Ion Conducting Behavior in $(Lu_{1-x}M_x)_2(WO_4)_3$ Solid Solutions (M = Sm, Ho, Er) with the $Sc_2(WO_4)_3$ Type Structure

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Solid solutions in the trivalent cationic conducting system $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Er, Ho, Sm) that crystallize in the $Sc_2(WO_4)_3$ type structure were prepared and their conducting behaviors were characterized electrochemically. The partial replacement of the Lu^{3+} cation site in $(Lu_{1-x}M_x)_2(WO_4)_3$ by larger M^{3+} cations caused a crystal lattice expansion. Due to the opened ion-migration pathways, the solid solutions generally exhibited an increased cationic conductivity relative to pure $Lu_2(WO_4)_3$. The ion conductivity can be optimized by substituting the appropriate amount of M^{3+} into $(Lu_{1-x}M_x)_2(WO_4)_3$ in order to adjust the expansion of the migration pathways for the Lu^{3+} cations. Furthermore, a relationship between the average ionic radius of the trivalent cations involved and the ionic conductivity was characterized which makes it possible to predict the composition of the optimum ion-conducting compound in each solid solution system with the $Sc_2(WO_4)_3$ type structure.

Introduction

Compounds that crystallize in the scandium tungstate $Sc_2(WO_4)_3$ type structure and behave as trivalent cationic solid electrolytes have been intensively studied in recent years.[1−9] This research has focused mainly on the synthesis of various isostructural compounds with $Sc_2(WO_4)_3$-type structures and their characterization with respect to the trivalent cationic conduction properties. The $Sc_2(WO_4)_3$-type structure, in general $M_2(XO_4)_3$, is adopted by a huge number of tungstates (X = W) and molybdates (X = Mo). Considering $M_2(WO_4)_3$, M can be represented by trivalent cations of the heavier rare earth metals Er−Lu, Sc or by trivalent cations of the main group elements In and Al;[10] the corresponding molybdates, $M_2(MoO_4)_3$, are formed by Ho−Lu, Sc, In and Al.[10] In addition, it is possible to synthesize solid solutions by the partial replacement of a given M^{3+} cation with another trivalent cation B^{3+} $[(M_{1-x}B_x)_2(XO_4)_3]$[11] or by replacing the anionic part of the structure to give $M_2(W_{1-y}Mo_yO_4)_3$.[12] Furthermore, simultaneous substitutions in both the cationic as well as anionic part can be performed resulting in solid solutions such as $[M_2(WO_4)_3]_{1-x}[B_2(MoO_4)_3]_x$.[13] The number of possible compounds further increases when trivalent cations that are not usually able to form tungstates with the $Sc_2(WO_4)_3$ structure type are substituted into the host lattice. For example, $Gd_2(WO_4)_3$ crystallizes with the insulating $Eu_2(WO_4)_3$-type structure. However, a certain amount of Gd^{3+} (up to 60% of the trivalent cations) can be incorporated into $Sc_2(WO_4)_3$ maintaining the $Sc_2(WO_4)_3$-type structure and exhibiting ionic conduction characteristics.[14]

The ion conducting properties of a remarkable number of compounds with the $Sc_2(WO_4)_3$ type structure have been determined. It has been shown that the ion-conducting behaviors are strongly dependent on the nature of the trivalent cations. However, ordering principles are needed to manage and to oversee the huge amount of different conduction data.

Recently, the existence of such a principle was indicated during systematic investigations in the solid solution systems $(Sc_{1-x}M_x)_2(WO_4)_3$ (M = Lu, Dy, Gd) and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ (M = Lu, Gd, Sm, Nd). In these compounds, the Sc^{3+} conductivity was shown to be dependent on the crystal lattice expansion.[13,15]

It is the aim of this paper to determine whether this relationship can be generalized and extended to other solid solution systems with another trivalent-cation conducting tungstate series, such as trivalent ion species with ionic radii appreciably larger than that of Sc^{3+}. For this purpose, solid solutions in the system $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Er, Ho, Sm), which behave as Lu^{3+} ion conductors, have been prepared and characterized for the first time. The Lu^{3+} ion conducting system has been chosen for two reasons: i) the cationic radius of Lu^{3+} ($r_{Lu^{3+}} = 0.1001$ nm)[16] is considerably larger than that of Sc^{3+} ($r_{Sc^{3+}} = 0.0885$ nm),[16] and ii) because of the fast ion-conduction properties of $Lu_2(WO_4)_3$ {among compounds with the $Sc_2(WO_4)_3$-type structure,

