ISSN 2224-087X. Електроніка та інформаційні технології. 2021. Випуск 16. С. 94–103
Electronics and information technologies. 2021. Issue 16. P. 94–103

УДК 537.226; 537.311.32 DOI: https://doi.org/10.30970/eli.16.10

INFLUENCE OF CATION SUBSTITUTION ON THE ION MIGRATION IN SCHEELITE-TYPE STRUCTURE

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A stereo-atomic crystals structure analysis was applied to AMO_4 (A=Ba, Ca, Cd, Pb, Sr; M=W, Mo) and solid solutions based on these compounds. The program package TOPOS was used for the calculation. 3D migration paths and migration channels for the W or Mo ions in AMO_4 with scheelite-type structure were considered.

Key words: TOPOS, Electro-migration, probable W/Mo migration, migration channel, AMO_4 (A=Ba, Ca, Cd, Pb, Sr; M=W, Mo), scheelite.

The computer calculations are important methods for investigations of structural, electronic, and other physical properties of real crystals. For ion electro-migration in crystals structure the specifically calculation program TOPOS is applied.

In previous works [1-3] we report on investigation of probable cation migration path and elementary channels in the undisordered scheelite-type structures. The calculation data were obtained by using TOPOS program package [4]. In the paper [3] in particular the $CaWO_4$ compound with partial substitution Eu→Ca were considered. In this case the influence of divalent cation substitution on maps of ion migration and lengths of the W ion elementary channels migration were analysed.

In the present paper the influence of cation substitution on the probable ion migration ways and elementary channels in AMO_4 (A=Ba, Ca, Cd, Pb, or Sr; M=W, or Mo) and solid solutions based on these compounds were considered. The program package TOPOS [4] for the calculation was used. 3D-migration paths and migration channels for the W or Mo ions in AMO_4 crystals with scheelite-type structure were analysed.

The $A_{(1-x)}M_xO_4$ ($0 \leq x \leq 1$) (A=Ba, Ca, Cd, Pb, or Sr; M=W, or Mo) compounds under study (scheelite-type structure, space group C_{4h}^{6} –$\boldsymbol{I}4_1/a$) were obtained by authors (see Table 1). The X-ray diffraction (XRD) data were taken from mentioned works (Table 1).

In this work using the TOPOS program package [4] were constructed the possible W or Mo ion migration maps for the AMO_4 crystals. The possible migration paths of W or Mo ions in the structure of crystals at room temperature (X-ray data from the ref. [5-8]) and variation of probable elementary channel migrations with variation of a x value were analysed.

Table 1. Methods of crystal growth of $A_{(1-x)}M_xO_4$ ($0 \le x \le 1$) used for the calculations.

Compound	**Method of growing**	**Ref.**
$Ba_{(1-x)}Pb_xWO_4$	Classical sol. st. chem. react.	[5]
$Sr_{(1-x)}Pb_xWO_4$	Convent. sol. st. chem. react.	[6]
$Sr_{(1-x)}Pb_xMoO_4$	Convent. sol. st. chem. react.	[7]
$(1-x)CaWO_4$ - $xCdWO_4$	Co-precipitation	[8]

To the analysis of the possible ion migration was used the Voronoi tessellation [9]. In this approach the atomic Voronoi polyhedron are constructed. The basic concept for description of the voids and channels are the following: elementary void (channel) and closely related terms of form and radius of void, significant elementary void (channel). The Voronoi polyhedron (VP) of an atom (geometric image atom) is defined [4] by the value of the second moment of inertia (G).

The elementary void is an area of the crystal unit cell, the center of which is one of the vertexes of a Voronoi polyhedron. The major (ZA) and minority (ZC) elementary voids with sequence numbers N (ZAN and ZNC) are considered. An atom can pass through an elementary channel if the sum of its radius (r_i) and the average radius of the atom forming the channel (r_a), is less than the radius of the channel cross section (r_c). In order to the take into account possible polarization (deformation) of the ion when they pass through the channel the coefficient of deformation $\gamma_{ia} \le 1$ was introduced. An ion passes through the channel if $\gamma_{ia}(r_i + r_a) \le r_c$.

