

# Distribution of Na ions in a solid electrolyte $\text{Na}_x(\text{Ti,Mg})_2(\text{O,F})_4$ with a one-dimensional conductivity

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The distribution of Na cations in the conduction channels of the compound  $\text{Na}_{0.82}(\text{Ti}_{1.20}\text{Mg}_{0.80})(\text{O}_{3.22}\text{F}_{0.78})$  at 153 K and 293 K has been determined from the x-ray diffraction data of a single crystal.

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The unique physical properties of ionic crystal conductors and their practical application have attracted the attention of investigators.<sup>1</sup> A number of single crystals of the nonstoichiometric phase of the compound  $\text{Na}_x\text{Mg}_y\text{Ti}_{2-y}\text{O}_{4-2y+x}\text{F}_{2y-x}$  were obtained in the study of the  $\text{Na}_2\text{O}-\text{NaF}-\text{MgO}-\text{TiO}_2$  system.<sup>2</sup> The one-dimensional conduction in Na cations, which was measured in these single crystals by Belyaev *et al.* over the temperature range up to 670 K, reaches  $10^{-2}\Omega^{-1}\cdot\text{cm}^{-1}$  (activation energy 0.3–0.5 eV). Atomic structures of such crystals have been investigated previously.<sup>3,4</sup> We see in Fig. 1 that (Ti,Mg) octahedra, which are connected by common edges and vertices, form a structure which is pierced by continuous, double-barreled channels. The Na cations which account for the conduction are situated in these channels. The conduction value indicated above pertains to the direction along the

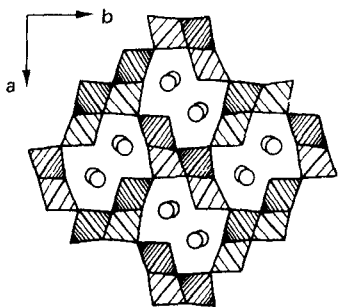


FIG. 1. Projection of the atomic structure of  $\text{Na}_{0.82}(\text{Ti}_{1.20}\text{Mg}_{0.80})(\text{O}_{3.22}\text{F}_{0.78})$  on the  $ab$  plane of the unit cell of the crystal.

channels. The conduction in the perpendicular direction is lower by at least three orders of magnitude.

Our goal in this paper is to determine the distribution of Na cations in the conduction channels at room temperature (293 K) and at nitrogen temperature (153 K), using experimental x-ray data. To solve the problem, we used various distributions of the electron density in crystals.<sup>5</sup> The integrated intensities of x-ray diffraction reflections were measured in automatically controlled x-ray diffractometers, using a single sample which was rounded into a ball ( $d = 0.20 \pm 3$  mm, Mo radiation, flat graphite monochromator,  $\theta/2\theta$  scanning method). We have measured 1206 and 1224 separate diffraction reflections, respectively, with  $I > 3\sigma_I$  and  $\sin \theta/\lambda \leq 0.99 \text{ \AA}^{-1}$  at nitrogen and room temperatures. The factors ultimately responsible for the divergence between the experimental structure-amplitude moduli and those calculated from the refined structure model amounted to 4.2% and 3.6% for the low temperature and room temperature. The structure parameters were refined by the least-squares method with allowance for the anomalous scattering of x-rays by matter, and by the method of Zachariasen's secondary extinction.<sup>6</sup>

The composition of the sample used in the experiment is  $\text{Na}_{0.82}(\text{Ti}_{1.20}\text{Mg}_{0.80})(\text{O}_{3.22}\text{F}_{0.78})$ . The dimensions of its unit cell are  $a = 9.238 \text{ \AA}$  (1),  $b = 11.333 \text{ \AA}$  (2),  $c = 2.9192 \text{ \AA}$  (3) at  $T = 153 \text{ K}$ . This sample belongs to the rhombic-symmetry Fedorov group  $\text{Pna}2_1$ . The unit cell of this sample contains four formula units of the indicated composition. Eight crystallographic positions in the unit cell are populated by 4.80 Ti atoms and 3.20 Mg atoms. Our first task was to determine the position of these cations in the structure. The scattering power of x radiation of Ti atoms differs markedly from that of Mg atoms ( $Z_{\text{Ti}} = 22$ ,  $Z_{\text{Mg}} = 12$ ). Within the accuracy of our experiment we have not been able to observe any order in the arrangement of Ti and Mg atoms in the eight crystallographic positions. All these positions are populated by statistically identical "atoms" ( $\text{Ti}_{0.60}\text{Mg}_{0.40}$ ). Because of the small difference in the scattering power of O and F atoms ( $Z_{\text{O}} = 8$ ,  $Z_{\text{F}} = 9$ ), we have made no attempt to differentiate them in the structure.

