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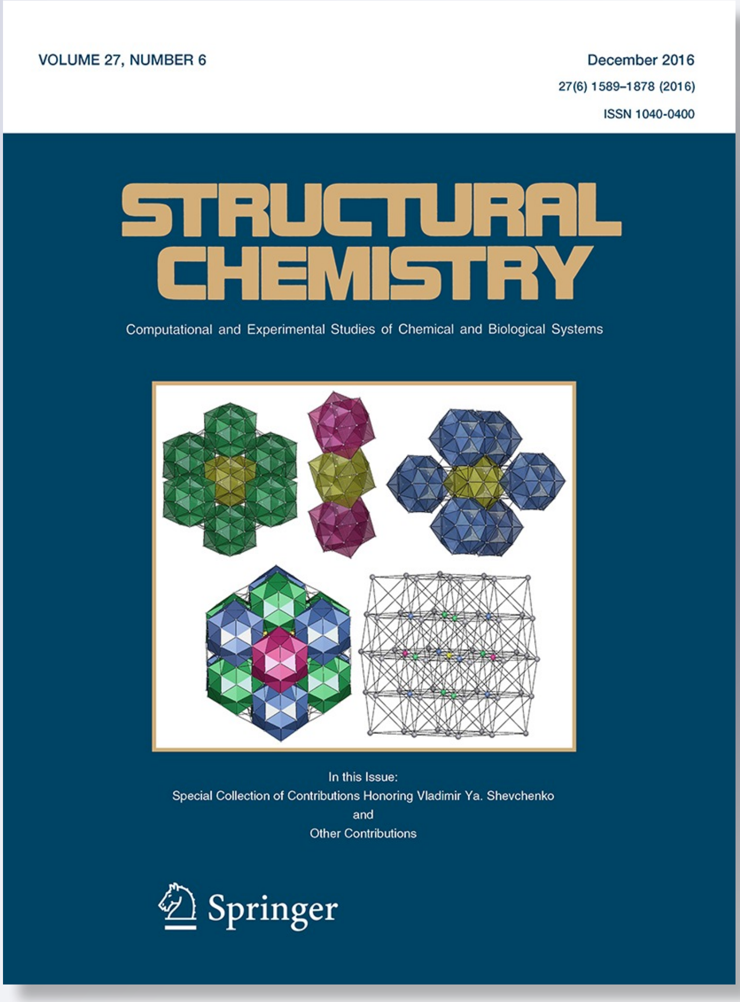

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ORIGINAL RESEARCH

Structure and real composition of undoped and Cr- and Ni-doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ single crystals

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Abstract Strontium barium niobate crystals with congruent melting composition $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN-61), both nominally pure and doped with Cr^{3+} и Ni^{3+} ions, have been investigated by neutron diffraction. Different strontium and barium contents as well as their different distribution over the Sr1, of Sr2 and Ba2 crystallographic sites of SBN-61 structure, caused by introduction of dopants, have been revealed. Coordination polyhedra of cations have been established based on the analysis of cation–anion internuclear distances together with the calculation of bond-valence sums for cations, which are equal to their formal charge. It was found that the Nb1 and Nb2 atoms are located in distorted octahedra with quadfurcated (the $Nb1O_6$ polyhedron) or bifurcated (the $Nb2O_6$ polyhedron) vertices, and the Sr1 atoms are located in a cuboctahedron with bifurcated vertices in the base plane. Different polyhedra have been revealed for the Sr2 and Ba2 atoms: Sr2 atoms are coordinated by 15 oxygen atoms to form a highly distorted five-capped pentagonal prism, whereas Ba2 atoms are located in a highly distorted three-capped trigonal prism with a coordination number 9. Comparison of interatomic and internuclear distances, determined by X-ray and neutron diffraction analyses, respectively, allowed to reveal a highly pronounced shift of electron density in Nb1 and Sr2 polyhedra, responsible for the covalent bond and properties of crystals. Location of Cr^{3+} и Ni^{3+} dopant ions in the SBN-61 structure as well as their formal charges has been discussed.

Keywords Strontium barium niobate · Ferroelectrics · Crystal structure · Coordination polyhedra · Neutron diffraction

Introduction

A congruent melting (CM) compound (one or several) with or without homogeneity regions is observed in systems with congruent melting (an isothermal or isobaric melting in which both the solid and liquid phases have the same composition throughout the transformation). Knowledge of CM composition is of great importance for growing high-quality uniform bulk crystals by technological melting techniques. When any information on CM composition is absent, a property of the object, in most cases, is attributed to a melt composition (a composition of initial charge or nominal composition) rather than a real composition of as-grown crystal, making it impossible to establish a correct structure-property correlations and, hence, to obtain functional materials with desired characteristics. The above also applies to single crystal solid solutions of relaxor ferroelectric strontium barium niobate with general chemical formula $Sr_xBa_{1-x}Nb_2O_6$ (SBN) where x varies from 0.25 to 0.75 (space group *P*4*bm*, $Z = 5$) [1–4].

Dedicated to 75th birth anniversary of RAS Academician Vladimir Ya. Shevchenko, a talented scientist best known for his fundamental works in the field of structural chemistry. He has made an invaluable contribution to the development of modern science.

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According to [5], the CM composition for SBN is found to be close to $(Sr_{0.61}Ba_{0.39}O)_{0.5007}(Nb_2O_5)_{0.4993}$. X-ray diffraction analysis (XDA) of $Sr_xBa_{1-x}Nb_2O_6$ single crystals with $x = 0.25$–0.75, grown by the Czochralski method, confirms the lack of niobium in all samples studied [6, 7]. However, doping of SBN with transition metal ions significantly reduces the maximum dielectric constant temperature, smears out the phase transition, increases relaxor properties [3, 8–11], and also leads to a change in the CM composition $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN-61) found for nominally pure crystals. In addition, growth of SBN crystal in an oxygen-deficient atmosphere contributes to deviation of its composition from CM one, as shown in [7, 12] as a result of the XDA of SBN microcrystals, both nominally pure and doped with Cr^{3+} and Ni^{3+} ions, and full-profile Rietveld analysis of the same crystals ground to a powder. However, the compositions of microcrystals, refined by the XDA, can not be attributed to all the crystal; for example, in case of growth effects, sectorial and/or zonal crystal growth. In addition, the formation of racemates for Cr- and Ni-doped SBN-61 crystals leads to the structure of microcrystals being refined by the XDA only for one of the two individuals [7]. It would therefore be useful to carry out a neutron diffraction investigation for the determination of real compositions and structure features of single crystals with initial composition $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61), both nominally pure and doped with Cr^{3+} and Ni^{3+} ions.

