

Infrared and Structural Studies of Micro and Nano-crystalline Ta Doped Lead Zirconate Titanate Ceramics

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ABSTRACT

In this paper, influence of additives on structural properties of Tantalum (*Ta*) doped PZT ceramics, prepared by solid-state oxide and mechanical activation (MA) routes, has been studied. The Fourier transformation infrared spectroscopy (FTIR) studies, are done to understand the structural interactions, confirmed that the wave number and bond energy decreases with the increase in Ta content accompanied by decrease in grain size. FTIR spectrum becomes broader in nanocrystalline Ta-PZT. The fraction of tetragonal phase decrease along with reduction in grain size as the *Ta* content increase. The remnant polarisation and coercive field also follows the similar trend on *Ta* doping. It is seen that infrared spectroscopy results corroborate the structure and ferroelectric properties of PZT materials.

Keywords: Ceramics; Fourier transform infrared spectroscopy; Piezoelectricity; Dielectric properties

1. INTRODUCTION

PZT ceramics with addition of dopants exhibit exceptional electromechanical properties in either bulk or thin film form for various potential applications¹⁻⁴. The advance in the field of material processing has resulted in to tailor made materials having specific grain size and properties for a desired application. PZT ceramics are generally prepared by conventional solid-state (SS) route. It results in large grain size and compositional in-homogeneity because of high temperature calcination and Lead (*Pb*) loss. To overcome these effects, there is a need of a process which can avoid Lead loss by eliminating calcination step. This can be achieved by mechanical activation (MA) process in which improved reactivity of the starting composition results in formation of desired ceramic phase at room temperature^{2,5,6}. The present study aims to investigate the effect of *Ta* dopant and grain size on the infrared spectra and structural properties of lead zirconate titanate ceramics.

In polycrystalline PZT ceramics, the dielectric and ferroelectric properties are dependent on combination of the intrinsic lattice response and extrinsic response originating from domain wall motion, phase boundary, space charge. The additives play a decisive role in intrinsic related mechanisms for modifying the microstructure and electro-mechanical properties⁷. In PZT based ceramics the piezoelectric properties is mainly reliant on the lattice interactions^{8,9}. IR spectra are an active method to investigate the forces in crystal lattices. In FTIR, the main spectra peak is identified by bonding energy of lattice interaction¹⁰. FTIR spectra studies to characterise the vibration of Ti-O bond has been carried out and reported for BaTiO₃ based ceramics¹¹⁻¹⁴ but not much similar research

studies have been reported extensively for PZT based ceramics with variation of dopant and grain size.

In this paper, we report synthesis of micro and nano-crystalline *Ta* doped PZT ceramics (1 to 4 mol. % *Ta*) by SS and MA routes. The lattice parameters and bonding energy shall modify when adding additives in the PZT, resulting in molecular interaction of the spectra. The concentration of additives and the grain size affects the lattice interactive forces that results in wave number shift and change in binding energy. The interactive forces and the crystal structure are correlated with ferroelectric properties for micro- and nano-crystalline *Ta* doped PZT ceramics which has rarely been studied.

2. EXPERIMENTAL METHOD

Lead zirconate titanate ceramics with general formula Pb_{1-x/2}(Zr_{0.53}Ti_{0.47})_{1-x}Ta_xO₃ (where X=0, 0.01, 0.02, 0.03 and 0.04) were prepared using analytical grades of PbO, ZrO₂, TiO₂ and Ta₂O₅ (Purity >99%) by conventional SS route. The mixture is ball milled for 24 h using ZrO₂ jars and media with distilled water. The mixture was calcined at 1050 °C for 2 h and again milled for homogeneity. Infrared spectroscopy was analysed to study the interactive forces of the lattices. The measurement of FTIR spectrum was carried out with Perkin Elmer FTIR system (resolution ~ 0.5 cm⁻¹). The region of wavenumber is from 400 to 4000 cm⁻¹. The main absorption peaks appear below 1500 cm⁻¹. The powders were subsequently pressed for pellets at 150 MPa. The pellets were sintered and electrode to study the ferroelectric properties. Based on the obtained results, selected composition (X = 0.01) was chosen as optimum composition and prepared by MA route using Fritsch (P5) Planetary ball mill. Milling was carried out for 10 h in toluene medium with tungsten carbide vial and media at a speed of 300 rpm and ball

to powder ratio of 15:1. The procedure discussed above was repeated for MA pellets as well. SEM (JEOL, JSM 5800) was used to determine the average grain size of the sintered PZT samples prepared by SS route. The MA prepared sintered PZT samples were thermally etched at 1050 °C and analysed for grain size using tapping mode of AFM (Agilent, Picoplus).

