Formation of Nickel Magnetic Nanoparticles and Modification of Nickel Phthalocyanine Matrix by Sodium Doping

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Abstract—Data for the vapor-phase doping (300 °C) of nickel phthalocyanine (NiPc) by sodium taken in different concentrations (x), as well as structural analysis data for Na_xNiPc, Na_x=1NiPc, and Na_x=3NiPc samples, have been reported. The structure of the samples and their atomic configuration versus the doping level have been studied by transmission electron microscopy, Raman scattering, X-ray diffraction, X-ray absorption spectroscopy, and extended X-ray absorption fine structure (EXAFS) spectroscopy. The structural parameters of Ni–N, Ni–C, and Ni–Ni bonds have been determined, and it has been found that, at a low level of doping by sodium, local structural distortions are observed in some molecules of the NiPc matrix near nickel atoms. The fraction of these molecules grows as the doping level rises from x = 0.2 to x = 1.0. It has been shown that doping changes the oscillation mode of light atoms, which indicates a rise in the electron concentration on five- and six-membered rings. At a high level of sodium doping (x = 3.0), nickel nanoparticles with a mean size of 20 nm and molecule decomposition products have been observed in the NiPc matrix. It has been found that the fraction of nickel atoms in the Na_x=3NiPc nanoparticles as estimated from EXAFS data is sufficient for the room-temperature magnetic properties of the samples to persist for a long time.

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INTRODUCTION

Magnetic nanoparticles of transition metals (Me = Fe, Co, Ni, etc.) stabilized in a phthalocyanine matrix (metal phthalocyanine, MePc) attracts much attention, since this composite is very promising for optoelectronic devices and devices made of organic semiconductors [1–4]. Also, these nanocomposites are used in photodynamic therapy due to their capacity for near-IR absorption [5]. In recent years, thin donor-doped phthalocyanine films have attracted much attention in those engaged in molecular spintronics and strongly correlated electronic systems [6].

The magnetic properties of alkali-doped metal phthalocyanines were studied in [7–9], where it was found that metal nanoparticles arise in the MePc matrix under certain doping conditions. In [10], nickel nanoparticles were prepared by vapor-phase doping of the NiPc matrix by potassium at 300°C and high doping levels. The resulting materials K_xNiPc (x = 1.8, 2.5, and 3.2) demonstrated persistent magnetic properties, which were attributed to nickel nanoparticles. It should be noted that our materials slightly doped by alkali metals also exhibited magnetic properties, but the nature of magnetism in them remains unclear.

In this work, we report the results of low and high doping of nickel phthalocyanine NiPc by sodium from the vapor phase at 300°C and also structural analysis data for the synthesized material. The method of sample preparation is presented in Section 1, along with the methods of testing their atomic configuration, namely, transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), and extended X-ray absorption fine structure spectroscopy (EXAFS). Using complementary data for the synthesized material that were gained by the above methods, we found local structural distortions (Section 2) in the NiPc matrix at low levels of sodium doping. As the dopant concentration increased, nickel nanoparticles appeared.

1. EXPERIMENTAL

Nickel phthalocyanine was synthesized by the Lin-
media and subsequently sublimated in vacuum. Vapor-phase doping [12] of phthalocyanine was carried out by heating in sodium vapor at 300°C. This was expected to cause the formation of phthalocyanine molecules according to the reaction

\[
\text{NiPc} + x\text{Na} \rightarrow (\text{Na}^+)_x(\text{NiPc})^{-x},
\]

where \(x\) is the doping level \((0 < x < 3)\). At a higher doping level, phthalocyanine molecules decompose (see below) to form Ni nanoparticles. The dopant distribution turns out to be nonuniform, so that areas of the initial (undoped) phthalocyanine matrix, doped matrix, and nickel nanoparticles may coexist. After the samples were prepared, they were annealed at 280°C and rinsed in distilled water. From the elemental composition of the samples determined using an InGa-Energy 300 energy-dispersive spectrometer, we found the mean values of the doping level in three samples, i.e., \(\text{Na}_x=0.2\text{NiPc}\), \(\text{Na}_x=1\text{NiPc}\), and \(\text{Na}_x=3\text{NiPc}\). Each of the samples is attracted to a permanent magnet.