Materials and methods

$Sr_{0.61}Ba_{0.39}Nb_2O_6$ crystals of congruent composition, both nominally pure (SBN61) and doped with Cr^{3+} ions (SBN61:0.01Cr) and Ni^{3+} ions (SBN61:0.05Ni and SBN61:1.0Ni with different Ni^{3+} ion concentration), were grown by the modified Stepanov technique (Table 1). Volume-profiled crystals were obtained using a capillary-type shaper. The impurities were introduced into the melt as Cr_2O_3 (0.01 wt%) and Ni_2O_3 (0.05 and 1.0 wt%). The crystals were grown without rotation; the pulling rate was 6 mm h^{-1}. In this matrix, the effective distribution coefficients for the Cr and Ni impurities are 0.9 and 0.6, respectively.

Table 1 Characteristics of the samples under investigation

Designation	Initial composition	Color
SBN61	$Sr_{0.61}Ba_{0.39}Nb_2O_6$	Light yellow
SBN61:0.01Cr	$Sr_{0.61}Ba_{0.39}Nb_2O_6$ (0.01 wt% Cr_2O_3)	Light green
SBN61:0.05Ni	$Sr_{0.61}Ba_{0.39}Nb_2O_6$ (0.05 wt% Ni_2O_3)	Light green
SBN61:1.0Ni	$Sr_{0.61}Ba_{0.39}Nb_2O_6$ (1.0 wt% Ni_2O_3)	Green

The neutron diffraction analysis (NDA) of SBN crystals with size no more than ~5 × 5 × 2 mm^3 was carried out at room temperature on the four-circle diffractometer installed at the hot source (5C2) of the Orphee reactor (LLB, France; $\lambda = 0.83$ Å, ω—scan mode). In preliminary data processing, we used the WinGX pack [13] with an empirical absorption correction [14].

The crystal structure was refined by the full-matrix least-squares method in the anisotropic approximation for all atoms using the SHELXL-97 software package [15] with consideration for the atomic scattering curves for neutral atoms. Friedel pairs were not averaged. The data collection and calculations were similar for all structures. SHELXL program allows refining the atomic coordinates and thermal parameters but also the site occupancy factors [16]. In the absence of disorder, the site occupancy factor is fixed to unity, which means that the atom site is fully occupied (in other words, the atom is present at that site in every unit cell). For atoms disordered over two sites in the unit cell or in the case of vacancies presence in the site, the ratio of two or one site occupancy factor, respectively, can be refined, but generally their sum is still constrained to unity.

Results and discussion

Structural characteristics of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN-61)

According to [7], there are two types of distorted octahedra in SBN-61 crystal structure: $Nb1O_6$ with four equal Nb1-O interatomic distances in the base plane and two different

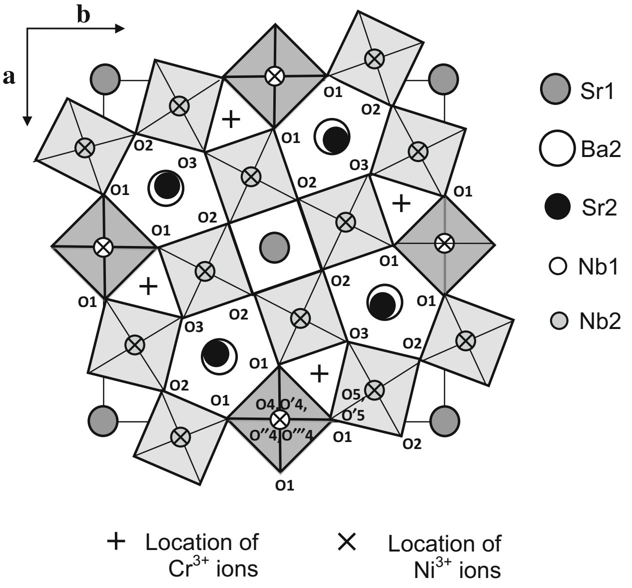


Fig. 1 Projection of the SBN-61 structure on the *XY* plane

apical Nb1-O interatomic distances, which allows to describe this polyhedron as semi-octahedron $Nb1O_5$ or octahedron $Nb1O_6$ depending on the ratio of two apical distances, and $Nb2O_6$ (rectangle in the base plane with bifurcated oxygen vertices) (Fig. 1). These octahedra are combined via their oxygen vertices to form three types of parallel channels along the polar axis *c*.

The medium-sized channels of square cross-section are statistically filled by the Sr1 atoms, forming a cuboctahedron with bifurcated oxygen vertices in the base plane. The Ba2 and Sr2 atoms with close (but different) atom coordinates statistically occupy the widest channels of pentagonal cross-section. According to [7, 17], the Ba2 and Sr2 atoms are coordinated by 15 oxygen atoms to form a five-capped pentagonal prism with four bifurcated vertices of the five in the base plane and with different interatomic distances which are longer in $Ba2O_{15}$ as compared with $Sr2O_{15}$ [which is consistent with atom sizes ($r_{Ba} > r_{Sr}$)]. It should be noted that, based on a number of high interatomic distances, the formation of a $Sr2O_9$ polyhedron is possible. Luna-Lopez et al. [18] indicate that both Ba2 and Sr2 atoms are coordinated by nine oxygen atoms to form a three-capped trigonal prism.

In SBN-61:Cr and SBN-61:Ni crystal structures, transition metal ions may occupy the smallest channels of triangular cross-section forming a distorted octahedron [7]. Volk et al. [19] suggested that the Ni^{3+} and Cr^{3+} ions occupy Nb sites, six-coordinated by oxygen atoms, without specifying Nb1 or Nb2 site. According to [7], based on the XDA data, the presence of these ions in the vicinity of the Nb2 atoms, i.e., in interstitial sites rather than substitutional ones, is possible. In the SBN-61 structure, there are five crystallochemically different O atoms coordinated by cations.

