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Structural, dielectric and electrical properties of Lead zirconate titanate and $CaCu_3Ti_4O_{12}$ ceramic composite

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ABSTRACT

In the present work, structural, dielectric and electrical properties of lead zirconate titanate and $CaCu_3Ti_4O_{12}$ ceramic composite with composition $(1\text{-}x)Pb(Zr_{0.65}Ti_{0.35})O_3$ - $xCaCu_3Ti_4O_{12}$ (where x = 0, 0.20, 0.40 and 0.60) has been reported. The sample was prepared by employing a high temperature solid state reaction technique. X-ray diffraction studies confirm the formation of pure phase for x = 0.00 concentration and composite phases for the x = 0.40, 0.60 compositions. Doublet of diffraction peaks suggests structural change for x = 0.20 composition. Scanning electron micrographs show a uniform grain distribution and the grain size and shape modified upon $CaCu_3Ti_4O_{12}$ addition. Dielectric measurement demonstrates a decrease in the dielectric constant with increase in $CaCu_3Ti_4O_{12}$ percentage. The prepared ceramic composites have high dielectric constant and low dielectric loss. The temperature dependence of the ac conductivity indicated that the conduction process is due to singly ionized (in ferroelectric region) and doubly ionized (in paraelectric region). Copyright © 2011 VBRI press.

Keywords: Ceramics; X-ray diffraction; PZT; dielectric properties; SEM.

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Introduction

Lead zirconate titanate (PZT) is a perovskite type ABO_3 (A = Mono –or divalent; B = Tri- hexavalent ion) structures material with A-site (Pb^{2+}) occupying the cubo-octahedral interstices described by the BO_6 site octahedral and has tetragonal, rhombohedral and orthorhombic phases at room temperature depending on the value of Zr/Ti ratio. It has two morphotropic phase boundaries (MPB) at 95/5 and

53/47 Zr/Ti ratio, where it undergo phase transition from orthorhombic to rhombhohedral at low temperature and high temperature rhombhohedral to tetragonal phases, respectively. It is a solid solution of ferroelectric $PbTiO_3$ (T_c = 490 ^oC) and anti ferroelectric $PbZrO_3$ (T_c = 230 ^oC) [**1**]. Existence of both phases near MPB leads to a higher polarizability due to presence of large number of possible polarization directions [**2**]. Because of its high dielectric properties it is being considered for micro-electro mechanical systems (MEMS), storage information devices, sensors etc. [**3-5**]. Low dielectric loss, good pyroelectric properties, room temperature permittivity makes them ideal for infra red sensors applications [**6-7**]. It is one of the most widely investigated ferroelectric systems.

$CaCu_3Ti_4O_{12}$ (CCTO) has drawn much interest recently due to its extraordinarily high dielectric constant ($\sim10^4$) which is practically frequency independent in the frequency range 10^2–10^6 Hz and possesses good temperature stability over a temperature range between 100 and 400K [**8-10**]. Oxides with the perovskite structure are well stabilized by their high dielectric constant (ε) which leads these classes of materials to big number of technological application [**8**]. However these behaviors are generally associated to ferroelectric, relaxor properties. In these cases the high value of ε is obtained during a phase transition (as a function of temperature) presented by the materials. The existence of the transition temperature event is generally a problem when one is talking about application of these materials .The reported results for CCTO show that the ε is high but with small dependence on temperature [**9**]. Such a materials is very promising for capacitor application and certainly for microelectronics, microwave devices (cell mobile phone example) where the miniaturization of the devices are crucial, high ε ceramics makes it possible to noticeably miniaturize passive microwave devices. Their size can be typically be reduced in comparison with classical resonators and filter by a factor of $(\varepsilon)^{1/2}$ (relative dielectric constant).

In the present work we are reporting the synthesis of (1-*x*) PZT-*x* $CaCu_3Ti_4O_{12}$ by solid state reaction route. These are characterized by powder X-ray diffraction (XRD), Field Scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX). The dielectric properties have also been studied.