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Table 1. Ionic radii of some selected trivalent cations corresponding to the coordination number of six[16]

Cation	Sc	In	Lu	Er	Ho	Dy	Gd	Sm	Nd
Radius / nm	0.0885	0.0940	0.1001	0.1030	0.1041	0.1052	0.1078	0.1098	0.1123

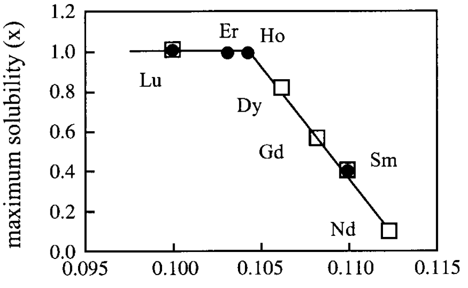

Figure 1. A plot of the maximum substitution rate in $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Sm, Ho, Er) (•) and in $(Sc_{1-x}M_x)_2(WO_4)_3$ (M = Lu, Dy, Gd) and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ (M = Lu, Gd, Sm, Nd) (□) solid solutions versus the ionic radius of the substituting cation M

$Lu_2(WO_4)_3$ exhibits the second highest conductivity [the optimum conducting compound is $Sc_2(WO_4)_3$ itself][1,5]}.

Results and Discussion

The ionic radii of several trivalent cations are summarized in Table 1 according to the coordination number of six in an octahedral environment.[16] Solid solutions between $Lu_2(WO_4)_3$ and $M_2(WO_4)_3$, with the $Sc_2(WO_4)_3$-type structure, are formed. Changing the size of the trivalent cation M^{3+} leads to drastically altered conditions for the formation of solid solutions. This relationship is displayed in Figure 1, where the solubility of $M_2(WO_4)_3$ in $Lu_2(WO_4)_3$ is given as a function of the ionic radius of M. For better illustration, the corresponding data of the previously described solid solutions in the systems $(Sc_{1-x}M_x)_2(WO_4)_3$ (M = Lu, Dy, Gd)[15] and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ (M = Lu, Gd, Sm, Nd)[13] are also shown. The ionic radii of W^{6+} (0.056 nm)[16] and Mo^{6+} (0.055 nm)[16] are almost identical and a corresponding influence on the mutual solubility can be neglected. For example, both $Gd_2(WO_4)_3$ and $Gd_2(MoO_4)_3$ can be dissolved into $Sc_2(WO_4)_3$ to about 60 mol %.[13,15] Thus, a direct comparison of the tungstate and molybdate systems, as shown in Figure 1, is possible. It can be seen that solid solutions between different tungstates/molybdates can be formed over the entire composition range ($0 < x < 1$) only for dopant cations M^{3+} with an ionic radius smaller than 0.105 nm. This value seems to be a stability limit for the $Sc_2(WO_4)_3$-type structure. The incorporation of larger cations causes a gradual decrease of the solid solution limit with increasing ionic radius of M^{3+}; for example, $x = 0.6$ for M = Gd ($r_{Gd}{}^{3+} = 0.1078$ nm[16]) and $x = 0.4$ for M = Sm ($r_{Sm}{}^{3+} = 0.1098$ nm[16]). Cations larger than Nd^{3+} cannot be dissolved into the $Sc_2(WO_4)_3$-type structure. The large cations cause strong local distortions in the crystal lattice which in turn collapses at a certain dopant level in order to release the strain and to form a new type of crystal structure. For example, pure $Gd_2(WO_4)_3$ and $Sm_2(WO_4)_3$ do not form the $Sc_2(WO_4)_3$-type structure but rather crystallize in the $Eu_2(WO_4)_3$-type structure.[10] Higher concentrations of M ($x > 0.6$ for M = Gd or $x > 0.4$ for M = Sm) in $(Lu_{1-x}M_x)_2(WO_4)_3$ destabilize the $Sc_2(WO_4)_3$ structure and favor the formation of either solid solutions in the corresponding $Eu_2(WO_4)_3$-type structure or mixtures of $Lu_2(WO_4)_3$ and $M_2(WO_4)_3$. On the other hand, $Er_2(WO_4)_3$ and $Ho_2(WO_4)_3$ crystallize in the $Sc_2(WO_4)_3$ type, and complete solid solution formation with $Lu_2(WO_4)_3$ becomes possible.

