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KDP:Mn piezoelectric coefficients obtained by X-ray diffraction

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Crystals of pure potassium dihydrogen phosphate KH_2PO_4 (KDP) and Mn-doped KDP (KDP:Mn) were grown from a water solution by the slow evaporation method and their piezoelectric properties were studied by X-ray diffraction methods. The results have shown an increase in the piezoelectric coefficients with the doping.

Keywords: piezoelectric properties; KDP; doped crystal.

1. Introduction

It is well known that various additives can considerably influence the physical properties of crystals, making them suitable for technological applications. The effect of a dopant in a crystal lattice has been extensively researched (Lai *et al.*, 2005; Remédios *et al.*, 2005; Parikh *et al.*, 2007). At room temperature, pure potassium dihydrogen phosphate, KH_2PO_4 (KDP), crystals (Lines & Glass, 2001) are piezoelectric with a tetragonal structure belonging to space group $I\bar{4}2d$. In order to modify and improve the properties of KDP, a number of dopants have been tested. Recently, two new articles were published revealing new information with respect to the structure of the Mn^{3+}-doped KDP crystal (Remédios *et al.*, 2010a,b). Strong evidence of major structural changes owing to Mn doping were obtained and attributed to the rotation of PO_4 units in the *ab* basal plane and consequent shortening of O—H—O bonds. For instance, since the two equivalent H^+ positions are much closer in doped samples, freezing out the hydrogen motion will be more difficult. It will lower significantly the Curie temperature, T_C, similar to that observed in high-pressure experiments (McMahon *et al.*, 1990). On the other hand, if the reduction in the O—H—O distance also leads to a reduction in the covalent H—O bond length, an increase in the piezoelectric coefficients is expected owing to higher polarizability of the molecules under an external applied field (van Reeuwijk *et al.*, 2001). Materials with their piezoelectric constants larger than the values for conventional piezoelectric materials are much more important for these applications (Almeida *et al.*, 2006).

In this work, Mn-doped KDP (KDP:Mn) crystals were studied by X-ray diffraction using synchrotron radiation as a function of the applied electric field. Since the KDP:Mn crystal has already had its structure characterized by Raman spectroscopy and X-ray diffraction in previous works, and the observed structural changes pointed to an increase in the piezoelectric coefficients, we decided to use Bhalla's method (Bhalla *et al.*, 1971) to determine the KDP:Mn piezoelectric constants.

2. Experimental

Pure and doped crystal samples of KDP were grown by slow evaporation from saturated aqueous solutions at a controlled temperature (313 K). Mn^{3+}-doped samples were prepared for 5 mol% solution concentrations by adding $KMnO_4$ and $MnCl_3$ at a 1:1 molar ratio to the growth solutions with a pH between 3.8 and 4. Elemental composition analysis of the sample was made using Rutherford backscattering spectroscopy (RBS) to detect O, P, K and Mn using a beam of singly ionized 2.4 MeV He atoms aligned normal to the film surface with detection at 10° off-normal. From the RBS data the real densities of the O, P, K and Mn atoms of the film were obtained using the *RUMP* computational program (Doolittle, 1985). The results of RBS analysis show that the doped KDP sample prepared had Mn^{3+} concentrations of 0.9%. These crystals were cut in parallelepipeds of dimensions $0.87 \times 3 \times 5$ mm. The parallelepiped faces were orthogonal to the crystallographic directions of the tetragonal structure. Silver electrodes were placed in both surfaces perpendicular to the *c* axis as schematically shown in Fig. 1. The voltage applied in the sample was supplied by a model 246 high-
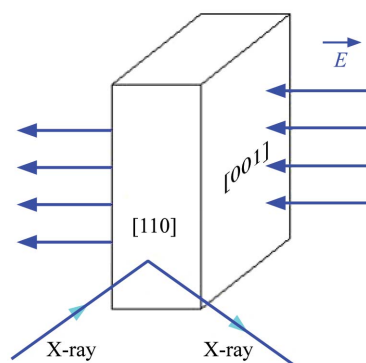

Figure 1
Sample representation for X-ray measurements.

voltage supply (Keithley Instruments) with a maximum output voltage of ±3 kV.

Data collection for this study was carried out in the XRD1 station of the Brazilian synchrotron radiation facility (LNLS) at wavelength λ = 1.88014 Å. This value was determined through the use of a silicon standard [111] crystal. A three-axis (θ, φ and 2θ) Huber goniometer was used. This goniometer provides Renninger scans with minimum step sizes of 0.0002° in the ω axis and 0.0004° in the φ axis.

The piezoelectric coefficients were determined by X-ray diffraction methods (Bhalla *et al.*, 1971) using the following equations,

$$-\Delta\theta \cot\theta = d_{36}E_3 \qquad (1)$$

$$-\Delta\theta \cot\theta = d_{25}E_2, \qquad (2)$$

where θ is the Bragg angle for reflections $(hh0)$ and $(0kk)$, d_{36} and d_{25} are elements of the piezoelectric tensor, and E_3 and E_2 are components of the electric field in the [001] and [010] directions, respectively.

