Energy of formation of intrinsic defects and their clusters in the powellite CaMoO$_4$

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Atomistic simulation of powellite crystals has been carried out. A system of parameters of interatomic potentials is proposed for the calculation of point defects in powellite. The formation energies of intrinsic defects and their clusters, which are spatially related combinations of defects, are estimated.

The most favorable localization of interstitial calcium and oxygen ions was determined. The formation energies of the Frenkel and Schottky defects are calculated. It was shown that the most energetically preferred in stoichiometric powellite are the oxygen Frenkel defects. Defects arising from deviations from stoichiometry are considered.

It is established that the clustering of defects allows to reduce the energy of their formation by 15−20%.

1. Introduction

Calcium molybdate, CaMoO$_4$ (powellite) has a scheelite structure (tetragonal syngony, space group $I4_1/a$) with unit cell parameters $a = 5.224$ and $b = 11.430$ Å [1]. Calcium atoms are surrounded by eight oxygen atoms (see figure) with two sets of interatomic distances (CN = 4 + 4). Molybdenum atoms are in a tetrahedral oxygen environment. Eight-vertex CaO$_8$ bind together along the edges, and each polyhedron is linked with four neighboring polyhedra CaO$_8$. Each calcium cation is surrounded by four similar cations and eight molybdenum cations. The radii of the Ca^{2+}, Mo^{6+}, O^{2-} ions are 1.12, 0.41 and 1.35 Å respectively [2]. The most probable interstitial positions in the scheelite structure are shown with crosses in the figure and have coordinates 0.5, 0.5, 0.125 (I1), 0.5, 0.5, 0.25 (I2) and 0.5, 0.5, 0.375 (I3). Molybdenum is an element of variable valence and under reducing conditions, Mo^{5+} ions may appear in powellite.

Calcium molybdate and solid solutions based on it, containing ions of rare earth and transition elements, are of interest as materials of laser technology [3,4], cryogenic phonon-scintillation detectors [5,6], acoustooptics [7,8] and phosphors [9,10]. The possibility of forming solid solutions of powellite with radioactive elements plays an important role in the burial of nuclear waste [11,12].

Although calcium molybdate is a long-known material (see, for example, [13]), its intensive research is still ongoing. A large number of experimental works are devoted to the synthesis of monocrystal, ceramic, powder and nanoparticle-containing samples, the study of their optical, luminescent and scintillation properties (see, for example, [14–18]).

Atomistic simulation has been successfully used to study the physical, thermodynamic properties of powellite [19,20], changes in the local structure around the activator ion [21].

The study of both intrinsic and impurity defects is one of the most important tasks in the field of atomistic simulation. Such practically demanded properties as spectroscopic, scintillation, electronic and ionic conductivity, as well as the processes of catalysis, ion exchange and immobilization of waste, are largely determined by the processes of defect formation. In all these phenomena, the crystals intrinsic defects play an important role. This role can be both positive, for example, charge compensation in the formation of heterovalent solid solutions, and undesirable, for example, in the formation of color centers. Coloring of crystals in the working range is an extremely undesirable phenomenon. Solving the problem of eliminating the color is one of the most important tasks of developing a technology for fabrication crystals.

Simulation of intrinsic defects by the method of atomistic potentials was previously carried out for some crystals isostructural with calcium molybdate, such as CaWO$_4$ [22], PbMoO$_4$ [23] and PbWO$_4$ [24,25]. This paper is devoted to the calculation of the energy of formation of intrinsic point defects and their clusters in CaMoO$_4$.

2. Simulation procedure

Simulation was carried out by the method of interatomic potentials using the program GULP 4.0.1 (General Utility

Table 1. The values of the parameters of interatomic potentials and charges of atoms in a powellite crystal used in the work

