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Atom States and Interatomic Interactions in Perovskite-Like Oxides: XXVII.[1] Influence of Strontium Concentration on Interatomic Interactions and Conductivity in Lanthanum Gallates Doped with Strontium and Chromium

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Abstract—Solid solutions based on lanthanum gallate and containing chromium and strontium in the ratio 2:1 as doping elements were studied by the method of static magnetic susceptibility, electron paramagnetic resonance spectroscopy, and impedance spectroscopy. Clustering of chromium atoms resulting in the formation of large aggregates of paramagnetic atoms is strengthened as the amount of strontium in the system increases.

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Compounds based on lanthanum gallate doped with diamagnetic elements, strontium (calcium and barium) in the lanthanum sublattice and magnesium together with a transition element in the gallium sublattice, are electron-ion conductors. They are gaining a growing acceptance mostly as the materials for solid-oxide fuel cells (SOFC) [2, 3]. This circumstance accounts for a recent sharp increase in the interest to such compounds of researchers involved in the study of ionic conductivity in solids.

A substitution for atoms in perovskite is performed rather easily, providing materials with a great variety of properties. However, up to now in published works there are no hypotheses about the role of the doping element nature and concentration in the realization of particular properties. The search for the materials with the best characteristics, namely with high conductivity, is carried out empirically. In rare cases we can see a particular explication of the properties of one or another material; more often there is only an establishment of the facts. And only a systematic study of these systems may answer the question which factors and how influence the electron structure of complex oxides and, as a consequence, the characteristics of the materials. In [4] it was suggested that the perovskite structure of lanthanum gallate containing chromium and strontium is stabilized only at the expense of oxidation of a fraction of chromium atoms equivalent to the quantity of introduced strontium to chromium(IV). The introduction of only strontium into lanthanum gallate [4] results in the formation of a foreign phase La_4SrO_7, which is not observed upon simultaneous introduction of strontium and chromium into $LaGaO_3$. A closeness of effective ionic radii of the replaceable an substituting ions in the sublattices of lanthanum and gallium, and also the introduction of a fortiori small quantities of the doping agents allow the doped gallates to be considered as diluted solid solutions [5, 6]. Hence, they can be studied by the magnetic dilution method.

The aim of this work was to study how the ratio [Cr]:[Sr] affects the state of chromium atoms, the character of interatomic interactions, and, as a consequence, the electrophysical characteristics of solid solutions (1).

$$La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3\ (0.01 \le x \le 0.1). \qquad (1)$$

The section of the La_2O_3–Ga_2O_3–SrO–Cr_2O_3 system was selected in such a manner that the ratio [Cr]:[Sr] remained constant (2:1). As the systems for com-

[1] For communication XXVI, see [1].

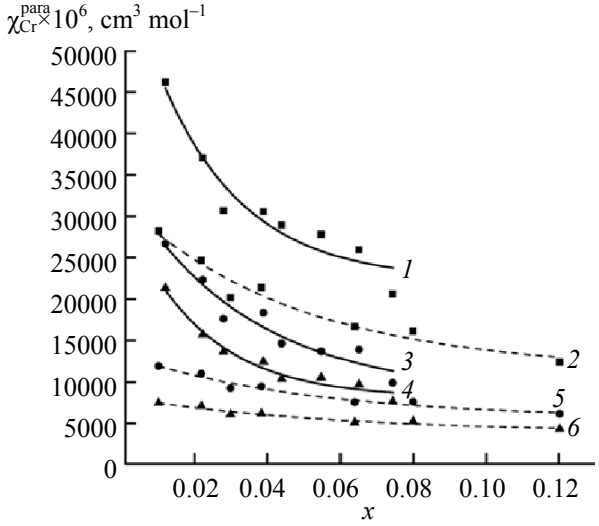

Fig. 1. Plot of paramagnetic component of magnetic susceptibility calculated per 1 mol of chromium atoms vs. chromium concentration for the systems: (*1, 3, 4*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ and (*2, 5, 6*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ for three temperatures: (■) 77; (●) 200; (▲) 320 K.