3. RESULTS AND DISCUSSION

Figure 1 shows the FTIR Spectrum of (SS) microcrystalline PZT powder. Figure 2 show the FTIR spectra of microcrystalline (SS) PZT powder with various Ta content and the magnified portion of Ti-O stretching mode absorption bands. Spectrum of all the Ta doped PZT are alike. But the wavenumber of the absorption band associated with stretching mode of Ti-O bond vibration of 1 per cent Ta doped PZT (624 cm^{-1}) is higher compared to undoped PZT (607 cm^{-1}). When Ta^{5+} is replaced for Zr^{4+} or Ti^{4+} , the absorption band is shifted to higher wavenumber due to smaller radius of Ta^{5+} ion and therefore the lattice parameter becomes smaller when Ta^{5+} substitutes Zr^{4+} or Ti^{4+} ion. It reduces the space between ions and strengthens the Ti-O bond. But further increase in Ta content shifts the absorption band to lower wavenumber and

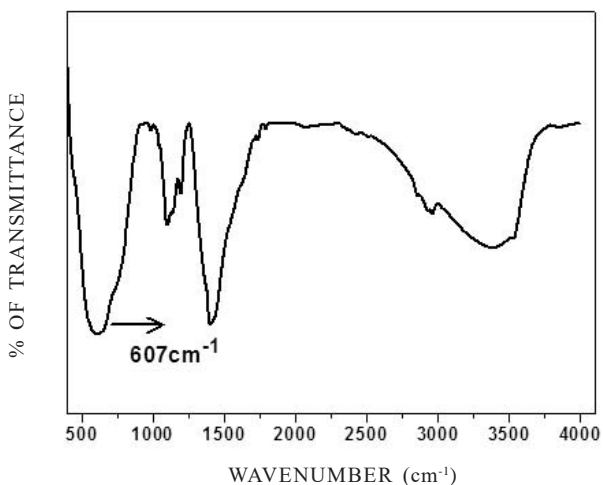
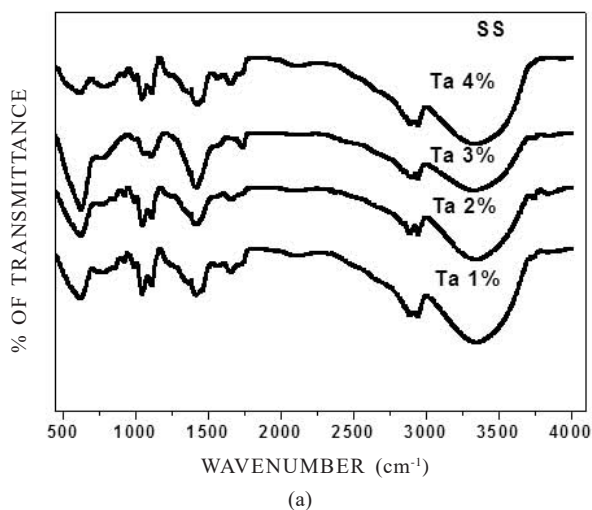


Figure 1. FTIR spectrum of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ powder.



that indicates the reduction in bond energy. When more Ta is added, it affected the Coulomb interaction amongst the ions^{15,16}. Because of this with increase in Ta, the related spectrum moves to lower frequency. This indicates the decrease in bond energy and the tetragonal phase in the material with increase in the Ta content.