$Sc_2(WO_4)_3$, $Lu_2(WO_4)_3$ as well as the corresponding solid solutions $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Er, Ho, Sm) behave as trivalent cation conductors[13] and the ion-conduction properties vary with changing size and concentration of the different M^{3+} cations. The main effect of the incorporated larger M^{3+} cations in the $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions is to increase the lattice parameters *a*, *b*, and *c*, as indicated by the corresponding shifted d-spacings of individual peaks in the X-ray diffraction pattern.[13] The size of the unit cell increases isotropically and linearly with increasing substitution ratio, as shown in Figure 2 for solid solutions in the $(Lu_{1-x}Er_x)_2(WO_4)_3$ system. The substitution ratio is directly related to the average radius of the trivalent cations r_m [$r_m = (1-x)\cdot r_{Lu}{}^{3+} + x\cdot r_M{}^{3+}$]. The linear dependence between the average cationic radius and the cell volume, as shown in Figure 2, will be of importance for the subsequent discussion.

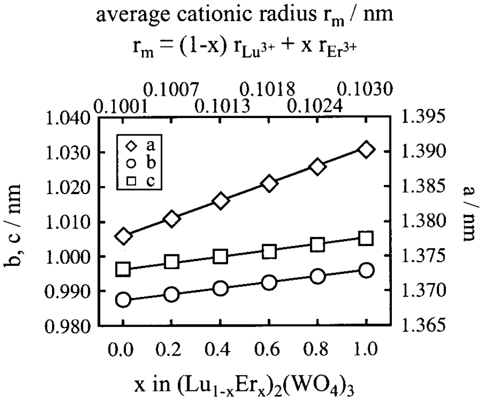

Figure 2. A plot of the lattice cell parameter of $(Lu_{1-x}Er_x)_2(WO_4)_3$ solid solutions versus the composition and the average trivalent cationic radius, r_m

Table 2. The trivalent-cation conducting properties of pure $Lu_2(WO_4)_3$ and $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions (M = Er, Ho, Sm) for different degrees of doping x; upper row: conductivity at 600 °C ($\log \sigma_{600\,°C}$); middle row: activation energy E_a in kJ/mol; bottom row: average trivalent-cation radius r_m in nm [$r_m = (1-x)\cdot r_{Lu}{}^{3+} + x \cdot r_M{}^{3+}$]; the compounds showing an optimum performance are marked in bold

M	x							
	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
	−4.413	−4.413	−4.413	−4.413	−4.413	−4.413	−4.413	−4.413
Lu	50.6	50.6	50.6	50.6	50.6	50.6	50.6	50.6
	0.1001	0.1001	0.1001	0.1001	0.1001	0.1001	0.1001	0.1001
		−4.350		−4.262	**−4.260**	−4.306	−4.384	−4.490
Er		48.7		45.7	**45.6**	48.5	52.5	55.9
	0.1007		0.1013	**0.1016**	0.1019	0.1024	0.1030	
		−4.307	−4.248	**−4.222**		−4.256	−4.286	−4.638
Ho		52.6	58.0	**44.1**		50.3	52.9	58.3
	0.1009	0.1013	**0.1017**		0.1025	0.1033	0.1041	
	−4.224	−4.435						
Sm	**47.5**	48.0						
	0.1011	0.1020						

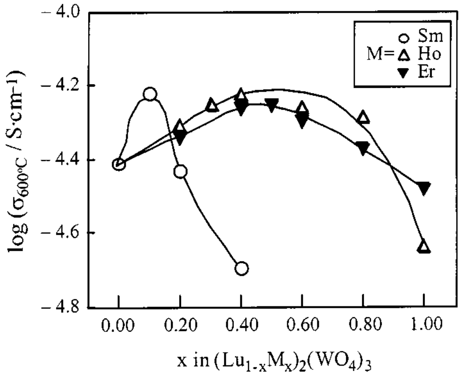

Figure 3. A plot of the trivalent cation conductivity at 600 °C ($\log \sigma_{600\,°C}$) versus the compositional parameter, x, for the $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions with M = Sm (○), Ho (□), Er (▼)