A TEM micrograph taken of the \(\text{Na}_x=3\text{NiPc}\) sample under an FEI Tecnai F20 electron microscope is presented in Fig. 1. X-ray diffraction patterns and Ni K-edge X-ray absorption fine-structure (Ni K-XAFS) spectra for pure NiPc samples and Na-doped NiPc samples were taken using a synchrotron source, which is an integral part of the Structural Materials Science end station at the National Scientific Center Kurchatov Institute in Moscow. X-ray diffraction reflections were taken in transmission mode at a radiation wavelength of 0.1072 nm using FujiFilm ImagePlate 2D detector. Ni K-XAFS spectra were also taken in transmission mode using an Si(111) monochromator and two ionization chambers. The scan step was equal to \(\delta E \sim 0.3\) eV for X-ray absorption near-edge structure (XANES) and \(\delta k \sim 0.005\) nm\(^{-1}\) for EXAFS domains. The total time of talking of one spectrum was about 30 min.

To take Raman spectra from the samples, we excited oscillations by an argon (\(\lambda = 514\) nm) or He–Ne laser (\(\lambda = 633\) nm). The spectra were recorded in backscattering mode by a Renishaw spectrometer equipped with a CCD detector. We used an objective lens with a 50× magnification, which focused the laser beam into a spot about 2 μm in diameter on the sample surface.

2. RESULTS AND DISCUSSION

2.1. TEM Images, Particle Size Distribution, and X-Ray Diffraction

Figure 1 shows the TEM micrograph of the \(\text{Na}_x=3\text{NiPc}\) sample. Extended rods are nickel phthalocyanine crystallites (or clusters of crystallites). Darker near-spherical areas with a mean size of about 20 nm may be nickel nanoparticles.

2.2. XRD Reflections

Figure 2 shows X-ray diffraction reflections from the doped \(\text{Na}_x\text{NiPc}\) \((x = 0.2, 1, 3)\) samples, undoped samples, and nickel foil. Here, a clear-cut reflection from the \(\text{Na}_x=3\text{NiPc}\) sample at 20 ~ 30.5° catches the eye (this reflection is absent in the diffraction patterns taken of the \(\text{Na}_x=0.2\text{NiPc}\) and \(\text{Na}_x=1\text{NiPc}\) samples and the undoped one). Comparing these patterns with those taken from nickel foil, one can suppose that this reflection is the (111) reflection from fcc nickel. This indicates the formation of nickel nanoparticles. Peaks at 20 < 25°, which are present in the diffraction patterns taken of both the doped and undoped NiPc samples, broaden with an increase in the doping level. Since the diffraction pattern of pure NiPc does not contain peaks typical of pure nickel, it can be con-
Table 1. Parameters of crystal phases in variously doped Na$_x$NiPc samples ($x = 0.2, 1.0, 3.0$) obtained from diffraction pattern analysis. $C$ is the weight fraction of nickel nanoparticles; $a$, $b$, $c$, and $\beta$ are the lattice parameters; and $D$ is the crystallite size.

| Sample | $R_{wp}$, % | Ni nanoparticles | NiPc |
|--------|-------------|------------------|------|
|        | $C$, wt % | $a$, nm | $b$, nm | $c$, nm | $\beta$, deg | $D$, nm |
| Na$_x$ = 0.2NiPc | 5.8 | 0.4 | 0.374 | $\infty$ | 1.988 | 0.472 | 1.483 | 121.8 | 83 |
| Na$_x$ = 1NiPc | 5.3 | 0.5 | 0.374 | 30 | 1.992 | 0.471 | 1.484 | 121.8 | 118 |
| Na$_x$ = 3NiPc | 3.8 | 3.0 | 0.354 | 22 | 1.997 | 0.470 | 1.485 | 122.0 | 66 |

cluded that nickel nanoparticles do form in NiPc at a doping level of $x \sim 3$ or greater.