FTIR spectra of micro- (SS) and nano-crystalline (MA) Ta-doped PZT and the magnified portion of Ti-O stretching mode absorption band are as shown in Fig. 3. The spectra of Ta-doped micro and nanocrystalline PZT clearly show the presence of absorption band associated with stretching of Ti-O. It is observed that the wavenumber of absorption band related to Ti-O stretching of microcrystalline PZT is higher as compared to nanocrystalline Ta doped PZT powder, which are 624 cm^{-1} and 613 cm^{-1} , respectively. It is also observed that absorption band in the nanocrystalline PZT prepared by MA route is broader when compared with microcrystalline PZT powder. The nature of absorption band differs because the frequency of vibration modes of atom is different for both micro and nanocrystalline materials because of dipole interactions, interfacial effects and surface free energy¹⁷. Because of small grain size and large surface to volume ratio of nanocrystals, the atomic arrangements on the boundaries could differ from that of the bulk crystals, showing some extent of disorder. This can result in the shifting of IR active modes and in the evolution of new bands. The decrease in wavenumber of absorption band as the particle size decreases is due to increase in repulsive dipolar interaction and variation in cation-oxygen bond length¹⁸.

The variation of tetragonal phase and grain size with Ta content in PZT powders prepared by SS and MA routes are shown, respectively in Fig. 4 (a) and 4(b). In donor doping, the two holes caused by the removal of Ti^{4+} or Zr^{4+} ion may be compensated by two electrons from the donor dopants instead of the formation of oxygen vacancies. It is observed that the increase in Ta (0 to 4 mol.%) content and reduction in grain size to nano scale, decreases the tetragonal phase in PZT. Increase in Ta content leads to structural deformation and that result in crystal structure changing from tetragonal perovskite to

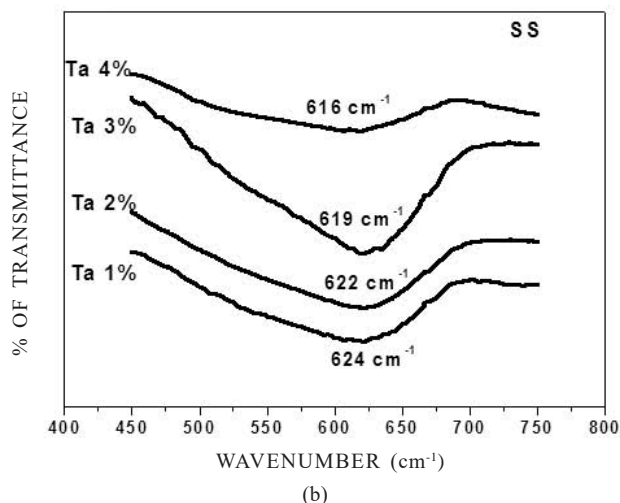


Figure 2. FTIR spectra of (a) microcrystalline (SS) Ta doped PZT and (b) magnified portion of absorption bands.

