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RESEARCH ARTICLE

Growth, structural, piezoelectric, ferroelectric and thermal properties of lead nitrate orthophosphate hydrate single crystals grown in silica gel

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Abstract

Lead nitrate phosphate hydrate single crystals were grown in silica gel at room temperature. A controlled reaction was employed between orthophosphoric acid and lead nitrate solution by the double diffusion process in the gel medium. The single crystal X ray diffraction spectrum was recorded to confirm the structural parameters. The piezoelectric properties of the grown crystal were recorded at room temperature. The ferroelectric behavior of the grown crystal was analysed by PE hysteresis loop. From the results of DTA and TG analysis pointed out the decomposing point of the material.

Keywords

Inorganic compounds
Growth from gels
Single crystals
Piezoelectricity
Thermogravimatric analysis

Introduction

In recent years, an increasing demand for the crystals with many interesting properties, such as electronic, dielectric, ferroelectric, piezoelectric, pyroelectric [l-4]. These crystals are used in transducers and in linear and nonlinear mechanical devices in the advanced laser technology and optoelectronics applications. They are also suitable for testing macroscopic theory of ferroelectricity. Lead nitrate phosphate hydrate abbreviated as LNPH, It finds application in transducers, pyroelectric detectors and optoelectronic devices [5-7]. Due to the low solubility, fast precipitation during synthesis and the presence of water molecules in the structure, it is difficult to grow LNPH crystals from conventional slow evaporation solution technique and other melt methods.

But, the crystal growth *via* gel medium has received much attention to grow such kind of materials [8-10] because of the gel characteristics such as nucleation control and suppressing nucleation centers. Further, as lead nitrate one of the starting components, Lead hydrogen phosphate (LHP) can also result in addition to the LNPH during the growth process of LNPH crystallization [11-14].

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In the present work efforts are taken to grow large size LNPH crystals by suppressing the LHP growth. This can be achieved by introducing higher nitrate transfer in gel media which leads to LNPH growth. Hence, the nitric acid is used for gelation of the growth of LNPH. The LNPH crystal was grown by double diffusion method, where. Silica gel (acidified with nitric acid) was used as the growth medium to suppress the fast reaction. Also, as per the author's knowledge, the piezoelectricity, ferroelectric and thermal properties of LNPH crystals have not been reported in the literature. In this context, we report the growth of LNPH single crystals by using double diffusion gel technique and an attempt has been made to study the structural, piezoelectric, ferroelectric and thermal properties of grown LNPH crystals.

Experimental

Commercially available AR grade chemicals (Merck, India) of lead nitrate, orthophosphoric acid and nitric acid were purchased and used to grow single crystals of LNPH by employing gel technique at room temperature (31˚C). In this technique, silica gel was used as the growth medium. The growth of LNPH single crystal was accomplished by the controlled diffusion of lead nitrate and phosphate ions through silica gel impregnated with nitric acid. Silica gel was prepared using sodium metasilicate. Silica gel of specific gravity in the range 1.03-1.06 g/cc was prepared by dissolving sodium metasilicate in double distilled water and Nitric acid (2M) was dissolved in it. The gel is acidified with 1M glacial nitric acid to obtain pH in the range of 6-9 and it was stirred well for 3 h using a magnetic stirrer.

After stirring, the solution was taken in U tube of length 15 cm and diameter 2.5 cm. To keep the solution free from dust and impurities, care was taken to cover the test tubes. The optimized pH value of gelation is found to be 8.5. The solution gelled within 48 h. It was left as such for another 3 days for gel aging and then the outer reagent, aqueous solution of 1.5 M lead nitrate and 1 M of orthophosphoric acid were added onto the top of the gel. The reaction between orthophosphoric acid and lead nitrate in gel medium resulted in the growth of pure LNPH crystals.. The experimental setup was kept at ambient temperature for crystallization. Crystal growth was observed within three days. The colorless transparent LNP crystals upto 9 x 5 x 3 mm^3 in size have been grown at room temperature after 60 days. The grown crystals are shown in **Fig 1**.

Fig 1 The Grown LNPH single crystals from silica gel.

Results and discussion

Single crystal XRD analysis

The single crystal X-ray diffraction data of the grown LNPH crystals was recorded using Enraf Nonius CAD4 diffractometer with MoKα Single crystal XRD instrument to determine the unit cell parameters and space group. We found that the crystal system is monoclinic with cell parameters a = 9.634 (Å); b = 7.364 (Å); c = 10.663 (Å), $\alpha = 90.00^0$, $\beta = 106.26^0$, $\gamma = 90.00^0$ and volume = 1290 $Å^3$ and the space group is $P2_1/C$. The present result is in close agreement with the reported results [14] and JCPDS card no. 53-0667 which are shown in **Table 1**.

Table 1 Single crystal XRD result of reported and present study.