Table 1 presents complete analytical data for the diffraction pattern of the samples. An analysis was based on the above qualitative comparison with model objects, i.e., with regard to two main phases, i.e., nickel phthalocyanine NiPc ($P12/1/a$ [13]) and nickel nanoparticles ($Fm\overline{3}m$ [14]). According to Table 1, the Na$_x$ = 0.2NiPc and Na$_x$ = 1NiPc samples are free of nickel crystal particles. It seems that their concentration in these samples is very low (below the resolution limit). However, they are detected in the Na$_x$ = 3NiPc sample, where their concentration is $3.0 \pm 0.3$ wt %.

2.3. EXAFS Data

The method of EXAFS spectroscopy was used to confirm the TEM and XRD qualitative conclusions concerning the structure of the Na$_x$NiPc samples and quantitatively characterize these samples. When constructing models of the nearest-neighbor environment of Ni atoms, which were applied for fitting Fourier transforms (FTs) $F(R)$ of experimental Ni K–EXAFS spectra, we took into account that the shortest Ni–Ni distance in the NiPc crystal structure equals 0.479 nm [13], which is almost twice as large as the length of the Ni–Ni bond in nickel foil (0.249 nm [14]). Because of this large difference, it becomes possible to separate the contributions of photoelectron multiple scattering by nickel atoms in nanoparticles and in the molecular crystal. To quantitatively characterize the structure of the nearest-neighbor environment of nickel atoms in the samples, we analyzed the Ni K–EXAFS spectra by applying the Fourier transformation to the experimental spectra and subsequently fitting the resulting Fourier transforms $F(R)$ by the method described in [15]. This method makes it possible to find structural parameters that strongly correlate with each other. To mitigate the influence of multiple scattering (MS) on the structural parameters being studied, the lower limit of the $k$ interval for the FT spectra was set equal to $k_{min} = 0.45$ nm$^{-1}$ [16].

To gain insight into the structure of the nearest-neighbor environment of Ni atoms in the Na$_x$ = 3NiPc sample, we used a model that takes into account that some of Ni atoms remain in NiPc molecules (according to XRD data), whereas the rest of Ni atoms are responsible for the production of nickel nanoparticles. Having denoted the contribution of Ni atoms that remain in NiPc molecules as NiPc$\chi_{NiPc}(k)$ and that of nanoparticles as $\chi_{Ni-NPs}(k)$, one can write (in terms of the adopted model) function $\chi(k)$ for the EXAFS spectrum of the doped sample as

$$
\chi(k) = C\chi_{Ni-NPs}(k) + (1 - C)\chi_{NiPc}(k),
$$

where $C$ is the relative concentration of absorbing Ni atoms that constitute nickel nanoparticles. The distance between molecular layers in the NiPc structure is roughly equal to 0.35 nm so that the contribution of intermolecular scattering can be neglected and fitting model (2) for $\chi_{NiPc}(k)$ can be employed when analyzing the FT of the Ni K–EXAFS spectrum. This model considers only one NiPc molecule. To mitigate the influence of photoelectron multiple scattering on the parameters of the first coordination sphere, fitting in the $R$ space was carried out in the interval $0.35 < R < 1$ nm$^{-1}$ using the IFEFFIT program package [17] for the function $F(R)$ obtained by applying the Fourier transformation to function $k^2\chi(k)$ in the interval $1.15 \leq k \leq 4.5$ nm$^{-1}$. The accuracy of the structural parameters determined from the Ni K–EXAFS spectra was checked in [10] based on the example of undoped NiPc and Ni foil spectra.