Based on the results of the refinement of structural parameters of single crystals with nominal composition $Sr_{0.61}Ba_{0.39}Nb_2O_6$ using X-ray and neutron diffraction [7, 20–25], several models of the crystal structures can be distinguished. These structures differ in coordinates of several atoms and distribution of cations over the crystallographic sites. Herewith, it was revealed that:

Table 2 Crystallographic data, experimental details and parameters of SBN-61 crystal structure refinement according to the NDA data

Chemical formula of the nominal composition	$Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN-61)			
Technique	NDA			
System, space group, *Z*	Tetragonal, *P4bm*, 5			
Sample	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni
a, Å	12.4599(2)	12.4604(3)	12.4597(2)	12.4723(2)
c, Å	3.93713(8)	3.9370(1)	3.9366(1)	3.9332(1)
V, Å^3	611.24	611.26	611.13	611.84
D_x, g/cm^3	5.282	5.281	5.282	5.276
λ, Å	0.83			
Absorption μ, mm^{-1}	0.01			
T, K	293			
Sample size, mm	~5 × 5 × 2			
Diffractometer	5C2, Orphee reactor			
Type of scan	ω			
θ_{max}, deg	42.445	42.725	43.05	42.995
Limits *h*, *k*, *l*	$0 \le h \le 20$ $-14 \le k \le 14$ $0 \le l \le 6$	$-20 \le h \le 20$ $-14 \le k \le 14$ $0 \le l \le 6$	$-20 \le h \le 20$ $0 \le k \le 14$ $0 \le l \le 6$	$-20 \le h \le 20$ $-9 \le k \le 14$ $-6 \le l \le 4$
Number of reflections: measured/unique $[I > 2\sigma(I)]$	1105/817	1089/818	1555/838	1521/865
Number of parameters in refinement	79			
Weighting scheme	$1/[\sigma^2(F_0^2) + (0.1360P)^2 + 0.05P]$, $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.1468P)^2 + 0.08P]$, $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.1290P)^2 + 0.07P]$, $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.1438P)^2 + 0.07P]$, $P = (F_0^2 + 2F_c^2)/3$
wR_2	0.2544	0.2788	0.2517	0.2936
R_1 $[I > 2\sigma(I)]$	0.0890	0.0929	0.0924	0.1024
S	1.183	1.086	1.068	1.179
Program	SHELXL-97 [15, 16]			

Table 3 Coordinates of atoms, their equivalent thermal parameters $U_{eq} \times 10^2$ (Å^2) and site occupancies P in the structures of SBN-61 crystals according to the NDA data

Parameter	Sample			
	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni
Nb1				
x	0	0	0	0
y	0.5	0.5	0.5	0.5
z	0.440(1)	0.435(1)	0.4323(4)	0.455(1)
P	0.250	0.250	0.250	0.250
U_{eq}	1.96(6)	1.97(7)	1.63(2)	2.89(4)
Nb2				
x	0.9256(1)	0.9256(1)	0.92554(5)	0.92533(6)
y	0.2114(1)	0.2117(1)	0.21157(5)	0.21179(6)
z	0.4546(6)	0.4509(6)	0.4500(2)	0.4562(4)
P	1.000	1.000	1.000	1.000
U_{eq}	2.15(4)	2.16(5)	1.90(1)	2.36(2)
Sr1				
x	0	0	0	0
y	0	0	0	0
z	−0.033(2)	−0.037(2)	−0.0413(6)	−0.0435(9)
P	0.171(6)	0.169(7)	0.166(8)	0.202(7)
U_{eq}	1.8(1)	1.8(1)	1.50(3)	2.1(1)
Sr2				
x	0.155(1)	0.152(2)	0.1651(3)	0.1549(3)
y	0.309(1)	0.313(2)	0.3217(3)	0.3129(3)
z	−0.032(5)	−0.034(7)	−0.0542(8)	−0.018(2)
P	0.219(9)	0.206(9)	0.231(9)	0.238(9)
U_{eq}	3.2(3)	2.8(4)	3.94(6)	3.55(9)
Ba2				
x	0.1703(7)	0.173(1)	0.1717(4)	0.1715(2)
y	0.3297(7)	0.327(1)	0.3283(4)	0.3285(2)
z	−0.055(4)	−0.051(5)	−0.021(2)	−0.062(1)
P	0.220(8)	0.225(9)	0.206(8)	0.21(1)
U_{eq}	2.1(5)	2.0(3)	1.8(2)	3.5(8)
O1				
x	0.0061(2)	0.0060(3)	0.00605(9)	0.0060(1)
y	0.3434(2)	0.3430(2)	0.34336(8)	0.34332(9)
z	0.484(2)	0.483(2)	0.4820(8)	0.463(1)
P	1.000	1.000	1.000	1.000
U_{eq}	5.1(1)	4.9(1)	4.76(5)	5.09(5)
O2				
x	0.0682(2)	0.0681(2)	0.06831(8)	0.06788(9)
y	0.1393(2)	0.1393(3)	0.13920(9)	0.1385(1)
z	0.488(2)	0.488(2)	0.4875(7)	0.4760(9)
P	1.000	1.000	1.000	1.000
U_{eq}	4.7(1)	4.5(1)	4.35(4)	4.52(4)
O3				
x	0.7813(2)	0.7814(2)	0.78170(9)	0.7811(1)
y	0.2813(2)	0.2814(2)	0.28170(9)	0.2811(1)
z	0.486(2)	0.470(2)	0.4724(7)	0.468(1)

