

## Analysis of electromigration and structure of $AWO_4$ ( $A = Ca, Cd, Pb, Zn$ ) crystals using the TOPOS program complex

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**A stereo-atomic crystal structure analysis of  $AWO_4$  ( $A = Ca, Cd, Pb, Zn$ ) crystals was carried out. The program package TOPOS was used for the calculation. The migration path of the W ions in  $AWO_4$  compounds at room and higher temperatures was visualized. The conditions for ionic conductivity in crystals with scheelite-type structure were discussed.**

**$AWO_4$  ( $A = Ca, Cd, Pb, Zn$ ) / TOPOS / Electromigration / Migration map / Scheelite / Wolframite**

### Introduction

Most of oxide crystals are characterized by mixed electron-ionic conductivity. In our previous papers [1,2] the electrical properties and migration of the charge carriers of complex oxide crystals were investigated in connection with the crystal structure. The electrical properties of  $AWO_4$  (where  $A$  is Ca, Cd, Pb, or Zn) compounds have not been studied sufficiently. In the book by Ivanov-Shits and Murin [3] data on the ionic conductivity of crystals of different structural types based on crystallographic characteristics are given. The effect of migration of tungstate complexes at high temperatures was observed for  $CaWO_4$  crystals in [4]. The ionic conductivity of crystals with scheelite-type structure was experimentally investigated for  $PbWO_4$  and  $PbMoO_4$  [5], but the mechanism of ionic conductivity and the migration paths of the mobile ions in these crystals were not ascertained.

A stereo-atomic crystal structure analysis using the program package TOPOS [6], with the aim to visualize the migration pathway of the mobile ions in oxide crystals-superionics was proposed in [7].

Different investigators have used different basic concepts and calculation methods for the visualization of the migration pathways of the ionic charge carriers in oxide compounds. Li *et al.* [8], for instance, applied computational simulations of the oxide ion mobility by *ab initio* molecular dynamics methods to fluorite-based  $Bi_8La_{10}O_{27}$ . The probable channels for the oxide ions at different high temperatures were analyzed visually using a large array manipulation program. The migration pathways of oxygen vacancies and oxygen interstitials in the  $La_2Ti_2SiO_9$  lattice was

determined by the atomistic computer simulation technique [9]. A cluster model was applied to describe the ionic conductivity in oxynitride compounds [10]. Geometry optimization and *ab initio* molecular dynamics simulations were performed at four temperatures to study the oxide ion migration pathways in bismuth-rhenium oxide [11]. Yashima *et al.* [12] obtained the equinuclear density and nuclear density distribution in planes of  $Pr_2NiO_4$ -based mixed conductors at different temperatures, which indicates the diffusion pathway of the oxide ions in the crystal lattice. The results were obtained by a combined technique that included the maximum-entropy method, pattern fitting, and Rietveld analysis of neutron powder diffraction data. Mavrocchelli *et al.* [13] used large-scale atomistic simulations to investigate the oxygen transport in  $SrTiO_3$ .

In the present work, using the program package TOPOS 4.0 [6], ionic migration maps for crystals with the general formula  $AWO_4$  ( $A = Ca, Cd, Pb, or Zn$ ) were constructed. Possible migration paths of the W ions in the structure of  $AWO_4$  crystals with scheelite- ( $Ca, Pb$ , space group  $I4_1/a$ ) and wolframite- ( $Cd, Zn$ , space group  $P2/c$ ) type structures at different temperatures (room and higher) were analyzed. Consideration of chemical and structural factors and visualization of the conduction pathways led to the determination of the mechanisms and other spatial features of the ion migration in the crystals. This approach also allowed predicting crystal properties and possible applications. Some basic concepts of micro-level investigation of the migration of mobile ion in crystal lattices, and previous results of calculations have been considered in earlier reports [14-16].

