SORPTION
AND ION EXCHANGE PROCESSES

Sorption of Strontium Ions on Potassium-Titanate Nanoparticles of Various Morphology Obtained under Hydrothermal Conditions

O. Yu. Sinelshchikova[a,*], T. P. Maslennikova[a,**], N. V. Besprozvannykh[a], and E. N. Gatina[a]

[a] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, 199034 Russia*
e-mail: *sinelshikova@mail.ru, **maslennikova.tp@iscras.ru

Abstract—The results of the study of the interaction of an aqueous solution of strontium nitrate with potassium–titanate nanoparticles of different morphology obtained by the hydrothermal method are reported. Comparative analysis showed the advantage of nanotubes as sorbents over nanolayers and nanowires. As can be seen from the experiment conducted with nanotubes containing aluminum, an amount of strontium sorbed from the solution rises with increasing temperature: at 50°C the absorption by the tubular matrix was $\sim 0.76 \times 10^{-3}$ mol g^{-1}, and at 80°C that was $\sim 2.02 \times 10^{-3}$ mol g^{-1}. Nanotube samples doped with magnesium had the best sorption characteristics: After 5 h of keeping in a solution at 80°C, the content of strontium in them was $\sim 3.65 \times 10^{-3}$ mol g^{-1}. The results show the promise of using potassium titanate nanoparticles to extract strontium from aqueous solutions.

Keywords: potassium titanates, nanoparticles, morphology, hydrothermal synthesis, sorption of strontium ions

DOI: 10.1134/S1070427219040116

The removal of heavy metals from aqueous solutions obtained as a result of reprocessing of spent nuclear fuel and such industrial processes as the production of textiles, paper, paints, batteries, etc., is a topical problem [1]. Over the past two decades, numerous studies have shown some prospects for the use of layered alkali metal titanates as ion exchangers for extracting and converting radioactive waste into a solid fraction, as well as for separating some cations [2]. In particular, potassium titanates exhibit intense adsorption properties with respect to ions Sr^{2+} [3], Hg^{2+}, Ba^{2+}, Cd^{2+} [2, 4, 5], Pb^{2+}, and Ni^{2+} [6]. In [7], it was found that by replacing K^{+} ions in potassium tetratitanate (K$_2$T$_4$O$_9$) with protons, layered H$_2$Ti$_4$O$_9 \cdot n$H$_2$O is obtained. This compound has a large ion-exchange capacity with respect to ions of alkali, alkaline earth, and bivalent transition metals.

Thus, the available data on the study of layered alkali metal titanates allow suggesting their high efficiency as adsorbents. The advantage of the above compounds is that they do not pose a danger of secondary pollution: the adsorbed cations, being embedded in the interlayer space, change its configuration, which prevents their release [8]. This property of titanates is especially valuable when isolating radionuclides from polluted solutions, which makes it possible to obtain powders that are convenient for long-term storage, processing or disposal.

The purpose of the work was the hydrothermal synthesis of nanoparticles based on potassium polytitanates K$_2$Ti$_n$O$_{2n+1}$ doped with ions of different valences, and the study of the influence of their composition and morphology on the sorption characteristics with respect to Sr^{2+} ions.