Table 3 continued

Parameter	Sample			
	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni
P	0.500	0.500	0.500	0.500
U_{eq}	3.32(9)	3.28(9)	3.01(3)	3.25(4)
O4				
x	0.002(2)	−0.001(2)	0.0000(4)	−0.0021(6)
y	0.519(1)	0.521(2)	0.5204(3)	0.5189(3)
z	0.974(2)	0.975(3)	0.9725(8)	0.9847(8)
P	0.28(2)	0.27(2)	0.262(4)	0.270(4)
U_{eq}	5.7(8)	4.8(9)	4.1(1)	4.5(2)
O5				
x	0.9053(5)	0.9047(6)	0.9054(2)	0.9060(2)
y	0.1945(5)	0.1954(5)	0.1956(2)	0.1956(2)
z	−0.016(2)	−0.022(2)	−0.0220(6)	−0.0281(8)
P	0.54(2)	0.55(2)	0.551(5)	0.562(5)
U_{eq}	3.2(1)	3.2(1)	2.96(4)	3.12(4)
O′5				
x	0.9456(7)	0.9460(7)	0.9458(2)	0.9445(3)
y	0.2157(6)	0.2151(7)	0.2152(2)	0.2155(3)
z	−0.020(2)	−0.024(3)	−0.0237(7)	−0.035(1)
P	0.46(2)	0.45(2)	0.449(5)	0.438(5)
U_{eq}	3.2(1)	3.2(1)	2.96(4)	3.12(4)

- the Sr1, Sr2 and Ba2 sites, as well as the Nb2 site [7], are occupied statistically with different site occupancies;
- the right systems of points (RSP) of the Sr1, Nb1 and Nb2 atoms are the same in all models, as well as RSP of O1, O2, O3 atoms, which are fully occupied their crystallographic sites;
- the Ba and Sr2 atoms occupy statistically only 4*c* sites with the same x $x + 1/2$ z coordinates (1A model) [23–25] or 8*d* sites with x y z coordinates (Sr2) and 4*c* sites with x $x + 1/2$ z coordinates (Ba2) with different site occupancies (2A model) [7, 20–22];
- the O4 atoms may fully occupy 2*b* sites with 0 ½ z coordinates (1O model) [7, 23–25] or occupy statistically a half of 4*c* sites with x $x + 1/2$ z coordinates (2O model) [20–22]. Analysis of the thermal parameters, obtained as a result of the XDA, shows clearly excessive values for the O4 atoms [7];
- the O5 atoms fully occupy 8*d* sites (3O model) [23–25] or 8*d* site is split into two 8*d* sites, O5 and O′5, with the close [20–22] or different [7] atomic coordinates and an equal [20–22] or different [7] distribution of the oxygen atoms in the structure sites (4O model).

Kuz'micheva et al. [7] reported the structure of SBN-61 microcrystals, both nominally pure and doped with Cr^{3+} and Ni^{3+} ions, refined by the XDA, where the Sr2 and Ba2 atoms occupy sites according to the 2A model, and the O5 and O4 atoms occupy RSP according to the 5O and 1O models, respectively.

Results of neutron diffraction analysis (NDA)

Refinement of positional and thermal parameters as well as occupancies of the Ba2 and Sr2 sites was carried out according to the 2A model, and that of the O5 site—according to the 5O model. Crystal structures of macroparts of all the crystals under investigation were refined for different RSP of the O4 atoms with 0 ½ z (2*b* sites are fully occupied) (model 1O) [7, 23–25], x $x + 1/2$ z (defective 4*c* sites) (Model 2O) [20–22] and x y z (defective 8*d* sites) coordinates. Real U_{eq}(O4) values, comparable with the thermal parameters of other oxygen atoms, have been achieved, providing that the 8*d* sites are partially occupied, that was not considered in the literature before. This confirms the possibility of using the U_{eq}(O4) values for the selection of structural model with defective O4 sites [12].

Due to the fact that the electroneutrality of system has not been achieved for the cation composition, the occupancies of all the oxygen sites were refined. As a result, it was found that the O1, O2 and O3 sites were defect-free, the O4 site was about 50–60 % full, while the O5 and O′5

Table 4 Main internuclear (NDA) or interatomic (XDA) distances d (Å) and bond angles (deg) in the structures of SBN-61 crystals according to the NDA and XDA [7] data

Method	NDA				XDA			
Crystal	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni	SBN61[b]	SBN61:0.01Cr[b]	SBN61:0.05Ni[b]	SBN61:1.0Ni[b]
Nb1								
−4 × ¼ O4 (1 × O4)[a]	1.848(11)	1.830(11)	1.828(3)	1.863(5)	1.795(8)	1.791(5)	1.776(6)	1.804(4)
−4 × O1	1.961(3)	1.967(3)	1.963(1)	1.956(1)	1.947(2)	1.964(2)	1.941(3)	1.962(2)
1) $[\text{Nb1-O}]_{\text{av.}}$	1.938	1.940	1.936	1.937	1.917	1.929	1.908	1.930
Σs—bond-valence sum								
(CN = 5)	4.68	4.68	4.73	4.68	5.00	4.85	5.13	4.82
−4 × ¼ O4 (1 × O4)[a]	2.118(11)	2.141(12)	2.142(3)	2.099(5)	2.142(8)	2.150(5)	2.158(6)	2.124(4)
2) $[\text{Nb1-O}]_{\text{av.}}$	1.968	1.973	1.970	1.964	1.954	1.966	1.950	1.963
Σs—bond-valence sum								
(CN = 6)	5.25	5.22	5.26	5.28	5.53	5.37	5.64	5.38
$\Delta = d_2 – d_1^c$	0.270	0.311	0.314	0.236	0.347	0.359	0.382	0.320
O4-Nb1-O4	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
O4-Nb1-O1	95.60(69)	96.08(68)	95.97(19)	95.46(22)	95.52	96.38	94.64	93.37
Nb2								
−1 × O1	1.930(3)	1.923(3)	1.928(1)	1.924(1)	1.935(2)	1.931(2)	1.940(3)	1.923(2)
−1 × O2	1.964(3)	1.969(3)	1.964(1)	1.965(1)	1.959(2)	1.966(2)	1.958(3)	1.967(2)
−1 × O3	1.999(2)	1.997(2)	1.9958(8)	1.996(1)	1.9947(8)	1.9959(8)	1.998(1)	1.9932(8)
−1 × O2	1.996(3)	1.998(3)	2.000(1)	2.001(3)	2.005(2)	1.998(2)	2.003(3)	2.005(2)
−1 × ½ O5	1.883(8)	1.885(11)	1.885(2)	1.931(4)	1.925(6)	1.897(4)	1.878(4)	1.937(5)
−1 × ½ O′5	1.886(9)	1.890(8)	1.882(3)	1.948(5)	2.107(4)	2.101(4)	2.118(4)	2.061(3)
−1 × ½ O5	2.109(7)	2.102(8)	2.103(2)	2.052(4)	2.073(6)	2.105(4)	2.141(4)	2.059(4)
−1 × ½ O′5	2.084(9)	2.086(11)	2.088(3)	2.015(5)	1.853(4)	1.865(4)	1.839(4)	1.895(3)
$[\text{Nb2-O}]_{\text{av.}}$	1.978	1.978	1.978	1.9765	1.979	1.979	1.981	1.977
O5-Nb2-O5	174.95(30)	174.93(33)	175.14(11)	175.30(12)	174.11	175.31	173.70	174.90
O2-Nb2-O3	173.64(34)	173.46(37)	173.19(12)	176.17(17)	172.99	173.09	173.91	175.05
O2-Nb2-O1	169.86(31)	169.22(34)	169.27(11)	171.79(10)	168.75	169.01	171.10	170.97
O1-Nb2-O5	95.06(33)	94.73(35)	94.48(12)	95.81(7)	95.19	94.28	97.72	101.96
O2-Nb2-O5	97.74(32)	98.45(33)	98.27(11)	99.73(17)	99.37	97.78	97.07	97.94
Σs—bond-valence sum								
(CN = 6)	5.08	5.08	5.08	5.05	5.07	5.08	5.08	5.06
Sr1								
−4 × O2	2.699(7)	2.689(8)	2.678(3)	2.697(4)	2.648(3)	2.692(3)	2.713(6)	2.692(3)
−4 × ½ O5	2.696(6)	2.710(7)	2.709(2)	2.708(3)	2.709(4)	2.707(4)	2.678(6)	2.710(4)
−4 × ½ O′5	2.772(7)	2.764(8)	2.766(3)	2.776(3)	2.767(4)	2.769(4)	2.773(7)	2.777(4)
−4 × O2	2.820(8)	2.829(9)	2.840(3)	2.806(4)	2.863(3)	2.835(3)	2.819(5)	2.825(3)