### Calculation procedure

To study the ion migration the Voronoi tessellation was used [15]. In this approach atomic Voronoi polyhedra with unambiguous physical meaning [17] are constructed. The map of voids and channels is based on experimental data. The basic concepts for the description of voids and channels are the following: elementary void (channel), and the closely related terms of form and radius of voids, and significant elementary void (channel). The Voronoi polyhedron (VP) of an atom (geometric image atom), is defined 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. Major (ZA) and minority (ZC) elementary voids with sequence numbers  $N$  (ZAN and ZCN) are considered. An atom can pass through an elementary channel if the sum of its radius ( $r_i$ ) and the average radius of the atoms forming the channel ( $r_a$ ), is less than the radius of the channel cross section ( $r_c$ ). In order to take into account possible polarization (deformation) of the ions when they pass through the channel the coefficient of deformation  $\gamma_{ia} \leq 1$  was introduced. An ion passes through the channel if  $\gamma_{ia}(r_i + r_a) \leq r_c$ .

In the program package 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

conductivity map is formed by the migration pathways. For superionics endless ways of migration are required. Knowledge about the conduction pathways enhances the determination of mechanisms and spatial features of the ion migration in crystals.

The algorithm based on the analysis of the adjacency matrix of the crystal structure [18] includes four steps: (i) construction of VP for all the atoms of the structure; (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.

The availability of structural data for the  $AWO_4$  ( $A = Ca, Cd, Pb, \text{ or } Zn$ ) compounds at room and higher temperatures [19-27] motivated the choice of this class of compounds as a model object for mapping the ion migration and calculating the structural elements of the coordination polyhedra. For the calculations we used the following radii of the ions:  $W^{6+}$  (0.56 Å) for coordination number 4,  $Ca^{2+}$  (1.26 Å),  $Cd^{2+}$  (1.24 Å),  $Pb^{2+}$  (1.43 Å), and  $Zn^{2+}$  (1.04 Å) for coordination number 8, and  $O^{2-}$  (1.36 Å) [28]. The value of the parameter  $G$  is 0.0830(1) for W, and, for example, for the Ca ion 0.084(2) [29]. The search for structural data was performed using *Pearson's Crystal Data* [19]. The basic oxygen polyhedra in scheelite-type structures are presented in Fig. 1, where the  $WO_4$  and  $AO_8$  elementary polyhedra are shown.

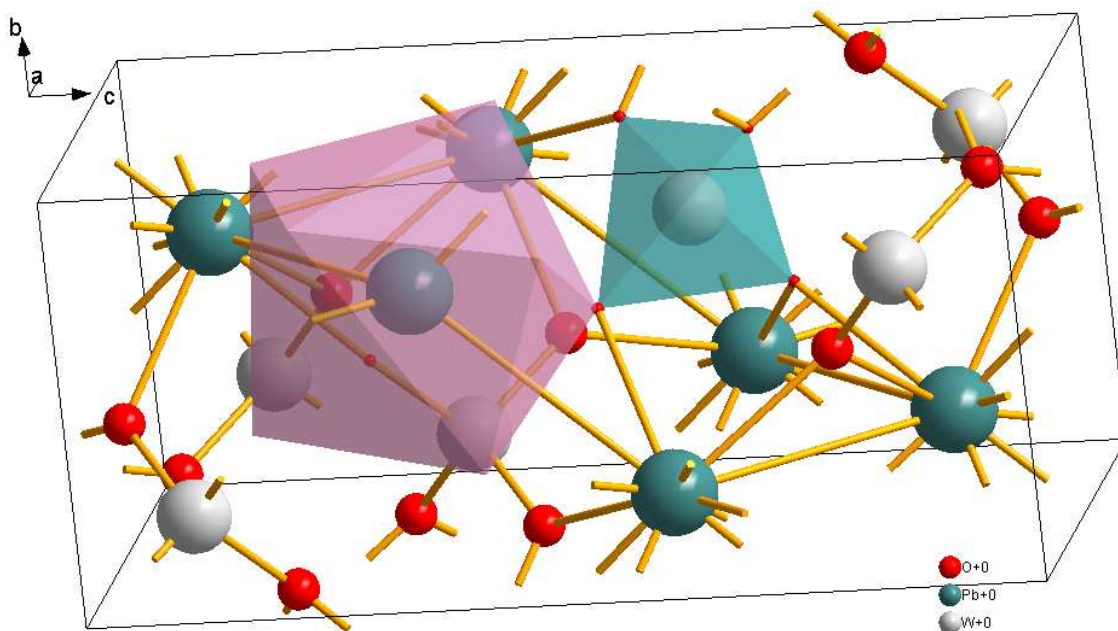


Fig. 1 Basic oxygen polyhedra in scheelite-type crystals.