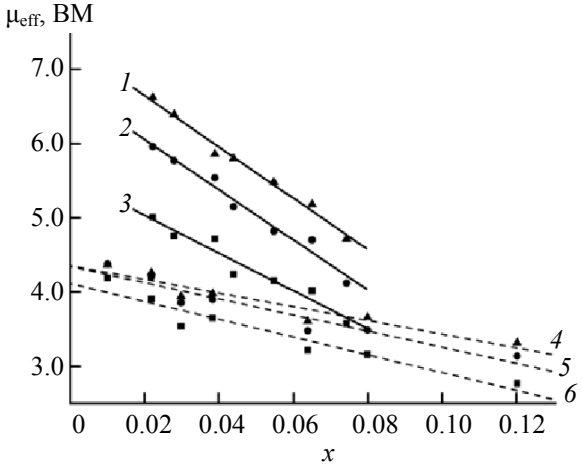

Fig. 2. Plot of effective magnetic moment vs. chromium concentration for the systems: (*1, 2, 3*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ and (*4, 5, 6*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ for three temperatures: (■) 77; (●) 200; (▲) 320 K.

parison we chose the solutions based on lanthanum gallate studied earlier and containing only chromium, $LaCr_xGa_{1-x}O_3$ [7], and chromium together with strontium in the ratio 5:1, $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ [8].

In the course of the work we synthesized the $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ solid solutions based on lanthanum gallate and containing chromium and strontium in the ratio 2:1 in the concentration range $0.01 \le x \le 0.10$. The X-ray analysis showed that all the solutions have the structure of cubic perovskite. We determined chromium and strontium concentrations by the X-ray fluorescent analysis and have chosen for the study of magnetic susceptibility only solutions with the chromium–strontium ratio close to 2. We have measured the magnetic susceptibility in the temperature range 77–400 K and the electron paramagnetic resonance and impedance spectra.

Using the resulting data on the magnetic susceptibility, we have plotted the temperature and concentration dependences of magnetic characteristics of $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ solid solutions.

Let us consider the dependences of the paramagnetic component of magnetic susceptibility calculated per 1 mole of a paramagnetic component on the chromium concentration for the systems with the [Cr]:[Sr] ratios of 5:1 and 2:1 (Fig. 1).

A comparison of the isotherms of paramagnetic component of magnetic susceptibility for the solutions with the [Cr]:[Sr] ratios of 2:1 and 5:1 shows that the isotherms for the systems with greater strontium content (2:1) lie much higher. First of all it points to the fact that chromium(III) is not oxidized to chromium(IV) and, moreover, shows how crucially the magnetic properties depend on the changes in the [Cr]:[Sr] ratio.

An essential difference in the behavior of the systems with various strontium content can be seen also on considering the dependence of the effective magnetic moment (μ_{eff}) on chromium concentration (Fig. 2).

When the effective magnetic moment is extrapolated to the infinite dilution characteristics of single paramagnetic atoms are usually obtained. This in essence is a hypothetic presentation, but the very procedure has an important significance in the examination of special features of interatomic interactions.

Extrapolating the effective magnetic moments to the infinite dilution for the $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ system under study, we see that the obtained values fit none of possible valence states (II–IV) of isolated chromium atoms.

Cr^{II}, configuration d^4, ^5E_g, μ_{eff} ~4.90 BM;
Cr^{III}, configuration d^3, $^4A_{2g}$, μ_{eff} ~3.87 BM;
Cr^{IV}, configuration d^2, $^3T_{1g}$, μ_{eff} ~2.83 BM.

In our case μ_{eff} is substantially higher and varies within the limits of 5.50–7.50 BM in the temperature

range 77–400 K. It means that even at infinite dilution no complete disaggregation of chromium atoms occurs, and chromium in the systems with the ratio [Cr]:[Sr] = 2:1 remains in the trivalent state.