The conductivities of several $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions differing in the compositional parameter x have been determined. The corresponding conductivity data at 600 °C ($\log \sigma_{600\,°C}$) are tabulated in Table 2 in addition to the corresponding activation energies (E_a) as well as the average ionic radii of the involved trivalent cations. The activation energies are calculated from the log σT vs. 1/T relationship in the temperature range of 400−700 °C by using the common Arrhenius equation. A plot of the trivalent ion conductivities (log σ) of $(Lu_{1-x}M_x)_2(WO_4)_3$ at 600 °C versus the $M_2(WO_4)_3$ content (x) in $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Er, Ho, Sm) is shown in Figure 3. As a result, by expanding the crystal lattice due to the incorporation of larger cations M^{3+} into $(Lu_{1-x}M_x)_2(WO_4)_3$, the migration pathways within the crystal structure become more opened, which leads to a reduction in the electrostatic interaction between the mobile trivalent cations and the anionic host lattice. Thus, the migration of the trivalent Lu^{3+} cations is improved and increased conductivities are obtained in comparison to pure lutetium tungstate.

However, although the unit cell expands continuously over the whole composition region ($0 < x < 1$) and a corresponding continuous enhancement of the conductivity would be expected, a more complex behavior of log σ is found depending on the concentration and the size of the substituting cation, M^{3+}. Starting from the viewpoint of pure $Lu_2(WO_4)_3$, the conductivity increases continuously with increasing x because of the opening of the migration pathways due to the incorporation of the larger cation M^{3+}. However, at a certain composition, log σ reaches a maximum and the addition of further $M_2(WO_4)_3$ only reduces the ion-conduction properties. In our previous studies, trivalent cations with an ionic radius larger than Lu^{3+} are shown to be less mobile due to steric reasons.[5] Thus, although the crystal lattice is continuously expanding with increasing substitution ratio, the ionic conductivity decreases after reaching a maximum due to the exchange of mobile Lu^{3+} cations by M^{3+} cations that show a less-mobile behavior in $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions. The corresponding activation energies seem to confirm the aforementioned assumption by exhibiting the same dependency on the composition in each single system as the conductivity. The lowest and highest activation energies were observed (see Table 2) in solid solutions with the best and worst conductivities, respectively. This behavior is fully consistent with the corresponding results in the solid solution systems $(Sc_{1-x}M_x)_2(WO_4)_3$ (M = Lu, Dy, Gd) and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ (M = Lu, Gd, Sm, Nd), where the Sc^{3+} cations have been unambiguously identified as the main charge-carrying species in the high ion-conducting compounds.[13,15]

Although the optimum conductivity in each single system (different systems refer to different M^{3+} cations) is observed for different compositions [different x in $(Lu_{1-x}M_x)_2(WO_4)_3$] in Table 2, the maximum appears at almost the same average ionic radius, r_m, of the concerned trivalent cations. A similar behavior was also observed during systematic investigations in the solid solution systems $(Sc_{1-x}M_x)_2(WO_4)_3$ (M = Lu, Dy, Gd) and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ (M = Lu, Gd, Sm, Nd).[13,15] The corresponding relationship between the conductivity (log σ) and the average ionic radius, r_m, is shown in Figure 4, with the Sc^{3+}-conducting systems included for comparison (Figures 4b and 4c). The maximum ion conductivity in each solid solution system, corresponding to the main conducting species (Sc^{3+} or Lu^{3+} cations), appears at a similar average trivalent cationic radius within the Sc^{3+}- and Lu^{3+}-conducting compounds, respectively. It amounts to approximately 0.0938−0.0943 nm in $(Sc_{1-x}M_x)_2(WO_4)_3$ and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ and to about 0.1011−0.1017 nm in the $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions. The size of the trivalent cations is directly related to the expansion of the crystal lattice (cf Figure 2), i.e. to the extension of the migration pathways. According to the different ionic size of Sc^{3+} and Lu^{3+}, the optimum conductivities in $(Lu_{1-x}M_x)_2(WO_4)_3$ appear for compounds with a larger lattice cell volume ($V_{opt-cell}$ = 1.41−1.42 nm^3) than the $(Sc_{1-x}M_x)_2(WO_4)_3$ and $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ solid solutions ($V_{opt-cell}$ = 1.29−1.31 nm^3). Comparing these optimum cell volume to the ionic size of the charge-carrying Lu^{3+} ($Vr_{Lu}{}^{3+}$ = 0.0042 nm^3) and Sc^{3+} ($Vr_{Sc}{}^{3+}$ = 0.0029 nm^3) cations by forming the corresponding quotients $V_{opt-cell}/Vr_M{}^{3+}$ leads to values of 0.00297 (Lu^{3+}) and 0.00223 (Sc^{3+}). The similarity of these values might indicate the existence of a certain cell volume/cation size relation of approximately 0.002−0.003, which is most appropriate for the transport of trivalent cations within the $Sc_2(WO_4)_3$-type structure series. While this simple model is based only on steric considerations and neglects a more complex situation including polarizabilities, electrostatic interactions, and local ordering of the different cation types, which might also influence the migration behavior of the cations within the conduction layers to some extent, it provides information which makes it possible to roughly predict the composition of the optimum conducting compound of mixed solid solutions crystallizing with $Sc_2(WO_4)_3$-type structures, despite its simplicity.

