PREDICTION OF ISOMORPHOUS SUBSTITUTIONS OF STRONTIUM OR BARIUM BY SODIUM AND ACTINIDES FOR THEIR IMMOBILIZATION IN MOLYBDATES WITH A SCHEELITE-TYPE STRUCTURE

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Highlights

- Calculated mixing energies, critical decomposition temperatures, substitution limits, and matrix capacities for actinide-containing solid solutions using the crystal-energy theory of isomorphous substitutions.
- Evaluated thermodynamic stability regions of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ and $Ba_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solutions, where An = actinides.
- Found continuous thermodynamic stability for $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solutions with actinides from Ac to Pu below 373 K (IAEA disposal conditions).
- Determined isomorphic capacities of $SrMoO_4$ matrix at 373 K for various actinides.
- Identified that $Ba_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ asymmetric solid solutions comply with Goldschmidt's polarity rule and the authors' second polarity rule.

Cation–Tetrahedral Anion Distances in the $Na_{0.5}An_{0.5}MoO_4$ Structures

Data for calculating the crystal radii of actinide ions $r_8(An^{3+})$ and the interatomic distances between the cation and tetrahedral anion in $Na_{0.5}An_{0.5}MoO_4$

Ln	Crystal ionic radii of lanthanide ions, Å			Crystal ionic radii of lanthanide ions, Å			$R(Na_{0.5}An_{0.5}MoO_4)$, Å
	$r_8(Ln^{3+})$	$r_6(Ln^{3+})$	r_8/r_6	An	$r_6(An^{3+})$	$r_8(An^{3+})$	
La	1.300	1.172	1.1092	Ac	1.26	1.400	3.905
Ce	1.283	1.15	1.1156	Th	–	–	3.879*
Pr	1.266	1.13	1.1203	Pa	1.18	1.311	3.853
Nd	1.249	1.123	1.1122	U	1.165	1.294	3.843
Pm	1.233	1.110	1.1108	Np	1.15	1.277	3.833
Sm	1.219	1.098	1.1102	Pu	1.14	1.266	3.826
Eu	1.206	1.087	1.1095	Am	1.115	1.239	3.811
Gd	1.193	1.078	1.1067	Cm	1.11	1.233	3.807
Tb	1.180	1.063	1.1101	Bk	1.10	1.222	3.800
Dy	1.167	1.052	1.1093	Cf	1.09	1.211	3.794

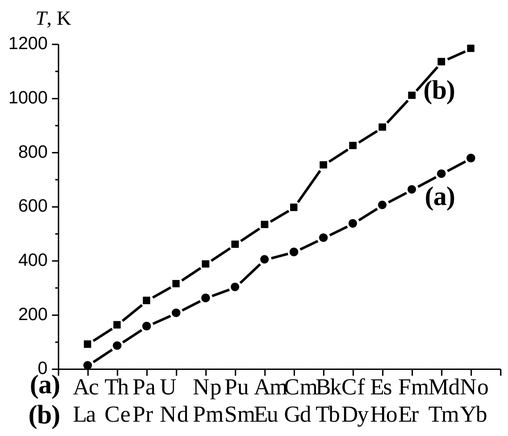
**Note:* The interatomic distance for $R(Na_{0.5}Th_{0.5}MoO_4)$ was calculated as the arithmetic mean of the values for $R(Na_{0.5}Ac_{0.5}MoO_4)$ and $R(Na_{0.5}Pa_{0.5}MoO_4)$.
Values of $r_8(Ln^{3+})$ and $r_6(Ln^{3+})$ are taken from: Shannon R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst. 1976. Vol. A32, No. 5. P. 751–767. https://doi.org/10.1107/S0567739476001551

Mixing Energies and Critical Decomposition (Stability) Temperatures of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ Solid Solutions

