Piezoelectric effect in $Cu_{0.5}In_{0.5}Cr_2S_4$ and $xCuCr_3S_4$–$(1-x)$ $Cu_{0.5}In_{0.5}Cr_2S_4$ compounds with a normal spinel structure

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The piezoelectric effect is observed for the first time in spinellide $Cu_{0.5}In_{0.5}Cr_2S_4$ (crystal symmetry T_d^2), which is comparable in magnitude to a piezoeffect in an X-cut quartz plate with a coefficient of electromechanical coupling of 10%. The piezoeffect may also occur in a solid solution of this compound with $CuCr_3S_4$, although its magnitude diminishes rapidly with increasing x in $xCuCr_3S_4$–$(1-x)Cu_{0.5}In_{0.5}Cr_2S_4$ and at $x > 0.05$ the effect cannot be observed.

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Neutron scattering data indicate that the $Cu_{0.5}In_{0.5}Cr_2S_4$ compound exhibits at low temperatures antiferromagnetic structure of the following type. [1–3] Each moment of the Cr^{3+} ions is ferromagnetically coupled with the movements of three neighboring ions with which it forms a ferromagnetic tetrahedron, and anti-ferrmagnetically coupled with the remaining three other ions. This magnetic structure is unusual for spinel and is associated with the lowering of the nuclear structure symmetry caused by the 1 : 1 ordering of Cu^{1+} and In^{3+} ions in the tetrahedral lattice points. [2] An identical lowering of the symmetry was observed earlier in x-ray spectra. [4] These experiments indicate that the crystal symmetry changes from O_h^7, that is characteristic for the $MgAl_2O_4$, to T_d^2 whose center is missing.

It is known that the necessary condition for the occurence of piezoelectricity in a crystal is the absence of a symmetry center. Therefore, the presence of the piezoelectric effect may be assumed in the $Cu_{0.5}In_{0.5}Cr_2S_4$ compound. Unfortunately, until now there are neither single crystals of this compound available, nor even a ceramic with a texture that would permit a quantitative study of this effect. An attempt was made to observe the latter in this and other materials having similar symmetries. [4] Negative results were obtained with polycrystals, causing the authors [4] to conclude that the long-range atomic order in A-modes is nonexistent.

In this work we qualitatively identify the piezoeffect in a polycrystalline compound $Cu_{0.5}In_{0.5}Cr_2S_4$ and its hard solutions with a ferromagnetic compound $CuCr_3S_4$, namely in $xCuCr_3S_4$-$(1-x)Cu_{0.5}In_{0.5}Cr_2S_4$, where $x = 0.005$; 0.01; 0.02 and 0.05. The samples were obtained by solid-phase synthesis in evacuated quartz ampoules. The starting materials for the synthesis were: powdered Cu and Cr with $\geqslant 99.9\%$ purity, elemental sulfur "OSCH-16-5" and indium sulfide In_2S_3 with $\geqslant 99.9\%$ purity. Calculated amounts of starting materials were homogenized in an agate beater under an ether layer. Heating was carried out at $T = 1400$ K during 200 hours with three intermediate homogenations. To obtain a highly stoichiometric anion composition the original mixture was 2% enriched with sulfur. The phase analysis of the

CuK$_\alpha$ x rays which was carried out in the DRON-1 device, showed all the compounds were single phase.

All the polycrystals we investigated belong to the $F\bar{4}3m$ (T_d^2) space group since we observed reflections of the same parity in all the planes, including [200], [420], etc. The R-factor minimum for Cu$_{0.5}$In$_{0.5}$Cr$_2$S$_4$ was observed at the following cation distribution: (1) all Cr atoms are in octahedral positions (16e), (2) 88% Cu and 12% In are found in the tetrahedral positions 4a, while the converse (88% In, 12% Cu) occurs in the tetrahedral positions 4c, i.e., the degree of atomic order in the 1 : 1-type tetrahedrons is 0.88.

The Cu$_{0.5}$In$_{0.5}$Cr$_2$S$_4$ samples obtained by Pinch using a method described in Ref. 4, could be anion non-stoichiometric, i.e., in the chemical formula for Cu$_{0.5}$In$_{0.5}$Cr$_2$S$_{4-\gamma}$, γ may, according to our data, be in the range from 0 to 0.16. Clearly, the degree of order in the A-sublattice of samples the obtained with our technique is higher than that achieved by Pinch. [4]

The different degree of order in the tetrahedral lattice points of samples with different thermal prehistory is fully understood if we allow for a very weak energy difference of positions 4 and 4c which exhibit the same symmetry. Thus, the energy threshold for the cation transition from a type 4a tetrahedron to type 4x tetrahedron is at least an order of magnitude lower than for a transition from any A-point to B-point at a varying degree of invertibility in spinel. It should be also noted that the data with respect to the Neely point (T_N = 26 K) obtained in Ref. 4 differ substantially from T_N = 39–35 K values in Refs. 1 and 3. Our measurements for Cu$_{0.5}$In$_{0.5}$Cr$_2$S$_4$ show T_N = 35 K. Evidently, this is related to the poor quality of the samples used by Pinch. [4]

To qualitatively observe the piezoeffect in this work we used pressed plates with a thickness ≤0.5 mm. Mechanical deformations of acoustic frequency were induced in a plate by a sharp pointer which set up an electrical potential in a sample. Upon amplification, this voltage was applied across the horizontal plates of an oscillograph while the vertical plates were supplied with a voltage of the same frequency as the mechanical vibrations. If a substance exhibits the piezoelectric effect, an ellipse will form on the oscillograph screen, whose vertical axis is proportional to the coefficient of electromechanical coupling.

Using this setup for the aforementioned samples we observed a piezoeffect that in terms of magnitude is comparable to the piezoeffect of an x-cut quartz plate with the coefficient of electromechanical coupling $K = 10\%$. As x increased, K decreased and the piezoeffect could not be observed in samples with $x > 0.05$, This means that this relatively small perturbation of order in the A-points leads to the disappearance of piezoelectricity; consequently, it is not surprising that this effect could not be observed by the other authors. [4] Thus, this work is responsible for identifying new spinellides characterized by the piezoelectric effect. These materials also exhibit magnetic order. Further quantitative investigations of piezoelectricity and the formulation of its possible coupling with the magnetic order require that high-quality single crystals be available.

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