

INVESTIGATION OF *s, p, d*-ELEMENT NIOBATES AND THEIR SOLID SOLUTION FORMATION PROCESSES BY THERMAL ANALYSIS

V. M. Zhukovsky and A. L. Podkorytov

Department of Chemistry, Ural State University, pr. Lenina 51, 620083, Ekaterinburg, Russia

(Received November 11, 1998; in revised form September 23, 1999)

Abstract

The binary and ternary systems $M'O(M'CO_3)-Nb_2O_5$ and $M'O(M'CO_3)-MO-Nb_2O_5$, where $M'=Ca, Sr$ and Ba and $M=Cu, Ni, Cd, Zn$ and Pb , were investigated by means of thermal analysis in the temperature range 20–1500°C. The boundaries of stability of the solid solutions $Sr_{2-x}Me_xNb_2O_7$, $Sr_{2-x}M_xNb_2O_7$, $Sr_{4-x}M_xNb_2O_9$ and $Sr_{6-x}M_xNb_2O_{11}$ were determined by means of X-ray diffraction, and IR and Raman spectroscopy. The possibility of prognostication of the phase fields of stable solid solutions by calculation from the diagrams of the 'comparative electronegativity of atoms vs. tolerance factor' was demonstrated. The kinetic parameters of the interactions in the $SrCO_3+MO+Nb_2O_5$ powder mixtures were established.

Keywords: fields of stability, kinetic parameters, niobates, solid solution, thermal analysis

Introduction

From a technological aspect, the niobates are of interest as materials for the production of ferroelectrics, solid electrolytes and electrochemical sensors. The conditions of synthesis, the fields of stability of the solid solutions, and the relations between the structures, compositions and characteristics of the niobates are further interesting topics.

The phase equilibria in the binary system $SrO-Nb_2O_5$ have been described in detail (Table 1) [1, 2]. $Sr_4Nb_2O_9$ has a perovskite-like structure, as does the neighbour phase $Sr_6Nb_2O_{11}$. The part of the $SrO-Nb_2O_5$ phase diagram between $Sr_4Nb_2O_9$ and $Sr_6Nb_2O_{11}$ has been considered to be a continuous series of solid solutions [3–5]. The composition $Sr_6Nb_2O_{11}$ is the boundary of these solid solutions. However, the existence of a narrow two-phase range, limited to the 1–3 mol% range, has been demonstrated [1, 6, 7].

The kinetics and mechanism of interaction of $SrCO_3(SrO)-Nb_2O_5$ have been investigated in detail [9–14]. It was concluded that the interaction of $SrCO_3(SrO)$ with Nb_2O_5 is a complex and multi-stage process, which at <900°C takes place without the direct decomposition of $SrCO_3$.

Table 1 Structures of the phases in the binary system SrO–Nb₂O₅ [1–7]

Niobates	Structures	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å
Sr ₆ Nb ₂ O ₁₁ (solid solution)	cubic	8.227		
Sr ₄ Nb ₂ O ₉	monoclinic	5.871	5.845	4.121 β=90.52°
Sr ₅ Nb ₄ O ₁₅	hexagonal	5.659		11.495
Sr ₂ Nb ₂ O ₇	orthorhombic	27.18	5.694	3.948
SrNb ₂ O ₆	monoclinic	10.987	7.724	5.595 β=90.38°
Sr ₂ Nb ₁₀ O ₂₇	orthorhombic	12.382	36.97	3.943

The available information concerning the phase equilibria and kinetics of interaction in the ternary systems SrO(SrCO₃)–MO–Nb₂O₅ (*M=d*-metal) is of a fragmentary character [8].

Experimental

The thermal analysis of the binary and ternary systems M'O(M'CO₃)–Nb₂O₅ and M'O(M'CO₃)–MO–Nb₂O₅, where *M'*=Ca, Sr and Ba; and *M*=Cu, Ni, Cd, Zn and Pb, was carried out with a derivatograph Q-1500.

The niobates and solid solutions based on strontium niobates were prepared by solid-state synthesis from the previously annealed extra-pure-grade oxides (Nb₂O₅ – 1200°C; CuO – 600°C; CdO – 500°C; NiO – 900°C; ZnO – 500°C) and SrCO₃ (600°C). Mixtures of definite composition were annealed in aluminum oxide crucibles. The temperature of synthesis was raised stepwise in the range from 600–700°C up to 1100–1500°C. The temperatures and duration of synthesis depended on the nature of the *d*-metal and the composition of the mixture.

The intermediate phases and final products were identified via the X-ray diffraction patterns and the determination of lattice parameters. X-ray diffraction patterns were obtained on DRON-2 and STADI-P (STOE) X-ray diffractometers (CuK_{α1} radiation) with an internal standard (Si, *a*=5.43075 Å) and a Guignet chamber monochromator. Infrared absorption was investigated on a UR-20 spectrometer (1000–400 cm⁻¹). Raman spectra were investigated on a DFS-24 spectrometer, with an LG-38 laser as excitation source.

The kinetic studies on powder mixtures of composition (4–*x*)SrCO₃+*x*MO+ Nb₂O₅ (*x*=0–1) were carried out by using isothermal thermogravimetry (VLR-200 balance and VRT temperature controller).

