



Low-temperature permittivity anomalies of Me/Me₂P₂S₆ family layered crystals

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Introduction: Layered crystals of the Me/Me₂P₂S(Se)₆ family have recently received increased attention. This is due to the expanded possibilities of using these materials as hydrogen storage, ionic conductors, substrates for photocells, etc. [1]. Of particular interest are ferroelectric crystals, for example, CuInP₂S₆ [2] or multiferroics, in which both ferromagnetic and ferroelectric ordering is observed simultaneously, such as CuCrP₂S₆ [3].

Methods: We investigated the temperature dependence of the dielectric constant of various Me/Me₂P₂S(Se)₆ family crystals, obtained by gas-transport reactions and using the Bridgeman method, in the temperature interval 80÷450 K and the frequency range 10÷10⁵ Hz. For this, the automated measuring system based on the GW Instek LCR-819 LCR Meter, the Measurement Computing USB-TEMP-AI temperature meter, and an OWON ODP3033 programmable power supply was used.

Results: As our studies have shown, in many crystals of the Me/Me₂P₂S(Se)₆ family in the vicinity of temperatures of 120-250K, an anomaly is observed on the temperature dependence of the dielectric constant (a characteristic step in the temperature dependence of the dielectric constant and a maximum on the dielectric loss curve), which shifts to the region of higher temperatures with an increase in the frequency of the measuring field. This behavior indicates the presence of a relaxation process in the selected temperature range but does not provide an answer to the mechanism of this relaxation. We observed a similar phenomenon in crystals CuInP₂S₆, CuGaP₂S₆, Cs₂Ag₂P₂Se₆, CuDyP₂S₆, and in Cu_{0.15}Fe_{1.7}PS₃ mixed material.

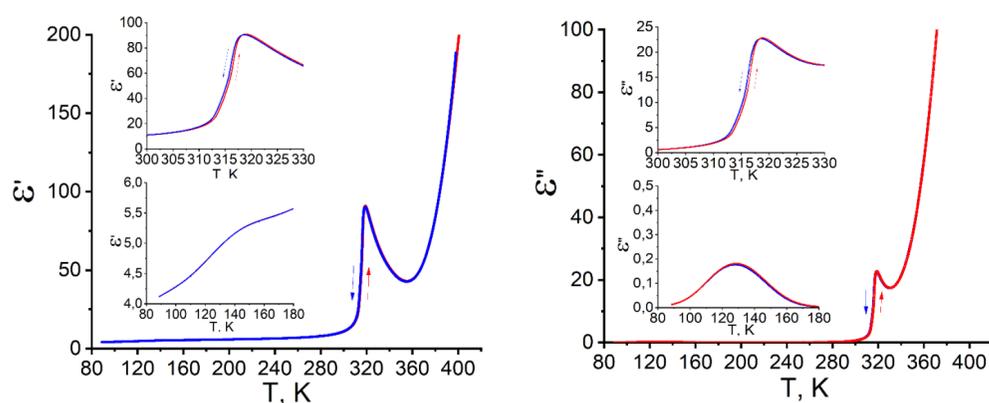


Fig 1. Temperature dependency of real and imaginary parts of complex dielectric permittivity of 80%CuInP₂S₆-20%CuGaP₂S₆ solid solution.

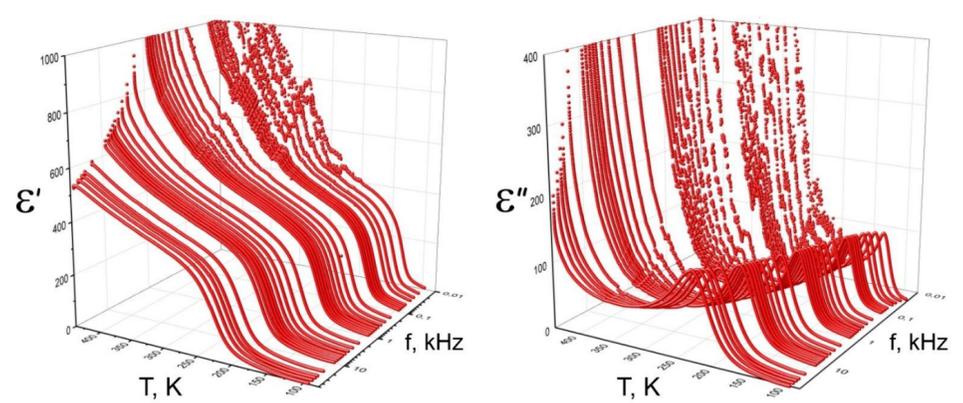


Fig. 2. Temperature dependence of real and imaginary parts of dielectric permittivity of Cu_{0.15}Fe_{1.7}PS₃.

Similar behavior is observed in crystals of the Sn₂P₂S(Se)₆ family, which is also surprising since these crystals are 3D uniaxial ferroelectrics. As shown in [4], this phenomenon can be explained by the creation and annihilation of a small hole and electron polarons with the participation of tin vacancies acceptor and sulfur vacancies donor in gap energy states.

As shown in [5], in the case of Cu_{0.15}Fe_{1.7}PS₃ mixed material, the low-frequency relaxation in the 120K region is due to the Maxwell-Wagner relaxation what is often found in heterogeneous systems in which components of the dielectric material have different conductivity.

For CuInP₂S₆ crystals enriched with indium in the article [6], this relaxation behavior is explained by the presence of a state similar to dipole glass. As can be seen only with these three examples, the relaxation behavior of the frequency-temperature dependence of the permittivity components is described by three different mechanisms, which, although possible, is unlikely, and probably should have a common cause.

Conclusion: Because the low-temperature relaxation phenomenon is observed in almost all materials of the Me/Me₂P₂S(Se)₆ family at the same temperature and frequency range, probably they have a common nature, the origin of which will need to be clarified. Since PS₃ or PSe₃ structural units are common for all of the listed materials, the described phenomenon is most likely associated with the relaxation mechanism of just this structural unit, for example, with sulfur vacancies, as in the case of Sn₂P₂S₆ crystals.

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