EXPERIMENTAL

Synthesis of potassium-titanate K$_2$Ti$_n$O$_{2n+1}$ nanoparticles doped with aluminum, iron, chromium, nickel, and magnesium ions was carried out as follows. To obtain initial mixtures, hydroxides were co-deposited with NH$_4$OH from aqueous solutions of titanyl chloride
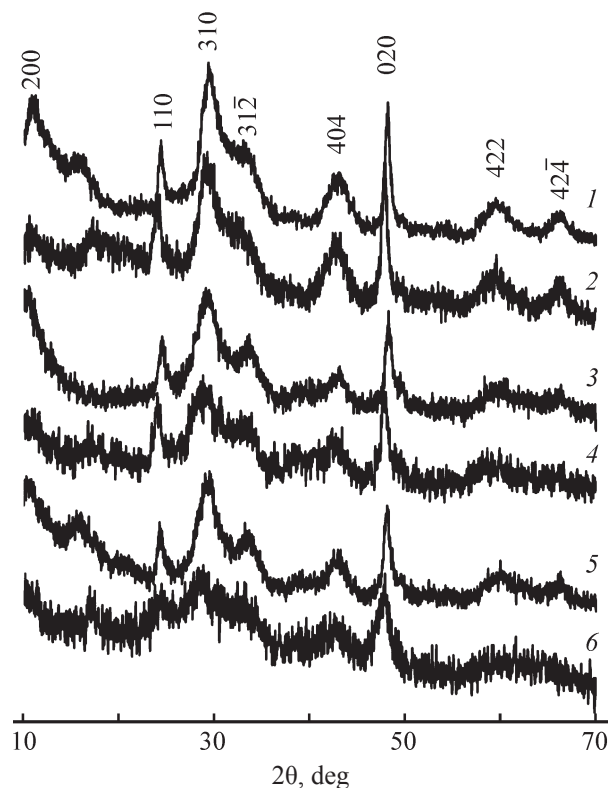
Fig. 1. X-ray diffraction patterns of nanoparticles obtained by hydrothermal treatment of (*1, 3, 5*) initial mixtures of the composition 0.95 TiO_2 : 0.05 MeO (Me_2O_3) in 10 M KOH solution for 24 h, as well as (*2, 4, 6*) products of their interaction with 0.1 M $Sr(NO_3)_2$ solution within 5 h, where Me = (*1, 2*) Al, (*3, 4*) Fe, (*5, 6*) Cr. The *hkl* indices are given according to [11].

($TiOCl_2$) and salts of doping elements—$Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $NiCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$. To produce $TiOCl_2$, $TiCl_4$ was dissolved in chilled distilled water, therewith a ratio of titanium chloride and water was 1 : 5 by volume. The content of titanium oxide in the resulting solution was controlled by weight analysis. A ratio of salts was chosen so that the content of the doping component was 5 mol % in the term of the corresponding oxides. Deposition was carried out at pH ~ 9, after which the resulting precipitates were thoroughly washed from soluble impurities with distilled water until a negative reaction to chlorine ions was achieved. Before the hydrothermal treatment, the obtained initial mixtures were dried at *T* = 100°C for 3 h and mechanically ground. Hydrothermal treatment of the samples was performed in the temperature range of 170–180°C in 10 M KOH solution for 24 h. The ratio of air-dry powder and alkaline solution was 1 g per 10 mL of solution, the volume of the resulting suspension was

chosen so that the degree of filling of the autoclaves was equal to 80% of the internal volume. For the synthesis autoclaves with Teflon liners were used. After the hydrothermal treatment, the samples were washed with distilled water until neutrality was reached, after which the resulting powders were dried at 100°C.

For sorption of strontium ions, the weighed sample of nanoparticles (0.1 g) was poured with 10 mL of 0.1 M $Sr(NO_3)_2$ solution, then placed in a thermostat and kept at 50 or 80°C from 1 to 5 h. After keeping at a given temperature, the solution was separated from the nanotubes by filtration through a double blue ribbon filter with four washing with distilled water. The content of strontium in the resulting plums was determined by the gravimetric method [9], for which purpose it was precipitated as carbonate by adding 0.1 M solution of $(NH_4)_2CO_3$ in the presence of ammonia. The precipitate was transferred to an ashless filter and calcined at *T* = 1000°C until a constant weight was reached to determine the SrO content.

The phase composition of the samples at various stages of the synthesis was determined by powder X-ray diffraction patterns (DRON-3 diffractometer, CuK_α radiation). Data processing and peak identification were performed using the DifWin 4.0 software package and the ICDD PDF-2 database. The shape and size of the nanoparticles were taken using high resolution transmission electron microscopy on a JEOL-2100F electron microscope at an accelerating voltage of 200 kV (wavelength 0.025 Å), and the elemental composition was simultaneously determined (an Oxford Instruments INCA attachment for energy dispersive X-ray microanalysis). To determine the specific surface, the method of low-temperature nitrogen adsorption (BET, gas analyzer Quantochrome, Nova-1200e) was used. The effective diameter of the agglomerates and the ζ-potential of the obtained nanoparticles were defined in aqueous suspension using the method of dynamic light scattering (NanoBrook 90 Plus Zeta); before measuring, the powders were dispersed in water by ultrasound for 40 min.