## Results and discussion

From our calculations continuous migration pathways for the  $A$ -ions in the  $AWO_4$  compounds were not obtained. Therefore we considered the probable migration path of the  $W$  ions in the same crystals (see Figs. 2-6). Calculations at RT for the  $W$  ions showed that they can pass through the channels if  $r_i > 0.9(0.56 + 1.36) = 1.728 \text{ \AA}$ . Note that the shape of all the voids in the cases under consideration is rather spherical ( $G < 0.1$ ).

We have analyzed the crystal structures (see Fig. 2a) and constructed the migration pathway using reference data [20,21] for  $CdWO_4$  (see Fig. 2b) and  $ZnWO_4$  (see Fig. 2c), respectively. In  $CdWO_4$  single crystals (see Fig. 2a,b) no significant channels cross the cleavage plane (010) [2].

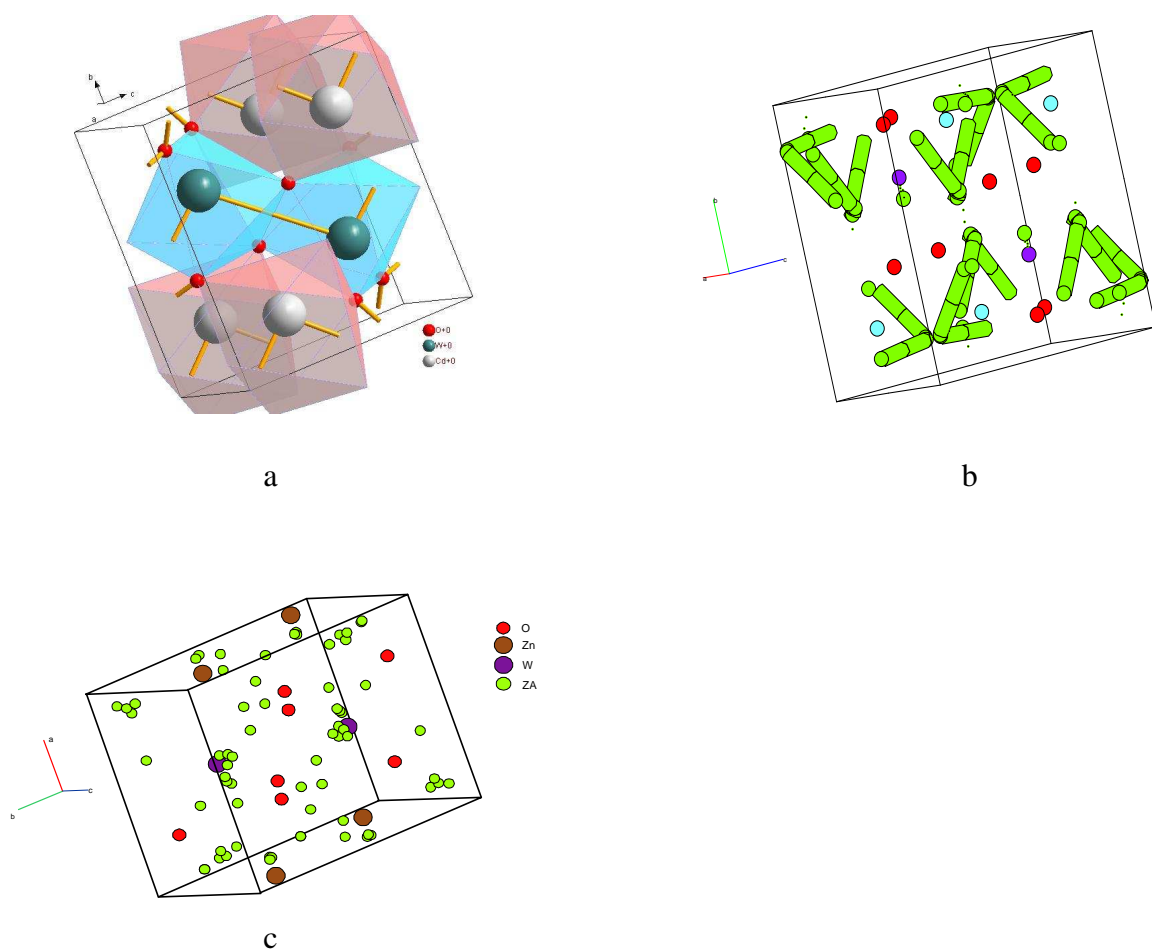
For the  $ZnWO_4$  crystal only separate probable voids were observed. At higher temperatures, as