Interaction	Potential parameters			Atom	Charge, e
	A, eV	ρ, Å	C, eV$\cdot$Å^6		
Ca$-$O$_S$	2157.414944	0.311170	0.000000		
Mo$_S-$O$_S$	1073.797588	0.368729	0.000000	Ca	2.000000
O$_S-$O$_S$	1868.561623	0.120368	10.909249	Mo$_C$	0.268423
	χ (eV/Å^{-2})			Mo$_S$	5.731577
Mo$_S-$Mo$_C$	74.480726			O$_C$	0.306187
O$_S-$O$_C$	13.804354			O$_S$	−2.306187
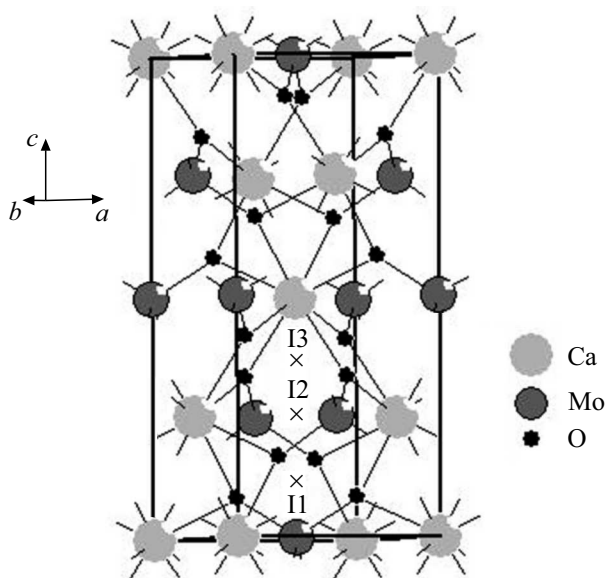
The structure of the powellite. Crosses indicate interstitial positions I1, I2, I3.

Lattice Program) [26], which is based on the procedure for minimizing the energy of the crystal structure.

The atomistic approach is based on the use of empirically determined interatomic potentials that describe the interaction between ions in a crystal. The paired potential U_{ij} of the interaction of ions i and j with charges q_i and q_j is the algebraic sum of several constituents

$$U_{ij}(R_{ij}) = q_i q_j e^2 / R_{ij} + A_{ij} \exp(-R_{ij}/\rho_{ij}) - C_{ij}/R_{ij}^6.$$

The first term takes into account the Coulomb interaction, the second — repulsion that occurs when the electron shells of neighboring atoms overlap, and the last one takes into account the van der Waals interaction, R_{ij} — interatomic distance, A_{ij}, ρ_{ij}, C_{ij} — empirical parameters of short-range potentials, the scope of which in this work was 15 Å for the oxygen−oxygen bond and 10 Å in other cases. The polarizability of molybdenum and oxygen ions was taken into account using the „shell model", in which the core (C) and the shell (S) are coupled by a harmonic elastic constant χ_i:

$$U_i^s = (1/2)\chi_i l_i^2,$$

where l_i — the distance between the centers of the core and the displaced shell.

The calculation of the defect energy was carried out according to the Mott–Littleton method [27], which is based on the model of „nested spheres". In our calculations, the central region had a radius of 10 Å, the following sphere had a radius of 20 Å.

3. Results and discussion

Empirical parameters of interatomic interactions were determined by an fitting procedure for optimizing interatomic potentials to provide the best description of structural and physical characteristics. Experimental values of structural [1] and elastic [28] properties of powellite were used as the main reference values. Table 1 shows the values of the parameters of interatomic potentials obtained in the work.

To verify the adequacy of the parameters, a comparison of the obtained calculated data concerning the structural and elastic properties of powellite with the experimental ones was carried out (Tables 2 and 3).

The difference between the calculated values and the experimental values for the lattice parameters is hundredths and thousandths of a percent, for the coordinates of atoms — tenths of a percent. For elastic constants, this difference in most cases does not exceed 5−10%, which is not bad, taking into account the errors of experimental determinations and their differences among themselves. Elastic constants c_{11} and c_{33} characterize the tensile strength along the directions [100] and [001], respectively. The calculation shows that the bond strength along the axis a is greater than along the axis c: $c_{11} > c_{33}$, which is consistent with the experimental data. Elastic constants c_{44} and c_{66} are associated with shear deformation in planes (001) and (100), respectively. The calculation,

Table 2. Comparison of computational and experimental structural data

Properties		Calculation	Experiment	
Parameters of an unit cell, Å^3	a	5.222	5.224	[1]
	c	11.431	11.430	
Coordinates of atoms of oxygen	x	0.259	0.257	
	y	0.146	0.145	
	z	0.166	0.167	

as well as the experiment, indicates that in the plane (001) the shear is easier than in (100): $c_{44} < c_{66}$. Thus, a comparison of the obtained calculated data related to the structural and elastic properties of powellite with the experimental ones indicates their good correspondence and we used the parameters presented in Table 1 to model defects.