After processing the Ni K–EXAFS data for pure NiPc and nickel foil, we analyzed the structure of Na$_x$ = 3NiPc by formula (2) using the values of structural parameters (factors $S_0^2$ and energy parameter $e_0$ [18]) obtained for reference samples. The contribution of nickel nanoparticles, $\chi_{Ni-NPs}(k)$, included contributions of two coordination spheres, i.e., the one nearest to an absorbing Ni atom and the following one. They have different coordination numbers $N_{Ni-Ni}$; coordination sphere radii $R_{Ni-Ni}$; and Debye–Waller parameter $\sigma_{Ni-Ni}^2$, which takes into account thermal and structural disordering. The contribution of $\chi_{NiPc}(k)$ in (2) included those of three near spheres around an absorbing Ni atom with different values of parameters $R$ and $\sigma^2$. The number $N$ of atoms in each electron shell was fixed in accordance with the XRD data for undoped NiPc, which show that a large number of NiPc molecules remain in doped Na$_x$ = 3NiPc. Param-
parameter $C$, which is the fraction of Ni atoms entering into Ni NPs, was varied as a global parameter. Figure 3 (curve d) compares $|F(R)|$ for the experimental Ni K-EXAFS spectrum taken of Na$_{x}$NiPc with the result of fitting carried out by the above technique. The same comparison for pure NiPc (Fig. 3 (curve a)) and Ni foil (Fig. 3 (curve e)) was made in [10]. The corresponding structural parameters for a number of spheres near an absorbing Ni atom in a Ni nanoparticle and NiPc molecule that were obtained from the EXAFS spectra are presented in Table 2.

It follows from Table 2 that the lengths of Ni–N bonds in Na$_{x}$NiPc agree with those in undoped NiPc within the experimental error. The values of Debye–Waller parameter $\sigma^2$ for the nearest-neighbor environment of Ni atoms equal those measured at room temperature both in Ni nanoparticles and in NiPc molecules [19]. This correspondence of the fitting indicates that the model used based on Eq. (2) correctly takes into account the main types of local environment of absorbing Ni atoms in Na$_{x}$NiPc.

The parameters listed in Table 2 unambiguously indicate the presence of Ni nanoparticles in sodium-doped Na$_{x}$NiPc and also suggest that the atomic configuration of the remaining doped NiPc molecules changes insignificantly. Fraction $C$ of Ni atoms that constitute Ni nanoparticles is roughly equal to 60%.

The same fitting procedure carried out for the Na$_{x}$NiPc and Na$_{x}$NiPc samples did not reveal Ni–Ni bonds, which indicates the absence of nickel nanoparticles at these doping levels. This inference is supported by the XRD and TEM data. At the same time, the poor quality of fitting based on expression (2) (in which only one type of Ni–N bond is used to reproduce the contribution from NiPc) led us to suppose the presence of local distortions in the first coordination sphere of Ni, which consists of N atoms and NiPc molecules. Therefore, fitting $F(R)$ for the Ni K-EXAFS spectra of Na$_{x}$NiPc and Na$_{x}$NiPc was made using $\chi_2(k)$ given by

$$\chi_2(k) = C\chi_{(Ni-Ni)}(k) + (1-C)\chi_{NiPc}(k)$$

Here, the first summand $C\chi_{(Ni-Ni)}(k)$ corresponds to distorted Ni–4N structures, the fraction of which is $C$, and the second summand $(1-C)\chi_{NiPc}(k)$ corresponds to NiPc molecules. The structural parameters of the nearest-neighbor environment of Ni in the Na$_{x}$NiPc and Na$_{x}$NiPc samples with distorted and undistorted Ni–4N structures are listed in Table 3.

The absence of Ni nanoparticles in the Na$_{x}$NiPc and Na$_{x}$NiPc samples and their appearance in Na$_{x}$NiPc are clearly demonstrated by the variations in the shape and position of the first main peak in Fig. 4, which compares Fourier transforms $|F(R)|$ for oscillating branches $\chi(k)$ of the experimental Ni K-EXAFS spectra for pure NiPc; Na$_{x}$NiPc, Na$_{x}$NiPc, and Na$_{x}$NiPc; and Ni foil.

