Structural characterization of mixed conducting perovskites $\text{La}(\text{Ga},\text{M})\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$)

N.P. Vyshatko^a, V. Kharton^{a,b,*}, A.L. Shaula^a, E.N. Naumovich^b, F.M.B. Marques^a

^a*Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

^b*Institute of Physicochemical Problems, Belarus State University, 14 Leningradskaya Str., Minsk 220050, Byelorussia*

Received 22 May 2002; received in revised form 20 November 2002; accepted 21 November 2002

Abstract

Comparative analysis of the structure refinement results of perovskite-like $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) and data on other LaGaO_3 -based phases, heavily doped with transition metal cations, shows that on doping the structural changes in these oxides follow common trends for the perovskite-type systems. The maximum ionic conductivity, observed in various perovskites when the tolerance factor values are approximately 0.96–0.97, was found to correlate with the transition from orthorhombic to rhombohedral structure and maximum lattice distortion. The perovskite unit cell distortion near the orthorhombic–rhombohedral phase boundary may hence play a positive role in the ionic transport processes.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oxides; X-ray diffraction; Crystal structure; Ionic conductivity

1. Introduction

Oxide solid electrolytes and mixed ionic-electronic conductors based on perovskite-type lanthanum gallate, LaGaO_3 , are of considerable interest for high-temperature electrochemical applications, such as intermediate-temperature solid oxide fuel cells (IT SOFCs), oxygen separation membranes and sensors [1–9]. Significant oxygen-ionic conduction can be achieved by doping the perovskite (ABO_3) with lower valence cations on the A and/or B sites, including the substitution of La with alkaline-earth cations (Sr, Ca, Ba) and Ga with bivalent metal cations (Mg, Ni). One of the highest oxygen-ion conductivities of any material occurs for the solid solution series $(\text{La},\text{Sr})(\text{Ga},\text{Mg})\text{O}_{3-\delta}$ (LSGM), preferably containing minor amounts of transition metal cations (Co, Fe) in the B sublattice [1–4,9]. Further substitution of gallium with the transition metal ions leads to increasing electronic conductivity, advantageous for

* Corresponding author. Tel.: +351-234-370263; fax: +351-234-425300.

E-mail address: kharton@cv.ua.pt (V. Kharton).

applications in oxygen membranes and SOFC electrodes [3,6–8]; the ionic conductivity may, however, decrease when the concentrations of Ga and transition metal dopant (M) are comparable [9–11]. Exact reasons for the latter phenomenon are still unclear; one possible hypothesis refers to the great difference in the covalency of Ga–O and M–O bonds, resulting in local structural distortions or enhanced defect cluster formation [9,11]. This hypothesis was supported by data on oxygen thermodynamics and Seebeck coefficient of $\text{La}_{0.3}\text{Sr}_{0.7}(\text{Fe,Ga})\text{O}_{3-\delta}$ [12], which indicated an appearance of local inhomogeneities in the perovskite lattice when gallium is incorporated in the iron sites.

Continuing our research on $\text{La}(\text{Ga,M})\text{O}_{3-\delta}$ based solid solutions [6–12], the present work is focused on the study of crystal structure and phase composition of materials where the concentrations of Ga and M cations are comparable. When the Ga:M concentration ratio is close to 1:1, phase separation or cation ordering may appear. In the case of single-phase compositions, it may be questionable if the behavior of the structural parameters as functions of the cation composition can be analyzed in terms of the classical approaches such as the tolerance factor, which is commonly used for perovskite-type systems, including LSGM (for example, [3,13,14]). The tolerance factor is defined as $t = (\bar{R}_A + R_O) / (\sqrt{2}(\bar{R}_B + R_O))$, where R_A , R_B , R_O are the average radii of A, B and O ions, respectively. The compositions $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_3$ (M = Mn, Fe, Co, Ni) were thus synthesized and their structure refinement was performed. The results are analyzed in combination with data on other LaGaO_3 -based phases. The physicochemical and transport properties of these materials were reported elsewhere [6–9,15,16]. Another goal of this work was to consider relationships between the tolerance factor and ionic conduction in the transition metal-containing gallates. Recently, a maximum of the oxygen-ionic conductivity in several perovskite-like systems was found at $t \approx 0.96$ [14]; this behavior was attributed to an optimum ratio between t and another conduction-affecting factor, specific free volume V_{sf} [13]. On the other hand, t and V_{sf} quantities are interrelated, both being functions of the radii of ions constituting the lattice; the maximum ionic conductivity at $t \approx 0.96$ may hence result from other factors, which were not taken into consideration in [14].