In the framework of the program TOPOS the migration pathway is determined as a set of elementary voids and lines of elementary channels. It can be infinite along a 1D-, 2D-, or 3D-channel network. The conduction map is formed by the totality of migration pathways.

The algorithm based on the analysis of the adjacency matrix of the crystal structure (see for example our previous paper [3]) includes four steps: (i) construction of the VP for all atoms; (ii) determination of the atomic coordinates of the vertices of the VP and the positions of elementary voids; (iii) identification of all the independent edges of the VP and all basic channels; (iv) calculation of the basic characteristics of the voids and channels.

For the calculation we used the following radii of the ions: W^{6+} and Mo^{6+} (0.56 and 0,55 Å respectively) for coordination number 4, Ba^{2+} (1,56 Å), Ca^{2+} (1.26 Å), Cd^{2+} (1.24 Å), Pb^{2+} (1,43 Å), Sr^{2+} (1,40 Å) for coordination number 8, and O^{2-} (1.36 Å) [10]. The value of the parameter G is 0.0830(1) for W (near the value of Mo) [11]. According to the same source the G parameter for other ions were used. The calculation procedure was described in our paper [12] in detail.

For some structural data of the AMO_4 compounds the probable migration paths of W or Mo ions were constructed (see Fig. 1 and Fig. 2). The continuous probable migration paths of the W ions in case Ba tungstate were visualised. The similar calculation data for $BaWO_4$ crystal with scheelite-type structure in the previous paper [13] were obtained. In other cases of AMO_4 compounds under consideration structural data the continuous migration ways of the W or Mo ions were not observed. The migration of the Ba, Ca, Cd, Pb, or Sr ions were excluded since the radii of these ions are too large.

Fig. 1 and Fig. 2 visually demonstrates that large A^{2+} ions as Ba^{2+} or Pb^{2+} caused the continuous or near continuous way for W ion migration in the crystals with scheelite-type structure. The Sr^{2+} ion at substitution of Pb^{2+} ion caused the deviation in structure parameters of crystals and changing of the shape of calculation migration maps of W^{6+} ions in the $Sr_{(1-}$

$_{x)}Pb_xWO_4$ ($0 \le x \le 1$) compounds. Sr tungstate owned by non-continuous migration way of W^{6+} ions. The probable migration ways of ions in these cases are considered.

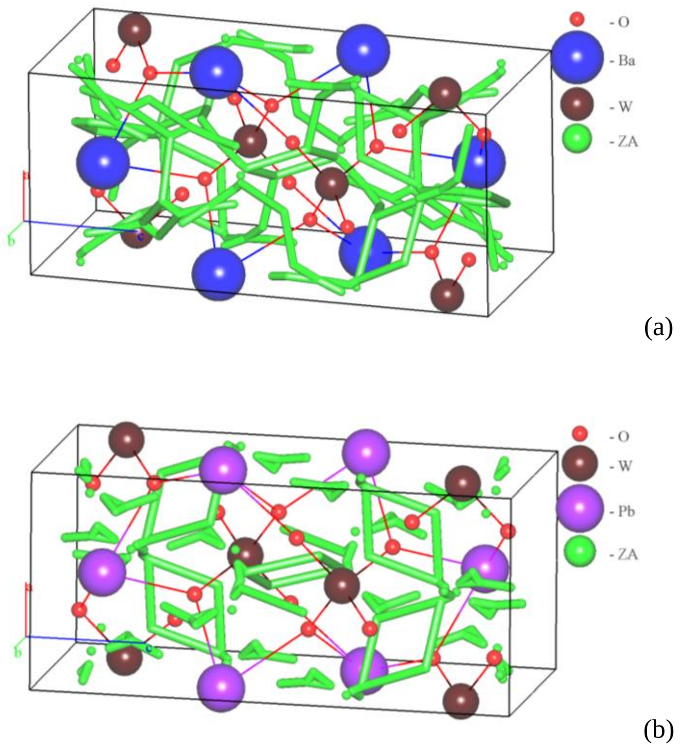


Fig. 1. Calculated migration maps of W ions in the structure $Ba_{(1-x)}Pb_xWO_4$ for x=0 (a) and x=1 (b).
X-ray data were taken from [5].