The fact that the effective magnetic moment at infinite dilution is so high directly points to a substantial influence of strontium on the formation, location, and special features of magnetic (exchange) interactions between chromium atoms. Therefore, we can state with assurance that strontium atoms are included into the cluster, and the exchange within the cluster is of the ferromagnetic type.

However, the assumption about the formation of the most probable type of aggregates of small dispersity, dimers, in the context of Heisenberg–Dirac–Van-Fleck model (HDVF) leads to the following inconsistencies. First, according to the HDVF model, the effective magnetic moment of a Cr(III)–Cr(III) dimer does not exceed 4.90 BM, and 6.30 BM, for a Cr(II)–Cr(II) dimer [9], whereas in the system under study the moment varies in the range 5.50–7.50 BM. Second, according to the same model, the effective magnetic moment of a ferromagnetically bound cluster can either be independent of temperature at high exchange parameters, or it must decrease as temperature increases [9]. This contradicts to the observed experimental dependence (Fig. 3): the magnetic moment increases as temperature increases. In this situation it is evident that invoking the classic HDVF model of exchange interactions is useless.

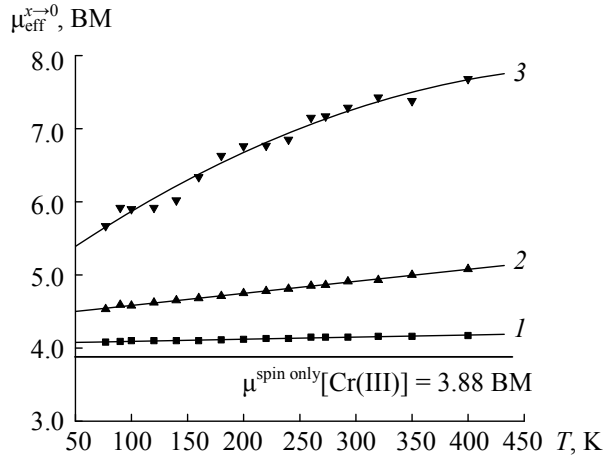

Fig. 3. Temperature dependence of effective magnetic moments at infinite dilution for the systems: (*1*) $LaCr_xGa_{1-x}O_3$, (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$, (*3*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$.

The formation of large paramagnetic clusters can be detected by the EPR spectroscopy. A comparison of EPR spectra for the systems with various ratio of chromium to strontium (Figs. 4a and 4b) allows a substantial difference to be detected: for the systems with the ratio [Cr]:[Sr] = 2:1 and almost the same chromium concentration as in the systems with the ratio [Cr]:[Sr] = 5:1 the line in the spectrum is noticeably less intensive and somewhat widened. Moreover, the approximation of the signal by Gauss and Lorentz distribution functions allows pure Lorentz shape of the line to be discussed.

