XAFS and XRD Study of the Atomic Displacements in Aurivillius Phase Ferroelectric $\text{Bi}_{2.25}\text{Ca}_{0.5}\text{Na}_{0.25}\text{Nb}_2\text{O}_9$

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Abstract. The novel layered perovskite-like oxide with Aurivillius phase structure $\text{Bi}_{2.25}\text{Ca}_{0.5}\text{Na}_{0.25}\text{Nb}_2\text{O}_9$ has been synthesized by solid-state reaction method. This compound is a ferroelectric with the Curie temperature 972 K. The crystal structure of $\text{Bi}_{2.25}\text{Ca}_{0.5}\text{Na}_{0.25}\text{Nb}_2\text{O}_9$ has been determined from powder diffraction data recorded at room temperature. The parameters of the orthorhombic cell (space group $A2_{1}am$) are: $a=5.4845$ Å, $b=5.4549$ Å, $c=24.9195$ Å. Using the profile of the X-ray diffraction pattern the atomic coordinates have been refined by Rietveld method and the Nb ion position in the oxygen octahedra has been found. It was shown that the Nb ion is displaced from the center of the oxygen octahedra by ~0.15 Å. Nb K-edge EXAFS spectra were measured over the temperature range 295 K - 960 K. The interatomic distances Nb-O and the mean-square relative displacements $\sigma^2$ have been determined. The interatomic distances Nb-O at room temperature obtained from XAFS analysis are in a good agreement with those found from XRD data. It was revealed that the temperature increase results in the decreasing of Nb ion displacements from the center of the oxygen octahedra. However, in the vicinity of the ferroelectric phase transition the displacement of Nb ion was preserved.

Keywords: Aurivillius phase, ferroelectric, XAFS, X-ray diffraction, ion displacement.

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INTRODUCTION

The layered bismuth oxides of the general formula $\text{Bi}_m\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$ are known as Aurivillius phases (APs) [1-3], where A is a large cations Bi$^{3+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Na$^+$, K$^+$, Th$^{4+}$ or rare earth ions and B is a highly charged small cations Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$, W$^{6+}$, Mo$^{6+}$, Fe$^{3+}$, Mn$^{4+}$, Cr$^{3+}$, Ga$^{3+}$, etc. The crystal structure of all Aurivillius phases consist of perovskite-like $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ units which regularly interleaved with $[\text{Bi}_3\text{O}_7]^{2+}$ layers. The value of $m$ indicates the number of perovskite-like layers, made up of oxygen octahedra, per slab. Although the structure of APs has been studied in detail by various techniques, including powder x-ray diffraction (XRD) and neutron diffraction, some issues pertaining to the distortion of the unit cell of APs from “ideal” tetragonal symmetry (sp. gr. $I4/mmm$, no. 139) and the origin of this distortion are still of scientific interest. Moreover, the key structural features of APs responsible for their ferroelectric properties are not yet fully understood. The ferroelectric state of these phases is commonly attributed to the displacement of the B ion (Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$) from the center position of the oxygen octahedral in the perovskite layers. The interest in the synthesis and study of new APs is also stimulated by the fact that APs find many device applications owing to their unique physical properties. The layered bismuth oxides are characterized by high ferroelectric transition temperatures (high Curie temperature $T_c$), low dielectric constants, low dielectric loss, large anisotropy in coupling factors, low fatigue rate and thus are good candidates for application in devices for ultrasonic non-destructive testing in chemical, metallurgical and nuclear industries. In this paper, we report the synthesis, structural characterization by EXAFS and powder X-ray diffraction (XRD) measurements of the new AP $\text{Bi}_{2.25}\text{Ca}_{0.5}\text{Na}_{0.25}\text{Nb}_2\text{O}_9$ ($m = 2$).

EXPERIMENTAL

Synthesis and characterization. Polycrystalline $\text{Bi}_{2.25}\text{Ca}_{0.5}\text{Na}_{0.25}\text{Nb}_2\text{O}_9$ was prepared by solid-state reaction, using extrapure-grade $\text{Bi}_2\text{O}_3$, $\text{NaHCO}_3$, $\text{CaCO}_3$, and $\text{Nb}_2\text{O}_5$ as starting reagents. A stoichiometric powder mixture was thoroughly homogenized by prolonged grinding and pressed into disks, which were fired in air for 3 h at 700–800°C.
and then, after intermediate grinding and mixing, at 1020°C.