Fig. 1 and Fig. 2 visually demonstrates that large A^{2+} ions as Ba^{2+} or Pb^{2+} caused the continuous or near continuous way for W ion migration in the crystals with scheelite-type structure. The Sr^{2+} ion at substitution of Pb^{2+} ion caused the deviation in structure parameters of crystals and changing of the shape of calculation migration maps of W^{6+} ions in the $Sr_{(1-x)}Pb_xWO_4$ ($0 \le x \le 1$) compounds. Sr tungstate owned by non-continuous migration way of W^{6+} ions. The probable migration ways of ions in these cases are considered.

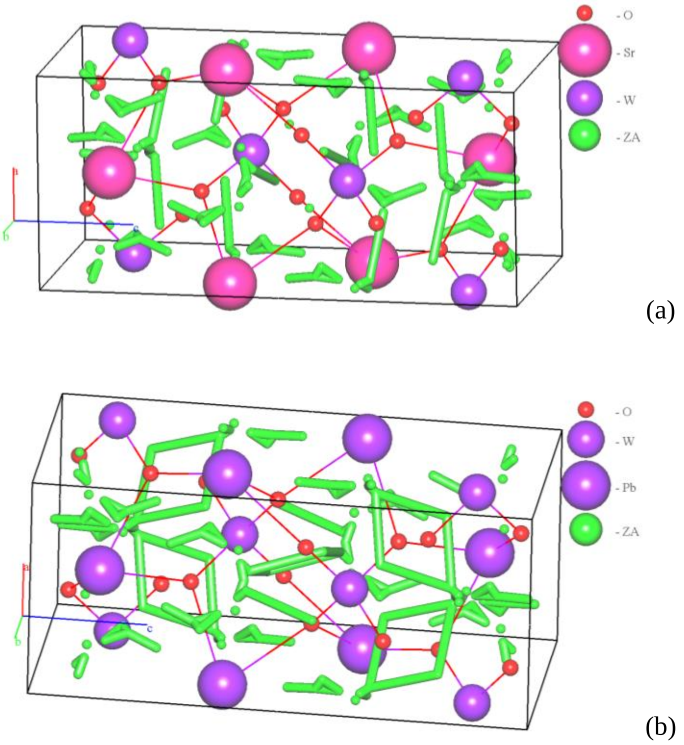


Fig. 2. Calculated migration maps of W ions in the structure $Sr_{(1-x)}Pb_xWO_4$ for x=0 (a) and x=1 (b).
X-ray data were taken from [6].

Some calculated data on channel lengths of migration ways for probable mobile W or Mo ions in $A_{(1-x)}M_xO_4$ ($0 \le x \le 1$) compounds in the Tabl. 2 are summarised. Composition and disordering (x variation) of crystals modify the shape of migration ways (Fig. 1 and Fig. 2) and lengths of elementary channels (see the Table 2).

The TOPOS program package used for calculation of mobile ion ways in superionics. This program used also for crystals with the aim to investigation their electrical ion migration features. In calculation procedure for disordered compounds sometimes the some simplify conditions were applied as e.g. for anion-mixed compound [14].

Our calculated data shows the influence of cation substitution in the $A_{(1-x)}M_xO_4$ with scheelite-type structure on W or Mo ions probable migration in crystal lattices. Fig. 3 (a, b, c, and d) shows the dependencies of the lengths of the distances between ZAN voids as a function of the x values of the replaced ions in $A_{(1-x)}M_xO_4$ ($0 \le x \le 1$) compounds.

For the $Ba_{(1-x)}Pb_xO_4$ system (Fig. 3, a) the near linear dependencies of calculated distances between ZAN voids as a increased/decreased function of the x varying between 0 and 1 for probable W ions migration at condition of formation the continuous ions move way in crystal lattice were observed. Two peculiar points at x=0.5 and x=0.8 are observed. In these cases the curves of calculated distances are crossed (see Fig. 3, a). For other compounds ($Sr_{(1-x)}Pb_xO_4$, $Sr_{(1-x)}Mo_xO_4$, and $(1\text{-}x)CaWO_4$–Pb_xWO_4, see curves on Fig. 3, b, c, and d accordingly) a few increased/decreased function of calculated distances between ZAN major voids at the x varying between 0 and 1 are observed.