Results and discussion

The interaction macrokinetics in the ternary systems *x*SrCO₃+*y*MO+Nb₂O₅ were investigated by using isothermal thermogravimetry. The experimental kinetic curves

were interpreted through formal kinetic analysis by the reduced coordinates method [22]. DTA revealed that the temperature of onset of interaction in the ternary mixtures lay in the range 750–850°C. As an example, Fig. 1 illustrates the kinetic interactions in the mixtures $x\text{SrCO}_3+y\text{MO}+z\text{Nb}_2\text{O}_5$ at 800°C.

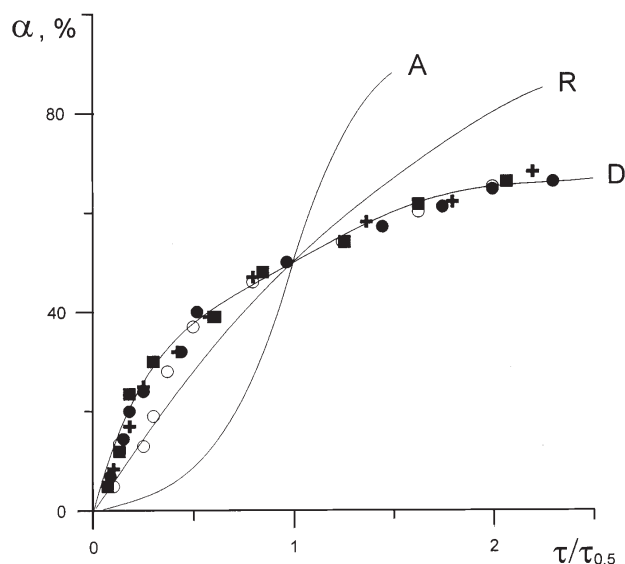
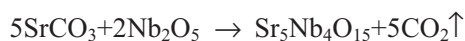


Fig. 1 Kinetic curves for mixtures $x\text{SrCO}_3+y\text{NiO}+z\text{Nb}_2\text{O}_5$ at $t=800^\circ\text{C}$:
 o – $4\text{SrCO}_3+\text{Nb}_2\text{O}_5$; + – $3.9\text{SrCO}_3+0.1\text{NiO}+\text{Nb}_2\text{O}_5$; ■ – $3.5\text{SrCO}_3+0.5\text{NiO}+\text{Nb}_2\text{O}_5$; ● – $3\text{SrCO}_3+\text{NiO}+\text{Nb}_2\text{O}_5$; The lines represent kinetic curves calculated on the assumption that the rate-limiting step is A – nucleation, R – direct chemical interaction, D – diffusion through the layer of reaction products (Ginstling-Brownstein model)

An analysis of the experimental data with respect to the conditions and the kinetic regularities in the mixtures of different compositions allowed the following conclusions:

1. The possible intermediate of the interaction is the phase $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ or the solid solution $(\text{Sr}_{1-x}\text{M}_x)_5\text{Nb}_4\text{O}_{15}$ based on it. Accordingly, we may express the process of interaction in the reaction mixtures $(4-x)\text{SrCO}_3+x\text{MO}+\text{Nb}_2\text{O}_5$ by the following scheme:



where $M=\text{Cd, Cu, Ni}$ or Zn .

The X-ray diffraction results and kinetic data for the binary mixtures confirm this scheme. The data indicated either the absence of interaction (SrCO_3+ZnO and SrCO_3+NiO) at 750–850°C, or a not very considerable interaction: the mixtures $\text{SrCO}_3+\text{TiO}_2$ and SrCO_3+CuO .

The extents of transformation and other kinetic parameters are slightly different (Table 2) for the ternary mixtures and the binary mixture $4\text{SrCO}_3+\text{Nb}_2\text{O}_5$. The similarity of the kinetic curves confirms the common nature of the intermediate phase in the ternary mixtures and the binary mixture [26]. Earlier [25], we calculated the Gibbs energy (ΔG_{298}°) for the formation of the individual strontium niobates. These thermodynamic data demonstrate the preference of formation of $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ or solid solutions based on it in the reaction mixture $\text{SrCO}_3+\text{CuO}+\text{Nb}_2\text{O}_5$.

Table 2 Kinetic parameters of interactions in mixtures $\text{SrCO}_3\text{--MO--Nb}_2\text{O}_5$ ($M=\text{Cu, Cd, Ni, Zn}$)