Table 4 continued

Method	NDA				XDA			
Crystal	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni	SBN61[b]	SBN61:0.01Cr[b]	SBN61:0.05Ni[b]	SBN61:1.0Ni[b]
$[\mathrm{Sr1\text{-}O}]_{\mathrm{av.}}$	2.751	2.752	2.752	2.748	2.750	2.761	2.753	2.754
Σs—bond-valence sum								
(CN = 12)	2.19	2.19	2.20	2.20	2.24	2.15	2.18	2.18
Sr2								
−1 × O1	2.692(21)	2.661(24)	2.708(4)	2.681(6)	2.588(4)	2.561(3)	2.650(7)	2.654(4)
−1 × O3	2.737(17)	2.790(27)	2.691(4)	2.740(6)	2.656(4)	2.687(4)	2.718(6)	2.753(4)
−1 × O1	2.784(19)	2.755(27)	2.820(4)	2.784(6)	2.802(4)	2.826(3)	2.807(7)	2.899(4)
−2 × ½ O5 (O′5)	2.714(16)	2.761(20)	2.857(4)	2.776(4)	2.797(4)	2.791(4)	2.738(7)	2.774(4)
−1 × O3	2.785(20)	2.813(24)	2.840(4)	2.818(6)	2.936(5)	2.916(4)	2.875(6)	2.862(4)
−1 × O1	2.991(18)	2.956(24)	2.908(4)	2.950(6)	2.902(5)	2.897(3)	2.893(6)	2.774(4)
−2 × ½ O5 (O′5)	2.853(19)	2.841(21)	2.840(3)	2.892(5)	2.976(4)	2.951(4)	2.942(9)	2.912(5)
−4 × ¼ O4	2.903(27)	2.804(31)	2.864(5)	2.834(7)	2.996(1)	3.006(1)	2.999(2)	2.990(1)
−1 × O1	2.944(27)	2.842(30)	2.849(5)	2.864(7)	3.095(4)	3.109(3)	3.038(7)	3.009(4)
1) $[\mathrm{Sr2\text{-}O}]_{\mathrm{av.}}$	2.823	2.803	2.820	2.815	2.828	2.860	2.851	2.847
Σs—bond-valence sum								
(CN = 9)	1.39	1.44	1.38	1.40	1.46	1.33	1.31	1.31
−1 × O2	3.032(18)	3.049(23)	3.004(4)	3.141(5)	3.018(3)	3.037(3)	3.053(6)	3.059(3)
−2 × ½ O5 (O′5)	3.073(18)	3.040(25)	3.013(4)	3.043(6)	3.070(4)	3.091(4)	3.065(7)	3.094(4)
−1 × O2	3.134(18)	3.161(24)	3.143(4)	3.134(5)	3.230(4)	3.249(4)	3.242(7)	3.269(4)
−1 × O2	3.260(17)	3.317(22)	3.261(5)	3.355(5)	3.387(5)	3.392(3)	3.362(6)	3.334(4)
−2 × ½ O5 (O′5)	3.421(19)	3.412(23)	3.329(4)	3.431(5)	3.290(4)	3.286(4)	3.268(7)	3.287(4)
−1 × O2	3.459(18)	3.536(23)	3.599(4)	3.579(5)	3.573(5)	3.577(3)	3.553(6)	3.517(4)
2) $[\mathrm{Sr2\text{-}O}]_{\mathrm{av.}}$	2.985	2.983	2.982	3.001	3.001	3.025	3.014	3.013
Σs—bond-valence sum								
(CN = 15)	1.71	1.76	1.72	1.69	1.77	1.63	1.62	1.61
Ba2								
−1 × O3	2.690(14)	2.684(21)	2.744(8)	2.675(6)	2.696(4)	2.709(4)	2.699(6)	2.715(4)
−1 × O3	2.864(17)	2.806(20)	2.781(8)	2.843(6)	2.774(4)	2.784(4)	2.777(6)	2.745(4)
−2 × O1	2.740(14)	2.781(17)	2.850(7)	2.789(5)	2.824(4)	2.808(3)	2.838(6)	2.858(4)
−4 × ½ O5 (O′5)	2.947(12)	2.904(17)	2.926(5)	2.942(4)	2.870(4)	2.884(4)	2.843(7)	2.855(4)
−2 × O1	2.952(14)	2.964(19)	2.867(7)	2.928(6)	2.927(4)	2.949(3)	2.908(6)	2.894(4)
−4 × ¼ O4	2.861(25)	2.863(30)	2.852(8)	2.850(7)	3.0511(5)	3.0525(5)	3.0506(7)	3.0696(5)
1) $[\mathrm{Ba2\text{-}O}]_{\mathrm{av.}}$	2.855	2.850	2.851	2.854	2.863	2.870	2.856	2.860