shown by the calculations, for this crystal the picture is rather changeable.

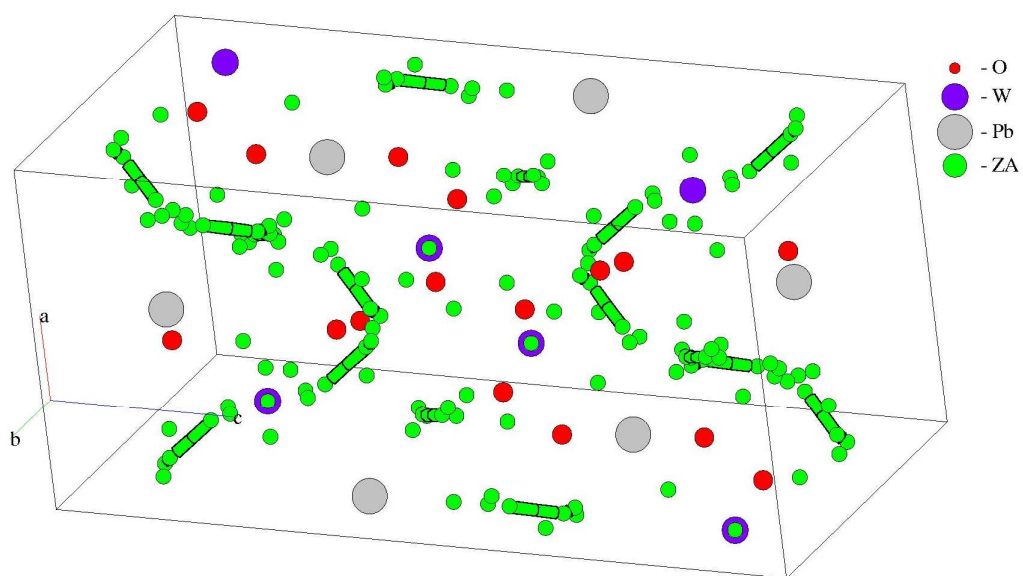
For the  $PbWO_4$  compound a large number of reference data was analyzed. For five of them [22-26], obtained by different experimental methods, crystallographic parameters are presented in Table 1 and conductivity maps in the extreme cases are shown in Figs. 3 and 4. The interrelation between the oxygen–oxygen and  $W$ – $O$  distances in the  $[WO_4]^{2-}$  tetrahedrons and the amount of channels can be seen on the figures. In the case of the  $PbWO_4$  compound a parallelogram at the center of the unit cell is observed as a characteristic element of the channels (see Fig 4, inset), by which the migration of the mobile ions is monitored. The sides of this parallelogram are determined by the distances  $ZA8$ – $ZA7$  ( $1.755 \text{ \AA}$ ) and  $ZA7$ – $ZA8$  ( $1.742 \text{ \AA}$ ).