2. Experimental

Powders of $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ (M = Mn, Fe, Co, Ni) were prepared by the standard ceramic synthesis method from high purity complex salt and binary oxide precursors. The solid state reactions were conducted in air at temperatures from 1520 to 1670 K for 30–40 h with multiple intermediate grinding steps. Details on the preparation route for other transition metal-containing phases considered in this work, including $\text{LaGa}_{1-y-z}\text{Mg}_y\text{Co}_z\text{O}_{3-\delta}$ ($y = 0.10\text{--}0.20$, $z = 0.35\text{--}0.60$) [8], $\text{LaGa}_{1-x}\text{M}_x\text{O}_{3-\delta}$ (M = Co, Ni, Mg; $x = 0.10\text{--}0.80$) [7,15,16] and $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.20\text{--}0.50$) [17], were previously reported. X-ray diffraction (XRD) revealed an absence of phase impurities for all compositions considered in this paper. Prior to the structural studies, the samples were annealed in air at 1300–1500 K for 2–3 h with subsequent slow cooling in order to ensure equilibration of the oxides with the gas phase at low temperatures. X-ray powder diffraction data were collected at the room temperature using a Rigaku D/Max-B diffractometer (CuK_α radiation, $10^\circ < 2\theta < 110^\circ$, step 0.02° , 10 s/step). Structural parameters were refined using Fullprof program [18]. Rietveld refinement consisted of 28 and 21 parameters for the orthorhombic and rhombohedral systems, respectively. The refined parameters included the scale factor, five-parameter background function, two peak-shape coefficients, detector zero-point, three lattice constants, and the coordinates and isotropic temperature factors for the four atoms in asymmetric

unit cell. The coordinates of B cations were fixed in order to define the origin of the polar axis. The values of the oxygen-ionic conductivity, used in this work for the analysis of structure—ionic transport relations, were calculated from the results on oxygen permeability and faradaic efficiency of dense ceramic materials; description of the experimental procedure and detailed results on the ionic conduction are found elsewhere [7–9,15,16].

3. Results and discussion

Selected results of the structure refinement of $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ are summarized in Tables 1–3; Fig. 1 shows an example of the final Rietveld plot. Single perovskite-type phases are formed in all cases; the lattice symmetry was found orthorhombic (Space Group $Pnma$ (No. 62)) for $\text{M} = \text{Mn}$ and Fe , and rhombohedral (S.G. $R\bar{3}C$ (No. 167)) for $\text{M} = \text{Co}$ and Ni . No cation ordering was observed; the results

Table 1
Selected structure refinement results for $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ solid solutions

	M = Mn	M = Fe	M = Co	M = Ni
Crystal system	Orthorhombic	Orthorhombic	Rhombohedral	Rhombohedral
Space Group	$Pnma$ (No. 62)	$Pnma$ (No. 62)	$R\bar{3}C$ (No. 167)	$R\bar{3}C$ (No. 167)
Unit cell parameters (Å)	$a = 5.495(3)$ $b = 7.784(6)$ $c = 5.530(4)$	$a = 5.530(8)$ $b = 7.822(1)$ $c = 5.542(1)$	$a = 5.469(5)$ $c = 13.196(5)$	$a = 5.492(9)$ $c = 13.224(3)$
Cell volume (Å ³)	236.58(7)	239.76(7)	341.89(9)	345.55(9)
Density (g/cm ³)	6.997	6.917	7.32	7.240
R_p (%)	8.07	7.35	10.4	8.24
R_{wp} (%)	14.7	11.9	13.8	10.9
χ^2	3.45	3.25	7.03	4.41
Bragg R-factor	3.38	3.41	6.82	6.13