Using these potential parameters, the energies of various intrinsic defects were determined, including vacancies of calcium (υ''_{Ca}), molybdenum (υ''''''_{Mo}) and oxygen ($\upsilon^{\bullet\bullet}_O$), interstitial atoms of calcium ($Ca^{\bullet\bullet}_I$) and oxygen (O''_I), as well as Frenkel and Schottky defects (Table 4). For defects, the symbols Kröger and Vink are used: the lower index denotes the position in the crystal, the upper — charge, the excess positive ($\bullet$), the excess negative ($'$) in relation to the charge of the undisturbed matrix ($\times$), υ — vacancy, I — interstitial atom.

From Table 4 it can be seen that among the vacancies in the powellite, oxygen vacancies are the most favorable, and slightly higher energies have calcium vacancies. At the same time the formation of vacancies of molybdenum significantly increases the energy of the crystal, since their appearance

leads to the formation of clusters consisting of four oxygen ions without a central cation, which significantly disrupts the local balance of the charge. The difficulty of formation of molybdenum vacancies is associated with the stability of molybdenum tetrahedra.

Comparison of the values of the energies of the same defect in different positions of the structure allows us to draw conclusions about its the most favorable location. The possible interstitial positions in the scheelite structure are shown in the figure. Among the interstitial ions that differ in structural localization, the minimum values of the energy of defects in Table 4 are highlighted in bold; the configurations corresponding to them are the most energetically favorable. From the results of the calculation it follows that the location of a calcium atom is most likely at position I3 with coordinates (0.500 0.500 0.375), and oxygen preferably at position I1 with coordinates (0.500 0.500 0.125). Calcium in the interstitial position is energetically more beneficial than oxygen in the interstitial position. Minimization of the energy of molybdenum located in different interstitial positions does not occur, which does not allow to calculate the energy of molybdenum ions in the interstitial position and molybdenum Frenkel defects in CaMoO$_4$. This seems to reflect the low probability of formation of these defects in the powellite. The study [24] also noted the absence of convergence while minimizing the defect energy in the case of placing tungsten in all interstitial positions in PbWO$_4$. In other works simulating intrinsic defects in crystals with a scheelite structure [22,23,25], there are also no data concerning molybdenum and tungsten ions in the interstitial positions and molybdenum and tungsten Frenkel defects.

For conjugate defects that include several point defects that ensure the electroneutrality of the crystal, the formation energies are given in Table 4 as average values per point defect.

**Table 3.** Comparison of computational and experimental elastic data

Specifications		Calculation	Experiment			
			[28]	[29]	[30]	[31]
Elastic constants, GPa	c_{11}	151.98	144.0	144.7 ± 2%	145.0	143.9
	c_{33}	114.07	127.0	126.5 ± 0.17%	128.2	125.8
	c_{44}	36.64	36.80	36.9 ± 0.17%	36.74	36.91
	c_{66}	47.74	45.80	45.1 ± 5%	45.58	46.07
	c_{12}	58.68	65.00	66.4 ± 50%	61.8	68.61
	c_{13}	51.17	47.00	44.6 ± 2%	49.6	48.43
	c_{16}	4.59	−13.50	+13.4 ± 50%	−14.6	12.72
Bulk modulus, GPa		81.25	81.00	81.70	81.9	−
Shift modulus, GPa		40.89	39.90	40.90	39.8	−

N o t e. The difference in the signs c_{16} is due to the different choice of the direction of the axis Z.

Table 4. The energies of intrinsic defects in the powellite in an isolated state

Defects	E/defect, eV
v_{Ca}''	23.96
v_{Mo}''''''	206.34
$v_O^{\bullet\bullet}$	22.15
$Ca_{I1}^{\bullet\bullet}$	−12.32
$Ca_{I2}^{\bullet\bullet}$	−12.61
$Ca_{I3}^{\bullet\bullet}$	**−12.62**
O_{I1}''	**−12.20**
O_{I2}''	−10.00
O_{I3}''	−10.02
v_{Ca}'', $Ca_I^{\bullet\bullet}$ Frenkel calcium defect	5.67
$v_O^{\bullet\bullet}$, O_I'' Frenkel oxygen defect	4.98
v_{Ca}'', v_{Mo}'''''', $4v_O^{\bullet\bullet}$ Schottky defect	6.52
v_{Ca}'', $v_O^{\bullet\bullet}$ defect CaO (Schottky)	4.96