RESULTS AND DISCUSSIONS

Under hydrothermal conditions based on the composition, nanotubes, nanosheets, or nanowires crystallize from hydroxide precipitated (see the table, Figs. 1, 2). The results of the microprobe analysis (EDX) [10] confirmed the uniform distribution of the doping
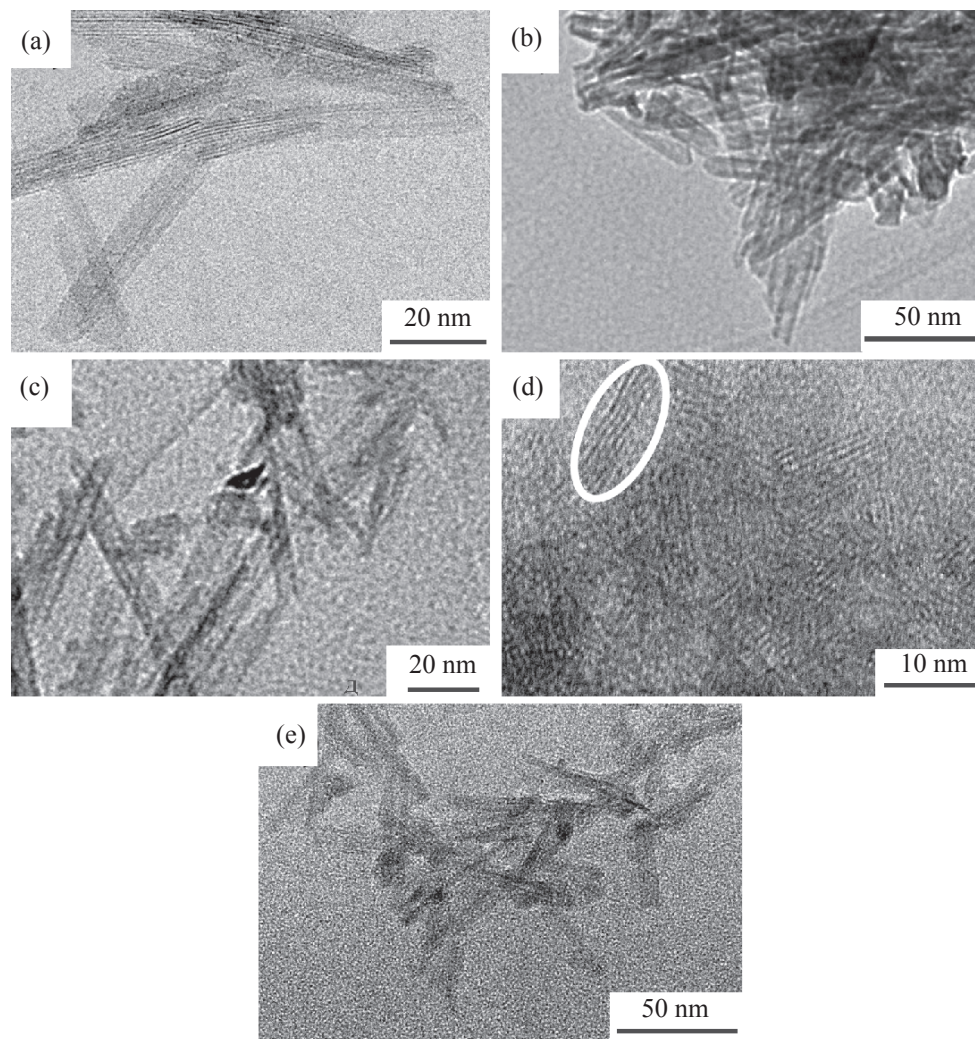
Fig. 2. Micrographs of potassium-titanate nanoparticles obtained by hydrothermal processing of precipitates of composition 0.95 TiO_2 : 0.05 MeO (Me_2O_3), where Me = (a) Ni, (b) Mg, (c) Al, (d) Cr, (e) Fe. In (d) an ellipse denotes a separate nanosheet in the agglomerate.