Table 4 continued

Method	NDA				XDA			
Crystal	SBN61	SBN61:0.01Cr	SBN61:0.05Ni	SBN61:1.0Ni	SBN61[b]	SBN61:0.01Cr[b]	SBN61:0.05Ni[b]	SBN61:1.0Ni[b]
Σs—bond-valence sum								
(CN = 9)	2.03	2.04	2.00	2.02	1.98	1.94	2.01	1.99
−4 × ½ O5 (O′5)	3.142(9)	3.155(11)	3.148(3)	3.164(3)	3.199(4)	3.193(4)	3.203(9)	3.182(5)
−2 × O2	3.238(9)	3.235(13)	3.210(8)	3.431(5)	3.265(4)	3.268(4)	3.266(6)	3.273(4)
−2 × O2	3.158(25)	3.160(25)	3.148(4)	3.254(5)	3.392(4)	3.405(4)	3.390(6)	3.381(4)
2) [Ba2-O]$_{av.}$	2.985	2.983	2.978	3.026	3.032	3.037	3.028	3.028
Σs—bond-valence sum								
(CN = 15)	2.58	2.58	2.57	2.44	2.40	2.36	2.42	2.41

[a] Interatomic distance according to the XDA [7]

[b] According to [7], the designation of samples was SBN-I, SBN-II(Cr), SBN-III(Ni), SBN-IV(Ni), respectively

[c] d_2 and d_1 are long and short Nb1-O4 apical distances, respectively

sites were ~54 and ~46 % full, respectively. Tables 2, 3 and 4 contain the crystallographic data, experimental details, structural parameters and internuclear distances of macroparts of all the SBN-64 crystals according to the NDA data.

Refined compositions of macroparts of SBN61, SBN61:0.01Cr, SBN61:0.05Ni crystals (Table 5) differ from the composition of initial charge in the barium content, which correlates with the Sr2 content. The greatest difference between the nominal and refined compositions was found for SBN61:1.0Ni crystal as a result of both XDA [7] and NDA (Table 5).

To clarify the coordination numbers (CN) and the shapes of coordination polyhedra of cations in SBN-61 structure, we used the equation $s = e^{(R1-R)/0.37}$, where s is the bond valence, $R1$ is a bond-valence empirical parameter characterizing the distance at which the bond is estimated to be one unit of bond valence (it is specific to each atom: $R1_{Nb} = 1.911$, $R1_{Sr} = 2.118$, $R1_{Ba} = 2.29$ Å), R—experimental cation-oxygen distance in observed crystal structures (Table 4), and $\sum s$ is equal to the formal charge (FC) of cation [26].

For the Nb1 cations, the calculation showed that the $\sum s$ values closest to the Nb formal charge [FC(Nb) = 5] are $\sum s = 5.22$–5.28, and, hence, the CN Nb1 = 6 (Table 4). Thus, according to the NDA, in the SBN-61 crystal structure, the Nb1 atoms are in distorted octahedra (Fig. 2a) with internuclear distances (d, Å) in the base plane 4 × O1 (these distances are similar in all the structures except for SBN61:1.0Ni, where they are shorter), and with four split apical O4 atoms (quadfurcated) with different distances $d_1 < d_2$ with $\Delta = d_2 – d_1$ (the smallest Δ value is observed in the SBN61:1.0Ni structure) (Table 4).

The calculation of bond-valence sums for Nb1 cation based on the cation–anion interatomic distances refined by the XDA [7] showed that the second O4 atom with long interatomic distance d_2 does not participate in bond formation (i.e., coordination polyhedron is $Nb1O_5$) as its contribution to bond formation is extremely small (Table 4; Fig. 2a).

The Nb2 atoms are six-coordinated by the O atoms with split vertices (O5 and O′5) to form a distorted octahedron $Nb2O_6$ (Fig. 2b). However, the Nb2-O5 and Nb2-O′5 distances in SBN61:1.0Ni structure are longer or shorter than the corresponding distances in other structures, while maintaining the similar average Nb-O2 distances in all the structures refined (Table 4). The calculation of bond-valence sums for the Nb2 cation confirmed that the CN Nb2 = 6 ($\sum s = 5.05$–5.08) both according to the NDA and XDA (Table 4).

Oxygen atoms surrounding Sr1 form a cuboctahedron with the CN Sr1 = 12 ($\sum s = 2.19$–2.20) with bifurcated

Table 5 Refined compositions of SBN-61 crystals determined by the NDA

Sample	Refined composition
SBN61	$Sr1_{0.273(6)}Sr2_{0.35(1)}Ba2_{0.35(1)}Nb_2(O_{5.97}\square_{0.03})^a \equiv Sr_{0.62(1)}Ba_{0.35(1)}Nb_2(O_{5.97}\square_{0.03})$
SBN61:0.01Cr	$Sr1_{0.270(7)}Sr2_{0.33(1)}Ba2_{0.36(1)}Nb_2(O_{5.96}\square_{0.04})^a \equiv Sr_{0.60(1)}Ba_{0.36(1)}Nb_2(O_{5.96}\square_{0.04})$
SBN61:0.05Ni	$Sr1_{0.265(8)}Sr2_{0.37(1)}Ba2_{0.33(1)}Nb_2(O_{5.97}\square_{0.03})^a \equiv Sr_{0.64(1)}Ba_{0.33(1)}Nb_2(O_{5.97}\square_{0.03})$
SBN61:1.0Ni	$Sr1_{0.323(7)}Sr2_{0.38(1)}Ba2_{0.34(2)}Nb_2O^a_{6.04} \equiv Sr_{0.70(1)}Ba_{0.34(2)}Nb_2O_{6.04}$

[a] Oxygen content was calculated based on the electroneutrality condition

☐ Vacancies

vertices (O5 and O′5) in the base plane (Fig. 2c), the most correct shape of $Sr1O_{12}$ polyhedron being observed for SBN61:1.0Ni structure (Table 4).