### Table 2. Structural parameters of the nearest-neighbor environment for Ni atoms in the Na$_{x}$NiPc sample. Parenthesized numbers are the values of the same parameters for undoped NiPc and nickel foil

| Sample    | Composition | $C$, % | Bonds  | $N$  | $R$, nm | $\sigma^2$, nm$^2$ |
|-----------|-------------|-------|--------|------|---------|-------------------|
| Na$_{x}$NiPc | NiPc        | 40    | Ni–N   | 4.0  | 0.191   | (0.191)          |
|           | NiNPs       | 60    | Ni–C   | 8.0  | 0.305   | (0.295)          |
|           |             |       | Ni–N   | 4.0  | 0.318   | (0.335)          |
|           |             |       | Ni–Ni  | 5.4  | 0.257   | (0.248)          |
|           |             |       | Ni–Ni  | 2.7  | 0.366   | (0.352)          |
2.4. Raman Spectroscopy Data

The structure of the NiPc molecule is schematically shown in Fig. 4. According to [20], this molecule belongs to the \(D_{4h}\) symmetry group, and the result of the factor group analysis of its normal oscillations can be represented in the form 14\(A_{1g}\) + 13\(A_{2g}\) + 14\(B_{1g}\) + 14\(B_{2g}\) + 13\(E_g\) + 6\(A_{1u}\) + 8\(A_{2u}\) + 7\(B_{1u}\) + 28\(E_u\). Modes that are active in the Raman spectra belong to the symmetry groups \(A_{1g}\), \(B_{1g}\), \(B_{2g}\), and \(E_g\). It was argued [21] that, in the interval of 300–1650 cm\(^{-1}\), Raman spectra contain lines that correspond to the oscillations of a macroscopic phthalocyanine ring, whereas intense lines that are assigned to the oscillations of aliphatic substituents are absent. As for oscillations that involve the central atom of the metal, they may be observed in the wavenumber interval 200–300 cm\(^{-1}\).

Figures 5a and 5b show Raman spectra taken at exciting radiation wavelengths of 514 and 633 nm, respectively. The differences between the Raman spectra for pure NiPc and those reported in [21, 22] lie both in the different numbers of lines and their various positions. These discrepancies may be associated with the fact that we used powdered samples, whereas samples used in the works cited were films.

The ranges in which the oscillations of nickel atoms are observed are nearly the same, regardless of samples and wavelengths. Therefore, we cannot directly conclude that the atomic structure is locally disordered. For radiation wavelength \(\lambda = 514\) nm (Fig. 5a), the spectra of the doped samples differed only slightly from those of nominally pure NiPc. In the interval 1445–1525 cm\(^{-1}\), the profile of a family of lines in all spectra of the doped samples somewhat changes. The spectra obtained at \(\lambda = 633\) nm (Fig. 5b) are compared in Table 4. Frequency shifts observed in the Raman spectra were identified based on data from [20]. In [20], the normal oscillations of metal phthalocyanine molecules were calculated and all experimental lines in the Raman spectra were correlated.

The redistribution of the line intensities and the frequency shifts indicate the presence of an extra elec-
tron concentration, which can be attributed to the electrons that were attached by nickel phthalocyanine molecules. Then, according to Table 4, the electrons that remain in the samples after doping by sodium localize largely near five-membered cycles \(-N_\alpha-C_\alpha-C_\beta-C_\beta-C_\alpha-\) (Fig. 4) and six-membered (aromatic) cycles consisting of only carbon atoms. The extra electrons present in the samples also influence the \(N_\alpha-C_\alpha-N_\beta\) bond angle, which shows up in frequency shifts of the corresponding lines. The appearance of new lines in the Raman spectrum can be explained twofold, i.e., (i) by a change in the resonance conditions (mainly for exciting radiation wavelength \(\lambda = 633 \text{ nm}\)) due to the reconstruction of the molecule’s electronic configuration or (ii) by the appearance of phthalocyanine molecule decomposition products. Since changes in the Raman spectrum (four new lines and decrease/increase in the intensities of old lines) are most significant in samples with the highest sodium concentration (under these conditions, a large amount of nickel nanoparticles arises), the second version seems to be more plausible.