Experimental

Materials and methods

A high temperature solid-state reaction technique was used to prepare the polycrystalline samples $Pb(Zr_{0.65}Ti_{0.35})O_3$ using high purity oxides; PbO, ZrO_2, TiO_2 (99.9% purity, M/S Loba Chemie, Inc. Bombay, India) in a suitable stoichiometry and with 3% excess of PbO was to compensate Pb losses during high temperature calcinations/sintering. The oxides were mixed thoroughly first in air atmosphere for 1 h and then acetone medium for 3h. The mixture was then calcined in high purity (99.9%) alumina crucible at 1050 ^oC for 2h.

$CaCu_3Ti_4O_{12}$ (CCTO) sample was prepared by standard solid state reaction technique. $CaCO_3$, TiO_2 and CuO (99.9% purity, M/S Loba Chemie, Inc, Bombay, India) were used as staring materials. Stoichiometric ratios of the regents were mixed in agate motor in acetone medium for 4h. The mixed powder was calcined in air at 900 ^0C for 12h and the calcined powder was again grinded in agate motor.

The prepared polycrystalline sample of $Pb(Zr_{0.65}Ti_{0.35})O_3$ and $CaCu_3Ti_4O_{12}$ were carefully weighed in stoichiometric proportion and mixed thoroughly in agate motor for 3h. The powder was calcined at 900 ^oC for 4h. This step is necessary to make sure that all composition reacts well with each other to form the desired phase. The calcined powder was then pressed into disks of thickness 1.2 mm and diameter 10 mm using polyvinyl alcohol (PVA) as a binder. The final sintering of the pellets was done at 1100 ^oC for 4h using a heating rate 5 ^oC/min.

Crystal structure and phase identification of sintered pellets was carried out by X- ray diffractometer (Bruker's D-8 Advance X-ray) with Cu K_α radiation (1.54 Å) in a wide range of Bragg's angles 2θ ($20 \leq 2\theta \leq 60$) at the scanning rate 1^o/min. The microstructure and grain morphology were directly imaged using field emission scanning electron microscope (FESEM). Sintered pellets were polished and flat surface were coated with high purity silver paste and then dried at 150 ^oC for 30 min to remove the moisture after that, the pellets were cooled at room temperature and the electrical measurements were performed. Dielectric measurements were measured by using LCR meter (HIOKI 3532-50 Hi-Tester) in a temperature range 50 to 400 ^oC.

Results and discussion

In the present study, powder X-Ray diffraction technique was used to determine the structure, crystalline size and phase of ceramics composition. The x-ray diffraction pattern of (1-*x*)$Pb(Zr_{0.65}Ti_{0.35})O_3$ - *x*$CaCu_3Ti_4O_{12}$, (where, x = 0, 0.20, 0.40, 0.60) powdered samples, sintered at 1100 ^oC for 4h is shown in **Fig. 1**. The XRD pattern for x = 0 clearly shows the formation of single phase, which was identified to be rhombohedral phase and the peaks were indexed accordingly. The doublet of peaks for x = 0.20 composition, suggests structural change from rhombohedral to cubic structure which may be due the cubic phase of $CaCu_3Ti_4O_{12}$. The XRD patterns for x = 0.40 and 0.60 compositions shows the composite phases of PZT(65/35) and CCTO. For $x \geq 0.40$ the XRD pattern of (1-*x*)PZT(65/35)-*x*CCTO compounds show some additional peaks (as the transient phase) in addition to PZT-CCTO peaks, which are called pyrochlore(s) [**10, 11**]. It has been reported that the pyrochlore phase is essential step in the formation of perovskites [**12**]. This type of the compound is considered as oxygen deficient compound with a metastable transient phase [**13**]. Whereas on increasing CCTO contents in $Pb(Zr_{0.65}Ti_{0.35})O_3$ pyrochlore/metastable phases were observed.

The Crystallite size (D) of PZT-CCTO compounds was determined by the Scherrer's formula, using equation $D = K\lambda/(\beta_{1/2}\cos\theta)$; where, K = 0.89, λ = 1.5405 Å and $\beta_{1/2}$ = peak width of the reflection at half intensity. As the powder sample was used for XRD, the effect of the strain, instruments and other unknown factor causing the broadening of the peak were ignored. The average value of the crystallite size of PZT-CCTO compounds under consideration was found to be .026 μm. Crystallite size was found to increase on increasing CCTO contents, this is shown in **Fig. 2** and **Table 1**.

