Preface

A solid-solution series is the continuous sequence of substances with compositions intermediate between two distinct mineral phases, called end members. In a solid-solution series, the components may be thought to substitute for one another on a molecular level in the crystal structure; the intermediate members have properties that vary continuously with composition from those of one end member to those of another. Solid-solution series are said to be complete if examples of complete variation exist in nature or have been synthesized in the laboratory...

... only the appearance of the computer provided a qualitative jump and made it possible to perform effective study of really complex systems in various areas of knowledge. Actually, the concern is with coarse qualitative criteria, differentiating simple systems from complex; if the structure and behaviour of a system can be studied by a single man in a reasonable time, the system is called simple. If the efforts of many persons and the use of special technical equipment (computers) are required to draw the whole picture, the system is called complex.

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In the last 10–15 years, crystallographic and compositional engineering has become an important tool in the developing functional materials and in enhancing their physical properties. Ferroelectrics represent a vast class of modern functional materials that find applications from medical equipment to aeronautics. Intricate domain, twin and heterophase structures, sequences of structural phase transitions (mainly the first-order phase transitions), complex systems of solid solutions with different structural and polar orderings, and outstanding electromechanical properties in the poled state make ferroelectric materials attractive for basic research within the framework of the well-known dependency triangle of 'composition–structure–properties'. As is known from numerous experimental studies, the first-order phase transitions in ferroelectrics are characterized by jumps of the spontaneous polarization, unit-cell parameters, by heterophase states concerned with an internal mechanical field, etc. The present book is intended to discuss recent experimental and theoretical results on heterophase states and to provide crystallographic interpretations of heterophase structures in the ferroelectric solid solutions, especially in the presence of heavily twinned phases.

The most studied group of ferroelectric solid solutions is characterized by the perovskite-type structure (from the mineral perovskite, $CaTiO_3$). Components of these solid solutions are perovskite oxides with a composition ABO_3, where A and B are cation elements or mixtures of two or more such elements, or vacancies. The importance of ferroelectric perovskite-type materials is concerned with the almost unlimited isomorphism of their crystal structure. As a consequence, a continuous change in the composition, structural characteristics, and physical properties is achieved by substitution of different elements at equivalent positions (A and/or B). The isomorphism favours the formation of the ferroelectric solid solutions with properties that can be varied within a wide range. It should be added that many of the ferroelectric perovskite-type solid solutions exhibit excellent piezoelectric properties. Experimental data on these solid solutions show that the heterophase states in them are observed in certain ranges of temperature, composition, and electric field strength, where volume densities of free energy of the coexisting phases approximately equal. Recent studies on the representative perovskite-type solid solutions (for instance, ferroelectric $Pb(Zr_{1-x}Ti_x)O_3$ and relaxor-ferroelectric $(1-x)Pb(A_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ with $A = Mg$ or Zn) show that the heterophase states therein are of particular interest because of the presence of intermediate phases and their considerable influence on the physical properties, phase coexistence, and stress relief near the morphotropic phase boundary. The three aforementioned solid solutions are the main subjects of research, comparison, and discussion in the present book.

This book has been written on the basis of the author's research results obtained mainly at the Rostov State University (Russia, until December 2006), Southern Federal University (Russia, since December 2006), and Karlsruhe Research Centre (Germany, 2003–2004). The academic style of presentation of the results and the discussion about them indicate that the book would be useful to researchers, engineers, postgraduate students, and lecturers working in the field of ferroelectrics, ferroelastics, multiferroics, and other modern functional materials. The present book fills a gap in materials science, crystallography of ferroelectrics and related materials, and in physics of heterogeneous ferroelectrics and, therefore, will be of benefit to all specialists trying to understand behaviour and physical properties of modern heterogeneous materials suitable for various applications. Some chapters and sections of the book could serve as a basis for a university course devoted to ferroelectric solid solutions.

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