### CONCLUSIONS

A technique for doping polycrystalline NiPc powders by sodium at relatively low temperatures (\(\sim 300^\circ \text{C}\)) was developed. TEM examinations showed that metal nanoparticles with a mean size of \(\sim 20 \text{ nm}\) are present in \(Na_x=3\)NiPc samples. Comparing X-ray patterns for pure NiPc and doped \(Na_x=0.2\)NiPc, \(Na_x=1\)NiPc, and \(Na_x=3\)NiPc phthalocyanines, one can conclude that nickel nanoparticles are only present in the \(Na_x=3\)NiPc sample. NiPc molecules are disordered, whereas the structure of an individual molecule remains stable. In the \(Na_x=0.2\)NiPc and \(Na_x=1\)NiPc samples, nickel nanoparticles are absent, but local structural distortions in the initial phthalocyanine matrix are observed. The results of diffraction pattern analysis are supported by the qualitative and quantitative analysis of the \(Na_x\)NiPc samples, which was carried out using Ni K-EXAFS spectroscopy. Processing the EXAFS spectra, we determined the structural parameters of Ni–N, Ni–C, and Ni–Ni bonds and found that local distortions of the initial phthalocyanine matrix occur in

### Table 4. Changes in the Raman spectra after doping of phthalocyanine by sodium. Oscillating atoms are denoted in the same way as in Fig. 4

| Frequency shifts, \(\text{cm}^{-1}\), (identification) | \(Na_x=0.2\)NiPc, \(Na_x=1\)NiPc | \(Na_x=3\)NiPc |
|------------------------------------------------------|---------------------------------|----------------|
| 1188 \(\rightarrow\) 1193 (C--C, H--C--C)            |                                 | 1452 \(\rightarrow\) 1457 (\(C_\alpha-N_\beta, C_\alpha-C, N_\alpha-C_\alpha-N_\beta, C_\alpha-N_\beta-C_\alpha, C_\alpha-N_\beta-C_\alpha\)) |
| 1105 \(\rightarrow\) 1108 (\(C_\alpha-C, C--C\))       |                                 | \(N_\beta-C_\alpha-C\)) |
| 1305 \(\rightarrow\) 1309 (C--C, C--C--C)            |                                 | \(N_\beta-C_\alpha-C\)) |
| 1467 \(\rightarrow\) 1471 (\(C_\alpha-N_\beta, C_\alpha-C, N_\alpha-C_\alpha-N_\beta, C_\alpha-N_\beta-C_\alpha, C_\alpha-N_\beta-C_\alpha\)) | | \(N_\beta-C_\alpha-C\)) |
| 1544 \(\rightarrow\) 1552 (\(C_\alpha-N_\beta, C_\alpha-N_\alpha, N_\alpha-C_\alpha-N_\beta, C_\alpha-N_\beta-C_\alpha, C_\alpha-N_\beta-C_\alpha\)) | | \(N_\beta-C_\alpha-C\)) |
| 1607 \(\rightarrow\) 1612 (\(C_\alpha-N_\beta, C_\alpha-N_\alpha, N_\alpha-C_\alpha-N_\beta, C_\alpha-N_\beta-C_\alpha, C_\alpha-N_\beta-C_\alpha\)) | | \(N_\beta-C_\alpha-C\)) |
| New lines, \(\text{cm}^{-1}\)                          | 636                             | 636, 723, 738, 779, 1372 |
| One more difference                                   | The line at 1338 \(\text{cm}^{-1}\) (NiPc) in the spectra of the doped samples splits into two: 1340 and 1346 \(\text{cm}^{-1}\) |
slightly doped (\(x = 0.2, 1.0\)) Na\(_x\)NiPc. When the doping level rises to \(x = 3\), nickel nanoparticles incorporated into the NiPc matrix appear. It follows from the Raman spectra that the lightly doped samples (\(x = 0.2, 1.0\)) contain an extra electron density at five-membered nitrogen–carbon and six-membered aromatic phthalocyanine rings. This shows up in frequency shifts of the corresponding lines. In the heavily doped sample (\(x = 3\)), new lines appear in the Raman spectra at \(\lambda = 633\) nm. They can be identified because they correspond to the oscillations of carbon and nitrogen atoms, which result from the phthalocyanine molecule decomposition. For the Na\(_3\)NiPc sample, the value of parameter \(C \sim 60\%\) (the ratio of the amount of Ni atoms in nickel nanoparticles to the total amount of Ni atoms in the sample) determined from the EXAFS spectrum was found to be \~60\%. It can be concluded that this value provides ferromagnetism, which persists in air at room temperature for a long time.

