Relaxor ferroelectrics were discovered almost 50 years ago among the complex oxides with perovskite structure. In recent years this field of research has experienced a revival of interest. In this paper we review the progress achieved. We consider the crystal structure including quenched compositional disorder and polar nanoregions (PNR), the phase transitions including compositional order-disorder transition, transition to nonergodic (probably spherical cluster glass) state and to ferroelectric phase. We discuss the lattice dynamics and the peculiar (especially dielectric) relaxation in relaxors. Modern theoretical models for the mechanisms of PNR formation and freezing into nonergodic glassy state are also presented.

1. Introduction

Relaxor ferroelectrics or relaxors are a class of disordered crystals possessing peculiar structure and properties. At high temperature they exist in a non-polar paraelectric (PE) phase, which is similar in many respects to the PE phase of normal ferroelectrics. Upon cooling they transform into the ergodic relaxor (ER) state in which polar regions of nanometer scale with randomly distributed directions of dipole moments appear. This transformation which occurs at the so-called Burns temperature ($T_B$) cannot be considered a structural phase transition because it is not accompanied by any change of crystal structure on the macroscopic or mesoscopic scale. Nevertheless, the polar nanoregions (PNRs) affect the behaviour of the crystal dramatically, giving rise to unique physical properties. For this reason the state of crystal at $T < T_B$ is often considered as the new phase different from the PE one.

At temperatures close to $T_B$ the PNRs are mobile and their behaviour is ergodic. On cooling, their dynamics slows down enormously and at a low enough temperature, $T_i$ (typically hundreds degrees below $T_B$), the PNRs in the canonical relaxors become frozen into a nonergodic state, while the average symmetry of the crystal still remains cubic. Similar kind of nonergodicity is characteristic of a dipole glass (or spin glass) phase. The existence in relaxors of an equilibrium phase transition into a low-temperature glassy phase is one of the most interesting hypotheses which has been intensively discussed. Freezing of the dipole dynamics is associated with a large and wide peak in the temperature dependence of the dielectric constant ($\varepsilon$) with characteristic dispersion observed at all frequencies practically available for dielectric measurements (Fig. 1). This peak is of the same order of magnitude as the peaks at the Curie point in the ordinary ferroelectric (FE) perovskites, but in contrast to ordinary ferroelectrics it is highly diffuse and its temperature $T_m (> T_i)$ shifts with frequency due to the dielectric dispersion. Because of the diffuseness of the dielectric anomaly and the anomalies in the temperature dependences of some other properties, relaxors are often called (especially in early literature) the “ferroelectrics with diffuse phase transition,” even though no transition into FE phase really occurs.

The nonergodic relaxor (NR) state existing below $T_i$ can be irreversibly transformed into a FE state by a strong enough external electric field. This is an important characteristic of relaxors which distinguishes them from typical dipole glasses. Upon heating the FE phase transforms to the ER one at the temperature $T_C$ which is very close to $T_i$. In many relaxors the spontaneous (i.e. without the application of an electric field) phase transition from the ER into a low-temperature FE phase still occurs at $T_C$ and thus the NR state does not exist.

Compositional disorder, i.e. the disorder in the arrangement of different ions on the crystallographically equivalent sites, is the common feature of relaxors. The relaxor behaviour was first observed in the perovskites with disorder of non-isovalent ions, including the stoichiometric complex perovskite compounds, e.g.
Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) [1] or Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST) [2] (in which Mg$^{2+}$, Sc$^{3+}$, Ta$^{5+}$ and Nb$^{5+}$ ions are fully or partially disordered in the B-sublattice of the perovskite ABO$_3$ structure) and nonstoichiometric solid solutions, e.g. Pb$_{1-x}$La$_x$(Zr$_{1-y}$Ti$_y$)$_{1-x/4}$O$_3$ (PLZT) [3, 4] where the substitution of La$^{3+}$ for Pb$^{2+}$ ions necessarily leads to vacancies on the A-sites. Recently an increasing amount of data has shown that many homovalent solid solutions, e.g. Ba(Ti$_{1-x}$Zr$_x$)$_3$O$_9$ (BTZ) [5, 6] and Ba(Ti$_{1-x}$Sn$_x$)$_3$O$_9$ [7] can also exhibit relaxor behaviour. Other examples of relaxor ferroelectrics are complex perovskites Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_9$ (PZN), Pb(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_9$ (PMT), Pb(Sc$_{1/2}$Nb$_{1/2}$)$_3$O$_9$ (PSN), Pb(In$_{1/2}$Nb$_{1/2}$)$_3$O$_9$ (PIN), Pb(Fe$_{1/2}$Nb$_{1/2}$)$_3$O$_9$ (PFN), Pb(Fe$_2$W$_1$)$_3$O$_9$ (PFW) and the solid solutions: (1−χ)Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_9$−χPbTiO$_3$ (PMN-PT) and (1−χ)Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_9$−χPbTiO$_3$ (PZN-PT).