Significant difference in cation-oxygen distances was found for Ba2 and Sr2 polyhedra. According to the Ba2-O internuclear/interatomic distances refined by both NDA and XDA, it is possible that the CN Ba2 = 15; however, the bond-valence sums for the Ba2 are $\sum s = 2.00–2.04$, according to the NDA, and $\sum s = 1.94–2.01$, according to XDA, which indicates that the CN Ba2 = 9 in all the structures (Table 4). For the CN Ba2 = 15, the bond-valence sums are too high (Table 4). On the other hand, for the Sr2 atoms with the CN = 9, the bond-valence sums, calculated according to both NDA and XDA, are too small even when possible deviations (10–20 %) are taken into account (Table 4). A high $\sum s$ values, but still far from the FC Sr, are achieved for CN Sr2 = 15. This indicates that the difference in coordinates of the Ba2 and Sr2 atoms (2A model) must inevitably lead to difference in their oxygen environments: several oxygen atoms are mutual for the Ba2 and Sr2, and additional oxygen atoms should be included in the Sr2 environment. This may be due to the splitting of the O1 site [the U_{eq}(O1) values are higher than the corresponding values for the remaining O atoms].

Therefore, the Ba2 and Sr2 atoms occupy the same 8*d* site but with different coordinates and coordination environments due to the difference in their sizes ($r^{XII}_{Ba} = 1.61$ Å, $r^{XII}_{Sr} = 1.44$ Å) [27]. The Sr2 atoms are coordinated by 15 oxygen atoms to form a highly distorted five-capped pentagonal prism with split vertices (O5 and O′5; O4, O′4, O″4 and O‴4) in the base plane (Fig. 2d). The Ba2 atoms are in a highly distorted three-capped trigonal prism with the CN = 9 (Fig. 2e), which was also established by Luna-Lopez et al. [18], but, in contrast to our results, it was supposed that the Sr2 atoms have the same coordination. It follows that the calculation of bond-valence sums based on the experimental cation–anion interatomic distances is needed for the determination of CN of highly distorted coordination polyhedra, which primarily include the Nb1, Sr2 and Ba2 polyhedra.

The refinement of structures of SBN61:0.01Cr, SBN61:0.05Ni, SBN61:1.0Ni macroparts allowed to reveal strong peaks with coordinates ~0.04 ~0.46 ~0.45 (SBN61:0.01Cr), ~0.90 ~0.23 ~0.96 (SBN61:0.05Ni) and 0 0.5 ~ 0.76 (SBN61:1.0Ni) in the residual nuclear density. Based on these data, the presence of Cr^{3+} ions in the triangular cavities with a distorted octahedral coordination (as is typical for Cr^{3+} ions) and the presence of Ni^{3+} ions in the vicinity of the Nb2 and Nb1 sites (Fig. 2) in a distorted semi-octahedron are possible (Fig. 2). Due to the fact that the Ni^{2+} ions are characterized by the CN = 4 with tetrahedral or square coordination and the Ni^{3+} ions, in turn, have octahedral environment, it is possible that the nickel ions are present in the form of Ni^{2+} and Ni^{3+} (with different FC) in the SBN:1.0Ni structure, which was also assumed in [7].

The difference in the interatomic and internuclear distances, obtained by the XDA and NDA (Table 4), is due to the fact that position of center of gravity of atom's electron density (XDA) or that of centroid of nucleus thermal fluctuations (NDA) is determined. A comparison of the distances, obtained as a result of the XDA and NDA, shows a highly pronounced shift of the electron density, responsible for the covalent bond, in the Nb1 and Sr2 polyhedra (Table 4). It is possible that the properties of SBN crystals will depend primarily from these atoms; for example, form the Sr2 content in the crystal composition, as confirmed in [1], and from interatomic distances in $Nb1O_6$ polyhedra [7].

Figure 3 shows a change in the difference of Δ, Å = d_2–d_1 value (d_2 и d_1 are long and short Nb1-O4 apical distances, respectively) in the $Nb1O_6$ polyhedra for all the crystals under investigation (Fig. 3a) and its correlation with the Sr content in the Sr1 site: the difference between long (d_2, Å) and short (d_1, Å) internuclear distances (Δ) increases with decreasing Sr content in the Sr1 site (Fig. 3b). It should be noted that the minimum Δ value was found for the $Nb1O_6$ polyhedra in SBN61:1.0Ni structure (Fig. 3a), and the Δ value is correlated with physical properties, in particular, the second-order nonlinear susceptibility (Fig. 4).

Therefore, NDA of macroparts of SBN-61 crystals showed different Sr and Ba content and their different distribution over the Sr1, of Sr2 and Ba2 crystallographic sites (the most pronounced for SBN:1.0Ni), caused by