No.	Composition of mixture	$t/^\circ\text{C}$	α_{max}	Regime of process	$E_a \pm 10/\text{kJ mol}^{-1}$
1	$4\text{SrCO}_3\text{--Nb}_2\text{O}_5$	750	0.45	to $\alpha=0.25$ – DCI	76
		800	0.61	$\alpha>0.25$ – G-B	
		850	0.81	G-B	
2	$3.9\text{SrCO}_3\text{--}0.1\text{ZnO--Nb}_2\text{O}_5$	750	0.48	to $\alpha=0.25$ – DCI	93
		800	0.63	$\alpha>0.25$ – G-B	
		850	0.82	G-B	
3	$3.5\text{SrCO}_3\text{--}0.5\text{ZnO--Nb}_2\text{O}_5$	750	0.40	to $\alpha=0.1$ – DCI	95
		800	0.59	$\alpha>0.1$ – G-B	
		850	0.80	G-B	
4	$3\text{SrCO}_3\text{--ZnO--Nb}_2\text{O}_5$	750	0.39	to $\alpha=0.08$ – DCI	98
		800	0.57	$\alpha>0.08$ – G-B	
		850	0.78	G-B	
5	$3.9\text{SrCO}_3\text{--}0.1\text{NiO--Nb}_2\text{O}_5$	750	0.47	to $\alpha=0.2$ – DCI	84
		800	0.62	$\alpha>0.2$ – G-B	
		850	0.85	G-B	
6	$3.5\text{SrCO}_3\text{--}0.5\text{NiO--Nb}_2\text{O}_5$	750	0.41	to $\alpha=0.15$ – DCI	86
		800	0.59	$\alpha>0.15$ – G-B	
		850	0.79	G-B	
7	$3\text{SrCO}_3\text{--NiO--Nb}_2\text{O}_5$	750	0.34	to $\alpha=0.08$ – DCI	87
		800	0.57	$\alpha>0.08$ – G-B	
		850	0.73	G-B	
8	$3.9\text{SrCO}_3\text{--}0.1\text{CuO--Nb}_2\text{O}_5$	750	0.40	to $\alpha=0.05$ – DCI	93
		800	0.57	$\alpha>0.05$ – G-B	
		850	0.79	G-B	

Table 2 Continued

No.	Composition of mixture	$t/^\circ\text{C}$	α_{\max}	Regime of process	$E_a \pm 10/\text{kJ mol}^{-1}$
9	3.5SrCO ₃ -0.5CuO-Nb ₂ O ₅	750	0.47	to $\alpha=0.05$ – DCI	94
		800	0.64	$\alpha>0.05$ – G-B	
		850	0.85	G-B	
10	3SrCO ₃ -CuO-Nb ₂ O ₅	750	0.49	to $\alpha=0.05$ – DCI	98
		800	0.65	$\alpha>0.05$ – G-B	
		850	0.87	G-B	
11	3.9SrCO ₃ -0.1CdO-Nb ₂ O ₅	750	0.42	to $\alpha=0.25$ – DCI	87
		800	0.57	$\alpha>0.25$ – G-B	
		850	0.79	G-B	
12	3.5SrCO ₃ -0.5CdO-Nb ₂ O ₅	750	0.50	to $\alpha=0.2$ – DCI	95
		800	0.65	$\alpha>0.2$ – G-B	
		850	0.84	G-B	
13	3SrCO ₃ -CdO-Nb ₂ O ₅	750	0.53	to $\alpha=0.2$ – DCI	101
		800	0.71	$\alpha>0.2$ – G-B	
		850	0.90	G-B	

2. The main characteristic of the macrokinetics in the investigated powder mixtures is the existence of undiffusion regions of direct chemical interaction (DCI) in the first stage. The diffusion region reactions (Fig. 1) were satisfactorily described by the Ginstling-Brownstein (G-B) equation [22]:

$$D_2(\alpha) = \left[1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} \right] = \frac{2k\tau}{r_B^2} = k_{G-B}\tau$$

where τ – time/s; α – extent of transformation, and r_B – radius of grain of B, cm.

The radiometric analysis data indicate that the mechanism of cation mass-transfer in these solid solutions occurs mainly through the octahedral positions.

3. For all mixtures, similar values of activation energy were obtained, which confirms the general mechanism of interaction and the single nature of the intermediates (Table 2). These data also agree as concerns the diffusion regime of interaction.

4. The addition of CuO and CdO to the reaction mixtures resulted in some increase in the degree of transformation, whereas the addition of NiO and ZnO resulted in a decrease. This is connected with the possibility of interaction MO+SrCO₃ (M =Cd or Cu) in the binary mixtures, and with the absolute absence of interaction in mixtures containing NiO and ZnO in the temperature range 750–850°C.

The boundaries of stability of the solid solutions based on the niobates Sr₂Nb₂O₇, Sr₄Nb₂O₉ and Sr₆Nb₂O₁₁ have been established. The solid solutions (Sr_{1-x}M_x)₂Nb₂O₇ (M =Ba, Ca, Cd and Pb) with the lamellar perovskite structure were studied by X-ray dif-

fraction, and by IR and Raman spectroscopy. The results are given in Table 3 and Fig. 2. Change of the value of x from 0.30 to 0.35 for the solid solutions $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Nb}_2\text{O}_7$ causes the occurrence of a new band with $\nu=300\text{ cm}^{-1}$, and change of the value of x to 0.40 results in the supplementary band with $\nu=805\text{ cm}^{-1}$.

The X-ray diffraction data reveal that, for $\text{Sr}_4\text{Nb}_2\text{O}_9$ - $'\text{M}_4\text{Nb}_2\text{O}_9'$ ($M=\text{Cd}, \text{Cu}, \text{Ni}$ and Zn) and $\text{Sr}_6\text{Nb}_2\text{O}_{11}$ - $'\text{M}_6\text{Nb}_2\text{O}_{11}'$ ($M=\text{Cd}$ and Zn), systems of solid solutions with perovskite-like structure are formed, with a double lattice parameter (a) of the cubic face-centred unit cell. The compositions and the widths of the homogeneity range of solid solutions are given in Table 4.