Table 2
Bond lengths (Å) and angles (°) between bonds for $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ solid solutions

	M = Mn	M = Fe	M = Co	M = Ni
La–O1	2.386	2.420	2.445	2.424
La–O2	2.478	2.463	–	–
B–O1	1.987	1.993	1.946	1.958
B–O2	1.976	1.980	–	–
O2–La–O2	118.21	116.16	120	120
O2–La–O1	84.55	84.65	–	–
O2–B–O2	180	180	180	180
O2–B–O2	91.51	91.31	91.20	91.42
O2–B–O2	90.25	90.61	88.80	88.58
O2–B–O1	90.13	90.31	–	–
O2–B–O1	89.87	89.39	–	–
O2–B–O1	89.75	88.69	–	–
O1–B–O1	180	180	–	–

Table 3

Fractional coordinates of selected ions in $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ lattice

M	Symmetry	Ion	x	y	z
Mn	Orthorhombic	La	0.0173 (7)	0.25	−0.0029 (7)
		O1	−0.0058 (3)	0.25	0.4277 (6)
		O2	−0.2275 (6)	0.4641 (4)	−0.2280 (9)
Fe	Orthorhombic	La	0.0251 (3)	0.25	−0.0047 (4)
		O1	−0.0083 (1)	0.25	0.4306 (7)
		O2	−0.2233 (7)	0.4619 (9)	−0.2202 (4)
Co	Rhombohedral	O	0.5529 (2)	0	14
Ni	Rhombohedral	O	0.5587 (9)	0	14

confirm, therefore, formation of a continuous solid solution series in the systems LaGaO_3 – $\text{LaMO}_{3-\delta}$, as reported elsewhere ([7,15] and references therein). Such a behavior results probably from the similar size and charge of gallium and transition metal cations; the role of these factors seems greater than that of the differences in the metal-oxygen bond covalency.

In order to compare variations of the lattice symmetry and unit cell volume of $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ with the literature data, Fig. 2 presents the dependence of the average lattice parameter (a_{av}) on the tolerance factor for various perovskite-type systems. Perovskite phases having the orthorhombic (O) and rhombohedral (R) perovskite structure are marked by open and closed symbols, respectively. The average unit cell parameter is defined as $a_{\text{av}} = (V/Z)^{1/3}$, where V is the cell volume and Z is the number of formula units. The definition of the tolerance factor is well known in the literature [3,13,14]; the ionic radii reported by Shannon [19] were used for the calculations. As expected from the tolerance factor definition, increasing t values leads to a higher symmetry and smaller unit cell volume of the perovskite phases. The transition from orthorhombic to rhombohedral structure is observed at $t \approx 0.96$.

Fig. 1. Observed, calculated and difference X-ray diffraction patterns of $\text{LaGa}_{0.5}\text{Fe}_{0.5}\text{O}_3$.

Fig. 2. Tolerance factor dependence of the average unit cell parameter of $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_3$ phases, compared to the data on other perovskite systems. Structural data on $\text{La}_2(\text{Cu,Ti})\text{O}_6$, $\text{LaMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$, $\text{LaCo}_{0.2}\text{Mn}_{0.8}\text{O}_3$, $\text{La}_2\text{NiRhO}_6$, $\text{LaNi}_{0.8}\text{Sb}_{0.2}\text{O}_3$, $\text{La}(\text{Fe,Ni})\text{O}_3$ and $\text{La}(\text{Al,Ni})\text{O}_3$ systems are taken from [24–31]; all other perovskite compounds were synthesized by the authors.