The formation of a Frenkel defect for calcium ions can be expressed by the following quasichemical reaction

$$Ca_{Ca}^\times \rightarrow v_{Ca}'' + Ca_I^{\bullet\bullet},$$

and for oxygen:

$$O_O^\times \rightarrow v_O^{\bullet\bullet} + O_I''.$$
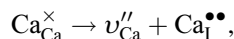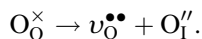
The Frenkel defect formation energy (E_F) is the sum of the energies of the formation of a vacancy and an interstitial atom, and on average per point defect can be expressed for calcium ions $E_F(Ca) = [E(v_{Ca}'') + E(Ca_I^{\bullet\bullet})]/2$, for oxygen $E_F(O) = [E(v_O^{\bullet\bullet}) + E(O_I'')]/2$. The most energy-advantageous configurations are selected for interstitial atoms. The obtained estimates of the energy of the formation of calcium and oxygen defects of Frenkel are given in Table 4.

The process of formation of the Schottky defect in powellite can be represented as follows:

$$Ca_{Ca}^\times + Mo_{Mo}^\times + 4O_O^\times \rightarrow v_{Ca}'' + v_{Mo}''''''+ 4v_O^{\bullet\bullet} + CaMoO_4.$$
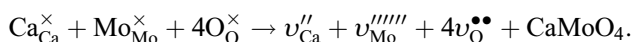
The formation energy of the Schottky defect, which falls on average per point defect, consists of the following components:

$$E_{Sch} = [E(v_{Ca}'') + E(v_{Mo}''''''') + 4E(v_O^{\bullet\bullet}) + E_L(CaMoO_4)]/6,$$

where $E_L(CaMoO_4)$ — the lattice energy of the powellite. The calculated value was $E_L(CaMoO_4) = -279.78\,eV$. The

value of the energy of the formation of the Schottky defect is also presented in Table 4. A comparison of the energy values of the formation of various intrinsic defects indicates that Frenkel defects in the powellite are more energetically favorable than the Schottky defect, which includes molybdenum vacancies. Frenkel oxygen defects have the lowest energy of formation, so they are the most likely defects in stoichiometric powellite. However, given the rather high energies of their formation, it can be assumed that defects can reach a noticeable concentration only at elevated temperatures. This is consistent with the results of the work [32], where the ionic conductivity in calcium molybdate was observed only at elevated temperatures.

Cationic stoichiometry deviation occurs during the formation of partial Schottky defects, when not the full formula unit of powellite is removed from the crystal, but only its part, MoO_3 or CaO. Due to the high volatility of MoO_3 when growing calcium molybdate from a melt, a deficiency of these elements may occur in the crystals, i.e. there may be an increased content of vacancies of molybdenum and oxygen. The usual practice of eliminating these defects in molybdates grown from melt is addition to the charge excess, quantities of MoO_3 over stoichiometry. Deficiency of CaO in calcium molybdate crystals can be achieved by annealing in pairs MoO_3 [33]. We calculated the formation energy of a partial Schottky defect for CaO when CaO is removed from the crystal, according to the following reaction: $Ca_{Ca}^\times + O_O^\times \rightarrow v_{Ca}'' + v_O^{\bullet\bullet} + CaO$. The calculated value of the energy of the CaO lattice was $E_L(CaO) = -36.19\,eV$. The energy of the formation of CaO defects (Schottky), in the powellite from an energy point of view, is more favorable than the complete Schottky defects (Table 4).

At the same time, the magnitude of the energy of the formation of CaO (Schottky) defects is quite large, which indicates their limited contribution to the processes of defect formation. This correlates with the results of the study of electrical conductivity. According to the data of the work [33] crystals with a deficit of CaO relative to the stoichiometric composition are essentially electronic conductors.

It is interesting to compare the intrinsic defect energies in $CaMoO_4$ with the defect energies of other isostructural molybdates and tungstates with the general formula ABO_4, where A — calcium or lead ions, B — tungsten or molybdenum ions. This data are presented in Table 5.