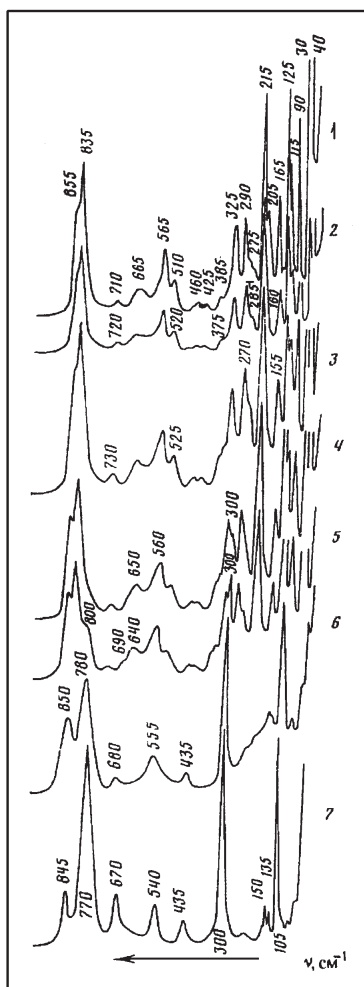


Fig. 2 Raman spectra of solid solution $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Nb}_2\text{O}_7$ where $x=0$ (1); 0.2 (2); 0.3 (3); 0.35 (4); 0.45 (5); 0.70 (6); $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (7)

Table 3 Solid solutions in the systems $\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}M_2\text{Nb}_2\text{O}_7$ ($M=\text{Ba, Ca, Zn, Cd, Pb, Cu}$)

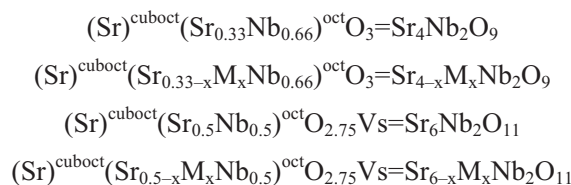
System	Investigated composition/mol%	Solid solution $(\text{Sr}_{1-x}M_x)_2\text{Nb}_2\text{O}_7$	Phases on boundaries
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Ba}_2\text{Nb}_2\text{O}_7'$	0–90, step=5	$0 \leq x \leq 0.35$	$(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Nb}_2\text{O}_7$ $\text{Ba}_5\text{Nb}_4\text{O}_{15}$
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Ca}_2\text{Nb}_2\text{O}_7'$	0–100, step=5–10	$0 \leq x \leq 1.00$	$\text{Ca}_2\text{Nb}_2\text{O}_7$
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Zn}_2\text{Nb}_2\text{O}_7'$	0–50, step=5	$0 \leq x \leq 0.25$	$(\text{Sr}_{1-x}\text{Zn}_x)_2\text{Nb}_2\text{O}_7$ ZnO
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Cd}_2\text{Nb}_2\text{O}_7'$	0–100, step=5–10	$0 \leq x \leq 0.30$	$(\text{Sr}_{1-x}\text{Cd}_x)_2\text{Nb}_2\text{O}_7$ $\text{Cd}_2\text{Nb}_2\text{O}_7$
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Cu}_2\text{Nb}_2\text{O}_7'$	0–100, step=5–10	$0 \leq x \leq 0.20$	$(\text{Sr}_{1-x}\text{Cu}_x)_2\text{Nb}_2\text{O}_7$ $\text{CuO, Nb}_2\text{O}_5$
$\text{Sr}_2\text{Nb}_2\text{O}_7\text{--}'\text{Pb}_2\text{Nb}_2\text{O}_7'$	0–50, step=5	$0 \leq x \leq 0.40$	$(\text{Sr}_{1-x}\text{Pb}_x)_2\text{Nb}_2\text{O}_7$ $\text{Pb}_2\text{Nb}_2\text{O}_7$ (pyrochlore)

Table 4 Solid solutions in the systems $\text{SrO--MO--Nb}_2\text{O}_5$ ($M=\text{Cd, Cu, Ni, Zn}$)

System	Investigated composition/mol%	Solid solutions	Width of homogeneity range
$\text{Sr}_4\text{Nb}_2\text{O}_9\text{--}'\text{Cu}_4\text{Nb}_2\text{O}_9'$	0–25	$(\text{Sr}_{1-x}\text{Cu}_x)_4\text{Nb}_2\text{O}_9$	$0 \leq x \leq 0.25$
$\text{Sr}_4\text{Nb}_2\text{O}_9\text{--}'\text{Zn}_4\text{Nb}_2\text{O}_9'$	0–37	$(\text{Sr}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$	$0 \leq x \leq 0.25$
$\text{Sr}_4\text{Nb}_2\text{O}_9\text{--}'\text{Cd}_4\text{Nb}_2\text{O}_9'$	0–25	$(\text{Sr}_{1-x}\text{Cd}_x)_4\text{Nb}_2\text{O}_9$	$0 \leq x \leq 0.25$
$\text{Sr}_4\text{Nb}_2\text{O}_9\text{--}'\text{Ni}_4\text{Nb}_2\text{O}_9'$	0–25	$(\text{Sr}_{1-x}\text{Ni}_x)_4\text{Nb}_2\text{O}_9$	$0 \leq x \leq 0.25$
$\text{Sr}_6\text{Nb}_2\text{O}_{11}\text{--}'\text{Cd}_6\text{Nb}_2\text{O}_{11}'$	0–33	$\text{Sr}_{6-x}\text{Cd}_x\text{Nb}_2\text{O}_{11}$	$0 \leq x \leq 2$
$\text{Sr}_6\text{Nb}_2\text{O}_{11}\text{--}'\text{Zn}_6\text{Nb}_2\text{O}_{11}'$	0–33	$\text{Sr}_{6-x}\text{Zn}_x\text{Nb}_2\text{O}_{11}$	$0 \leq x \leq 0.50$