Geometrical dimensions and textural characteristics of nanoparticles obtained by hydrothermal treatment of precipitate of composition of 0.95 TiO_2 : 0.05 MeO (Me_2O_3) vs. on the type of doping element

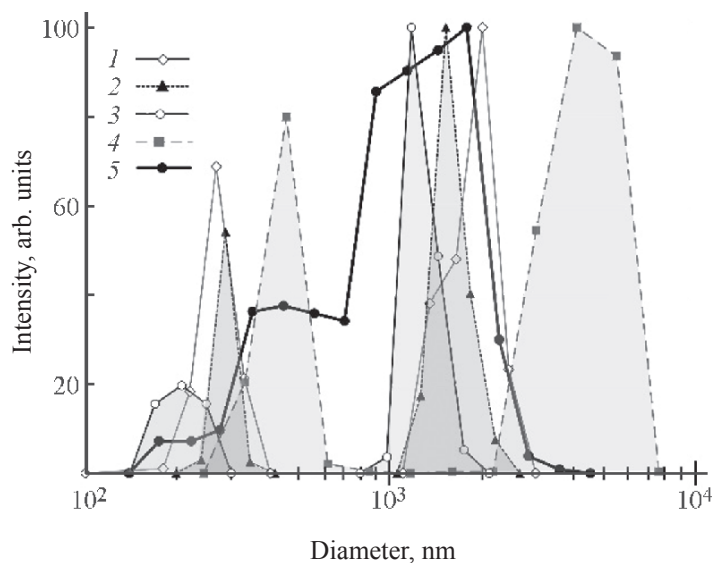| Doping element	Morphology	Length, nm	External diameter (thickness)/internal diameter, nm	The average effective diameter of the agglomerates, nm	ζ-Potential, mV	Specific surface, $m^2\ g^{-1}$
Ni	Nanotubes	60–130	7–10/2–2.5	635	–27	301
Mg	"	45–100	8–10/3–3.5	617	–29	294
Al	"	40–100	5–6/1.5–1.7	672	–30	220
Cr	Nanosheets	6–14	3–4	841	–30	266
Fe	Nanowires	15–60	4–5	1149	–23	286

Fig. 3. Size distribution of agglomerates of nanoparticles containing (*1*) Al , (*2*) Ni, (*3*) Mg, (*4*) Fe, (*5*) Cr according to dynamic light scattering.

elements in the obtained nanoparticles, which, in our opinion, indicates their isomorphic incorporation in the titanium–oxygen layers.

All investigated compounds with water form suspensions of microdisperse aggregates with a ζ-potential modulus less than or equal to 30 mV (see the table), which allows to refer them to systems in which rapid sedimentation takes place that facilitates the separation of the sorbent from the interacting solution, therewith despite of a sufficiently strong agglomeration of nanoparticles as well as regardless of their morphology the obtained samples have high specific surface. As can be seen from Fig. 3

according to dynamic light scattering the size distribution of agglomerates is bimodal for nanotubes and nanowires, which is evidence for a strong anisotropy of their sizes.

The kinetic curves of sorption of Sr^{2+} ions (Fig. 4) exhibit that absorption on aluminum-containing nanotubes at 50°C (curve *1*) occurs mainly in the first 2 h of contact with the solution, after which an equilibrium is established at 0.76×10^{-3} mol g^{-1}. When the temperature rises to 80°C (curve *2*), the amount of strontium adsorbed on these nanotubes increases and after 5 h of exposure to the solution is about 2.02×10^{-3} mol g^{-1}.

The maximum extraction of Sr^{2+} ions from the solution is demonstrated by the Mg-containing sample (~3.65×10^{-3} mol g^{-1}), which corresponds to the almost complete replacement of potassium ions by strontium ions in the considered nanoparticles, assuming that the composition of nanotubes is close to potassium tetratitanate ($K_2Ti_4O_9$). The results of the interaction of nanotubes containing nickel with a solution of $Sr(NO_3)_2$ are not reported since the separation of the nanotubes and the solution by the filtration method failed. Changes in the morphology of the obtained nanoparticles affect the nature of the sorption curves. Nanowires obtained at doping nanoparticles with iron absorbed a smaller amount of strontium ions than nanotubes (Fig. 4, curve *4*). And agglomerates of nanosheets synthesized from chromium-containing precipitates, gradually react with $Sr(NO_3)_2$ solution; probably, this effect is associated with stronger agglomeration of nanowires and layers (see the table).
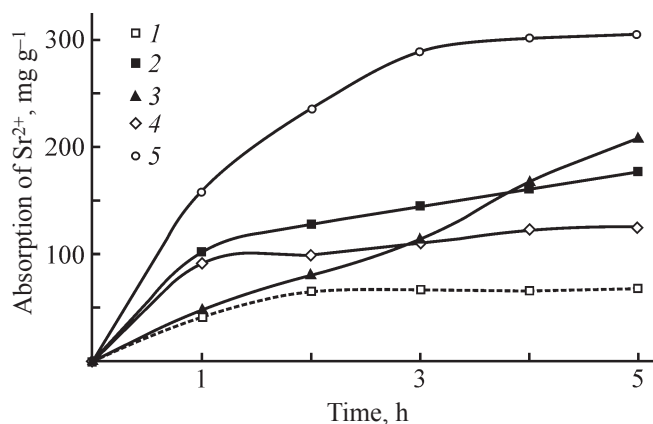