Table 2. Calculated channel lengths of migration ways for $Ba_{(1-x)}Pb_xWO_4$ (I), $Sr_{(1-x)}Pb_xWO_4$ (II), $Sr_{(1-x)}Pb_xMoO_4$ (III), and (1-x)$CaWO_4$ – x$CdWO_4$ (IV) ($0 \le x \le 1$).

№	**X**	**ZAN_1 - ZAN_2 Void distances (Å)**				
		ZA_1 - ZA_4	***ZA_3 - ZA_5***	***ZA_3 - ZA_4***	***ZA_4 - ZA_5***	***ZA_6 - ZA_8***
I	0.1	0.752	0.607	0.335	0.603	0.290
	0.2	0.743	0.632	0.347	0.828	0.285
	0.3	0.725	0.656	0.358	0.652	0.282
	0.4	0.707	0.681	0.371	0.676	0.278
	0.5	0.688	0.706	0.383	0.702	0.273
	0.6	0.670	0.731	0.395	0.726	0..270
	0.7	0.649	0.752	0.404	0.748	0.269
	0.8	0.628	0.775	0.415	0.771	0.267
	0.9	0.610	0.797	0.420	0.790	0.270
	1.0	0.585	0.819	0.433	0.817	0.268
II	0.1	0.770	0.575	0.317	0.571	0.294
	0.3	0.771	0.575	0.317	0.572	0.295
	0.5	0.772	0.575	0.317	0.572	0.295
	0.7	0.773	0.576	0.317	0.573	0.296
	0.9	0.774	0.577	0.318	0.573	0.297
III	0.1	-	-	-	-	0.596
	0.3	-	-	-	-	0.595
	0.5	-	-	-	-	0.595
	0.7	0.733	0.594	0.332	0.589	-
	0.9	0.743	0.594	0.332	0.588	-
IV	0.1	-	0.225	-	0.223	0.238
	0.2	-	0.222	-	0.220	0.239
	0.3	-	0.219	-	0.217	0.239
	0.4	-	0.215	-	0.214	0.240
	0.5	-	0.213	-	0.211	0.240

Thus the introduction of the large ion (Ba) in crystal lattice and $Ba^{2+} \to Pb^{2+}$ substitution in case of probable mobile W ions the considerable changing of migration way shape (Fig. 1) and of elementary channel lengths or bond of neighbouring voids (Fig. 3, a, and Tabl. 2) are observed. Introduction of Eu^{3+} ions replacing Ca^{2+} ions in the crystal structure of $CaWO_4$ according to X-ray data [15] caused also considerable changing of elementary channel lengths as non-linear function of the x [3]. In other substitution when radius of introduced ion is similar to lattice ion (see Fig. 2, and Fig. 3, b, c, d, and Tabl. 2) these changes are small.