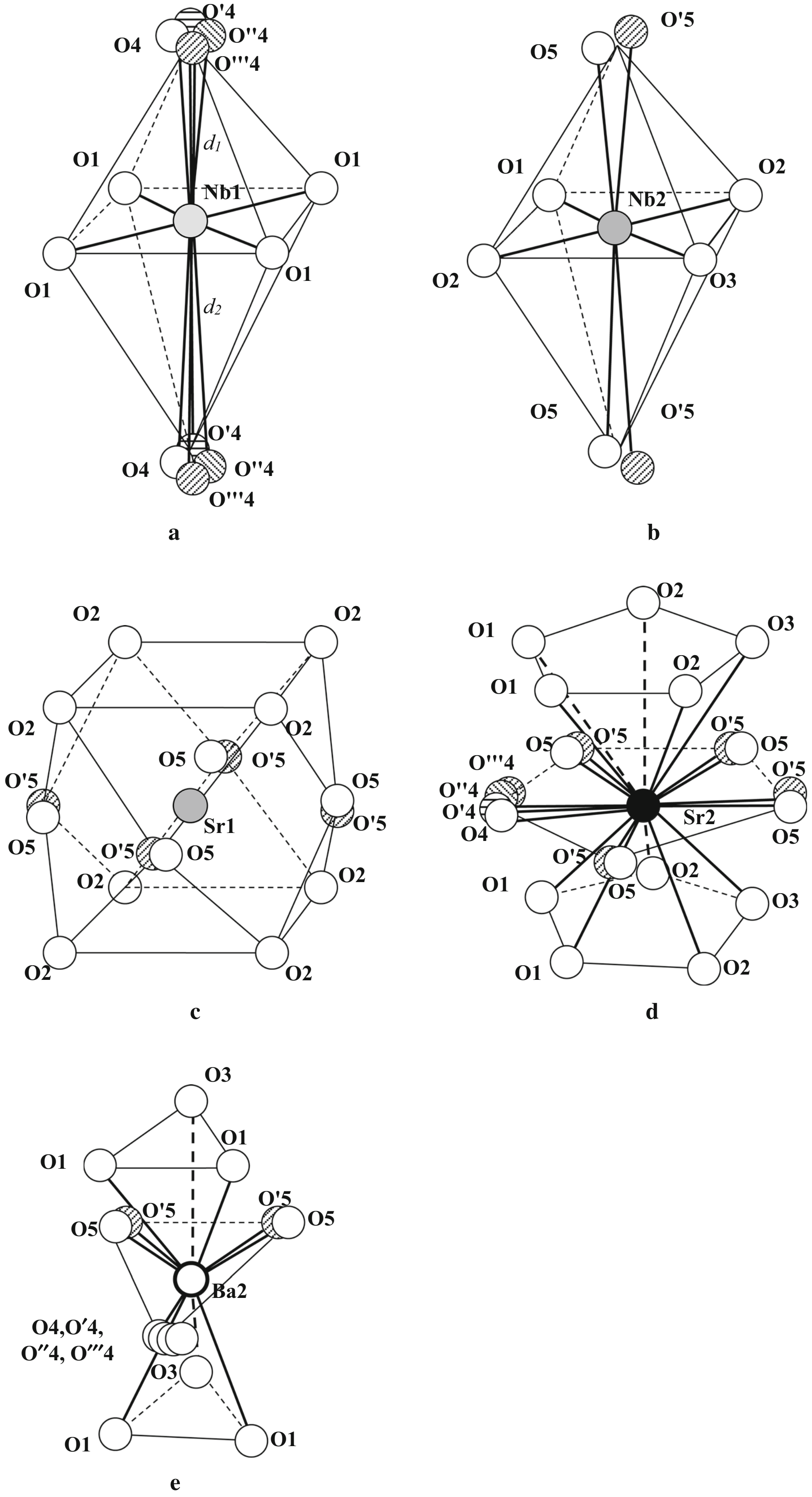
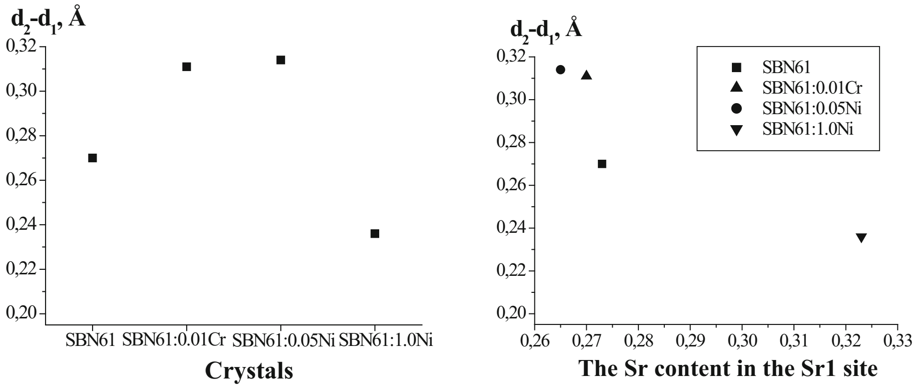


Fig. 2 Coordination polyhedra of the cations in the SBN-61 structure: Nb1 (**a**) Nb2 (**b**), Sr1 (**c**), Sr2 (**d**) and Ba2 (**e**)

Fig. 3 Change in the difference of Nb1-O4 internuclear distances (Δ, Å = d_2–d_1) in the $Nb1O_6$ polyhedron (**a**) and its correlation with the Sr content in the Sr1 site (**b**)



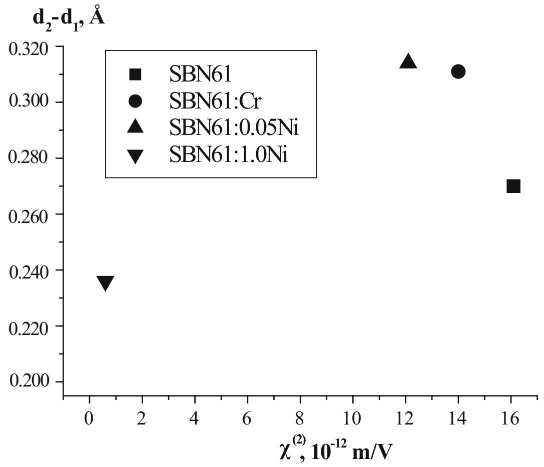


Fig. 4 Correlation between the difference of Nb1-O4 internuclear distances (Δ, Å = d_2–d_1) in the $Nb1O_6$ polyhedron and the second-order nonlinear susceptibility values, $\chi^{(2)}$, in SBN-61 crystals

introduction of dopants. Moreover, the Ba content in crystal macroparts differs from that in the CM compositions. It was found that the Sr2 and Ba2 atoms occupy close (but different) RSP, which leads to their different coordination environment by O atoms, established as a result of calculation of bond-valence sums for cations. The Nb1 and Nb2 atoms are six-coordinated by O atoms to form distorted octahedra, and the Sr1 atoms are located at the center of cuboctahedrons. The most disordered coordination environment was found for Sr2 atoms, surrounded by 15 O atoms to form a highly distorted five-capped pentagonal prism with split vertices in the base plane, and for Ba2 atoms, located in a highly distorted three-capped trigonal prism with split vertices in the base plane. Analysis of the NDA results obtained indicates a different behavior of Cr^{3+} and Ni^{3+} ions in the SBN-61 structure and a highly pronounced shift of the electron density in the Nb1 and Sr2 polyhedra, responsible for the covalent bond and SBN-61 physical properties.

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