Fig. 4. Kinetic curves of sorption of Sr^{2+} ions from a solution of potassium-titanate nanoparticles doped with (*1, 2*) Al, (*3*) Cr, (*4*) Fe, (*5*) Mg at a temperature of (*2–5*) 80 and (*1*) 50°C.

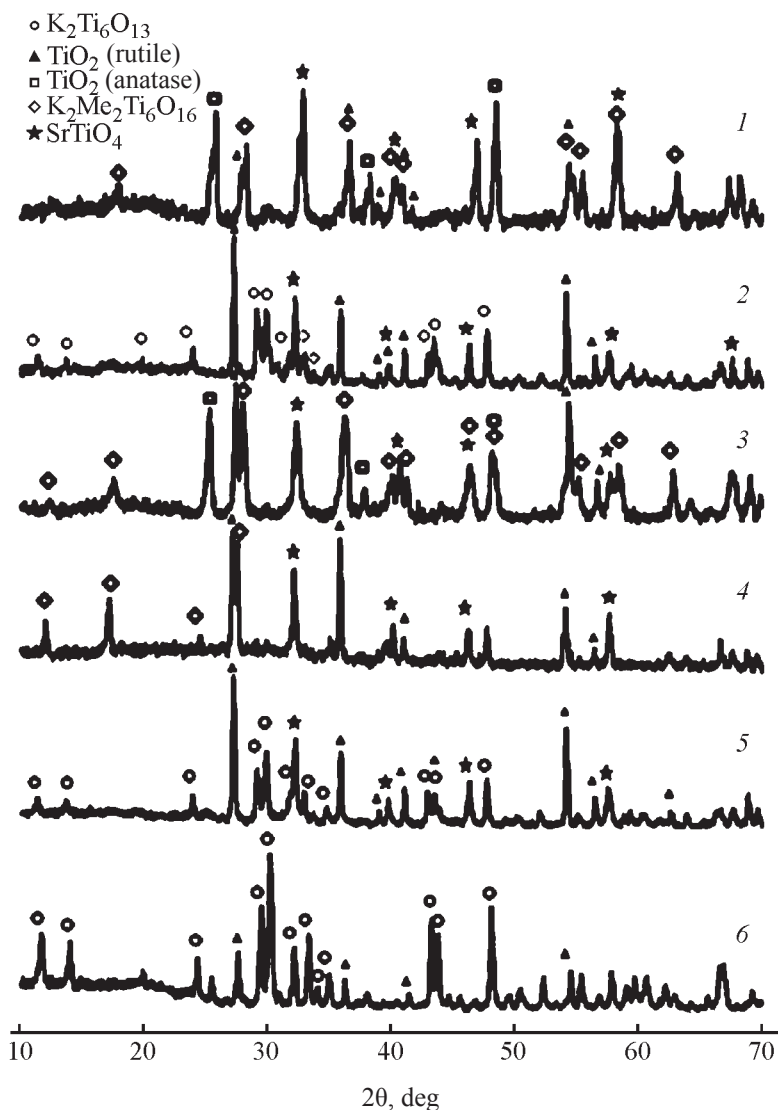**Fig. 5.** X-ray diffraction patterns of titanate nanoparticles obtained by hydrothermal treatment of precipitates of composition 0.95 TiO$_2$: 0.05 MeO (Me$_2$O$_3$), where Me = (*1*) Ni, (*2*) Mg, (*3*) Cr, (*4*) Fe, (*5*) Al, after sorption of strontium ions (80°C, 4 h) and calcination at 950°C. (*6*) Calcined samples of nanotubes containing Al, prior to sorption.

Practically all the examined samples in the studied time range do not reach saturation.