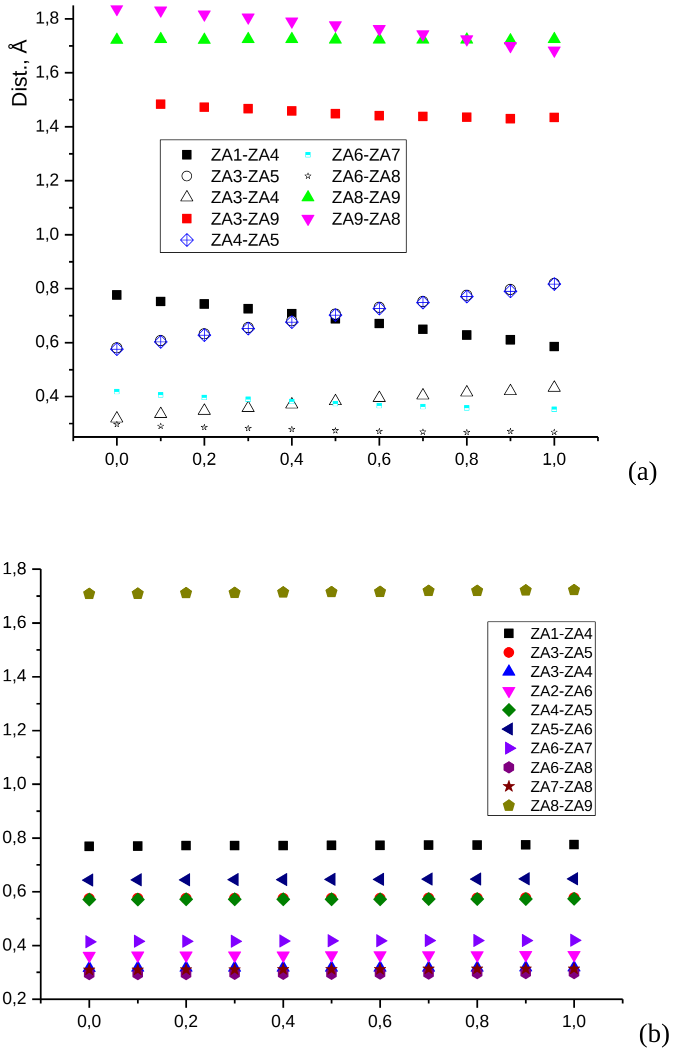
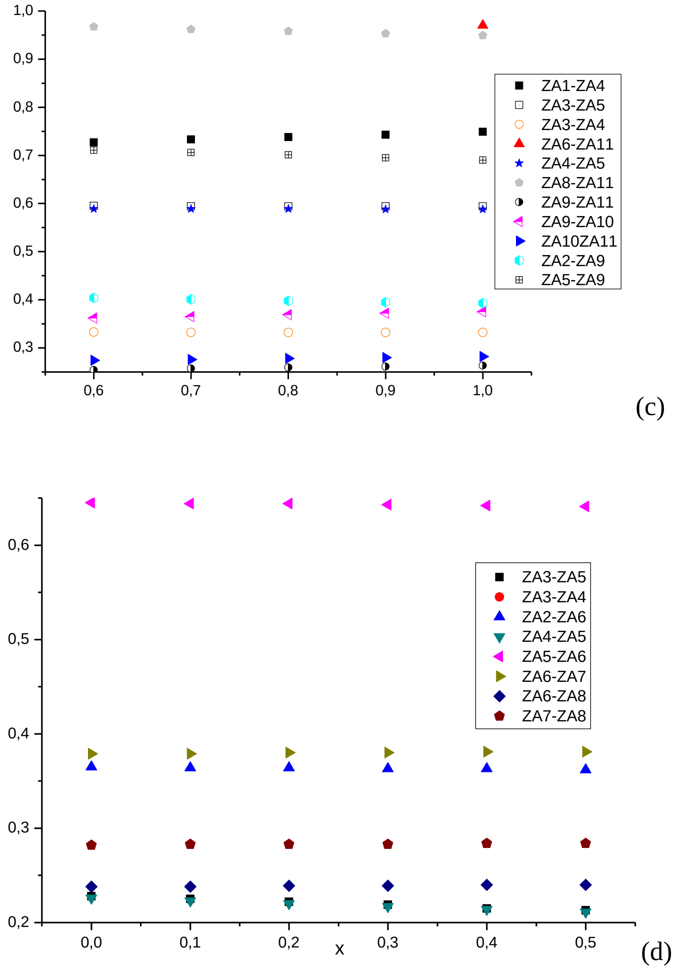


Fig. 3. Selected calculated distances between ZAN voids at RT as a function of compositions with x varying between 0 and 1 for W mobile ions (a, b, and d curves) and Mo (c curves) in the compounds $Ba_{(1-x)}Pb_xWO_4$ (a), $Sr_{(1-x)}Pb_xWO_4$ (b), $Sr_{(1-x)}Pb_xMoO_4$ (c), and (1-x)$CaWO_4$ – Pb_xWO_4 (d). (Continuation is below).



(c)

(d)

Fig. 3. (Continuation).

