α-quartz type $M^{III}X^{V}O_4$ (M= Al, Ga and X= P, As) piezoelectric single crystals – a review

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Quartz is the most widely used piezoelectric single crystal. Nevertheless, its applications are limited due to a relatively low piezoelectric coupling coefficient (8%) and low thermal stability due to the α-β phase transition at 846K. The structure of $M^{III}X^{V}O_4$ quartz isotypes (space group $P3_121$ or $P3_221$, Z=3, as for α-quartz) corresponds to a cation-ordered derivative of the α-quartz type with a doubled c parameter due to the alternating of MO_4 and XO_4 tetrahedra in the helical chain along the z-axis. Structure-property relationships have been developed for α-quartz and its $M^{III}X^{V}O_4$ isotypes (with M^{III} = Al, Ga and X^{V} = P, As) in order to identify new materials with better intrinsic properties. Indeed, piezoelectric performances and thermal stability of the α-quartz form were found to be a function of the structural distortion with respect to the β-quartz structure type. New theoretical calculations using DFT theory were developed to better understand the lattice dynamic disorder. The structural distortion of the quartz isotypes can be tuned by the nature of the cations M and/or X in the tetrahedral for growing crystals with piezoelectric properties adapted to industrial applications. In this way, α-berlinite ($AlPO_4$), with a similar structural distortion than that of quartz, exhibits a coupling coefficient of 11% and a α-β phase transition at 859K. By replacing Al^{III} with a bigger cation like Ga^{III}, the distortion is increased; the coupling coefficient reaches 16% and the α-quartz $GaPO_4$ is stable up to 1206K. The structural distortion is still increased by replacing P^{V} by As^{V} in $GaAsO_4$. α-quartz-type $GaAsO_4$ has a remarkable thermal stability up to 1273K and the highest electromechanical coupling coefficient (21%) in this family. All these materials were grown by hydrothermal routes in acidic solvents at low pressure (P<200MPa) in the 180°C-250°C temperature range. Large $AlPO_4$ single crystals have been grown between 1980-1990 with excellent crystalline quality (low –OH and low dislocation content). Piezoelectric devices like filters for radio-telecommunication applications have been studied at an industrial level. The crystal growth process of $GaPO_4$ and chemical etching process for high frequency resonators were later developed with the financial help of the E.U. Large single crystals are now obtained by the Piezocryst Company for the unique use of the AVL group for manufacturing pressure sensors at high temperature. $GaAsO_4$ is produced at the laboratory level. This presentation summarizes the scientific evolution of the knowledge in the α-quartz type materials. Crystal growth processes and crystals will be presented. The results will show how fundamental research can improve our understanding of the structures of these materials and their links to piezoelectric applications.