There is no common opinion relating to the type of unit cell (cubic or monoclinic) for the phase $\text{Sr}_4\text{Nb}_2\text{O}_9$ [1, 3–7]. In the present paper, X-ray diffraction shows that stabilization of the cubic structure occurs when the octahedrally (*oct*) coordinated strontium is substituted by an ion with smaller radius (*d*-metal).

The boundary composition of the solid solutions $\text{Sr}_{4-x}M_x\text{Nb}_2\text{O}_9$ and $\text{Sr}_{6-x}M_x\text{Nb}_2\text{O}_{11}$ corresponds to the complete substitution of strontium in octahedral positions by a *d*-metal. The substitution of strontium does not occur in the cubic-octahedral (*cuboct*) position [1]. This mechanism is illustrated as follows:



Exceptions from the given patterns are the solid solutions $\text{Sr}_{4-x}\text{Ni}_x\text{Nb}_2\text{O}_9$ and $\text{Sr}_{6-x}\text{Zn}_x\text{Nb}_2\text{O}_{11}$, for which the homogeneity ranges are narrower than the predicted

ranges. The formation of solid solutions in these systems was accompanied by decreases in the lattice parameters, which is obviously connected with the smaller ionic radius of the incoming *d*-metal ion as compared with that of Sr^{2+} ($r(\text{Sr}^{2+})(\text{c.n.6}) = 1.18 \text{ \AA}$) [16]. For example, for the solid solution $\text{Sr}_{4-x}\text{Cd}_x\text{Nb}_2\text{O}_9$ *a* can be described by the following equation:

$$a = 8.2690 - 0.1085x \text{ (\AA)}$$

The tolerance factor (*t*) is the most essential crystal-chemical parameter determining whether a structure is of a definite type. *t* was assumed by Goldsmidt [13] and was studied in detail for the perovskite structure [18–21]. The possible range of values of *t* is $0.8 \leq t \leq 1.05$. According to the data [19], the tolerance factor lies between 0.72 and 1.06 for the perovskite-like structure with the cubic unit cell.

The values of *t* were calculated by using Shannon's ionic radii [16] according to the equation

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

where R_A is the ionic radius of the atom in the *A*-sublattice of the ABO_3 structure (cubic-octahedral coordination); R_B is the ionic radius of the atom in the *B*-sublattice of the ABO_3 structure (octahedral coordination); and R_O is the ionic radius of oxygen.

Apart from the dimension parameter, we use an energy criterion, which includes the electronic structure of the atoms and the bond character. The values of comparative electronegativities of atoms $\bar{\chi}_A/\bar{\chi}_B$ were earlier used for the analysis of the region of existence of the $\text{A}_2\text{B}_2\text{O}_7$ phases (pyrochlore, fluorite and layered perovskite) [23, 24]. In [25], the region of existence of the perovskite-related phases for the criterion $\bar{\chi}_A/\bar{\chi}_B > 0.72$ was indicated.

We have attempted to unite both criteria by plotting diagrams of $\bar{\chi}_A/\bar{\chi}_B$ vs. *t*. The range of values of $\bar{\chi}_A/\bar{\chi}_B$ and *t* for the solid solutions in question, $\text{Sr}_{4-x}\text{M}_x\text{Nb}_2\text{O}_9$ and $\text{Sr}_{6-x}\text{M}_x\text{Nb}_2\text{O}_{11}$, are given in Table 5.

Table 5 Values of *t* factor and $\bar{\chi}_A/\bar{\chi}_B$ for solid solutions $(\text{Sr}_{1-x}\text{M}_x)_4\text{Nb}_2\text{O}_9$ and $(\text{Sr}_{1-x}\text{M}_x)_6\text{Nb}_2\text{O}_{11}$

Composition	Range of <i>t</i> -factor	Range of $\bar{\chi}_A/\bar{\chi}_B$
$(\text{Sr}_{1-x}\text{Cu}_x)_4\text{Nb}_2\text{O}_9$	0.909–0.968	0.71–0.84
$(\text{Sr}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$	0.909–0.966	0.72–0.84
$(\text{Sr}_{1-x}\text{Cd}_x)_4\text{Nb}_2\text{O}_9$	0.906–0.935	0.79–0.85
$(\text{Sr}_{1-x}\text{Ni}_x)_4\text{Nb}_2\text{O}_9$	0.903–0.974	0.71–0.86
$\text{Sr}_{6-x}\text{Cd}_x\text{Nb}_2\text{O}_{11}$	0.888–0.924	0.74–0.85
$\text{Sr}_{6-x}\text{Zn}_x\text{Nb}_2\text{O}_{11}$	0.898–0.973	0.69–0.83