It is known the scheelite-type crystal structure is characterised by two types of oxygen polyhedron with central W^{6+} (Mo^{6+}) or A^{2+} ions surrounded by four and eight oxygen polyhedron ions, respectively. The present calculated data shows increase of possibility formation of the continuous channels of ionic conductivity (probable mobile W or Mo ions) at introduction of ions with large radius (e.g. Ba) to the scheelite-type crystal lattice in oxygen polyhedron with central A^{2+} ions surrounded by eight O^{2-} oxygen ions. Experimental investigation of ionic electrical conductivity of scheelite-type crystals were realised in work [16] and the tungstate polyatomic anion migration at high temperatures were discussed by authors [17].

Hence possible migration map at RT for the W or Mo ions in $A_{(1-x)}M_xO_4$ (A=Ba, Ca, Cd, Pb, or Sr; M=W, or Mo; $0 \le x \le 1$) compounds with scheelite-type structure using the TOPOS program package were visualised. The near linear dependencies of distances between ZAN voids as a increased/decreased function of the x varying between 0 and 1 for probable W or Mo ions migration were observed.

Influence of the cation substitutions in $A_{(1-x)}M_xO_4$ scheelite-type matrix on the shape of possible migration paths of probably mobile (W or Mo) ions and elementary channel lengths of migration ways in mentioned compounds were observed. In case of the large ion (e.g. Ba) in crystal and specifically Ba^{2+} replaced Pb^{2+} for probable mobile W ions the considerable changing of migration way shape and of elementary channel lengths were demonstrated. The calculated data shows increase of possibility formation of the continuous migration ways of probable mobile W or Mo ions at introduction of Ba^{2+} as ion with large radius to the scheelite-type crystals.

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ВПЛИВ КАТІОННОГО ЗАМІЩЕННЯ НА ІОННУ МІГРАЦІЮ В СТРУКТУРІ ТИПУ ШЕЄЛІТУ

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Стерео-атомний аналіз структури кристалів застосований до сполук AMO_4 (A=Ba, Ca, Cd, Pb, Sr; M=W, Mo) та твердих розчинів на їхній основі. Для розрахунків використано комплекс програм TOPOS. Розглядаються 3D міграційні карти та елементарні канали міграції для іонів W в AMO_4 зі структурою типу шеєліту.

Комп'ютерний розрахунок є важливим методом для дослідження структурних, електронних та інших фізичних властивостей реальних кристалів. Для іонної електроміграції в структурі кристалів застосовують спеціальну розрахункову програму TOPOS. На основі рентгеноструктурних та елетронних властивостей іонів – вузлів гратки сполук AMO_4 за допомогою вказаної програми розрахунку отримані карти провідності ймовірно мобільного іона. В статті візуалізовані шляхи міграції катіонів W/Mo і вивчаються канали ймовірної міграції катіонів, координованих вісьмома іонами кисню. Міграція двовалентних катіонів, тетредрично координованих киснем, малоймовірна в силу великого їхнього радіуса. При заміщенні іонів двовалентних металів в тетраедричних положеннях структури іншими, співрозмірними за величиною іонного радіуса, спостерігаємо близькі до лінійних зростаючі/спадні залежності довжини елементарних каналів міграції від зміни концетрації домішкових катіонів (зміни стехіометричних коефіцієнтів сполук від 0 до 1).

В статті показано, що розглянуті катіонні заміщення впливають також на форму каналів міграції катіонів W/Mo в структурі кристалів типу шеєліту. У випадку іонів великого радіуса, які заміщують іон з меншим радіусом (наприклад, $Ba^{2+} \rightarrow Pb^{2+}$) спостерігаємо суттєві зміни форми шляху міграції ймовірних мобільних іонів та розмірів елементарних каналів міграції. Розрахунки показують, що зростання можливості формування каналів катіонної міграції в матриці кристалу, близьких до суцільних (такий тип шляху міграції вказує на реалізацію високоймовірної іонної провідності сполуки) при введенні іонів Ba^{2+} з великим іонним радіусом.

Ключові слова: TOPOS, електро-міграція, ймовірна W/Mo міграція, міграційний канал, AMO_4 (A=Ba, Ca, Cd, Pb, Sr; M=W, Mo), шеєліт.

Стаття: надійшла до редакції 15.12.2021,
доопрацьована 20.12.2021,
прийнята до друку 21.12.2021