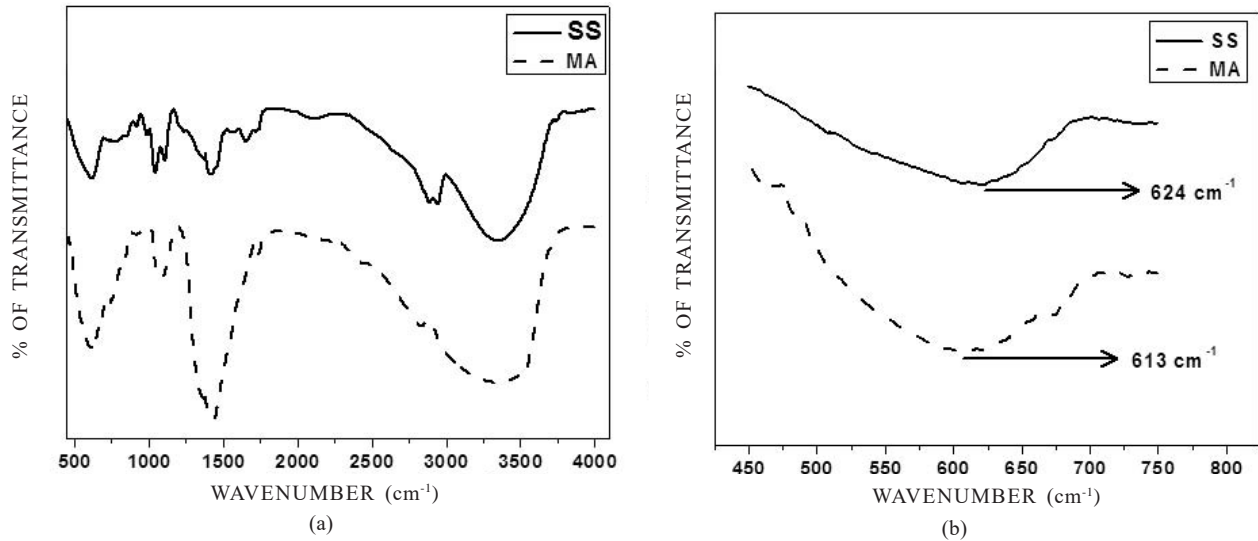


Figure 3. FTIR spectra of (a) micro (SS) and nanocrystalline (MA) Ta (1 mol %) doped PZT.

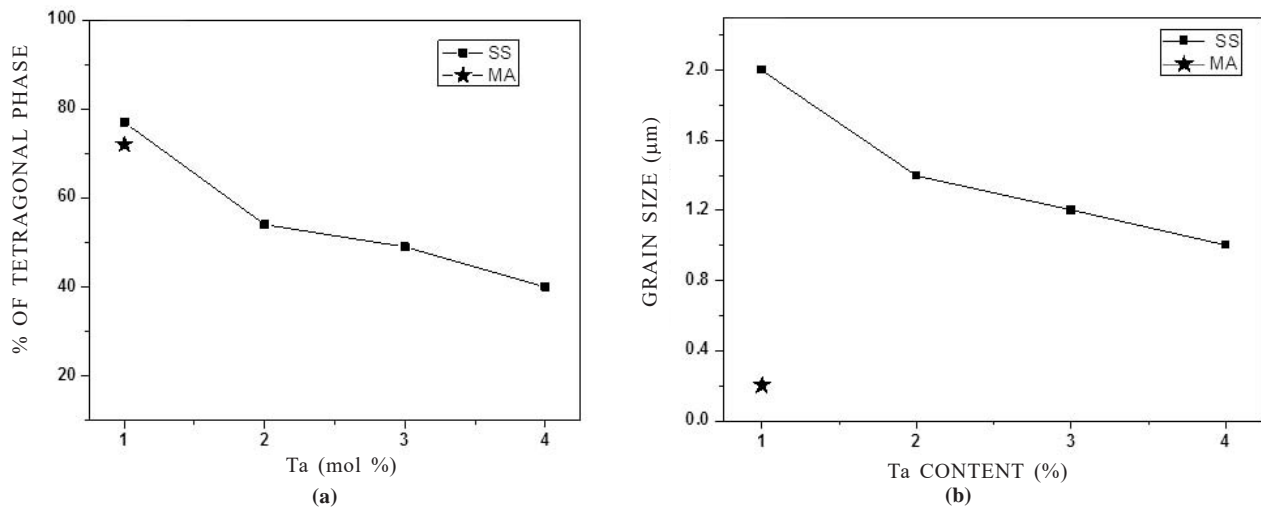


Figure 4. Variation of (a) tetragonal phase and (b) grain size with Ta %.

rhombohedral perovskite¹⁶. It is due to the stronger Ta-O bond and smaller ionic radius of Ta^{5+} , the O^{2-} will move towards Ta^{5+} . Pb^{2+} will also leave from its normal position towards Ta^{5+} because of Pb-O bond restriction. In the case of Ta doped PZT, partial substitution of Ta ions induces the conversion of intensified tetragonal structure to the coexistence of rhombohedral and tetrahedral structure. Subsequently, decrease in grain size to nano scale reduces the presence of tetragonal phase because of the formation of compressive micro stresses in nanoparticles and slight reduction in depolarisation energy of mechanically

activated PZT powders¹⁹⁻²². The dielectric and ferroelectric properties of Ta doped PZT obtained by MA and SS route are as shown in Table 1.