**Table 1** Some calculated distances and angles in the coordination polyhedra of  $PbWO_4$  and  $CaWO_4$  crystals (scheelite type, space group  $I4_1/a$ ).

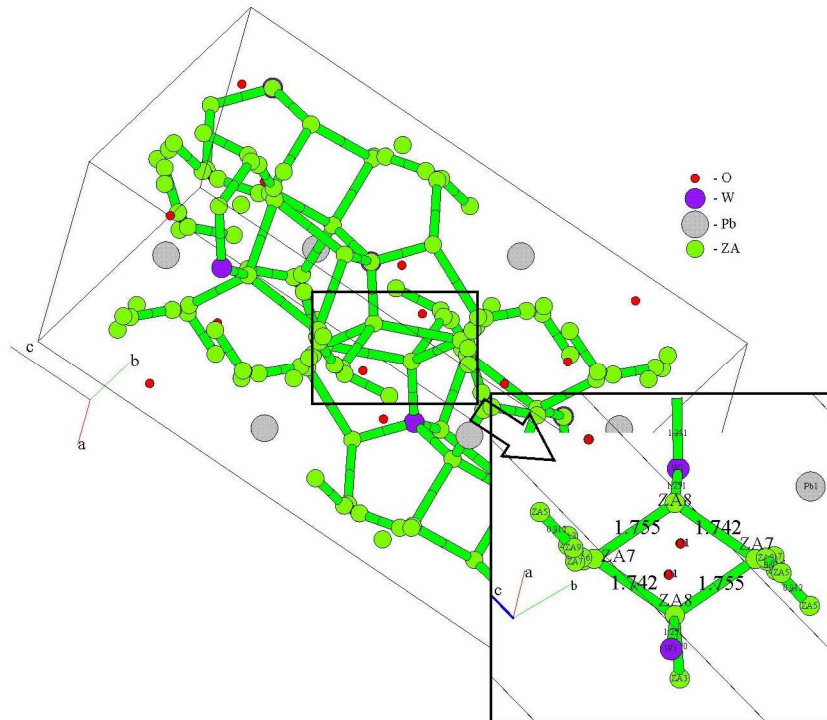
| Data (ref.) used for the calculations | O–O distance (nm) |            | O–W distance (nm) | O–W–O angle ( $^\circ$ ) |
|---------------------------------------|-------------------|------------|-------------------|--------------------------|
|                                       | tetrahedron       | octahedron |                   |                          |
| $PbWO_4$ [22]                         | 0.28782           | 0.39073    | 0.1779            | 112.404                  |
|                                       | 0.29560           | 0.32434    |                   |                          |
|                                       |                   | 0.30330    |                   |                          |
|                                       |                   | 0.28558    |                   |                          |
|                                       |                   | 0.33201    |                   |                          |
| $PbWO_4$ [23]                         | 0.28788           | 0.33223    | 0.1781            | 112.763                  |
|                                       | 0.29660           | 0.31306    |                   |                          |
|                                       |                   | 0.32956    |                   |                          |
|                                       |                   | 0.39836    |                   |                          |
|                                       |                   | 0.29207    |                   |                          |
| $PbWO_4$ [24]                         | 0.31273           | 0.28557    | 0.1780            | 103.202                  |
|                                       | 0.27901           | 0.32471    |                   |                          |
|                                       |                   | 0.38800    |                   |                          |
|                                       |                   | 0.31917    |                   |                          |
|                                       |                   | 0.30217    |                   |                          |
| $PbWO_4$ [25]                         | 0.28242           | 0.37979    | 0.1790            | 120.761                  |
|                                       | 0.31126           | 0.31010    |                   |                          |
|                                       |                   | 0.32160    |                   |                          |
|                                       |                   | 0.31466    |                   |                          |
|                                       |                   | 0.29791    |                   |                          |
| $PbWO_4$ [26]                         | 0.32357           | 0.30569    | 0.1900            | 116.777                  |
|                                       | 0.30333           | 0.31258    |                   |                          |
|                                       |                   | 0.38731    |                   |                          |
|                                       |                   | 0.29178    |                   |                          |
|                                       |                   | 0.30731    |                   |                          |
| $CaWO_4$ [27]                         | 0.30016           | 0.29357    | 0.1789            | 114.015                  |
|                                       | 0.28813           | 0.27707    |                   |                          |
|                                       |                   | 0.31377    |                   |                          |
|                                       |                   | 0.30258    |                   |                          |
|                                       |                   | 0.37555    |                   |                          |
| $CaWO_4$ [27] (1773 K)                | 0.30004           | 0.31397    | 0.1790            | 113.840                  |
|                                       | 0.28846           | 0.30531    |                   |                          |
|                                       |                   | 0.31179    |                   |                          |
|                                       |                   | 0.38715    |                   |                          |
|                                       |                   | 0.28460    |                   |                          |