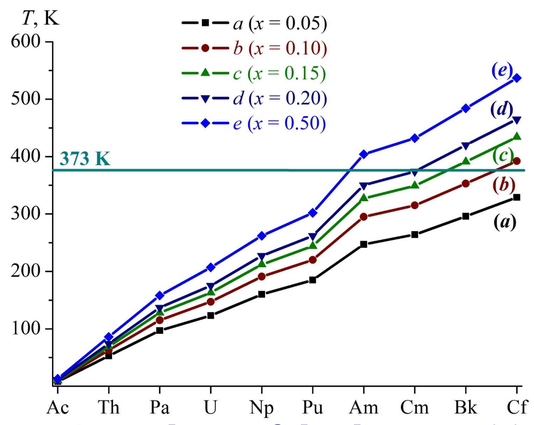
Data for calculating mixing energies, critical decomposition temperatures, and isomorphic capacity of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solution matrices towards actinoids

An	$R(Na_{0.5}An_{0.5}MoO_4)$, Å	$\Delta R/R_1$	Q_R, J/mol	T_{cr}, K (x = 0.5)	Isomorphic capacity (x) for $SrMoO_4$
Ac	3.905	0.0054	217	13	< 1.0
Th	–	–	1436	86	< 1.0
Pa	3.853	0.0189	2656	158	< 1.0
U	3.843	0.0216	3469	207	< 1.0
Np	3.833	0.0243	4391	262	< 1.0
Pu	3.826	0.0261	5065	302	< 1.0
Am	3.811	0.0302	6782	404	≤ 0.265
Cm	3.807	0.0312	7238	432	≤ 0.197
Bk	3.800	0.0331	8121	485	≤ 0.124
Cf	3.794	0.0348	9005	537	≤ 0.083
Es				605	
Fm				663	
Md				721	
No				779	

Substitution Limits and Thermodynamic Stability of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ Solid Solutions

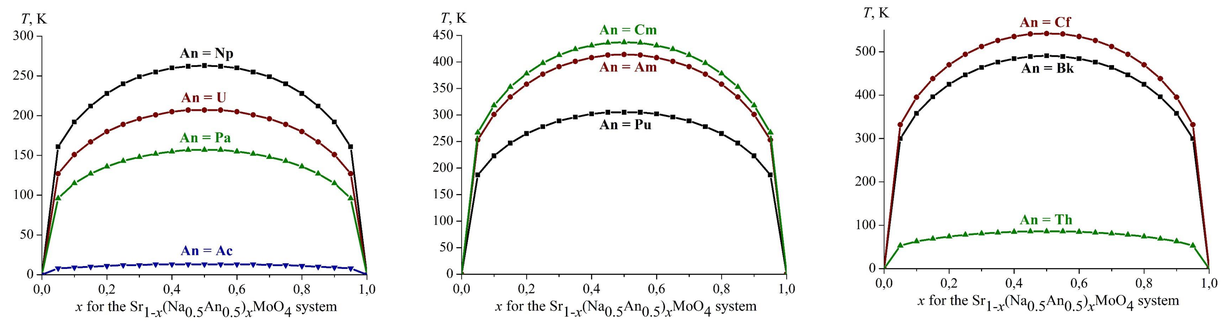


Critical decomposition temperatures of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ (a) and $Sr_{1-x}(Na_{0.5}Ln_{0.5})_xMoO_4$ (b) solid solutions for actinides and lanthanides



Dependence of the decomposition temperatures of $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solutions on the actinide atomic number (thermodynamic stability diagram) for substitution limits x = 0.05 (*a*), 0.10 (*b*), 0.15 (*c*), 0.20 (*d*), and 0.50 (*e*)

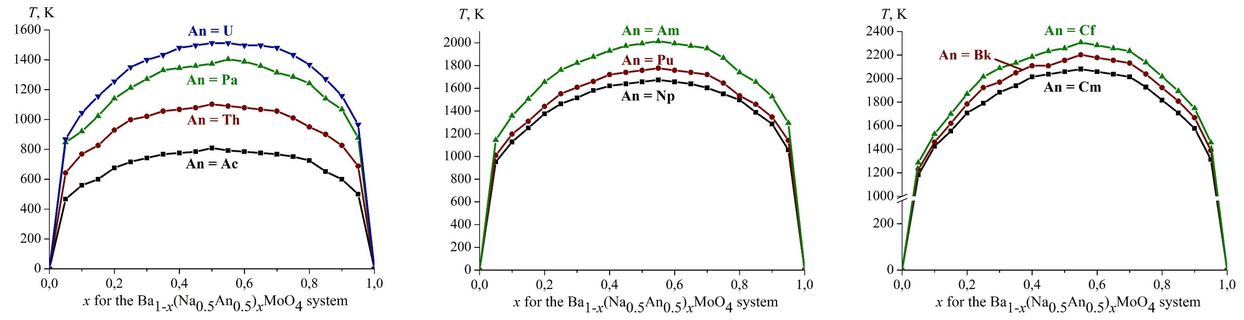
Decomposition domes for $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solutions