The results on $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ and other phases derived from LaGaO_3 are in a good agreement with the literature (Fig. 2); the structural changes in LaGaO_3 -based systems follow, therefore, common trends for other perovskite systems. Another conclusion is that the maximum in oxygen-ionic conductivity, reported at $t \approx 0.96$ [14], is close to the transition from orthorhombic to rhombohedral. One should note that the morphotropic phase boundary, existing in a number of perovskite-like solid solutions where the end members have different distortions of the structure, often results in anomalous physicochemical properties due to the lattice instability (for example, [20–22]). As the maximum ionic conductivity at $t \approx 0.96$ [14] might have a similar nature, an attempt to analyze lattice distortions around the O–R transition was performed.

Table 3 lists coordinates of ions shifted from their crystallographic positions in the lattice of $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$; the data on ions located in their ideal sites are skipped for simplicity. For the orthorhombic phases, the displacement of La cations decreases with increasing tolerance factor and becomes equal to zero at $t > 0.96$ when the structure transforms into rhombohedral. Increasing t values leads also to a greater displacement of the oxygen-ions; tilting of the metal-oxygen octahedra and, hence, orthorhombic distortion increase with the tolerance factor around O–R transition. For the rhombohedral solid solutions, no direct correlation between atomic displacement and tolerance factor was found.

A quantitative estimation of the orthorhombic distortion level in a perovskite lattice is possible using the parameters Δ_1 and Δ_2 , related to the orthorhombic unit cell constants as $\Delta_1 = a/b$ and $\Delta_2 = \sqrt{2} \times (a/c)$ [23]. When $\Delta_1 = 1$, the parameters a and b are equal, and the monoclinic angle (β) is 90° . If $\Delta_1 = 1$ and $\Delta_2 = 1$, the lattice can be considered as pseudocubic. For the rhombohedral structure, the distortion can be expressed by the parameter $\Delta = \sqrt{6} \times (a/c)$, where a and c are the unit

Fig. 3. Unit cell parameters, perovskite lattice distortion and ionic conductivity at 1223 K vs. tolerance factor for the $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ system. The average cell constant and distortion parameters are calculated from the structural results [24]. The ionic conductivity is determined from the oxygen permeation data, published elsewhere [17].

cell parameters in the hexagonal setting. This unit cell is close to cubic when $\Delta = 1$. The quantities Δ_1 , Δ_2 and Δ were used for the analysis of perovskite lattice distortion as a function of the tolerance factor.

A typical behavior of the distortion parameters versus tolerance factor is illustrated in Fig. 3 using one typical system, $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$, which was selected due to the detailed structural data available in a wide compositional range [24]. Fig. 4 illustrates similar trends for LaGaO_3 - and LaAlO_3 -based perovskites. The values of the oxygen-ionic conductivity of $\text{La}(\text{Fe},\text{Ni})\text{O}_{3-\delta}$ at elevated temperatures were calculated from the results on the oxygen permeability, published earlier [17]. As for other perovskite systems, increasing with the nickel content in $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ leads to increasing tolerance factor and decreasing unit cell volume; the O–R transition is observed when the concentrations of Fe and Ni cations are comparable (Fig. 3 and [17]). However, the distortion of the perovskite lattice, either orthorhombic or rhombohedral, also increases with the tolerance factor. The ionic conductivity of $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ perovskites increases with t and x , but tends to a maximum at $t = 0.96$ – 0.97 , near the O–R transition. Although the observed behavior of ionic transport should be attributed mainly to increasing oxygen nonstoichiometry when x increases [17], the trends in the ionic conductivity as a function of the tolerance factor clearly correlate with the observations reported in [14].