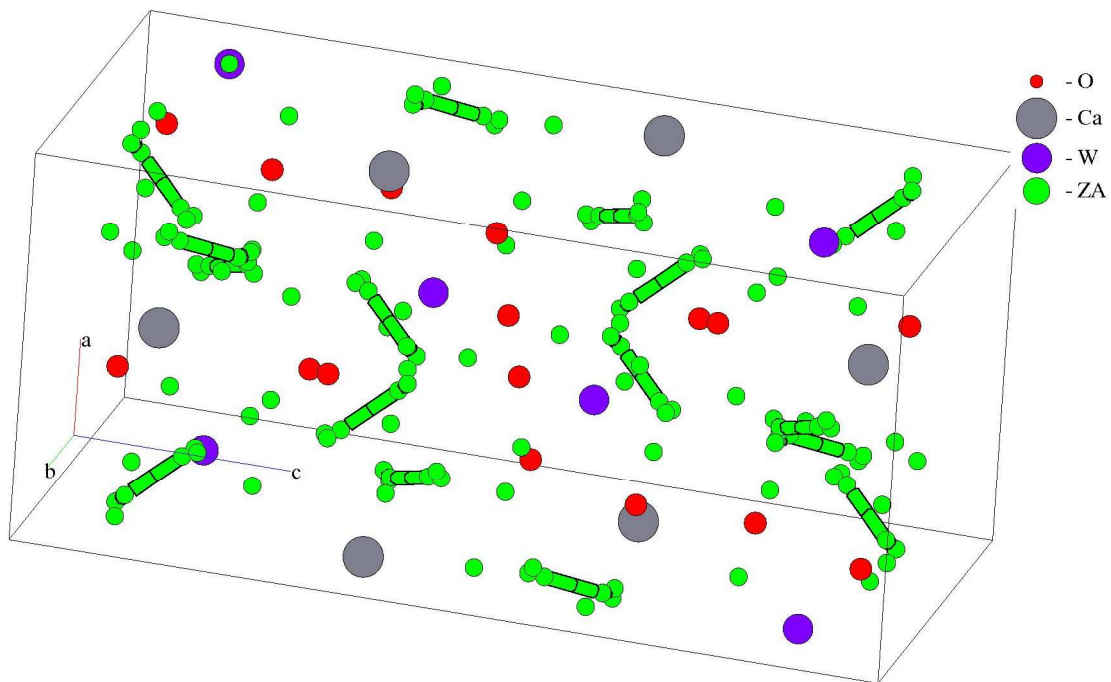
**Fig. 2** Wolframite-type structure of  $CdWO_4$  (a) and probable migration map calculated for the W ions in  $CdWO_4$  (b) and  $ZnWO_4$  (c) at RT.



