

Hydrothermal synthesis of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ α -quartz single crystal

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α -Quartz type materials are of major interest due to their piezoelectric properties. Structure-property relationships have been evidenced in these materials, in which a series of physical, thermodynamic, dielectric and piezoelectric properties have been linked to the distortion present in their crystal structures. Single crystals in the AlPO_4 - GaPO_4 and FePO_4 - GaPO_4 systems were prepared by hydrothermal process using H_2SO_4 , 6 M/l, and H_3PO_4 , 6M/l solutions. The crystal growth method is slow temperature rise used at temperature from 150 °C up to 250 °C (the retrograde solubility of AlPO_4 - GaPO_4 and FePO_4 - GaPO_4 systems). The single crystals were characterized by electron probe microanalysis and X-ray diffraction. The present results open the possibility to growth of high quality single crystal and to tune the piezoelectric properties of these materials by varying the chemical composition.

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1. Introduction

α -Quartz type materials are of major interest due to their piezoelectric properties. In addition to α -quartz itself, this family is composed of GeO_2 and compounds with the general formula $\text{M}^{\text{III}}\text{X}^{\text{V}}\text{O}_4$ where $\text{M} = \text{Al, Ga, Fe, B, and X} = \text{P and As}$. The α -quartz structure, space group $P 3_121$ (or $P 3_221$), is built up of left-handed (or right-handed) helical chains of RO_4 ($\text{R} = \text{M or X}$) parallel to the c -axis. Each MO_4 tetrahedron shares its four corners with XO_4 tetrahedra.

The structural distortion present can be described by two interrelated angles: the intertetrahedral bridging angle M-O-X , θ , and the tetrahedral tilt angle δ [1]. In the case of undistorted tetrahedra, the relation between these two parameters is given by:

$$\cos \theta = \frac{3}{4} - \left[\cos \delta + \frac{1}{2\sqrt{3}} \right]^2 \quad (1)$$

For very well characterized crystals (SiO_2 , AlPO_4 and GaPO_4), it proved possible to relate linearly their M-O-X values (143.7, 142.8 and 134.6 respectively) to their piezoelectric properties [2]. The more distortion structure, the more θ and δ values decrease and increase, respectively. One of main way to obtain a more distortion structure, it is to increase the average size of $\langle r_{\text{M}} \rangle$ of M -site cations.

Therefore, in the present paper, the $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ series, powder and single crystal, with $x=0.1, 0.7, 0.9$, and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series, powder and single crystal, with $x=0.1, 0.7$, were obtained by hydrothermal method and the crystal

structure was determined by X-ray diffraction. These results can be used to tune the piezoelectric properties of these materials by varying the chemical composition.

2. Experimental

The powder of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ were prepared by hydrothermal process using H_2SO_4 , 3 and 6 M/l, and H_3PO_4 , 6M/l solutions. Suitable quantities of solutions AlPO_4 and GaPO_4 (FePO_4 and GaPO_4 , respectively), in sulfuric acid (phosphoric acid respectively) were mixed, sealed in quartz tubes with a filling capacity of 70% and heated at 170°C, for 24 h. Hydrothermal reaction temperature was 170°C due to the higher solubility of AlPO_4 and GaPO_4 compounds at this temperature.

This powder was used like a precursor material in the growth of single crystal which has the same stoichiometric composition.

Single crystals in the AlPO_4 - GaPO_4 and FePO_4 - GaPO_4 systems were prepared by hydrothermal process using H_2SO_4 , 6 M/l, and H_3PO_4 , 6M/l solutions. The crystal growth method is slow temperature rise used at temperature from 180 °C up to 250 °C (the retrograde solubility of AlPO_4 - GaPO_4 and FePO_4 - GaPO_4 systems), the temperature increases with 5 °C/day.

For all the samples, the room temperature X-ray patterns were obtained using $\text{Cu-K}\alpha$ radiation. The cell parameters were refined and the intensity data were indexed using the Fullprof program [3].

The chemical composition was analyzed by electron probe microanalysis (EPMA) along the crystal.

3. Results and discussion

The processing parameters of hydrothermal reaction to the powders of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series were the nature and molarity of growth medium. For all the samples of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ series, it was obtained a single α -quartz phase (fig.1.), regardless of the nature and molarity of growth medium, in according with good solubility of AlPO_4 and GaPO_4 compounds in these solutions.

However, for the powder of $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series, the nature and molarity of growth medium are mainly parameters which depend the appearance of the single α -quartz phase, i.e., only solution of H_2SO_4 , 6 M/l and H_2SO_4 , 3 M/l, for $\text{Ga}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ and $\text{Ga}_{0.3}\text{Fe}_{0.7}\text{PO}_4$, respectively. Also, $\text{Ga}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ cannot be obtained using

these processing parameters of hydrothermal reaction. This result can be explained by the low solubility of FePO_4 in these solutions, the behavior that occurs with the rise of Fe^{3+} content.

The structural data for $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ ($x=0.1, 0.7, 0.9$) and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ ($x=0.1, 0.7$), table 1, are found to vary continuously as a function of composition.