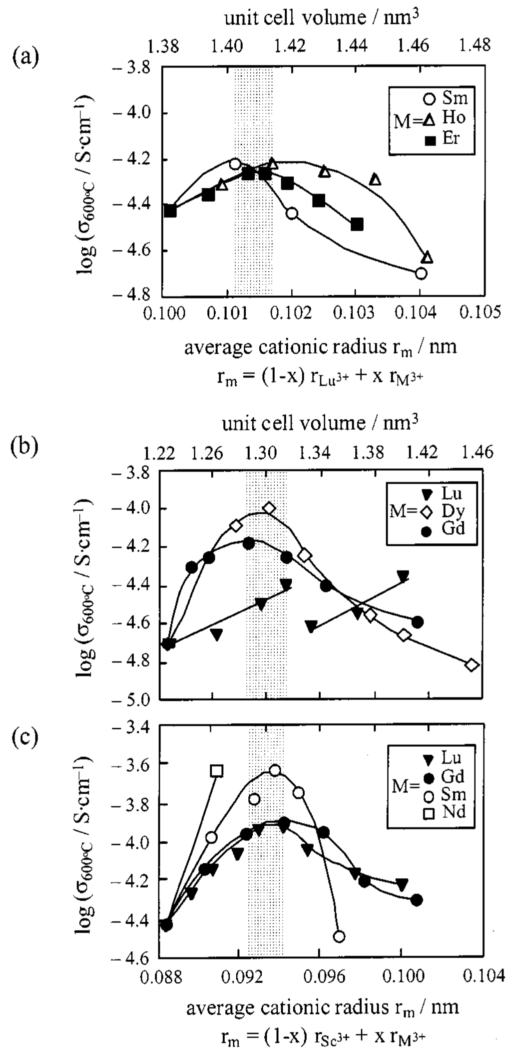

Figure 4. A plot of the trivalent cation conductivity at 600 °C (log $\sigma_{600\ °C}$) versus the average trivalent cationic radius, r_m, for: (a) $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions [M = Sm (○), Ho (□), Er (■)]; (b) $(Sc_{1-x}M_x)_2(WO_4)_3$ solid solutions[12] [M = Lu (▼), Dy (◇), Gd (•)]; (c) $[Sc_2(WO_4)_3]_{1-x}[M_2(MoO_4)_3]_x$ solid solutions[13] [M = Lu (▼), Gd (•), Sm (○), Nd (□)]; the shaded region corresponds to the optimal cationic radius where the highest conductivity data can be observed

Conclusions

The trivalent-cation conducting solid solution system of $(Lu_{1-x}M_x)_2(WO_4)_3$ (M = Er, Ho, Sm) shows a monotonous expansion of crystal lattice by substituting Lu^{3+} cation site for larger M^{3+} cations. Due to the linear relationship between the average cationic radius and the unit cell volume of the solid solutions, the optimum ion-conducting compound in a certain solid solution system with a given M^{3+} cation can be easily elucidated only by calculating the $V_{opt-cell}/Vr_M{}^{3+}$ quotient (0.002−0.003) to adjust the expansion of the crystal lattice in an optimum surroundings for the mobile cations. Ideally, only the compound with the composition which corresponds to that optimum unit cell volume need be prepared. This provides a helpful tool for the understanding of the trivalent cationic conduction characteristics in the various tungstate and molybdate compounds with the $Sc_2(WO_4)_3$-type crystal structure.