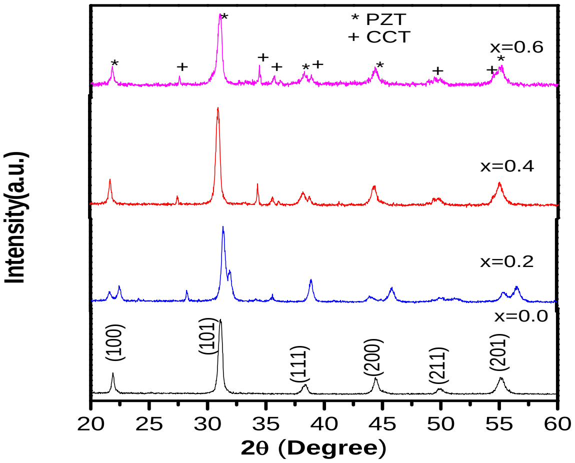

Fig. 1. X-ray diffraction pattern of (1-x)PZT- xCaCu$_3$Ti$_4$O$_{12}$ systems (x = 0, 0.20, 0.40, 0.60).

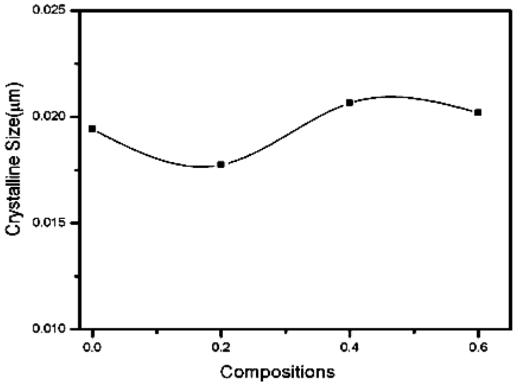

Fig. 2. Crystallite size for different composition (1−x) PZT–x CaCu$_3$Ti$_4$O$_{12}$ (x = 0, 0.20, 0.40, and 0.60).

Table 1. Crystallite size, grain size and activation energy for different compositions of (1−x) PZT (65/35)–xCCTO ceramics.

Sl. No.	Composition name	Crystallite size (µm)	Activation energy (eV)	Grain size (µm)	Diffusivity γ
1	PZT	0.01942	0.46	1.125	1.12
2	0.80PZT-0.20CCTO	0.01774	0.61	.5625	1.16
3	0.60PZT-0.40CCTO	0.02065	0.43	.752	1.25
4	0.40PZT-0.60CCTO	0.02019	0.52	.9375	1.50

In the present study surface microstructure of sintered samples observed by FE-SEM is shown in **Fig. 3**. It was found that the grain of different size is uniformly and densely distributed over the entire surface of the sample most of the grains of the sample were found in spherical in nature. The shape, size and distribution of grain of the microstructures of all the samples confirmed the polycrystalline nature of the sample and well developed grains were observed in all the compositions. The grain size increased on increasing the CCTO contents. And the variation of average grain size with composition is shown in **Fig. 4** and **Table 1**.

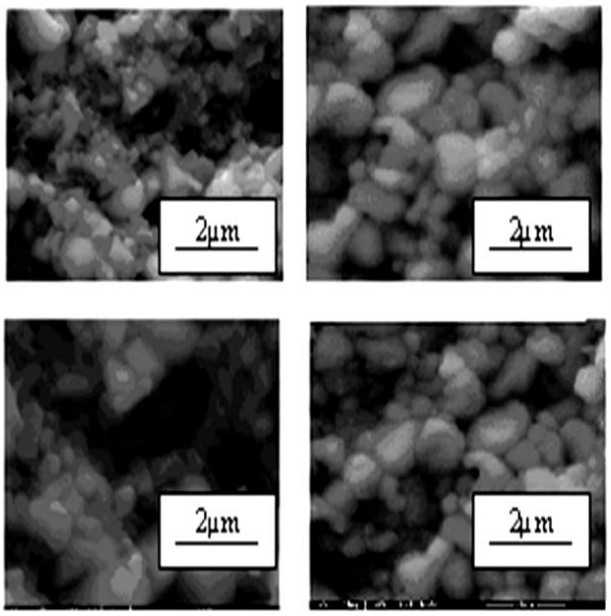

Fig. 3. FESEM micrographs (1-x) PZT-xCaCu$_3$Ti$_4$O$_{12}$ for x = 0, 0.20, 0.40 and 0.60.

