ON THE DISCOVERY OF THE DIELECTRIC RELAXATION AND FERROELECTRICITY IN Pb-CONTAINING COMPLEX PEROVSKITES

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In the end of 1940s young soviet scientist Georgii Smolenskii discovered ferroelectric properties in lead titanate ($PbTiO_3$) [1] and found an anomaly in the temperature dependence of the dielectric constant in lead zirconate ($PbZrO_3$) [1,2]. This encouraging result was also independently obtained by G. Shirane [3] and G. Roberts [4]. Based on this data, Smolenskii came to the conclusion that Pb^{2+} ions are essential for the appearance of ferroelectricity in perovskite-type materials, i.e., that they are "ferroelectrically active". However, it was clear from the very beginning that the number of simple perovskites is very limited. So, only few new ferroelectric materials could be obtained. At the same time, some reports on sintering ceramic samples of complex perovskites with different ions in the octahedral positions appeared in literature. These ceramics were not ferroelectric and contained Ba^{2+} and Sr^{2} ions. Probably, these two observations stimulated Smolenskii to sinter first Pb-containing complex perovskites where ferroelectric state could apparently be expected. This conclusion was probably drawn already in 1953-54, since in his 1954 scientific report the principles of sintering of such compounds were already formulated. During these years, Smolenskii worked in the Institute for Chemistry of Silicates of the Academy of Science of the USSR on his second scientific degree (Doctor of Sciences). In fact, experimental work on complex perovskites started as early as 1956. At this time, several new young researchers just entered his laboratory. This allowed intensifying research work in this area greatly. However, at that moment some technical problems arose due to the move of the laboratory to the Institute of Semiconductors that was newly established in Leningrad. The relocation to a new place somehow hampered the experimental work and took a lot of time and effort. In spite of these problems, the first compounds including $PbNi_{1/3}Nb_{2/3}O_3$ (PNN) and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) were successfully sintered and investigated by the end of 1957 already. At this time, it was thought that the latter material is a relaxator (due to its pronounced dielectric relaxation) and the former is a ferroelectric.

Already in November 1957 the first results have been reported at the Soviet Conference on Ferroelectricity in Rostov-on-Don. Later the results were published in the Journal of Technical Physics (or Zhurnal Tekhnicheskoi Fiziki, in Russian) [5]. This was followed by the detailed investigation of the continuous solid solutions of these materials [5,6]. First results were obtained on ceramics that were sintered by Agranovskaya and studied by Popov. When Stanislav Popov first showed the results of the dielectric permittivity measurements at different frequencies to Smolenskii, he first did not believe in them and referred them as incorrect measurements. When the measurements were repeated and confirmed, a new concept was soon born where phase transition was suggested to occur in the broad temperature range. In Ref. [7] the phase transition in such systems was first called a diffuse phase transition. At this moment, Natalia Krainik and Vladislav Isupov joined the investigation of these materials. The number of the investigated materials grew vastly during these years: $Pb(Fe_{1/2}Nb_{1/2})O3$ (PFN), $Pb(Yb_{1/2}Nb_{1/2})O_3$ (PYN) [8], $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN), $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) [9], $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW), $Pb(Fe_{1/2}W_{1/2})O_3$ (PFW), $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) [10], as well as $Pb(Lu_{1/2}Nb_{1/2})O_3$ (PLN), $Pb(Lu_{1/2}Ta_{1/2})O_3$ (PLT) [11] which were found to be antiferroelectrics similar to $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW).

In the first half of 1958 Irina Myl'nikova from the same laboratory had grown the first single crystals of $PbNi_{1/3}Nb_{2/3}O_3$ [12]. Later a number of single crystals of new complex perovskites were grown and diffuse phase transition in this system was confirmed. Only one exclusion was found: $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) which was closer to classical ferroelectrics. Many years after, solid solutions of these materials with $PbTiO_3$ were recognized as having a giant piezoelectric effect and are now investigated extensively. Single crystals were successfully grown by the spontaneous crystallization from the melt. The size of the first single crystals was very small (~0.15 mm) and, therefore, only few measurements were done. These measurements were of great importance to justify the first results on ceramics. XRD studies have shown that significant disorder present in the distribution of octahedral ions in the perovskite cell. Previously, it was believed that ions in the octahedral sites are completely ordered and, therefore, the nature of the diffuse phase transition was not clear. First electrical and optical measurements by Vladimir Bokov on single crystals [13, 14] not only confirmed the initial results on ceramics but resulted in qualitatively new conclusions that: (i) PMN is optically isotropic when cooled under applied field but has some remanent birefringence when the field is removed, (ii) ferroelectric domains can be observed under application of electric field and polarization process is due to domain motion like in classical ferroelectrics. (iii) PMN demonstrates non-ergodicity at low temperatures.

At the same time first models of diffuse phase transition in ferroelectrics were suggested. It was understood that the origin of unusual dielectric properties of ferroelectrics with diffuse phase transition (or relaxors) are due to disorder in the distribution of B-ions in the perovskite unit cell. This may lead to the appearance of the composition fluctuations and, as a consequence, to different local Curie temperatures in the different regions of ceramics or single crystals. This concept was first introduced by Vladislav Isupov in 1963 [16]. Relaxation behavior of complex perovskites was explained either by relaxation of polar microregions [16] or by domain wall motion [13]. The walls were suggested to be very thick and domains to be very fine and optically not detectable [13].

Soon after the discovery of complex perovskites and first publications of Smolenskii with co-authors, similar investigations have started in Rostov-on-Don and Moscow (Russia) as well as in Japan.

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