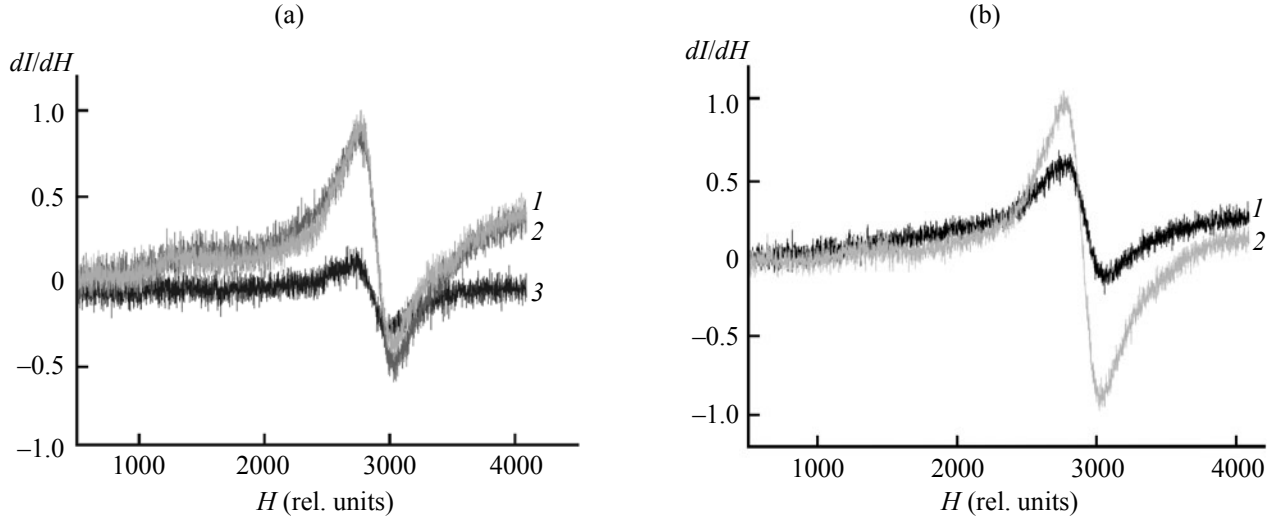

Fig. 4. Electron paramagnetic resonance spectra: (a) for solid solutions (*1*) $LaGa_{1-x}Cr_xO_3$, (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ (5:1), (*3*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ (2:1), containing ~4 mol % Cr; (b) for solid solutions with various strontium content and chromium concentration of ~6.5 mol %, (*1*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ (2:1), (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ (5:1).

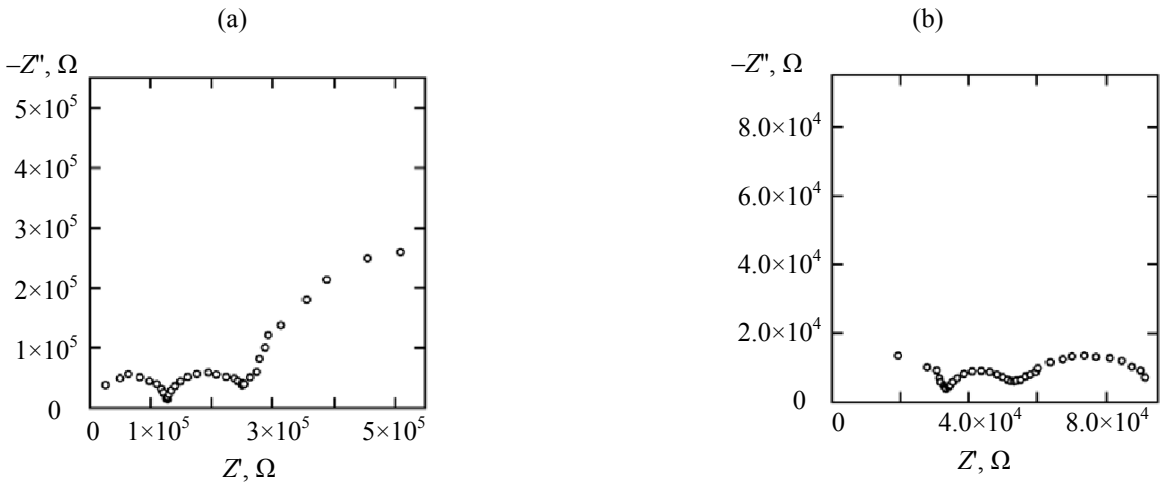

Fig. 5. Impedance spectra measured at the temperatures: (a) 403 and (b) 503 K.

These data to a large extent point to the formation of large aggregates of paramagnetic atoms, since the wider is the line in the spectrum and the less intensive it is, the greater number of paramagnetic centers is in the immediate interaction with each other.

It is evident that not only paramagnetic chromium atoms take part in the formation of clusters in the lanthanum gallate structure, but also diamagnetic strontium located near a vacancy and probably an "extra" electron.

