X-ray Absorption Spectroscopy study for understanding the dielectric behaviour of $ErFeO_3$ orthoferrites

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Introduction

Research on rare-earth orthoferrites $RFeO_3$ (R = rare earth ions) has gained the considerable attention of material researchers owing to interesting dielectric properties exhibited by them across the wide temperature range. Colossal dielectric (CD) response is one of the unusual properties exhibited by $RFeO_3$ (R = La, Pr and Sm). A common feature observed in the samples exhibiting CD response is the existence of the mixed valent state of Fe due to the doping of mono/di/tetra-valent ions at Fe-site in $LaFeO_3$ and/or presence of oxygen vacancies (Vo) to maintain the charge neutrality. Large number of reports claim the dependence of CD response on the Fe^n/Fe^{n+1} ratio and the hopping of electrons between $Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^{3+} \rightarrow Fe^{4+}$ leading to polaronic relaxation. In the present work, information about the crystal field symmetry and valance state of the Fe-ions in the La-doped $ErFeO_3$ orthoferrites have been obtained by the Soft X-ray Absorption Spectroscopy (SXAS) technique. The potentialities of XAS to understand the dielectric properties of the orthoferrites has been presented.

Methods

Polycrystalline samples of $Er_{1-x}La_xFeO_3$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized using co-precipitation method. Temperature-dependent dielectric measurements were performed using Agilent E4980A precision LCR meter. X-ray Absorption Spectroscopy measurements were carried out at Fe $L_{3,2}$ and La $M_{4,5}$ -edges in total electron yield (TEY) mode at Soft X-ray Absorption Spectroscopy beamline (BL-1) of the INDUS–2, a 2.5 GeV synchrotron radiation source, RRCAT, Indore, India.

Results and discussion

The spectral shape of Fe $L_{3,2}$ -edge XAS spectra of all the samples match with that of Fe_2O_3 reference spectra confirming the presence of the Fe^{3+} valance state. Values of 10 Dq for all the samples vary in the range of 1.62-1.75 eV. Comparison between the experimental and simulated La $M_{4,5}$ -edge XAS spectra show the presence of the La^{3+} state. Till date, the CD behaviour is observed only in the materials wherein Fe-ions exist in mixed-valent states (i.e. Fe^{2+}/Fe^{3+}). In the present study, CD behaviour is observed only in La-doped $ErFeO_3$ samples which is similar as observed for colossal dielectric materials such as $Ba(Fe_{0.5}Nb_{0.5})O_3$, $Sr(Fe_{0.5}Nb_{0.5})O_3$ and $Cu_3CaTi_4O_{12}$. Our findings reveal that, the CDC behaviour is also present in materials with the mono-valent state (Fe^{3+}) and could be a material specific property. Also, it may not require special sample preparation procedure as suggested by Adams et al [1]. $ErFeO_3$ shows typical dielectric behaviour as reported in literature whereas the value of dielectric constant increases with La-doping in $ErFeO_3$.

Conclusion(s)

Electronic structure and dielectric properties of La-doped $ErFeO_3$ samples have been studied systematically. XAS study reveals the presence of the Fe^{3+} state in octahedral symmetry. The existence of thermally activated relaxation at low temperature has been attributed to the hopping mechanism. The lower value of activation energy indicates the polaronic relaxation due to hopping motion of trapped electrons. The obtained higher value of dielectric constant for La-doped $ErFeO_3$ samples may be due to the major contribution from the modified grain boundary.

Reference

1. T.B. Adams, D.C. Sinclair and A.R. West, "Influence of Processing Conditions on the Electrical Properties of $CaCu_3Ti_4O_{12}$ Ceramics", *J. Am. Ceram. Soc.*, **89** [10] 3129–3135 (2006)