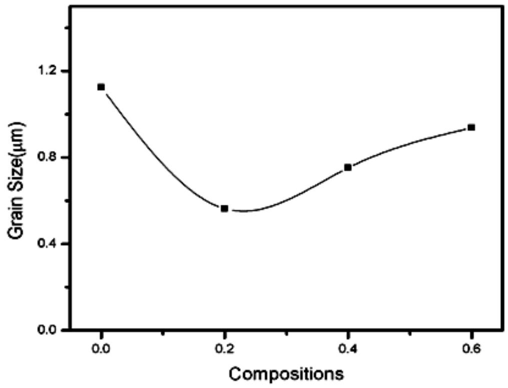

Fig. 4. Variation Average grain size of (1−x) PZT–xCaCu$_3$Ti$_4$O$_{12}$ ceramics (x = 0, 0.20, 0.40 and 0.60).

Fig. 5 shows the temperature dependence of dielectric constant (ε) at three different frequencies ranging from 1 kHz to 100 kHz for (1-x)PZT- xCCTO system (x = 0, 0.20, 0.40 and 0.60). The dielectric constant was almost constant up to 250 ^{o}C, then ε increases gradually attaining a maximum value ε_{max} at Curie temperature and thereafter it decreases with the further increase in temperature. This dielectric anomaly indicates a phase transition from ferroelectric to paraelectric phase at that particular temperature (Curie temperature, T_c). The Curie temperature of pure PZT is 370 ^{o}C. With increase of CaCu$_3$Ti$_4$O$_{12}$ content, Curie temperature shift towards lower temperatures (T_c~340^{o}C) and further no shift was found in Curie temperature (T_c) for all the compositions as determined from dielectric constant vs. temperature plots. From **Fig. 5**, it is evident that the value of ε decreases with increase of CaCu$_3$Ti$_4$O$_{12}$ content. The dielectric peaks broadened rather than a sharp peak (as in normal ferroelectrics) around T_c, which is one of the characteristic of disordered perovskite structure with diffuse phase transition. This broadening is believed to be due to the compositional fluctuation [**14**] or substitution disordering in the arrangement of cation in one or more crystallographic sites [**15**] in the structure leading to a microscopic heterogeneity in the composition and thus in a distribution of different local Curie points.

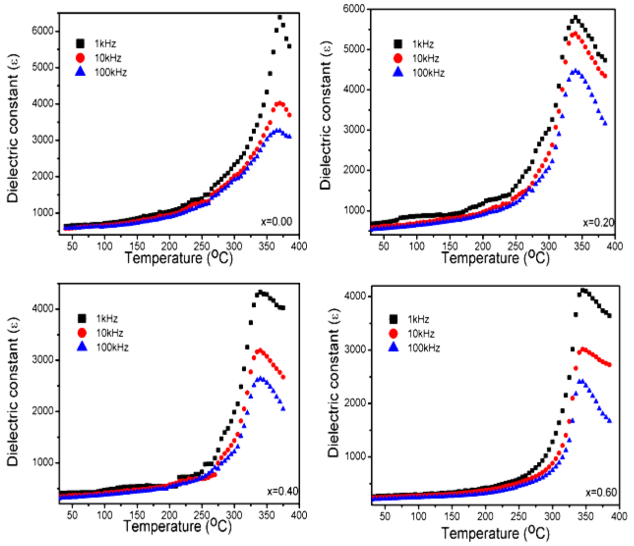

Fig. 5. Dielectric constant versus temperature plot for the (1-*x*) PZT-*x*$CaCu_3Ti_4O_{12}$ system (*x* = 0, 0.20, 0.40 and 0.60).