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REFERENCES

1. J. D. Aiken III and R. G. Finke, J. Mol. Catal. A: Chem. 145, 1 (1999).
2. R. Reisfeld, T. Saraidarov, and V. Levchenko, Opt. Appl. 38, 83 (2008).
3. C.-J. Jia and F. Schuth, Phys. Chem. Chem. Phys. 13, 2457 (2011).
4. C.-X. Liu, Q. Liu, C.-C. Guo, and Z. Tan, J. Porphyrrins Phthalocyanines 14, 825 (2010).
5. M. Idowu and T. Nyokong, Int. J. Nanosci. 11, 1250018 (2012).
6. J. G. Guan, W. Wang, R. Z. Gong, R. Z. Yuan, L. H. Gan, and K. C. Tam, Langmuir 18, 4198 (2002).
7. B. Brauer, Y. Vaynzof, W. Zhao, A. Kahn, W. Li, D. R. T. Zahn, C. de Julian Fernandez, C. Sangregorio, and G. J. Salvan, J. Phys. Chem. 113, 4565 (2009).
8. R. E. Schaak, A. K. Sra, B. M. Leonard, R. E. Cable, J. C. Bauer, Y.-F. Han, J. Means, W. Teizer, Y. Vasquez, and E. S. Funck, J. Am. Chem. Soc. 127, 3506 (2005).
9. F. Li, X. Yu, H. Pan, M. Wang, and X. Xin, Solid State Sci. 2, 767 (2000).
10. N. A. Kolpacheva, L. A. Avakyan, A. S. Manukyan, A. A. Mirzakhanyan, E. G. Sharoyan, V. V. Pryadchenko, Yu. V. Zubovich, A. L. Trigubenko, and L. A. Bugaev, Phys. Solid State 58, 1004 (2016).
11. S. Zhou, Y. Li, Z. Chen, X. Li, N. Chen, and G. Du, Ceram. Int. 39, 6763 (2013).
12. L. Grigoryan, M. Simonyan, and E. Sharoyan, SU Patent No. 120686 (1984).
13. J. M. Robertson and I. Woodward, J. Chem. Soc. 36, 219 (1937).
14. A. V. Chichagov, D. A. Varlamanov, R. A. Dilanyan, T. N. Dokina, N. A. Drozhzhina, O. L. Samokhvalova, and T. V. Ushakovskaya, Crystallogr. Rep. 46, 876 (2001).
15. V. V. Pryadchenko, V. V. Srbionyan, E. B. Mikheikina, L. A. Avakyan, V. Y. Murzin, Y. V. Zubovich, I. Zizak, V. E. Guterman, and L. A. Bugaev, J. Phys. Chem. C 119, 3217 (2015).
16. V. V. Srbionyan, A. L. Bugaev, V. V. Pryadchenko, A. V. Makhbiroruda, E. B. Rusakova, L. A. Avakyan, R. Schneider, M. Dubiel, and L. A. Bugaev, J. Non-Cryst. Solids 382, 24 (2013).
17. M. Newville, B. Ravel, D. Haskel, J. J. Rehr, E. A. Stern, and Y. Yacoby, Phys. B (Amsterdam, Neth.) 208–209, 154 (1995).
18. D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen, and D. E. Ramaker, Top. Catal. 10, 143 (2000).
19. A. V. Poiarkova and J. J. Rehr, Phys. Rev. B: Condens. Matter Mater. Phys. 59, 948 (1999).
20. C. A. Melendres and V. A. Maroni, J. Raman Spectrosc. 15, 319 (1984).
21. T. V. Basova, B. A. Kolesov, A. G. Gürek, and V. Ahsen, Thin Solid Films 385, 246 (2001).
22. I. V. Aleksandrov, Ya. S. Bobovich, V. G. Maslov, and A. N. Sidorov, Opt. Spektrosk. 37, 467 (1974).

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