For the $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ solid solution (x = 0.0223) we measured the impedance spectra in the region of frequencies from 3GHz up to 1 Hz in the temperature range 25–630°C with at 20 degree steps (Figs. 5a and 5b). We constructed an equivalent electric circuit consisting of three elements connected in parallel: volume resistance of the grains (R_b), volume capacitance (C_b), and the element of the phase shift constant angle (CPE) [10]. Based on this circuit the volume resistances and specific conductivity (σ_{sp}) were determined.

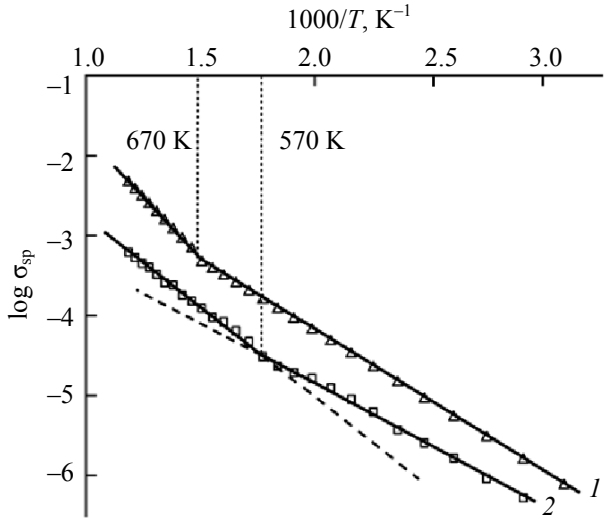

Fig. 6. Plot of logarithm of specific conductivity vs. inverse temperature for the solutions: (*1*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ (x = 0.0429, Cr:Sr 5:1) and (*2*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ (x = 0.0223, Cr:Sr 2:1).

In the temperature dependence of specific conductivity in the log σ_{sp}–1000/T coordinates (Fig. 6) a certain "break" is observed at 570 K, Arrhenius equation being satisfied for each site of the curve. For comparison a similar dependence is given for the sample of $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ (x = 0.0429) with the ratio [Cr]:[Sr] = 5:1, for which the "break" is observed at 670 K [7].

The activation energy in the T < 570 K region is 13.6 kJ mol^{-1} and in the T > 570 K: 17.2kJ mol^{-1}. The specific conductivity σ_{sp} at 383 K is 4.55×10^{-6} S cm^{-1}; at 843 K: 1.45×10^{-3} S cm^{-1}. Different activation energies for two portions of the straight line seem to point to the predominance of different types of conductivity. As temperature increases, the ion transfer becomes more pronounced, whereas at low temperatures the electron type of conductivity prevails.

The doping ions are assumed in [11] to act not only as traps for isolated oxygen vacancies, but also as nucleators of ordered clusters of vacancies. At low temperatures oxygen vacancies are grouped into clusters, and as temperature increases they can disintegrate giving rise to substantial ion conductivity. It confirms once more the conception about clustering in doped lanthanum gallates and a participation of vacancies in clustering, which we have offered on the

basis of studying the magnetic properties. In other words we can state with assurance that an increase in the fraction of diamagnetic heterovalent additions in lanthanum gallate doped with chromium results in a sharp increase in chromium atom clustering, which does not disappear even at infinite dilution. The stabilization of the structure is not associated with the transfer of a fraction of chromium atoms into the tetravalent state, but in all likelihood is associated with the formation of stable clusters including the atoms of chromium and strontium located in the vicinity of vacancies.

EXPERIMENTAL

The $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_3$ solid solutions ($0.01 \le x \le 0.1$) were obtained by the sol–gel method. For the synthesis we used the following reagents: special-purity grade lanthanum and gallium oxides; analytical-pure grade strontium carbonate. Chromium oxide was obtained by the reduction of stoichiometric amounts of analytical-pure grade ammonium dichromate with hydrogen peroxide in acid medium.

