

[o.m1.p5] Evolution of the structural and mean square displacement parameters in $(\text{NH}_4)_x\text{K}_{1-x}\text{H}_2\text{PO}_4$ solid solutions versus concentration and temperature. A. Boukhris^{*}, C. Lecomte^{*}, A. Thalal^{*}. ^{*}*Faculté des Sciences d'Agadir (Laboratoire des Sciences des Matériaux, Faculté des Sciences Semlalia Marrakech) - Maroc* - ^{*}*Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques (LCM³B), Nancy -France*. ^{*}*Laboratoire des Sciences des Matériaux, Faculté des Sciences Semlalia Marrakech -Maroc* -
Keywords: ferro-electricity, NLO materials.

The study of $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (KADPx) mixed crystals have been carried out not only to bring additional elements to explain the phase transition phenomena but also enlightenment of this particular physics of frustrations existing in these materials for intermediate concentrations.

Although KADPx appeared to be correctly characterised by dielectric measurements and IR spectroscopy^{1,2,3}, the crystallographic results were very few and in general issued from low resolution diffraction data^{4,5}. We have then carried out high resolution crystallographic studies on these materials in particular in the phase diagram $0.4 < x < 1.0$ range.

For each solid solution, X-Ray diffraction data of a single crystal have been used for determination of the electron deformation density using a multipolar model⁶ which uses an expansion of the electron density around each nucleus in order to have an insight in the chemical bond. This procedure leads to a better evaluation of the structure factors in comparison to that based on spherical model and thus permits more precise structure parameter estimations which are essential in the interpretation of any physical transformation process.

The thermal displacement parameters analysis with respect to the temperature and the ammonium ion concentration has revealed phosphorus and oxygen atom site disorders especially for intermediate concentration whatever the temperature value, $U^{33}(\text{P})$ and $U^{33}(\text{O})$ values are maximum for $x = 0.5$.

The non-linearity of U^{33}_{tot} ($U^{33}_{\text{tot}} = U^{33}_{\text{dyn}} + U^{33}_{\text{stat}}$) versus the concentration is entirely due to the static behaviour. This behaviour, mainly due to the atomic thermal displacement U^{33} tensor component, being a consequence of conflicting ferroelectric-antiferroelectric tendencies.

It seems necessary to investigate the whole phase diagram. For this purpose, precise structure parameter determinations have to be considered in the total ammonium ion concentration range ($0 < x < 1$).

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[o.m1.p6] High temperature ferro-paraelectric phase transition in tris(trimethylammonium) nonachlorodiantimonate(III) (TMACA) studied by X-ray diffraction method. M. Bujak, J. Zaleski, *Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland; E-mail: zaleski@uni.opole.pl.*

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The group of alkylammonium halogenoantimonates(III) and bismuthates(III), organic-inorganic salts, evokes recently much interest. It is due to the discovery in some of them phase transitions to polar phases. Those phase transitions are mainly connected with changes in the dynamic of cationic sublattices¹.

One of most interesting from the dielectric point of view are compounds of the general formula $\text{R}_3\text{M}_2\text{X}_9$ (R-organic cation; M-Sb, Bi; X-Cl, Br, I) with relatively small alkylammonium cations (eg. methyl-, dimethyl- and trimethylammonium). The ferroelectric phases in these salts, among others, have been found in: $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$ DMACA² and $[\text{NH}(\text{CH}_3)_3]_3\text{Sb}_2\text{Cl}_9$ TMACA³.

The TMACA crystals have been reported to undergo four phase transitions at: 125, 203, 363 and 364 K. The ferro-paraelectric phase transition takes place at 363 K. The presence of an incommensurate, intermediate phase (between 363 and 364 K) has been suggested from the dielectric and linear birefringence studies.

The structure of $[\text{NH}(\text{CH}_3)_3]_3\text{Sb}_2\text{Cl}_9$ has been determined at 295 K and 373 K, below and above the high temperature ferro-paraelectric phase transition. In both phases the anionic sublattice of TMACA is built of characteristic two-dimensional $(\text{Sb}_2\text{Cl}_9^{3-})_n$ polyanionic layers lying in the bc plane. In the room temperature ferroelectric phase (monoclinic Pc space group) there are three crystallographically non-equivalent $[\text{NH}(\text{CH}_3)_3]^+$ trimethylammonium cations in the crystal structure. Two of them located between polyanionic layers are ordered. The third one lying inside the cavity formed by six SbCl_6^{3-} octahedra is disordered. In the high temperature paraelectric phase (monoclinic P2₁/c space group) there are only two crystallographically non-equivalent trimethylammonium cations in the crystal structure. One of them is located between the inorganic layers while the second one is placed inside the polyanionic cavity. Both cations are disordered. Temperature dependencies of the lattice parameters determined between 295 and 375 K have confirmed the presence of phase transition in TMACA in the high temperature region. The mechanism of the ferro-paraelectric phase transition has been proposed.

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