The SEM image of a fractured cross section of Ta doped (1 mol %) SS PZT is as shown in Fig. 5. The image illustrates the dense microstructure and the average grain size measured by linear intercept method is found to be $\sim 2 \mu m$. The AFM image of the sintered MA Ta doped (mol 1%) PZT is shown in Fig. 6. AFM image reveals the average grain size of around $\sim 200 nm$. It clearly reflects that mechanically activated PZT

Table 1. Variation of dielectric and ferroelectric properties of Ta doped PZT prepared by SS and MA

Sample	Dielectric constant (ϵ)	Coupling coefficient (k_p)	Remnant polarisation ($\mu C/cm^2$)	Coercive voltage (V)	Curie temp ($^{\circ}C$)
SS Ta – 1%	1470	0.549	26.7	1290	385
SS Ta – 2%	1410	0.496	21.7	1210	360
SS Ta – 3%	1280	0.452	17.1	1150	340
SS Ta – 4%	980	0.38	9.2	850	300
MA Ta – 1%	1930	0.46	14.6	1040	370

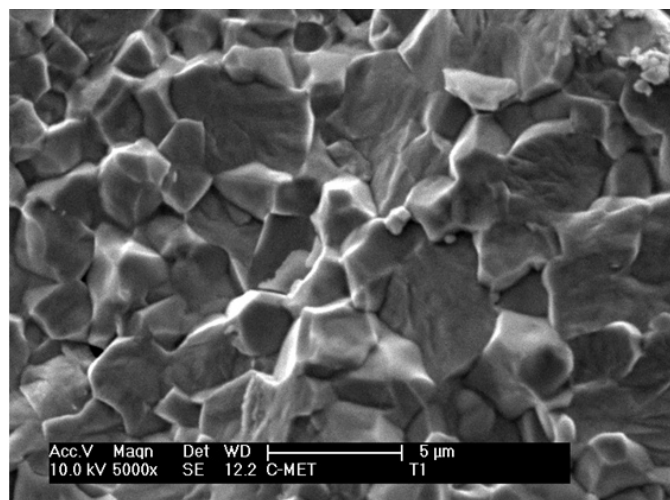


Figure 5. SEM Micrograph of Ta (1 mol %) doped sintered PZT.

powders, after sintering reduces the sintered grain size significantly. The reduction in grain size in MA PZT is due to the effect of high kinetic energy involved during mechanical activation route.

The variation of bonding energy with Ta content in PZT powders prepared by SS and MA routes are as shown in Fig. 7. The bonding energy decreases with increase in Ta content and decrease in grain size. It could be due to the decrease in the tetragonal phase observed with increment in Ta content. Consequently, decrease in particle size to nano scale also reduces the bonding energy of Ta doped PZT powders because of increase in repulsive dipolar interaction and variation in cation-oxygen bond length. In PZT based ferroelectric materials, the bond strength and bonding energy of Ti-O bond is influenced by particle size and tetragonal phase formation.

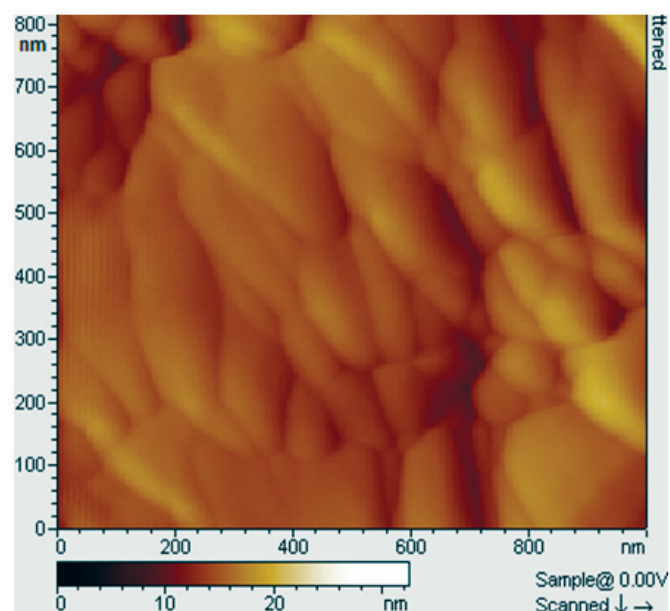


Figure 6. AFM of Ta (1 mol %) doped sintered PZT.