Based on the results of X-ray diffraction analysis, obtained after the interaction of nanoparticles with the solution of Sr(NO$_3$)$_2$, it can be concluded that with increasing the interaction time, the initial crystalline structures of nanoparticles formed at the synthesis stage are gradually destroyed. This is manifested by a decrease in the frequency of reflections on diffraction patterns (Fig. 1, curves *2, 4, 6*), which is especially evidence for the nanosheet samples that are initially of the smallest size and are characterized by greater amorphization.

The data of X-ray phase analysis of samples calcined at 950°C, on which sorption was carried out, confirm the replacement of potassium by strontium (Fig. 5). In all the samples after sorption for 4 h in addition to potassium hexatitanate, the main phase crystallized during calcination of the nanoparticles, reflections corresponding to strontium metatitanate (SrTiO$_3$) are observed. Moreover, the content of TiO$_2$ in both rutile and anatase forms (curves *1, 3*) significantly increases, and in the cakes obtained from nanoparticles containing Fe and Cr hollandite phases (K$_2$Me$_2$Ti$_6$O$_{16}$) crystallized instead of potassium hexatitanate (curves *3, 4*).

CONCLUSIONS

Potassium-titanate nanoparticles synthesized under hydrothermal conditions are promising sorbents of water-soluble metal compounds, the sorption capacity of which strongly depends on the composition and morphology. Tests on the sorption of strontium ions from an aqueous solution of 0.1 M $Sr(NO_3)_2$ on synthesized potassium-titanate nanoparticles showed a higher sorption capacity of nanotubes as compared to aggregates of nanowires and nanolayers. The maximum extraction of strontium ions from the solution was demonstrated by the Mg-containing sample at 80°C: $\sim3.65 \times 10^{-3}$ mol g^{-1}. The sample of nanotubes doped with aluminum demonstrated that a rise in the temperature of the interaction of the sorbent with the solution increases the amount of sorbed strontium from 0.76×10^{-3} at 50°C to $\sim2.02 \times 10^{-3}$ mol g^{-1} at 80°C.

REFERENCES

1. Agilar-Gonzalez, M.A., Gorokhovsky, A.V., and Aguilar-Elguezabal, A., *Bull. Soc. Esp. Ceram. V*, 2008, vol. 47, no. 1, pp. 29–34.

2. Mishra, S.P. and Upadhyaya, S., *J. Radioanalit. Nucl. Chem.*, 1995, vol. 189, no. 2, pp. 247–256.

3. Mishra, S.P. and Srinivasu, N., *Radiochim. Acta*, 1993, vol. 61, no. 1, pp. 47–52.

4. Mishra, S.P., Singh, V.K., and Tiwari, D., *Appl. Rad. Isot.*, 1998, vol. 49, no. 12, pp. 1467–1475.

5. Magalhaes, N.L., Nunes, L.M., Gouveia de Souza, A., and Fernandes de Farias, R., *J. Alloys Compd.*, 2001, vol. 319, no. 1–2, pp. 94–99.

6. Aguilar-González, M.A., Gorokhovsky, A.V., and Aguilar-Elguezabal, A., *Mater. Sci. Eng. B*, 2010, vol. 174, pp. 105–113.

7. Jung, K.T., Shul, Y.G., and Moon, J.K., Oh, W.J., *IAEA–ECDOC-947. International Atomic Energy Agency (IAEA) Waste Treatment and Immobilization Technologies Involving Inorganic Sorbents. Final Report of a Coordinated Research Programme*, 1997, pp. 163–182.

8. Dean, J.G., Bosqui, F.L., and Lanouette, K.H., *Environ. Sci. Technol.*, 1972, vol. 6, no. 6, pp. 518–522.

9. Poluektov, V.T., Mishchenko, V.T., Kononenko, L.I., and Beltyukova, S.V., *Analiticheskaya khimiya strontsiya* (Analytical Chemistry of Strontium), Moscow: Science, 1978.

10. Sinel'shchikova, O.Yu., Maslennikova, T.P., Besprozvannykh, N.V., and Gatina, E.N., Vlasov, E.A., *Glass Phys. Chem.,* 2018, vol. 44, no. 4, pp. 329–332.

11. Zhang, J., Wang, Y., Yang, J., Chen, J., and Zhanget, Z., *Mater. Lett.*, 2006, vol. 60, no. 24, pp. 3015–3017.