The phase fields of existence of the solid solutions are illustrated in Figs 3 and 4. The theoretical predictions for all compositions of the Cd-containing solid solutions are in full agreement with the experimental data, e.g. the range of the homogeneity re-

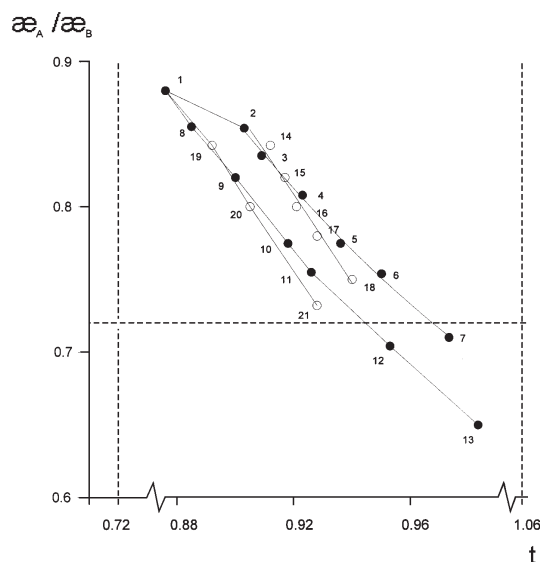


Fig. 3 Region of existence of solid solutions: $\text{Sr}_{4-x}\text{Cd}_x\text{Nb}_2\text{O}_9$, $\text{Sr}_{6-x}\text{Cd}_x\text{Nb}_2\text{O}_{11}$, $\text{Sr}_{4-x}\text{Ni}_x\text{Nb}_2\text{O}_9$, $\text{Sr}_{6-x}\text{Ni}_x\text{Nb}_2\text{O}_{11}$: 1 – $\text{Sr}_6\text{Nb}_2\text{O}_{11}$; 2 – $\text{Sr}_4\text{Nb}_2\text{O}_9$; 3 – $\text{Sr}_{3.9}\text{Ni}_{0.1}\text{Nb}_2\text{O}_9$; 4 – $\text{Sr}_{3.7}\text{Ni}_{0.3}\text{Nb}_2\text{O}_9$; 5 – $\text{Sr}_{3.5}\text{Ni}_{0.5}\text{Nb}_2\text{O}_9$; 6 – $\text{Sr}_{3.3}\text{Ni}_{0.7}\text{Nb}_2\text{O}_9$; 7 – $\text{Sr}_3\text{NiNb}_2\text{O}_9$; 8 – $\text{Sr}_{5.8}\text{Ni}_{0.2}\text{Nb}_2\text{O}_{11}$; 9 – $\text{Sr}_{5.5}\text{Ni}_{0.5}\text{Nb}_2\text{O}_{11}$; 10 – $\text{Sr}_{5.2}\text{Ni}_{0.8}\text{Nb}_2\text{O}_{11}$; 11 – $\text{Sr}_5\text{NiNb}_2\text{O}_{11}$; 12 – $\text{Sr}_{4.5}\text{Ni}_{1.5}\text{Nb}_2\text{O}_{11}$; 13 – $\text{Sr}_4\text{Ni}_2\text{Nb}_2\text{O}_{11}$; 14 – $\text{Sr}_{3.9}\text{Cd}_{0.1}\text{Nb}_2\text{O}_9$; 15 – $\text{Sr}_{3.7}\text{Cd}_{0.3}\text{Nb}_2\text{O}_9$; 16 – $\text{Sr}_{3.5}\text{Cd}_{0.5}\text{Nb}_2\text{O}_9$; 17 – $\text{Sr}_{3.3}\text{Cd}_{0.7}\text{Nb}_2\text{O}_9$; 18 – $\text{Sr}_3\text{CdNb}_2\text{O}_9$; 19 – $\text{Sr}_{5.5}\text{Cd}_{0.5}\text{Nb}_2\text{O}_{11}$; 20 – $\text{Sr}_5\text{CdNb}_2\text{O}_{11}$; 21 – $\text{Sr}_4\text{Cd}_2\text{Nb}_2\text{O}_{11}$

region is within the permitted boundaries both for the tolerance factor and for the criterion of electronegativity.

The theoretical estimation of the phase fields for the Ni-containing solid solutions is likewise in good agreement with the experimental results. The multi-phase composition ‘ $\text{Sr}_3\text{NiNb}_2\text{O}_9$ ’ lies outside the range for cubic perovskite.

The composition $\text{Sr}_3\text{CuNb}_2\text{O}_9$ for the Cu-containing solid solutions does not fall within the range for cubic perovskite. In fact, such a phase was obtained as the phase with the tetrahedral unit cell. Therefore, the range of comparative electronegativity for the perovskite-like structures with lower symmetry of the unit cell must be wider, as for the t criterion. The compositions ‘ $\text{Sr}_{4.5}\text{Cu}_{1.5}\text{Nb}_2\text{O}_{11}$ ’ and ‘ $\text{Sr}_4\text{Cu}_2\text{Nb}_2\text{O}_{11}$ ’ do not fall within the permitted range of the tolerance factor, because they do not satisfy the conditions, which is in full agreement with earlier experimental results [25].