To obtain a gel, we dissolved stoichiometric amounts of starting components in nitric acid on heating. The resulting solution was cooled and neutralized with ammonium hydroxide to pH ~7. The acidity of the medium was controlled using a litmus paper. After the neutralization we added citric acid and ethylene glycol to the solution [12]. A highly dispersed powder obtained after decomposition of citrate gel was ground in a jasper mold, then pressed into pellets, and sintered in air for 50 h at 1450°C. The time of sintering for obtaining single-phase samples was determined by the X-ray phase analysis. Using the method of static magnetic susceptibility, we found that the state of all the obtained solid solutions is close to equilibrium.

We carried out the X-ray phase analysis on a URS-50 N diffractometer using CuK_α emission. We simultaneously determined the quantitative content of chromium and strontium in the samples by the method of X-ray fluorescent analysis. The accuracy of the analysis was 2% of x in the solid solution formula.

We measured the specific magnetic susceptibility of the solid solutions in the temperature range 77–400 K by the Faraday method. The accuracy of relative measurements of specific magnetic susceptibility was 1%. We calculated the paramagnetic component of magnetic susceptibility, having introduced the diamagnetic corrections with regard to the susceptibility of lanthanum gallate matrix measured in the same temperature range as the samples under study.

We recorded the spectra of electron paramagnetic resonance on an SEPR-2 + KMYa (a small-scale mobile measuring analytical complex). The operation, control over the work, and recording of the spectra were carried out with the help of an original program package developed by the stuff of the quantum magnetic phenomena department of the physical faculty of St. Petersburg State University. The operating frequency of the spectrometer was 9.29 GHz (X-diapason). We carried out the measurements of the spectra in the magnetic induction diapason from ~100 up to 4500 Gs at room temperature. To estimate quantitative relationships, we carried out the measurements in the same quarts ampoule (~3.5 mm in diameter). We determined the quantity of the sample as a value proportional to the height of the substance bar in the ampoule. The modulation amplitude maximal for the moment of measurements was ~5–10 Gs.

We recorded the impedance spectra on an Impedancemeter–Z3000 device in the range of frequencies from 3GHz up to 1 Hz in the temperature range 298–903 K.

REFERENCES

1. Chezhina, N.V. and Fedorova, A.V., *Zh. Obshch. Khim*., 2010, vol. 80, no. 5, p. 739.
2. Yamaji, K., Horita, T., and Sakai, N., *Solid State Ionics*, 2002, vols. 152–153, p. 517.
3. Ishihara, T., Matsuda, H., and Takita, Y., *J. Am. Chem. Soc*., 1994, vol. 116, no. 9, p. 3801.
4. Baker, R.T., Gharbage, B., and Marques, F.M.B., *J. Eur. Ceram. Soc*., 1998, vol. 18, p. 105.
5. Shannon, R.D., *Acta Cryst. A,* 1976, vol. 32, p. 751.
6. Shannon, R.D. and Prewitt, C.T., *Acta Cryst. B*, 1969, vol. 25, p. 925.
7. Chezhina, N.V., Zolotukhina, N.V., and Bodritskaya, E.V., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 8, p. 1233.
8. Chezhina, N.V., Piir, I.V., and Zolotukhina, N.V., *Zh. Obshch. Khim*., 2006, vol. 76, no. 10, p. 1585.
9. Kalinnikov, V.T. and Rakitin, Yu.V., *Vvedenie v magnetokhimiyu. Metod staticheskoi magnitnoi vospriimchivosti* (Introduction to Magnetochemistry. Method of Static Magnetic Susceptibility), Moscow: Nauka, 1980.
10. Li, Z.-C, Zhang, H., Bergman, B., and Zou, X., *J. Eur. Ceram. Soc*., 2006, vol. 26, p. 2357.
11. Huang, K., Ticky, R.S., and Goodenough, J.B., *J. Am. Ceram. Soc*., 1998, vol. 81, p. 2565.
12. Kharton, V.V., Yaremchenko, A.A., Viskup, A.P., Mather, G.C., Naumovich, E.N., and Marques, F.M.B., *J. Electrocheramics*, 2001, vol. 7, p. 57.