Nb K-edge EXAFS spectra of Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ were measured in the Siberian Synchrotron Radiation Centre (Novosibirsk). The storage ring VEPP-3 with the electron beam energy of 2 GeV and current of 70–90 mA has been used as the source of radiation. All the spectra were recorded in a transmission mode using a double-crystal Si(111) monochromator and two ionization chambers as detectors. EXAFS data were analyzed using the IFEFFIT data analysis package [4]. The radial pair distribution functions around Nb atoms were obtained by the Fourier transformation (FT) of the $k^2$-weighted spectra over the range of photoelectron wave numbers 2.8–12.8 Å$^{-1}$. The structural parameters of the local Nb environment were determined using nonlinear least squares fitting of the data for coordination shells, by comparing the calculated EXAFS signal of a model compound with the FT obtained from the total EXAFS spectrum by Fourier filtering. The atomic position coordinates of the model compound were taken from the Rietveld powder diffraction analysis results. Theoretical spectra were simulated by means of FEFF7 [5]. The quality of fit was estimated from discrepancy factors between the experimental and simulated functions ($Q$-factor).

XRD patterns were collected on a DRON-4 diffractometer equipped with a GP-13 sample spinner (BSV21-Cu x-ray tube, Ni-filtered Cu K$_\alpha$ radiation, 20 = 5°–120°, scan step of 0.02°, counting time of 40 s per data point). No diffraction peaks from phases other than Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ were detected in the x-ray patterns. The crystal structure of Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ was determined by the Rietveld method using the General Structure Analysis System (GSAS) program [6].

The dielectric properties of the new compound have been studied between room temperature and 1200 K at frequencies from 1 to 50 kHz. Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ is shown to be a ferroelectric with a Curie temperature of 972 K.

### RESULTS AND DISCUSSION

Figure 1 shows the temperature-dependent FT of Nb K-edge EXAFS data for Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ in the temperature range from 295 to 960 K. As shown in figure 1, the FT of AP at 295 K has three well-defined peaks corresponding to the near neighbors of ion Nb$^{5+}$. The first coordination shell of Nb is made up of six oxygens in the form of an octahedron, the second shell corresponds to the distance between Nb and the A (Na, Ca, Bi) ions on the cuboctahedral site, and the third shell is formed by the Nb$^{5+}$ ions residing in the neighboring octahedra. Multishell fitting, carried out only for the first peak, allowed us to determine the six Nb–O bond distances, which are listed in Table 1 together with the Debye–Wall factor characterizing the relative mean-square displacements of the oxygen and niobium atoms. For comparison, Table 1 also lists the Nb–O bond distances inferred from the Rietveld analysis results.

The data sets obtained by the two techniques are seen to agree well. The Rietveld analysis of XRD patterns indicated that in each oxygen octahedron, the Nb$^{5+}$ ion is displaced from the center position by 0.15 Å, forming short ($R = 1.92–1.96$ Å) and long ($R = 2.21$ Å) Nb–O bonds. The shortest Nb–O bond, $R = 1.92$ Å, involves the oxygen ion shared with the neighboring Bi$_2$O$_2$ layer, and the longest Nb–O bond involves the oxygen ion shared with the neighboring perovskite-like layer. These Nb–O bond distances in the oxygen octahedron and the displacement of Nb$^{5+}$ from the center position are close to those reported for APs with $m = 2$ [7, 8] (in Bi$_2$Na$_{0.3}$Nb$_2$O$_9$, the displacement of Nb$^{5+}$ from the center of the oxygen octahedron is 0.19 Å).
Å [7]). The Debye–Waller factor has the lowest value for the shortest Nb–O bond and the highest value for the longest Nb–O bond (Table 1). From XRD data, the Nb–O–Nb bond angle was found to be 151°, which indicates that the oxygen octahedra are tilted about the c axis. In CaBi$_2$Nb$_2$O$_6$, an AP close in composition to the one under consideration, the Nb–O–Nb angle is 154.2° [9], which is close to the above value.

To follow temperature-induced structural changes in Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$, we measured its EXAFS spectrum at temperatures from 295 to 960 K. The Nb–O bond distances $R$ and the corresponding $\sigma^2$ values in the first coordination shell of Nb$^{5+}$ (six oxygens) are listed in Table 2. Analysis of the Nb–O bond distances indicates that, with increasing temperature, the short bonds ($R_{1-2}$) become longer, while the long bonds ($R_5-R_6$) become shorter. However, even at 960 K, i.e., about the phase-transition temperature, there are different Nb–O bond distances, and the difference in length between the shortest ($R_{1-2} = 1.97$ Å) and longest ($R_{5-6} = 2.15$ Å) bonds remains rather large.

**CONCLUSION**

The new AP Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ is a ferroelectric with a high Curie temperature, $T_C = 972$K. At room temperature, Bi$_{2.25}$Ca$_{0.5}$Na$_{0.25}$Nb$_2$O$_9$ has an orthorhombic unit cell (sp. gr. $A21am$, no. 36). The atomic positional parameters in its structure, determined by the Rietveld method, and the corresponding Nb–O bond lengths agree well with EXAFS results. EXAFS measurements demonstrate that, with increasing temperature, the displacement of the niobium ions from the center position in the oxygen octahedral of the perovskite block decreases. However, even at $T = 960$ K near the phase-transition temperature, the displacements of Nb ions from the center oxygen octahedral are large.

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**REFERENCES**


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