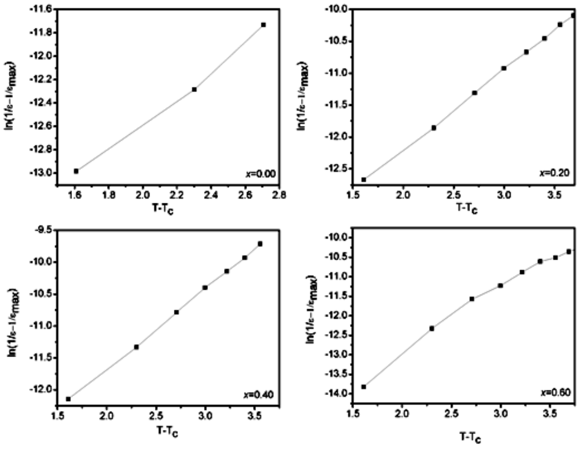

Fig. 6. Plots of ln ($1/\varepsilon$-$1/\varepsilon_{max}$) vs. ln (T-Tc) for (1-*x*) PZT- *x*$CaCu_3Ti_4O_{12}$ system (*x* = 0, 0.20, 0.40, 0.60).

As described above, a combination of PZT with CCTO introduces dielectric peak broadening. For better understanding of the dielectric behavior of (1-*x*)PZT-*x*CCTO system, we look at these behaviors through Curie–Weiss law. For a normal ferroelectric such as (1-*x*)PZT-*x* CCTO above the Curie temperature the dielectric constant follows the Curie–Weiss law:

$$\varepsilon = \frac{c}{T - T_0} \qquad (1)$$

where *c* is the Curie constant and T_0 is the Curie–Weiss temperature [**16**]. For a ferroelectric with a diffuse phase transition (broad peak), the following equation:

$$\frac{1}{\varepsilon} = (T - T_m)^2 \qquad (2)$$

It has been shown to be valid over a wide temperature range instead of the normal Curie–Weiss law, Eq. (1) [**17**]. In Eq. (2), T_m is the temperature at which maximum is the dielectric constant. Further examination of the diffuseness in the studied materials was carried out by using the following expression [**18, 19**]:

$$\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}}\right) \propto (T - T_C)^{\gamma} \qquad (3)$$

where ε_{max} is the maximum value of ε at T_c. The value of γ (diffusivity) was found to be between 1 and 2, which confirms the diffuse phase transition in the material.

The diffusivity (γ) can be estimated from the slope of the dielectric data shown in **Fig. 6**, which should be linear. The values of γ are material constants depending on the composition and structure of materials. The value of *γ* is the expression of the degree of dielectric relaxation. In a material with the “pure” diffuse phase transition described by the Smolenskii–Isutov relation, the value of *γ* is expected to be 2. The values of *γ* (diffusivity) was found to be between 1 to 2, which was extracted from the plot shown in **Fig. 6** of ln($1/\varepsilon$-$1/\varepsilon_{max}$) vs. ln$(T\text{-}T_c)^2$ by fitting a straight line equation. This confirms that diffuse phase transition occur in materials with a higher degree of disorder and there is a deviation from Curie-Weiss type of phase transition. The degree of diffuseness increases with the increase in CCTO content. The values of γ (diffusivity) were found to be 1.126, 1.1636, 1.254 and 1.5041 at 10 kHz for *x* = 0.00, 0.20, 0.40 and 0.60.

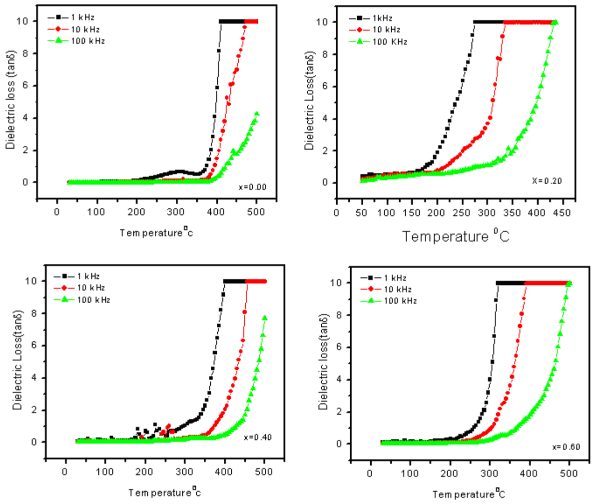

Fig. 7. Variation of Dielectric Loss versus temperature plot for the (1-*x*) PZT- *x*$CaCu_3Ti_4O_{12}$ system (*x* = 0, 0.20, 0.40 and 0.60).