Parameter	Reported result [14]	Present result
a (Å)	10.551	9.634
b (Å)	7.299	7.364
c (Å)	9.551	10.663
α	90.00^0	90.00^0
β	106.30^0	106.26^0
γ	90.00^0	90.00^0
System	Monoclinic	Monoclinic
Space group	$P2_1/C$	$P2_1/C$

Piezoelectric measurements

Piezoelectric studies were made using piezometer system. A precision force generator applied a calibrated force (0.25 N) which generated a charge on the piezoelectric material under test. The output was measured directly from oscilloscope which gives the d_{33} coefficient in units of pC/N. With out poling the crystal the piezoelectric measurement was carried out for the grown crystals. A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied. The piezoelectric property is related to the polarity of the material [15]. The obtained piezoelectric coefficient (d_{33}) value for before and after polling of grown LNPH crystal is 0.61 pC/N and 2.13 pC/N respectively. Approximately seven times higher d_{33} value has been obtained for the LNPH crystals than the conventional method grown pure ADP and KDP crystals.

Ferroelectric measurements

The variation of the polarization signal with respect to the DC field to the ferroelectric specimen is given by hysteres is loop. **Fig 2** shows the PE hysteres is loop for LNPH single crystals. When electric field is applied, domain switching occurs, leading to a gradual increase of polarization. When the field reaches maximum, an almost single domain configuration is observed, which corresponds to the maximum polarization. We observed an interesting reversible domain-switching process during electric field cycling. It corresponds well to the peculiar double PE hysteresis loop, which is contrasting with the well-known normal hysteresis loop. The measured parameters of the loop are coercivity = 5.245 kV/cm, remnance =4.329 μC/cm^2, Max. electric field =5.805 kV/cm and Max. polarisation = 5.288 μC/cm^2.

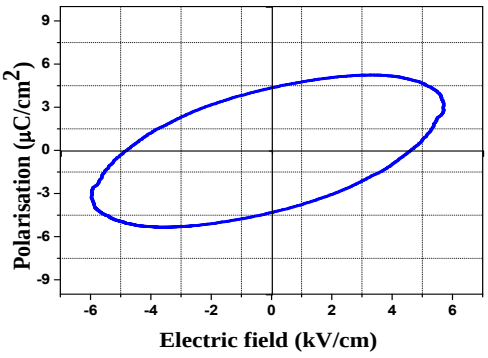

Fig 2 P- E Hysteresis loop of LNPH single crystals.

Thermal analysis

The TGA/DTA of the sample was conducted in nitrogen atmosphere at a heating rate of 10 °C /min between 35 and 400 °C at a heating rate 10 °C min^{-1} in nitrogen ambient using Perkin Elmer Diamond TG/DTA instrument. The thermal analyses are used to find out the weight loss (TGA) and melting point (DTA) of the grown LNPH single crystal. The TG/DTA curves are shown in the **Fig 3**. In differential thermal analysis, the material undergoes an irreversible sharp endothermic transition at 151^{0}C, which corresponds to its decomposing point indicating the removal of water molecules in the compund. The first decomposition (151 °C) is due to the loss of one water molecules (observed 3.5 %, calculated 3.0 %). Below the melting point there is no endothermic or exothermic peak, which illustrates the absence of isothermic transition in grown single crystal. The TGA curve indicates that the sample is stable and there is no phase transition upto 150 ^{0}C.

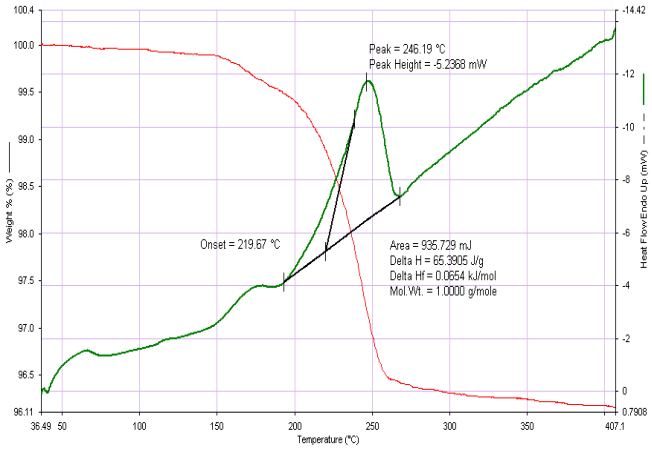

Fig 3 TG/DTA spectrum of grown LNPH single crystals.

Conclusions

LNPH single crystals upto 9 x 5 x 3 mm^3 in size were successfully grown using the double diffusion gel technique . The Single crystal XRD analysis confirms its lattice parameter and it is compared with the reported results. They belong to the monoclinic system and having the space group $P2_1/C$. Interestingly, the higher piezoelectric coefficient was found which is quit higher than materials of this category. The ferroelectric behavior of the grown crystal was studied from the P-E loop analysis. The crystal is found to be thermally stable up to 150 °C.

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