Experimental Section

Polycrystalline $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions (M = Er, Ho, Sm) were prepared in conventional solid-state reactions by heating a thoroughly ground mixture of reagent grade Lu_2O_3, WO_3, and the lanthanide oxides M_2O_3 (purity of all reagents 99.9% or higher) in the corresponding stoichiometric ratio at a temperature of 1200 °C for 24 h in an oxygen atmosphere. After regrinding, the procedure was repeated with the same experimental conditions. The colors of the obtained powders are white (Lu/Gd compounds), pink (Lu/Er), slight yellow (Lu/Ho), and salmon-pink (Lu/Sm). The resulting materials were characterized by X-ray powder diffraction analysis (XRD) using Cu-K_α radiation (Mac Science M18XHF diffractometer).

For the electrical conductivity measurements, pelletized samples of $(Lu_{1-x}M_x)_2(WO_4)_3$ were sintered in an oxygen atmosphere for 12 h at 1200 °C, and sputtered on opposite faces with ionically blocking platinum. Electrical conductivity measurements such as impedance analysis and time-dependent dc-polarization measurements of all samples were performed following the usual procedures as reported elsewhere.[1−9] In dc electrolysis experiments, the $(Lu_{1-x}M_x)_2(WO_4)_3$ samples were exposed to a direct voltage of 6V for about 4−6 weeks at 800−850 °C in air, using ion-blocking Pt electrodes. After the electrolysis procedure, the cathodic and anodic surfaces as well as the bulk of the samples were characterized by electron-probe microanalysis(EPMA).

Acknowledgments

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[1] J. Köhler, N. Imanaka, G. Adachi, *Chem. Mater.* **1998**, *10*, 3790−3812.

[2] N. Imanaka, Y. Kobayashi, G. Adachi, *Chem. Lett.* **1995**, 433−434.

[3] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, *Chem. Mater.* **1997**, *9*, 1649−1654.

[4] N. Imanaka, G. Adachi, *J. Alloys and Comp.* **1997**, *250*, 492−500.

[5] N. Imanaka, Y. Kobayashi, K. Fujiwara, T. Asano, Y. Okazaki, G. Adachi, *Chem. Mater.* **1998**, *10*, 2006−2012.

[6] N. Imanaka, M. Hiraiwa, S. Tamura, G. Adachi, H. Dabkowska, A. Dabkowski, J. E. Greedan, *Chem. Mater.* **1998**, *10*, 2542−2545.

[7] Y. Kobayashi, S. Tamura, N. Imanaka, G. Adachi, *Solid State Ionics* **1998**, *113−115*, 545−552.

[8] N. Imanaka, S. Tamura, Y. Kobayashi, Y. Okazaki, M. Hiraiwa, T. Ueda, G. Adachi, *J. Alloys and Comp.* **2000**, *303−304*, 303−306.

[9] N. Imanaka, T. Ueda, Y. Okazaki, S. Tamura, G. Adachi, *Chem. Mater.* **2000**, *12*, 1910−1913.

[10] K. Nassau, H. J. Levinstein, G. M. Loiacono, *J. Phys. Chem. Solids* **1965**, *26*, 1805−1816.

[11] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, *Solid State Ionics* **1999**, *118*, 325−330.

[12] Y. Kobayashi, PhD Thesis of Osaka University **1998**.

[13] J. Köhler, N. Imanaka, G. Adachi, *J. Mater. Chem.* **1999**, *9*, 1357−1362.

[14] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, *Solid State Ionics* **1998**, *111*, 59−65.

[15] G. Adachi, J. Köhler, N. Imanaka, *Electrochemistry* **1999**, *67*, 744−751.

[16] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

[17] As in previous reports on trivalent cation compounds with the $Sc_2(WO_4)_3$-type structure,[1−9] the conducting properties of the $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions (M = Er, Ho, Sm) have been characterized by several electrochemical methods, including time-dependent polarization measurements (under various atmospheres) and dc electrolysis experiments. As a main result, the electrical conductivity in the $(Lu_{1-x}M_x)_2(WO_4)_3$ solid solutions is found to be purely cationic with an ion-transference number higher than $t_i^+ = 0.99$. No electronic or anionic O^{2-} conduction has been observed. The migrating cations have been directly identified by EPMA for the samples after the dc electrolysis using the same experimental setup as reported elsewhere.[1−9] Thus, the data presented are discussed in terms of trivalent cationic conduction.

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