No significant increase in cell volume as a function of x is observed as the volume of α -quartz-type structures is found to depend on the cube of the cation–cation nonbonded distance [8], which in the case of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ is almost constant due to the very similar nonbonded radii of Al^{3+} (1.62 Å) and Ga^{3+} (1.63 Å) [9], and maybe the same situation occurs for $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$, because the cell volume is slowly modified when x increases.

Table. 1. Experimental data – X-ray powder diffraction for $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Al}_x\text{PO}_4$ single series at room temperature.

Crystal data	$\text{Ga}_{0.9}\text{Fe}_{0.1}\text{PO}_4$	$\text{Ga}_{0.3}\text{Fe}_{0.7}\text{PO}_4$	$\text{Al}_{0.9}\text{Ga}_{0.1}\text{PO}_4$	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{PO}_4$	$\text{Al}_{0.1}\text{Ga}_{0.9}\text{PO}_4$
T (K)	296	296	296	296	296
Cell setting	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P3_121$	$P3_221$	$P3_221$	$P3_221$	$P3_221$
a (Å)	4.94984 (1)	4.95185 (1)	4.94247 (1)	4.91628 (1)	4.91031 (1)
c (Å)	10.96284 (1)	10.97275 (1)	10.97123 (1)	11.03573 (1)	11.05823 (1)
V (Å ³)	232.615 (1)	233.014 (1)	232.1 (1)	230.996 (1)	230.19 (1)

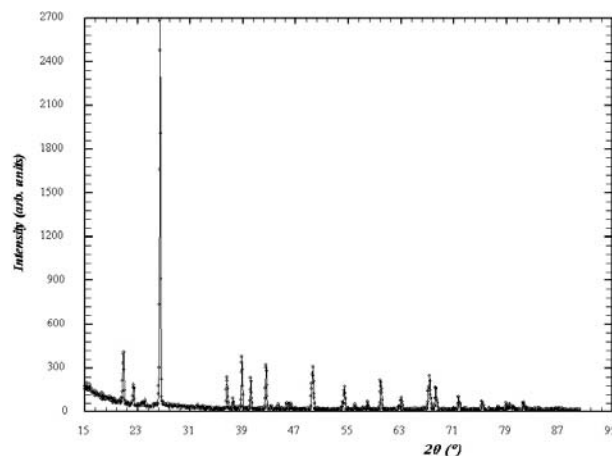


Fig. 1. XRD pattern of α -quartz structure of $\text{Al}_{0.1}\text{Ga}_{0.9}\text{PO}_4$ single crystal obtained by hydrothermal method (170 °C, H_2SO_4 , 6 M/l).

Thus, the structure must increasingly distort in order to pack the larger tetrahedra in an essentially identical unit cell volume, in according with ionic radius of Al^{3+} (0.52 Å), Ga^{3+} (0.61 Å) and Fe^{3+} (0.63 Å).

Due to the increase of the radius of the M-site cations, the structural distortion of $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series is larger than that of the $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and thus better piezoelectric properties.

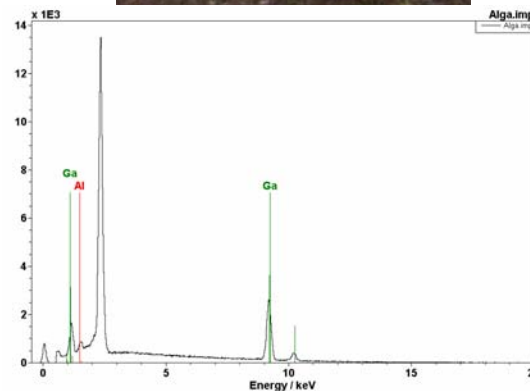


Fig. 2. (a) A $\text{Ga}_{0.9}\text{Al}_{0.1}\text{PO}_4$ single crystal; (b) Electron probe spectrum for a $\text{Ga}_{0.9}\text{Al}_{0.1}\text{PO}_4$ single crystal.

Single crystals of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series with linear dimensions of the order of 1-3 mm were obtained (Fig. 2a).

The electron probe microanalysis was performed at different points in the sample and was confirmed the uniformity and the closely stoichiometric composition with the precursor material for all single crystals of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series (Fig. 2b).

The best single crystals were obtained when it was used H_2SO_4 , 6 M/l solution like a growth medium. The growth rate was 0.2 mm/day for the H_2SO_4 , 6 M/l solution, and comparative with 0.05 mm/day for the H_3PO_4 , 6 M/l solution. This result is in correlation with the higher solubility of the $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series in H_2SO_4 , 6 M/l solution.

4. Conclusion

The single crystals and powder in the AlPO_4 - GaPO_4 and FePO_4 - GaPO_4 systems were prepared by hydrothermal method and studied by X-ray diffraction and electron microprobe analysis. The processing parameters of hydrothermal process emphasized the information about solubility of these compounds, which were used in the single crystal growth.

The structural data for these crystals indicates that their structures are α -quartz-type structures with the intermediate parameters between those of the pure end members.

This preliminary study of $\text{Al}_{1-x}\text{Ga}_x\text{PO}_4$ and $\text{Ga}_{1-x}\text{Fe}_x\text{PO}_4$ series open the possibility to growth of large single crystal and to tune the piezoelectric properties of these materials by varying the chemical composition and this way to improve the piezoelectric applications.

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