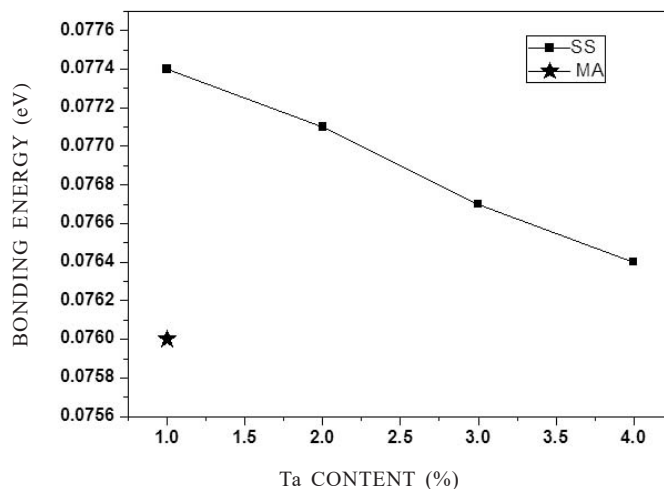


Figure 7. Variation of bonding energy with Ta %.

4. CONCLUSIONS

Ta doped PZT powder has been synthesised by solid-state and mechanical activation routes. FTIR studies reveal that the addition of dopant affects the vibration of crystal lattices. Ta doped PZT ceramics has higher wavenumber when compare to undoped ceramics but with increase in Ta content the wavenumber decreases. Decrease in wavenumber and broader absorption bands are observed in nanocrystalline Ta-PZT prepared by MA route. It is also observed that the increase in Ta content and reduction in grain size decreases the tetragonal phase in Ta doped PZT. It is concluded that the ferroelectric and dielectric properties are closely related with the vibrational forces of crystal lattice.

REFERENCES

- Jaffe, H. & Berlincourt D.A. Piezoelectric transducer materials. *In Proceedings of IEEE*, 1965, **53**(10), 1372-86. doi: 10.1109/PROC.1965.4253
- Hu, T.; Wang, Z.; Ma, N. & Du, P. Two stage formation of silver nanoparticles in PZT thin films controlled by re-nucleation through transition phase of Ag-Pb alloy. *Thin Solid Films*, 2016, **616**, 252-59. doi: 10.1016/j.tsf.2016.08.048
- Wu, C.; Cai, G.; Luo, W.; Peng, Q.; Sun, X & Zhang, W. Enhancement of pyroelectric properties of composite thick films using Mn-doped PZT. *Sensors Actuators A: Phys.*, 2013, **199**, 24-29. doi: 10.1016/j.sna.2013.04.025
- Han, C.S.; Park, K.S.; Choi, H.J. & Cho, Y.S. Enhanced piezoelectric and imprint characteristics of in situ sputtered Ta-doped Pb(Zr,Ti)O₃ thin films on Ir/TiW/SiO₂/Si substrates. *J. Alloys Compounds*, 2017, **720**, 369-75. doi: 10.1016/j.jallcom.2017.05.288
- Kumar, A.; Bhanu Prasad, V.V.; James, Raju K.C. & James A.R. Lanthanum induced diffuse phase transition in high energy mechanochemically processed and poled PLZT 8/60/40 ceramics. *J. Alloys Compounds*, 2016, **654**, 95-102. doi: 10.1016/j.jallcom.2015.09.081
- Goudarzi, H. & Baghshahi, S. PZT ceramics prepared