For the Zn-containing solid solutions, full analogy with the system ‘ $\text{Sr}_4\text{Nb}_2\text{O}_9$ – $\text{Cu}_4\text{Nb}_2\text{O}_9$ ’ was observed. The compositions with $x \geq 1$ do not fall within the homogeneity range for the solid solution $\text{Sr}_{6-x}\text{Zn}_x\text{Nb}_2\text{O}_{11}$, as the compositions with $x \geq 2$ lie outside the theoretical calculated range with respect to the t and $\bar{\chi}_A / \bar{\chi}_B$ criteria.

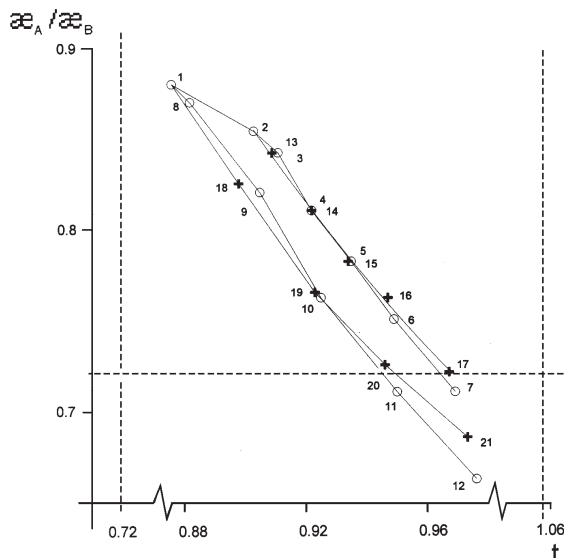


Fig. 4 Region of existence of solid solutions: $\text{Sr}_{4-x}\text{Cu}_x\text{Nb}_2\text{O}_9$, $\text{Sr}_{6-x}\text{Cu}_x\text{Nb}_2\text{O}_{11}$, $\text{Sr}_{4-x}\text{Zn}_x\text{Nb}_2\text{O}_9$, $\text{Sr}_{6-x}\text{Zn}_x\text{Nb}_2\text{O}_{11}$: 1 – $\text{Sr}_6\text{Nb}_2\text{O}_{11}$; 2 – $\text{Sr}_4\text{Nb}_2\text{O}_9$; 3 – $\text{Sr}_{3.9}\text{Cu}_{0.1}\text{Nb}_2\text{O}_9$; 4 – $\text{Sr}_{3.7}\text{Cu}_{0.3}\text{Nb}_2\text{O}_9$; 5 – $\text{Sr}_{3.5}\text{Cu}_{0.5}\text{Nb}_2\text{O}_9$; 6 – $\text{Sr}_{3.3}\text{Cu}_{0.7}\text{Nb}_2\text{O}_9$; 7 – $\text{Sr}_3\text{CuNb}_2\text{O}_9$; 8 – $\text{Sr}_{5.9}\text{Cu}_{0.1}\text{Nb}_2\text{O}_{11}$; 9 – $\text{Sr}_{5.5}\text{Cu}_{0.5}\text{Nb}_2\text{O}_{11}$; 10 – $\text{Sr}_5\text{CuNb}_2\text{O}_{11}$; 11 – $\text{Sr}_{4.5}\text{Cu}_{1.5}\text{Nb}_2\text{O}_{11}$; 12 – $\text{Sr}_4\text{Cu}_2\text{Nb}_2\text{O}_{11}$; 13 – $\text{Sr}_{3.9}\text{Zn}_{0.1}\text{Nb}_2\text{O}_9$; 14 – $\text{Sr}_{3.7}\text{Zn}_{0.3}\text{Nb}_2\text{O}_9$; 15 – $\text{Sr}_{3.5}\text{Zn}_{0.5}\text{Nb}_2\text{O}_9$; 16 – $\text{Sr}_{3.3}\text{Zn}_{0.7}\text{Nb}_2\text{O}_9$; 17 – $\text{Sr}_3\text{ZnNb}_2\text{O}_9$; 18 – $\text{Sr}_{5.5}\text{Zn}_{0.5}\text{Nb}_2\text{O}_{11}$; 19 – $\text{Sr}_5\text{ZnNb}_2\text{O}_{11}$; 20 – $\text{Sr}_{4.5}\text{Zn}_{1.5}\text{Nb}_2\text{O}_{11}$; 21 – $\text{Sr}_4\text{Zn}_2\text{Nb}_2\text{O}_{11}$

Thus, the suggested theoretical estimation of the possibility of formation of solid solutions allows prediction of the homogeneity ranges for other solid solutions on the basis of a phase with a perovskite-related structure.

Conclusions

The regularities of synthesis of the individual niobates ($x=0$) and their solid solutions were studied by thermal analysis. The single nature of intermediates based on the phase $(\text{Sr}_{1-x}\text{M}_x)_5\text{Nb}_4\text{O}_{15}$ in the powder mixtures was demonstrated. The behaviour of the solid-state interactions and the main kinetic parameters (α – extent of transformation and E – activation energy) were established.

