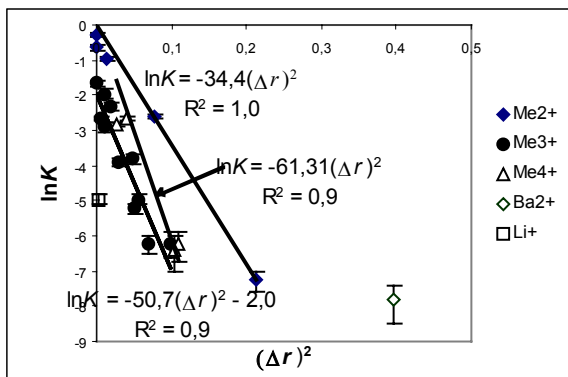
impurity	$\text{Me}^+$				$\text{Me}^{2+}$							
	Li	Na	K	Rb	Ni	Co	Fe	Mn	Ca	Sr	Ba	
$K$	0,007				0,75	0,53		0,39	0,073	$7 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	
technique	ICP, FP				EM	EM		EM	EM	ICP, AA	ICP, AA	
$E_{sol}$	2,2	3,0	5,2	6,6	-0,1	-0,1	-0,2	-0,3	0,01	0,9	1,8	
impurity	$\text{Me}^{3+}$											
	Cr	Ga	Ti	Sc	Lu	Yb	Er	Y	Gd	Eu	Sm	
$K$	0,18	0,055		0,19	0,1		0,02		0,022	0,0054	0,007	
technique	EM	NAA		NAA	NAA		NAA		EM	NAA	HAA	
$E_{sol}$	2,0		1,8	1,7		1,8		1,9	2,1	2,1		
impurity	$\text{Me}^{3+}$				$\text{Me}^{4+}$							
	Nd	Pu	La	Ge	Ti	V	Hf	Zr	Ce	U	Th	
$K$	0,002		0,002		0,06	0,07	0,0017	0,002				
technique	NAA		NAA		ICP, EM	EM	NAA	ICP, NAA				
$E_{sol}$	2,3	2,3		-0,4	1,0	-0,3	3,0	5,1	6,5	7,3	7,2	

Computer simulation has been used for calculation of the intrinsic and impurity defects in forsterite crystals, as well as for calculation of solution energies ( $E_{sol}$ ) impurities of different valencies. Calculations have been proceeded in static approximation in the dilute limit by the GULP program using the ionic Me-O interaction potentials from Ref. [1-3]. Energy of formation of Frenkel magnesium defect, the most favorite defects in forsterite is equal to 3,7 eV. The results of the calculation of the impurity solution energies are given in Table 1.

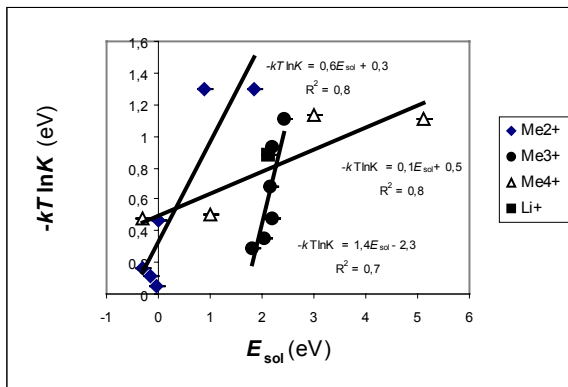
Partition coefficients and impurity solution energies have parabolic dependencies upon the difference between impurity ionic radius and ionic radius of substituted matrix cation ( $\Delta r$ ) (Figs. 1,2).  $K$  and  $E_{sol}$  demonstrate parabolic dependencies also upon charge of impurity ion. Plots of linear correlation  $E_{sol} - (\Delta r)^2$  and  $\ln K - (\Delta r)^2$  for  $\text{Me}^{4+}$  impurities are steeper than for  $\text{Me}^+$ ,  $\text{Me}^{2+}$  and  $\text{Me}^{3+}$  impurities. It is apparently connected with higher rigidity of tetrahedral site compared to octahedral sites.



**Fig. 1.** Dependences impurity solution energy  $E_{sol}$  in forsterite crystal upon  $(\Delta r)^2$



**Fig. 2.** Dependences between  $\ln K$  and  $(\Delta r)^2$  for impurities of different valencies in forsterite



**Fig. 3.** Correlation dependences between partition coefficients of impurities and their solution energy in forsterite

For isovalent substitution the linear dependencies  $E_{sol} - (\Delta r)^2$  and  $\ln K - (\Delta r)^2$  can be represented by straight lines, passing through the origin of coordinates. For heterovalent substitutions they are significantly shifted from the origin. For the dependence  $E_{sol} - (\Delta r)^2$  this displacement is equal to about 2 eV, which is close to one half of energy of magnesium Frenkel defect formation.

The displacement from the origin for dependence of solution heat of  $Me^{2+}$  in alcahalide crystals upon  $(\Delta r)^2$  is equal to 1 eV [4], what is close to the formation energy of intrinsic Schottky defect, the most favorite defect in those crystals.

Correlation dependencies between partition coefficients of impurities and their solution energies in forsterite have been found (see Fig. 3). Heterovalent substitutions are characterized by an essential larger displacement from the origin what is apparently connected with the influence of intrinsic defects playing role of charge compensators.

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## References

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