In all stoichiometric crystals, the predominant defects are Frenkel oxygen defects. At the same time, in $CaWO_4$ crystals and especially in $PbMoO_4$ the energy of their formation is relatively small, and therefore the concentration of Frenkel oxygen defects in these crystals will be significant. Crystals $PbWO_4$ and $CaMoO_4$ are characterized by higher values of the energy of formation of Frenkel oxygen defects, therefore they will be less defective compared to crystals $PbMoO_4$ and $CaWO_4$.

Schottky defects and WO_3 (Schottky) defects are characterized by the highest values of the energy of formation, so

Table 5. Comparing the energy of intrinsic defects in CaMoO$_4$ with the defect energies of other isostructural molybdates and tungstates

Defect	E/defect, eV				
	CaWO$_4$	PbWO$_4$		PbMoO$_4$	CaMoO$_4$
	[22]	[24]	[25]	[23]	This paper
v_A''	24.02	25.55	25.55	21.885	23.96
v_B''''''	195.85	178.67	178.67	–	206.34
$v_O^{\bullet\bullet}$	20.30	18.72	18.72	18.950	22.15
$A_I^{\bullet\bullet}$	−15.95	−13.19	−13.30	−12.860	−12.62
$B_I^{\bullet\bullet\bullet\bullet\bullet\bullet}$	–	–	–	–	–
O_I''	−17.85	−9.46	−9.56	−17.066	−12.20
A (Frenkel)	4.04	6.13	6.13	4.51	5.67
O (Frenkel)	1.23	4.63	4.63	0.942	4.98
Schottky	5.72	5.24	5.24	–	6.52
AO (Schottky)	3.70	2.74	2.74	3.67	4.96
BO$_3$ (Schottky)	7.02	5.36	5.36	–	–

their contribution to the formation of their intrinsic defects is small. Attention is drawn to the low value of the energy of formation of AO (Schottky) defects leading to cationic non-stoichiometry in PbWO$_4$ crystals, which indicates a noticeable contribution of PbO disorder. According to experimental data [34] it can reach 1000 ppm.

Cationic vacancies in position A are most easily formed in crystals of PbMoO$_4$. Based on this, it can be assumed that they, as charge compensators, will play a more important role in the formation of heterovalent substitutions in these crystals compared to other crystals.

Clustering additionally reduces the energies of differently charged defects, due to the contribution of communication energy. The communication energy in a cluster (E_b) is the difference between the formation energy of the cluster and the sum of the formation energies of its constituent point defects. The energies of the clusters of Frenkel calcium and oxygen defects and Schottky SaO defect in powellite are 9.04, 8.50 and 8.36 eV, respectively. Table 6 presents this data, as in the previous cases, on average per point defect. The sums of the energy of formation of isolated point defects that do not interact and are distributed statistically for Frenkel calcium and oxygen defects and Schottky SaO defect in calcium molybdate are 11.34, 9.95 and 9.92 eV. Thus, the clustering of defects allows you to reduce the energy of their formation by 15−20%.

Since defects that occur during thermodynamic equilibrium increase the entropy of the crystal, this increases the likelihood of their formation even at relatively high energies (enthalpies) of formation.

Table 6. The energies of intrinsic defects in the powellite in the form of clusters, the binding energy in the cluster (E_b)

Clusters	E_b, eV	E/defect, eV
$(v_{Ca}'' + Ca_I^{\bullet\bullet})$ Frenkel calcium defect	−2.30	4.52
$(v_O^{\bullet\bullet} + O_I'')$ Frenkel oxygen defect	−1.46	4.25
$(v_{Ca}'' + v_O^{\bullet\bullet})$ Schottky defect CaO	−1.56	4.18

The concentration of intrinsic defects in powellite may depend on the partial pressure of oxygen. If the oxygen pressure in the surrounding atmosphere P_{O2} is lower than the P_{O2}^0, corresponding to the exact cation-anionic stoichiometry, the oxygen will leave the crystal, forming oxygen vacancies, that is accompanied by the appearance of electrons in the conduction band: $2O_O^\times \rightarrow 2v_O^{\bullet\bullet} + O_2 \uparrow +4e'$. Thus, crystals obtained at low partial pressures of oxygen will be characterized by an increased concentration of oxygen vacancies $(v_O^{\bullet\bullet})$ and electrons (e′). The conductivity of CaMoO$_4$ under reducing conditions is the conductivity of *n*-type and greatly increases compared to the conductivity of oxidized crystals [32].