The difference distributions of the electron density, from which all atoms except sodium were removed, were used to localize the Na atoms. To eliminate the series-cutoff values in the experimental distribution of the electron density in the

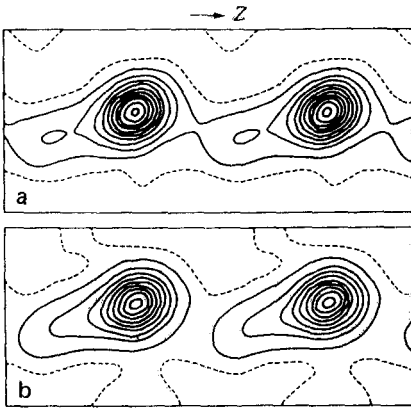


FIG. 2. Two-dimensional cross section of the difference electron density, showing the distribution of Na atoms in the conduction channels. a— $T = 153$  K,  $7.696$ ,  $x - 6.269$  plane,  $y = 2.379$ ; b— $T = 293$  K;  $7.352$   $x - 6.940$  plane,  $y = 2.170$ .

crystal, we used the  $\sigma$  factor to modify the corresponding Fourier coefficients.<sup>7</sup> Figure 2 shows the two-dimensional cross sections of the difference electron density along the conductance channels of the structure at 153 K (a) and 293 K (b). These cross sections (especially the low-temperature cross section) clearly reveal two locations in the conduction channels at which the Na atoms are concentrated. The behavior of the electron density in Fig. 2 indicates that the degree of population of the Na atoms is different at the two positions. The structure parameters were further refined by the least-squares method.<sup>6</sup>

At 153 K the population coefficients of the Na (1) and Na (2) positions turned out to be equal to 0.64 (1) and 0.18 (1), respectively, and the distance between them was only 1.20 Å, completely ruling out the possibility of simultaneously locating the pair of Na atoms in the neighboring positions. This situation can occur because the population of these two crystallographic positions is less than unity. The population of the Na (1) and Na (2) positions turned out to be 0.55 (3) and 0.28 (3), respectively, at a higher temperature (293 K). In other words, as the temperature is increased, the distribution of the Na cations flattens out along the conduction channel. An almost total agreement of the sum of the populations for the two experiments, which was obtained in an independent calculation of all four coefficients, is an additional argument in favor of the accuracy of our results. The anisotropy of thermal vibrations of the atoms in the harmonic approximation was taken into account in the refinement of the parameters of the atomic model of the crystal. The ellipsoids of thermal vibrations of the Na (1) atoms, and especially of the Na (2) atoms, turned out to be highly prolate: at  $T = 293$  K their major axes are equal to 0.52, 0.38, and 0.24 Å and 1.52, 0.38, and 0.19 Å, respectively. For comparison, we show that analogous parameters of thermal vibrations of the atoms (Ti, Mg) (1) and (Ti, Mg) (2) corresponds to 0.22, 0.21, and 0.18 Å and 0.26, 0.22, 0.18 Å. The major axes of the ellipsoids of the thermal vibrations of the Na (1) and Na (2) atoms deviate from the channel axis by 33° and 16°, respectively. It is reasonable to assume that these deviations indicate that the

Na atoms move in a zigzag manner in the channel during conduction. We should emphasize that the major axis of the ellipsoid of thermal vibrations of the Na (2) atom is very large, 1.52 Å. This shows that the model used by us does not describe all the specific features of the behavior of the Na atoms in the crystal, such as "sticking" of these atoms in other parts of the channel, deviation of the thermal motion of the sodium atoms from the harmonic motion, jumping of Na atoms from one position to another. An attempt to increase the complexity of the refined model of the atomic structure of the crystal in question at the precision level of the diffraction experiment, however, did not yield physically justifiable results.

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