The temperature dependence of tangent loss (tan δ) of (1-*x*)PZT-*x*CCT ceramics sample with x = 0, 0.20, 0.40 and 0.60 at selected frequency (1 kHz, 10 kHz and 100 kHz) is shown in **Fig. 7**. It was observed that the values of tan(δ), for all the composition were very low and remained almost constant until transition temperature (T_c), beyond which they exhibited a significant increase due to space charge polarization [**15**]. Also we found that the value of tangent loss decrease on increasing frequency [**20**] this is shown in **Fig. 7**.

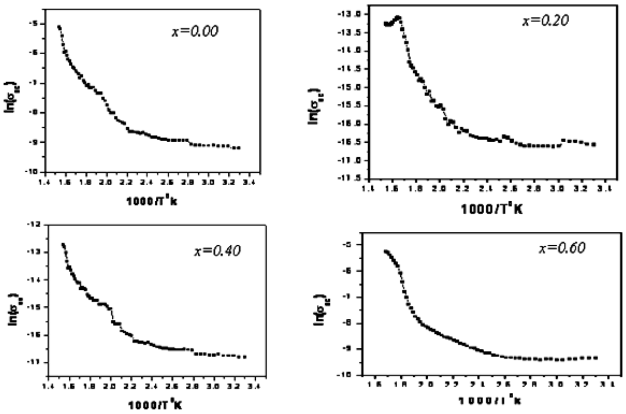

Fig. 8. Variation of conductivity with Temperature dependence of (1-*x*) PZT- xCaCu$_3$Ti$_4$O$_{12}$ ceramics ($x = 0$, 0.20, 0.40 and 0.60) at 100 KHZ.

Fig. 8 show the plot of ac conductivity of (1-*x*) PZT- *x* CCTO ceramic $x = 0$, 0.20, 0.40 and 0.60 at 100 kHZ against inverse of absolute temperature $10^3/T^o$ K at 10 kHz. A nature of variation of curves over a wide temperature range supports the temperature dependence of transport properties of the materials obeying Arrhenius equation (4):

$$\sigma_{ac} = \sigma_0 \exp(-\frac{E_a}{K_B T}) \tag{4}$$

where σ_0, E_a and K_B represent the pre-exponential factor, activation energy of the mobile charge carriers and Boltzmann constant, respectively. It is observed that there is an increase in conductivity above T_c on increasing the CCTO contents. This increase in the conductivity is attributed to the increase in polarizability of the materials around T_c. Above T_c the conductivity data trends to fall onto a straight line. This is the typical behavior of the dc component of the conductivity [**15**].

Conclusion

In the present work, we have prepared (1-*x*)PZT-xCaCu$_3$Ti$_4$O$_{12}$ system with composition $x = 0$, 0.20, 0.40 and 0.60 by standard solid state reaction method. X- ray diffraction pattern shows pure phase formation for $x = 0$ composition and composite phases for $x = 0.40$, 0.60 compositions. Doublet of diffraction peaks shows the structural change from rhombohedral to cubic structure for $x = 0.20$. A study of dielectric constant suggests diffuse type of phase transition in the material and the degree of diffusivity increases with increase of CaCu$_3$Ti$_4$O$_{12}$ concentration. With increasing *x*, dielectric constant was found to decrease, whereas Curie temperature was found to be 370 ^{o}C for $x = 0$ composition and with increase of CaCu$_3$Ti$_4$O$_{12}$ content, Curie temperature shift towards lower temperatures (T_c~340^{o}C) and further no shift was found in Curie temperature (T_c) for all the compositions. The dielectric loss for all the composition were very low and remained almost constant until transition temperature (T_c) It is observed that there is a increase in conductivity above T_C on increasing the PZT contents. This increase in the conductivity is attributed to the increase in polarizability of the materials around T_c.

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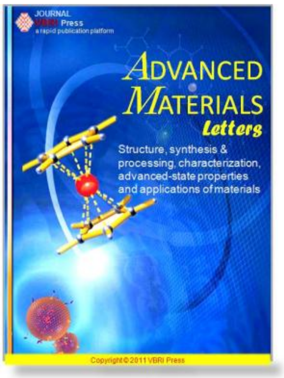
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