Although relaxor ferroelectrics were first reported nearly half a century ago, this field of research has experienced a revival of interest in recent years. In this paper, we try to provide an overview of the current understanding of the various issues of relaxors. Emphasis is put on the latest developments. For a review of the earlier studies, readers can refer to Refs. [8–11].

2. Compositional order-disorder phase transitions and quenched disorder in complex perovskites

As mentioned above, the disordered distribution of different ions on the equivalent lattice sites (i.e. compositional disorder, also called chemical, ionic or substitutional disorder) is the essential structural characteristic of relaxors. The ground state of the complex perovskites should be compositionally ordered, e.g. in the A(B$^{2+}$B$''_{1/2}$)O$_3$ compounds each type of the cations, B$'$ or B$''$, should be located in its own sublattice, creating a superstructure with complete translational symmetry. This is because the electrostatic and elastic energies of the structure are minimized in the ordered state due to the difference in both the charge and the size of B$'$ and B$''$ ions. Thermal motion is capable of destroying the order at a certain nonzero temperature ($T_c$). This occurs in the form of structural phase transition, the order parameter (compositional long-range order, $s$) of which can be measured by the X-ray or other diffraction methods. Such kind of phase transitions had been known long ago (e.g. in many metallic alloys) and was also discovered comparatively recently at $T_c \sim 1500$ K in PST, PSN [12] and several other complex perovskites. Ordering implies the site exchange between B$'$ and B$''$ cations via diffusion. It is a relaxation process with a nearly infinite characteristic time at low temperatures, but at 1500 K it can be quite fast. As a result, in some perovskites (e.g. in PST, PSN, PIN), by annealing at temperatures around $T_c$ and subsequent quenching, one can obtain the metastable states with different $s$ at low temperatures. In some other materials (e.g. in PFN and PMN) the compositional disorder cannot be changed by any heat treatment because the relaxation time of ordering is too long. However in all known relaxors, at $T_B$ and below, the compositional order is frozen (quenched), i.e. cannot vary during practically reasonable time.

In the real complex perovskite crystals and ceramics the quenched compositional disorder is often inhomogeneous, e.g. small regions of the ordered state are embedded in a disordered matrix. These regions can be regarded as a result of incomplete compositional order-disorder phase transformation or as quenched phase fluctuations. In the prototypical relaxor PMN this kind of inhomogeneous structure always exists and cannot be changed by any heat treatment.

In Pb(B$^2_{1/2}$B$''_{1/2}$)O$_3$ perovskites the ordering of B-site ions converts the disordered PE $Pm\bar{3}m$ structure into the ordered $Fm\bar{3}m$ structure in which B$'$ ions alternate with B$''$ ions along the ⟨100⟩ directions (1:1 ordering). In the ordered phase of many non-ferroelectric A(B$^{2+}$B$^+_{1/3}$B$''_{2/3}$)O$_3$ perovskites, B$^{2+}$ ions alternate with two B$^+$ ions along the ⟨100⟩ directions (1:2 ordering). The type of ordering in lead-containing relaxor perovskites, Pb(B$^{2+}_{1/3}$B$^+_1$B$''_{2/3}$)O$_3$, has been the subject of debates. In the early works only inhomogeneous ordering (ordered regions within disordered regions) was found in the samples studied. High-resolution electron microscopy of PMN revealed nano-size (~2–5 nm) regions in which the ordering of 1:1 type ($Fm\bar{3}m$) was observed (see e.g. Refs. [13, 14]).