Extending the considered range of tolerance factor up to 1.01 (Fig. 4) shows that the maximum lattice distortions in the perovskite systems is observed at $t = 0.97$ – 0.98 . Further increase of the t values results in a transition of the rhombohedral structure into cubic when the tolerance factor becomes close

Fig. 4. Unit cell parameters, lattice distortion and ionic conductivity vs. tolerance factor for the perovskite-type $\text{LaGa}_{1-x}\text{Co}_x\text{O}_{3-\delta}$, $\text{LaGa}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ and $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ systems. Structural data on $\text{La}(\text{Al},\text{Ni})\text{O}_{3-\delta}$ are taken from [25].

to unity. In this situation rhombohedral distortion decreases down to zero ($\Delta \approx 1$), as illustrated in Fig. 4 by the example of $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ phases [25]. The similarity in behavior, exhibited for the solid solutions $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$, $\text{LaGa}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ and $\text{LaGa}_{1-x}\text{Co}_x\text{O}_{3-\delta}$, suggests that these trends are common for perovskite-type oxides. Again, the maximum ionic conductivity is observed at $t = 0.970$ – 0.975 (Fig. 4), which is quite close to the literature data [14] and to the O–R phase transition. The location of this maximum is, of course, temperature-dependent due to the variations of the lattice parameters and oxygen nonstoichiometry on heating. Nevertheless, these data unambiguously indicate correlation between the maximum distortion of the perovskite lattice and the maximum ionic conductivity. Such a correlation may result either from the lattice instability, characteristic of morphotropic phase transformations, or from shortening of some distances between oxygen anions, thus enhancing ionic mobility.

Finally, one should mention that the observed correlations are characterized by a relatively large uncertainty, particularly due to the variations with temperature of the oxygen nonstoichiometry, transition metal oxidation state and lattice parameters, and can therefore be used only for qualitative analysis. For example, the differences in t values corresponding to the maximum ionic conductivity, which was reported at $t \approx 0.96$ [14] and appears at slightly higher values of the tolerance factor (e.g. Figs. 3 and 4), may result from this uncertainty. In any case, however, the maximum ionic transport at $t \approx 0.96$ – 0.97 unambiguously correlate with the O–R phase transition and maximum lattice distortion, the effect of which on the ion mobility may be dominant.

4. Conclusions

Single-phase perovskite-type $\text{LaGa}_{0.5}\text{M}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn, Fe, Co, Ni}$) were synthesized and their structure refinement was performed using X-ray powder diffraction data. The observed variation of the unit cell parameters and lattice distortion, and the transition from orthorhombic to rhombohedral structure are consistent with data on other perovskite-like systems, including LaGaO_3 -based phases. Comparative analysis of the results on B site substituted LaGaO_3 suggests that the maximum ionic conductivity, observed when the tolerance factor is approximately 0.96–0.97, may be related to the O–R transition and/or maximum lattice distortion, which appear at similar t values. The perovskite unit cell distortion near the orthorhombic–rhombohedral phase boundary may thus play a critical role in the ionic conduction processes.

Acknowledgements

This work was supported by the FCT, Portugal: (PRAXIS and POCTI programs, and project BD/6595/2001); INTAS (project 00276); JCPDS Grant-in-Aid 00-09; and the Belarus Ministry of Education and Science. The authors are sincerely grateful to M. Avdeev, A. Yaremchenko and A. Viskup for helpful discussions and experimental assistance.