**Fig. 3** Probable migration pathways calculated at RT for the W ions in  $PbWO_4$  using crystal data from [22].

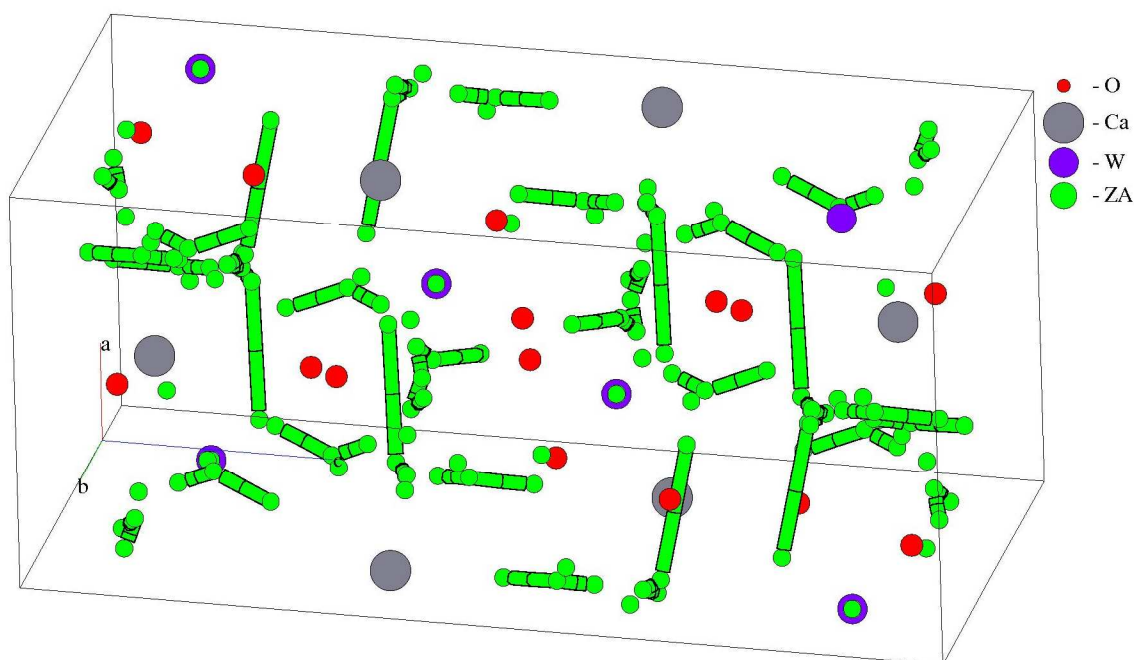


**Fig. 4** Probable migration pathways calculated at RT for the W ions in  $PbWO_4$  using crystal data from the literature [26] and the characteristic junction of migration pathways (inset).



**Fig. 5** Conductivity map calculated at RT for the W ions in a  $CaWO_4$  crystal.





**Fig. 6** Conductivity pattern calculated for the W ions in the  $CaWO_4$  crystal at 1773 K.

For the crystallographic data  $CaWO_4$  [27] conductivity maps were calculated at 298 and 1773 K and are presented in Fig. 5 and Fig. 6. The migration path slightly increases with increasing temperature. This influence of temperature was expected since the parameters of the crystalline cell are larger and similar results were observed in the case of  $CaMoO_4$  [14].

According to the approach used here, at RT in the perfect structure of  $AWO_4$  (for  $A = Ca, Cd, Zn$ ) the ionic conductivity is probably low. For the  $PbWO_4$  compound even at RT the W ions are mobile and in this case continuous ways of ion migration form (see Fig. 4). Higher temperatures and structural defects, which are always present in real crystals, provide significant opportunities to increase the mobility of the ions.

## Conclusions

The probable migration pathways for the W ions as possible mobile ionic charge carriers in crystals with the general formula  $AWO_4$  ( $A = Ca, Cd, Pb, Zn$ ) were visualized using the program package TOPOS. In the investigated compounds continuous migration paths of the A-ions are not formed. In  $PbWO_4$  for some selected structural data determined at RT a probable continuous 3D-network of migration pathways of W-ions in the crystalline matrix is formed. The length of the elementary channels of the migration path increases with increasing temperature,

as shown by the calculations for the  $CaWO_4$  compound. The oxygen ions in  $AWO_4$  crystals are always the mobile ions within the framework of the used model. This case was not analyzed in the present paper.

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