Recent studies conducted in the work [35] on sodium-gadolinium molybdate Na$_{0.5}$Gd$_{0.5}$MoO$_4$, which is derived from calcium molybdate, have shown that the number of oxygen vacancies in crystals grown from a charge of stoichiometric composition at low oxygen content does not

exceed 0.5% of the number of anionic sites. At the same time, under cationic disorder with an increase in the fraction of gadolinium, the oxygen non-stoichiometry can reach 5%.

As a result of the capture of one or two electrons by oxygen vacancies, color centers F^+ or F, respectively, can be formed.

It is also possible to interact with the electrons of part of the hexavalent molybdenum ions, leading to their transition to a pentavalent state: $Mo_{Mo}^{\times} + e' = Mo_{Mo}'$. This can also be the cause of crystal coloration.

Calcium molybdate crystals grown at low oxygen levels or subjected to reductive annealing have a blue color. Absorption spectra show significant anisotropy. In the absorption spectra of $CaMoO_4$ with polarization of incident light relative to the axis of the crystal $E \parallel c$, absorption bands with maxima in the region of 480 and $720-750$ nm are observed. When the incident light $E \parallel a$ is polarized the absorption band at 480 nm disappears, and the other band shifts toward shorter wavelengths [36]. Crystals can be bleached by high-temperature annealing in air or in an oxygen atmosphere.

With oxidative annealing, there is both oxidation of molybdenum and the disappearance of oxygen vacancies. This situation leads to difficulties in interpreting the nature of the color centers in calcium molybdate.

In the study [32] the colored centers in $CaMoO_4$, grown in reductive conditions or subjected to reductive annealing, are associated with ions Mo^{5+}. The argument supporting this relationship is the similarity in the behavior of the absorption spectra associated with the color centers and the absorption spectra of molybdenum-containing solutions $CCl_4/MoCl_5$. At the same time, theoretical study [37] connects the color centers in calcium molybdate with oxygen vacancies. In the study [37] using the CASTEP program, the electronic structure and absorption spectra of ideal $CaMoO_4$ crystals and crystals containing an oxygen vacancy were calculated. It has been shown that the additional absorption in crystals with a vacancy corresponds well to the experimentally observed absorption of the color centers.

When $P_{O2} > P_{O2}^0$, a relative excess of oxygen can be obtained in the crystal due to the formation of interstitial oxygen atoms and holes in the valence band: $O_2 \rightarrow 2O_I'' + 4h^{\bullet}$. The creation of a relative excess of oxygen is also possible due to the formation of cationic vacancies and holes: $2O_2 \rightarrow 4O_O^{\times} + \upsilon_{Ca}'' + \upsilon_{Mo}'''''' + 8h^{\bullet}$, but energetically it is less favorable. Therefore, crystals produced under conditions of relative excess of oxygen must contain higher concentrations of defects such as interstitial oxygen atoms and holes in the valence band. There is also the probability of the formation of interstitial atoms of atomic oxygen. The authors Ref. [38], studied in the context of the density functional theory the electronic structure of defects associated with oxygen in $CaMoO_4$ crystals. They found that neutral interstitial oxygen atoms can easily enter the lattice, forming a weak bond that connects two oxygen atoms belonging to neighboring $[MoO_4]^{2-}$ tetrahedra.

4. Conclusion

The energies of various intrinsic defects are determined, including the vacancies of calcium molybdenum and oxygen, as well as interstitial calcium and oxygen atoms, and the energy of the formation of Frenkel and Schottky defects. It is shown that the most energetically favorable in stoichiometric powellite are Frenkel oxygen defects.

In case of deviation from cationic stoichiometry, Schottky CaO defects are likely to appear. Violation of oxygen stoichiometry with a lack of oxygen entails the formation of oxygen vacancies and electrons in the conduction band, which can lead to the formation of color centers and the appearance of pentavalent molybdenum ions. In the case of excess oxygen, interstitial oxygen atoms and holes in the valence band are formed,

Combining defects into clusters allows to reduce the energy of their formation by $15-20$% due to the binding energy in the cluster, and therefore the clustering of defects in powellite becomes very likely.

Conflict of interest

The authors declare that they have no conflict of interest.

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