- through a combined method of B-site precursor and wet mechanically activated calcinate in a planetary ball mill. *Ceram. Int.*, 2017, **43**(4), 3873-78.
doi: 10.1016/j.ceramint.2016.12.050
7. Yang, Z. & Zu, J. Comparison of PZN-PT, PMN-PT single crystal and PZT ceramic for vibration energy harvesting. *Energy Conversion Manag.*, 2016, **122**, 321-29.
doi: 10.1016/j.enconman.2016.05.085
 8. Kong, L.B.; Ma, J.; Zhu, W. & Tan, O.K. Reaction sintering of partially reacted system for PZT ceramics via a high energy ball milling. *Scripta Mater.*, 2001, **44**, 345-50.
doi: 10.1016/S1359-6462(00)00567-4
 9. Perry, C.H.; Khanna, B.N. & Rupprecht, G. Infrared studies of perovskititanates. *Phys. Rev.*, 1964, **135**(2A), 408-12. doi: 10.1103/PhysRev.135.A408
 10. Ghasemifard, M.; Hosseini, S.M. & Khorani, G.H. Synthesis and structure of PMN-PT ceramic nanopowder free from pyrochlore phase. *Ceram. Int.*, 2009, **35**, 2899-905. doi: 10.1016/j.ceramint.2009.03.036
 11. Last, J.T. Infrared-absorption studies on barium titanate and related materials. *Phys. Rev.*, 1957, **105**, 1740-1750.
doi: 10.1103/PhysRev.105.1740
 12. Babooram, K. & Ye, Z.G. Polyethylene Glycol-based new solution route to relaxor ferroelectric $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.35\text{PbTiO}_3$. *Chem. Mater.*, 2004, **16**, 5365-71.
doi: 10.1021/cm049134s
 13. Perrin, F.X.; Nguyen, V. & Vernet, J.L. FT-IR spectroscopy of acid-modified Titanium Alkoxides: Investigations on the nature of Carboxylate coordination and degree of complexation. *J. Sol-Gel Sci. Techn.*, 2003, **28**, 205-15.
doi: 10.1023/A:1026081100860
 14. Jin, X, Sun, D, Zhang, M, Zhu, Y & Qian, J. Investigation on FTIR spectra of barium calcium titanate ceramics. *J. Electroceram.*, 2009, **22**, 285-290.
doi: 10.1007/s10832-007-9402-1
 15. Hammer, D.M. & Hoffmann, M.J. Detailed X-ray diffraction analyses and correlation of microstructural and electromechanical properties of La doped PZT ceramics. *J. Electroceram.*, 1998, **2**, 75-84.
doi: 10.1023/A:1009954822076
 16. Choi, G.P.; Ahn, J.H.; Lee, W.J.; Sung, T.H. & Kim H.G. Phase formations and electrical properties of doped PZT/PbTiO₃ films deposited by reactive sputtering using multi targets. *Mater. Sci. Eng.*, 1996, **B 41**, 16-22.
doi: 10.1016/S0921-5107(96)01616-9
 17. Yang, C.Q. & Fateley, W.G. The effect of particle size on peak intensities of FT-IR photoacoustic spectra. *J. Mol. Struct.*, 1986, **141**, 279-84.
doi: 10.1016/0022-2860(86)80334-9
 18. Adak, A.K.; Saha, S.K. & Pramnik, P. Synthesis and characterization of MgAl₂O₄ spinel by PVA evaporation technique. *J. Mater. Sci. Lett.*, 1997, **16**, 234-35.
doi: 10.1023/A:1018512025919
 19. Maison, W.; Kleeberg, R.; Heimann, R.B. & Phanichphant, S. Phase content, tetragonality, and crystallite size of nanoscaled barium titanate synthesized by the catecholate process: effect of calcination temperature. *J. Eur. Ceram. Soc.*, 2003, **23**, 127-32.
doi: 10.1016/S0955-2219(02)00071-7
 20. Yen, F.S.; Chang, C.T. & Chang, Y.H. Characterization of Barium titanate oxalate tetrahydrate. *J. Am. Ceram. Soc.*, 1990, **73**, 3422-27.
doi: 10.1111/j.1151-2916.1990.tb06470.x
 21. Ur, S.C.; Mahmud, I. & Yoon, M.S. Effect of high energy milling process on microstructure and piezoelectric/dielectric properties of $\text{K}_{0.475}\text{Na}_{0.475}\text{Li}_{0.05}\text{NbO}_3$ solid solution. *Ceram. Inter.*, 2013, **39**(1), 691-99.
doi: 10.1016/j.ceramint.2012.06.080
 22. Kumar, A.; Bhanu Prasad, V.V.; James Raju K.C. & James A.R. Ultra high strain properties of lanthanum substituted PZT electro-ceramics prepared via mechanical activation. *J. Alloys Compounds*, 2014, **599**, 53-59.
doi: 10.1016/j.jallcom.2014.02.037

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