The boundaries of stability of the solid solutions $\text{Sr}_{2-x}\text{Me}_x\text{Nb}_2\text{O}_7$, $\text{Sr}_{2-x}\text{M}_x\text{Nb}_2\text{O}_7$, $\text{Sr}_{4-x}\text{M}_x\text{Nb}_2\text{O}_9$ and $\text{Sr}_{6-x}\text{M}_x\text{Nb}_2\text{O}_{11}$ were determined by means of X-ray diffraction, IR spectroscopy and Raman spectroscopy. The possibility of prognostication of the phase fields of stable solid solutions with the perovskite-like structure by calculation from the diagrams comparative electronegativity of atoms vs. tolerance factor was revealed. The substitution of strontium by a *d*-metal ion in this structure appeared to oc-

cur through the octahedral positions. The general regularities of interaction in the binary compounds and solid solutions were established.

* * *

This work was supported by Grant 98-03-32538 from the Russian Fundamental Research Foundation.

References

- 1 P. P. Leschenko, Ph.D. Thesis, Moscow State University (1981) (in Russian).
- 2 P. Appendino and A. Burlando, *Atti Acad. delle Science, Torino*, 107 (1973) 98.
- 3 J. Lecomte, J. P. Loup, M. Hervieu and B. Raveau, *Phys. Stat. Sol. A65* (1981) 743.
- 4 J. Lecomte, J. P. Loup, M. Hervieu and B. Raveau, *Phys. Stat. Sol. A66* (1981) 551.
- 5 J. Lecomte, J. P. Loup, M. Hervieu and B. Raveau, *Phys. Stat. Sol. A69* (1982) 359.
- 6 V. I. Spizyn, E. A. Ippolitova, L. M. Kovba, L. N. Lykoba and P. P. Leschenko, *J. Inorg. Chem.*, 27 (1982) 827 (in Russian).
- 7 P. P. Leschenko, L. N. Lykoba, L. M. Kovba and E. A. Ippolitova, *J. Inorg. Chem.*, 27 (1982) 1285 (in Russian).
- 8 F. Gallasso and J. J. Pyle, *Phys. Chem.*, 67 (1963) 1560.
- 9 A. L. Podkorytov, Ph.D. Thesis, Ural State University (1984) (in Russian).
- 10 A. Ya. Neiman, A. L. Podkorytov, A. A. Ostroushko and L. A. Kotok, *Inorg. Mater.*, 19 (1983) 648 (in Russian).
- 11 K. W. Browall, O. Muller and R. H. Doremus, *Mat. Res. Bull.*, 11 (1976) 1475.
- 12 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, 25 (1969) 925.
- 13 V. M. Goldsmidt, *Geochem. vert. Elem. V, VII, VIII.* (1927) p. 140
- 14 E. G. Fesenko and A. T. Shuvaev, *News of Academy of Sciences of USSR, Part physical.*, 33 (1969) 1133 (in Russian).
- 15 E. G. Fesenko, V. S. Filip'ev and M. F. Kupriyanov, *News of Academy of Sciences of USSR, Part. physical.*, 31 (1967) 1790 (in Russian).
- 16 Yu. P. Vorob'yov, A. N. Men and V. B. Fetisov, *Calculation and prediction of properties of oxide*, Science Moscow (1983) p. 283 (in Russian).
- 17 Yu. N. Venevzev and A. T. Kapsyshev, *News of Academy of Sciences of USSR, Part physical.*, 33 (1969) 1206 (in Russian).
- 18 V. V. Garbuz, A. M. Sych and Yu. A. Titov, *Proc. of the II All-Union Conference of physical-chemical foundations of technology of ferroelectric and related materials*, Zvenigorod (1983) 30 (in Russian).
- 19 S. S. Lopatin, I. N. Belyaev and L. N. Aver'yanova, *Proc. of the II All-Union Conference of physical-chemical foundations of technology of ferroelectric and related materials*, Zvenigorod (1983) 25 (in Russian).
- 20 I. E. Animitsa, Ph.D. Thesis, Ural State University 1991 (in Russian).
- 21 A. L. Podkorytov, V. M. Zhukovsky and S. V. Avdon'kina, *Inorg. Mater.*, 27 (1991) 2606 (in Russian).
- 22 B. Delmon, *Introduction à la cinétique hétérogène*, Technip, Paris 1969 (in French).
- 23 A. L. Podkorytov, M. I. Pantyukhina, V. M. Zhukovsky, N. V. Sherstnyova and V. V. Simonov, *Inorg. Mater.*, 32 (1996) 95 (in Russian).

- 24 A. Ya. Neiman, A. L. Podkorytov, I. E. Animitsa, A. S. Zhukovsky and V. M. Zhukovsky, *J. Inorg. Chem.*, 32 (1987) 359 (in Russian).
- 25 A. L. Podkorytov, V. M. Zhukovsky, P. A. Hatypova and T. O. Andryeva, *Melts*, 5 (1994) 67 (in Russian).
- 26 A. Ya. Neiman, A. L. Podkorytov and V. M. Zhukovsky, IV Intern. Conf. of Solid State Ionics, Grenoble (France) (1983) 32.