In each of the $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ systems, where An = Ac, Pa, U, Np, Pu, and Th, under disposal conditions below the 373 K isotherm but above the peaks of the decomposition domes, continuous series of solid solutions may be thermodynamically stable. Below the peaks but above the dome lines, two limited solubility regions narrow with decreasing temperature. Below the dome lines, mixtures of two solid solutions are formed based on each system component. In the $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ systems where An = Am, Cm, Bk, and Cf, under disposal conditions below 373 K, only limited series of solid solutions can be thermodynamically stable, since the decomposition domes lie above the 373 K isotherm. Due to the low diffusion rates at these temperatures, the solid solutions and solubility regions may persist as metastable phases.

Solid Solutions of $Ba_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ Systems

An	$R(Na_{0.5}An_{0.5}MoO_4)$, Å	$\Delta R/R_1$	Q_R, J/mol	T_{cr}, K	Isomorphic capacity (x) for $BaMoO_4$
Ac	3.905	0.0432	13974	834	≤ 0.01264
Th		0.0502	19236	1148	≤ 0.00218
Pa	3.853	0.0572	24499	1462	≤ 0.00040
U	3.843	0.0600	26957	1609	≤ 0.00018
Np	3.833	0.0628	29531	1763	≤ 0.00008
Pu	3.826	0.0647	31345	1871	≤ 0.00005
Am	3.811	0.0689	35547	2122	≤ 0.00002
Cm	3.807	0.0700	36691	2191	≤ 0.00001
Bk	3.800	0.0720	38817	2318	≤ 0.00001
Cf	3.794	0.0737	40672	2429	≤ 0.00001



The very high critical decomposition temperatures of 834–2429 K for $Ba_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ solid solutions indicate that under the IAEA-recommended waste disposal conditions, they will either be metastable or decompose into limited series of solid solutions based on components whose substitution limits and thermodynamic stability regions can be estimated from the decomposition domes. At the same time, the isomorphic capacity of $BaMoO_4$ for actinides lies within the range of 0.00001–0.01264 (see Table), suggesting that using $BaMoO_4$ for actinide waste immobilization is not advisable.

CONCLUSIONS

1. Within the framework of the crystal-energy theory of isomorphous substitutions, under the regular solution approximation, the mixing energies (interaction parameters), critical decomposition (stability) temperatures, limits of isomorphous substitutions, thermodynamic stability regions, and isomorphic capacities of $SrMoO_4$ matrices for actinides were calculated.

2. A thermodynamic stability diagram was constructed for the $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ system, along with decomposition domes of solid solutions over the concentration range from x = 0 to x = 1.0 in increments of x = 0.05. These allow for determining the decomposition temperatures for a given composition, equilibrium substitution limits at a given temperature, thermodynamic stability regions, and assessing the isomorphic capacities of matrices for actinides.

3. Under the temperature conditions recommended by the IAEA for radioactive waste disposal (373 K and below), a continuous series of solid solutions $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ containing actinides from Ac to Pu are thermodynamically stable. Solid solutions with heavier actinides (Am–No) may decompose or become metastable under these conditions.

4. Lanthanides from La to Gd may serve as imitators of actinides in the $Sr_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ system since the critical decomposition temperatures of the corresponding solid solutions differ insignificantly (~100–200 K) from those with actinides.

5. For the $Ba_{1-x}(Na_{0.5}An_{0.5})_xMoO_4$ systems, mixing energies, critical decomposition temperatures, and substitution limits were calculated, and the thermodynamic stability of the solid solutions was assessed. Asymmetric decomposition domes were presented, and these solid solutions were shown to follow Goldschmidt's polarity rule and the second polarity rule for decomposition temperatures previously proposed by the authors.