References

- [1] T. Ishihara, H. Matsuda, Y. Takita, J. Am. Chem. Soc. 116 (1994) 3801.
- [2] K. Huang, R.S. Tichy, J.B. Goodenough, J. Am. Ceram. Soc. 81 (1998) 2565.
- [3] N. Trofimenko, H. Ullmann, Solid State Ionics 118 (1999) 215.
- [4] T. Ishihara, T. Akbay, H. Furutani, Y. Takita, Solid State Ionics 113/115 (1998) 585.
- [5] Y. Tsuruta, T. Todaka, H. Nisiguchi, T. Ishihara, Y. Takita, Electrochem. Solid-State Lett. 4 (2001) E13–E15.
- [6] V.V. Kharton, E.N. Naumovich, A.V. Kovalevsky, A.A. Yaremchenko, A.P. Viskup, P.F. Kerko, J. Membrane Sci. 163 (1999) 307.
- [7] A.A. Yaremchenko, V.V. Kharton, A.P. Viskup, E.N. Naumovich, N.M. Lapchuk, V.N. Tikhonovich, J. Sol. State Chem. 142 (1999) 325.
- [8] A.A. Yaremchenko, V.V. Kharton, A.P. Viskup, E.N. Naumovich, V.N. Tikhonovich, N.M. Lapchuk, Solid State Ionics 120 (1999) 65.
- [9] V.V. Kharton, A.P. Viskup, A.A. Yaremchenko, R.T. Baker, B. Gharbage, G.C. Mather, F.M. Figueiredo, E.N. Naumovich, F.M.B. Marques, Solid State Ionics 132 (2000) 119.
- [10] I.A. Leonidov, V.L. Kozhevnikov, E.B. Mitberg, M.V. Patrakeev, V.V. Kharton, F.M.B. Marques, J. Mater. Chem. 11 (2001) 1202.
- [11] V.V. Kharton, A.A. Yaremchenko, A.P. Viskup, M.V. Patrakeev, I.A. Leonidov, V.L. Kozhevnikov, F.M. Figueiredo, A.L. Shaula, E.N. Naumovich, F.M.B. Marques, J. Electrochem. Soc. 149 (2002) E125.
- [12] M.V. Patrakeev, E.B. Mitberg, A.A. Lakhtin, I.A. Leonidov, V.L. Kozhevnikov, V.V. Kharton, M. Avdeev, F.M.B. Marques, J. Solid State Chem., accepted for publication (2002).
- [13] R.L. Cook, A.F. Sammells, Solid State Ionics 45 (1991) 311.
- [14] H. Hayashi, H. Inaba, M. Matsuyama, N.G. Lan, M. Dokiya, H. Tagawa, Solid State Ionics 122 (1999) 1.
- [15] V.V. Kharton, A.P. Viskup, E.N. Naumovich, N.M. Lapchuk, Solid State Ionics 104 (1997) 67.
- [16] V.V. Kharton, A.A. Yaremchenko, A.P. Viskup, G.C. Mather, E.N. Naumovich, F.M.B. Marques, Solid State Ionics 128 (2000) 79.
- [17] V.V. Kharton, A.P. Viskup, E.N. Naumovich, V.N. Tikhonovich, Mater. Res. Bull. 34 (1999) 1311.

- [18] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.
- [19] R.D. Shannon, *Acta Cryst.* A32 (1976) 751.
- [20] Y.J. Kim, S.W. Choi, *Ferroelectrics* 173 (1995) 87.
- [21] W.W. Cao, L.E. Cross, *Phys. Rev. B* 47 (1993) 4825.
- [22] J.C. Ho, K.S. Liu, I.N. Liu, *J. Mater. Sci.* 28 (1993) 4497.
- [23] E.G. Fesenko, *Perovskite Family and Ferroelectricity*, Atomizdat, Moscow, 1972 (in Russian).
- [24] H. Falcon, A.E. Goeta, G. Punte, R.E. Carbonio, *J. Solid State Chem.* 133 (1997) 379.
- [25] S. Geller, V.B. Bala, *Acta Cryst.* 9 (1956) 1019.
- [26] M.R. Palacin, J. Bassas, J. Rodriguez-Carvajal, P. Gomez-Romero, *J. Mater. Chem.* 3 (1993) 1171.
- [27] M.R. Palacin, J. Bassas, J. Rodriguez-Carvajal, A. Fuertes, N. Casan-Pastor, P. Gomez-Romero, *Mater. Sci. Forum* 152 (1994) 293.
- [28] A. Meden, M. Ceh, *Mater. Sci. Forum* 278 (1998) 773.
- [29] M.A. Gilleo, *Acta Cryst.* 10 (1957) 161.
- [30] P.D. Battle, J.F. Vente, *J. Solid State Chem.* 146 (1999) 163.
- [31] I. Alvarez, M.L. Veiga, C. Pico, *J. Alloys Compd.* 255 (1997) 74.