3. Results and discussion

Several rocking curves for KDP and KDP:Mn were obtained in the absence of an electric field for two reflections, (440) and (066). We fit all the curves with Lorentzians and from these fittings we obtained the central angular positions of each peak. The peak shifts were obtained in the absence of the electric field to an accuracy better than 0.1 arcsec; the piezoelectric coefficients d_{25} and d_{36} could be determined to better than 1% at field strengths of the order of 10^5 V m^{-1}. After measurement of the rocking curves as a function of the electric field, the peak position returned to its initial position, indicating the reversibility feature of the E effect for both crystals. The centre peak
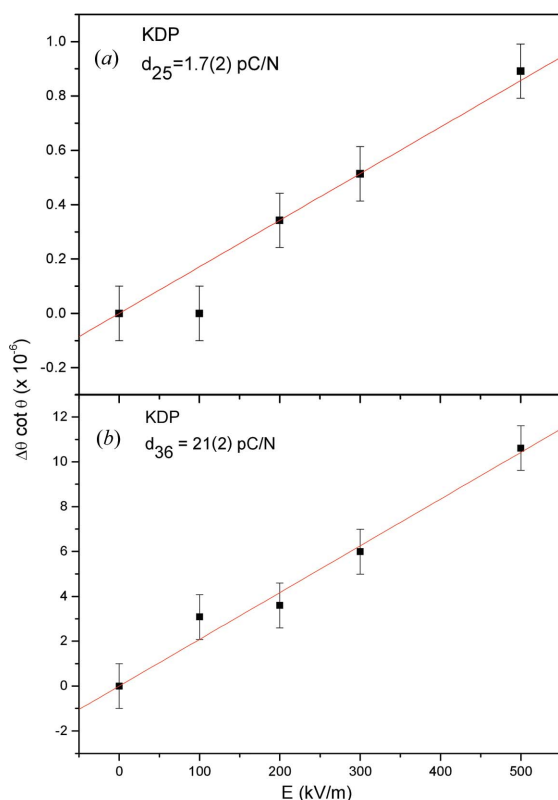

Figure 2
Pure KDP lattice strain *versus* electric field to obtain (*a*) the d_{25} piezoelectric coefficient and (*b*) the d_{36} piezoelectric coefficient.
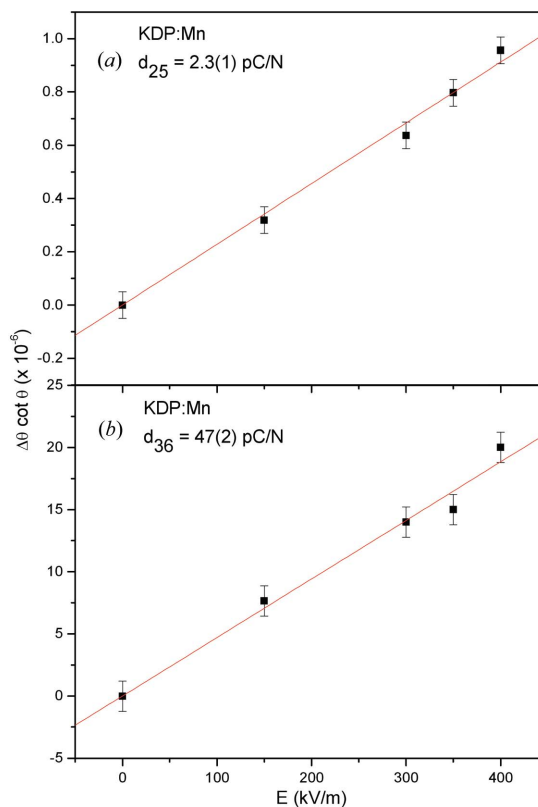

Figure 3
KDP:Mn lattice strain *versus* electric field to obtain (*a*) the d_{25} piezoelectric coefficient and (*b*) the d_{36} piezoelectric coefficient.

positions were transformed into lattice strain *via* equations (1) and (2). From the slope of $-\Delta\theta \cot\theta \times E$ plotted in Figs. 2(*a*) and 3(*a*) we obtain d_{25} = 1.7 (2) pC N^{-1} for pure KDP and d_{25} = 2.3 (1) pC N^{-1} for KDP:Mn. From the slope of $-\Delta\theta \cot\theta \times E$ plotted in Figs. 2(*b*) and 3(*b*) we obtain d_{36} = 21 (2) pC N^{-1} for pure KDP and d_{36} = 47 (2) pC N^{-1} for KDP:Mn. The piezoelectric coefficients obtained for KDP agree well with literature values (Lang, 1987).

It should be pointed out that the values obtained for the KDP:Mn d_{36} and d_{25} piezoelectric coefficients are higher than those of the well known pure KDP values. In preliminary results we have observed a reduction in the bridge length (H—O distance) in KDP:Mn. It is known that reduction in the bridge length (H—O) enhances the d_{36} KDP piezoelectric coefficients (McMahon *et al.*, 1990).

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