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Relation between photoluminescence emission and local order-disorder in the CaTiO$_3$ lattice modifier

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In this letter, the authors propose that photoluminescence emission in CaTiO$_3$ is affected not only by disorder in the lattice former but also by structural disorder in the lattice modifier. Structural disorder was evaluated by Ti, Ca K-edge x-ray absorption near-edge structure experiments and by photoluminescence emission. The preedge feature of the Ca K edge was related to the intensity of photoluminescence emission. The results of the preedge feature of the Ca K-edge x-ray absorption near-edge structure confirm the presence of different Ca coordination numbers, namely, Ca–O$_{11}$ and Ca–O$_{12}$.

The literature contains several studies on photoluminescence (PL) in titanates and structural disorder. This disorder has been attributed to the presence of different coordination modes in titanium. X-ray absorption near-edge structure (XANES) spectroscopy has been used to obtain information about coordination environment of metal in oxide materials, since the XANES region is highly sensitive to disorder in the short and medium ranges of metal. For instance, Ti K-edge XANES experimental results of PL titanates have revealed the coexistence of two types of environments in titanium, namely, fivefold coordination (TiO$_5$, square-base pyramid) and sixfold coordination (TiO$_6$, octahedron) before reaching the complete structural order. Asokan et al. $^{1,3}$ reported changes in the local environment of Ca sites in perovskite structures based on Ca K- and L$_{3,2}$-XANES spectra. These changes were related to electronic properties inferred from those XANES spectra.

With regard to the PL phenomenon at room temperature, Orhan et al.$^5$ proposed two conditions for this phenomenon to occur in disordered titanates, i.e., (i) they must possess at least two types of differently charged clusters creating a polarization of the structure and (ii) they must present some localized levels inside the band gap resulting from some structural disorders.

In this letter, we put forward an interpretation of PL emission based on an analysis of Ti and Ca XANES preedge intensities. Experimental observations suggest that PL emission is related to the TiO$_5$ and CaO$_{11}$ concentrations, as was determined by the preedge feature in our Ti and Ca K-edge XANES spectra. This interpretation of XANES data proposes the direct influence of lattice modifiers on the PL of oxide-type titanates.

Our main objective is not to explain all the possible mechanisms that occur during the photon excitation and decay processes, since the literature already offers many valid hypotheses, $^6$–$^8$ but to discuss the conditions that favor the generation of intense PL emission before the excitation process in structurally disordered CaTiO$_3$ (CT) powders.

CT ordered and disordered powders were prepared by the polymeric precursor method $^9$ and annealed at 450, 475, 500, 550, and 600 °C for 2 h. CT annealed at 600 °C is fully ordered. The PL measurements were collected using 350.7 nm exciting wavelengths of a krypton ion laser (Coherent Innova), with the nominal output power of the laser kept at 200 mW. The monochromator slit width was 200 μm. Calcium and titanium XANES spectra were collected using the D04B-XAS1 beamline. The storage ring was operated at 1.36 GeV and around 160 mA. XANES spectra were collected at the Ca and Ti K edge (4205 and 4966 eV, respectively) in a transmission mode, using a Si(111) channel-cut monochromator. For comparison, all the spectra were background removed and normalized using as unity the first extended x-ray absorption fine structure oscillation. All the measurements were taken at room temperature.

The PL curve depicted in Fig. 1(a) was obtained for CT powder annealed at 500 °C. This particular temperature represented the maximum intensity for PL emission of the CT samples. The inset Fig. 1(a) shows the PL curve for a fully ordered (600 °C) and a disordered CT (500 °C). Figure 1(b) illustrates the dependence of maximum PL intensity on temperatures in the range of 450–600 °C. Using the Gaussian method, the PL curve of the CT sample annealed at 500 °C was decomposed into three components, herein called blue component (maximum below 430 nm, 7%), green component (maximum below 600 nm, 85%), and red component (maximum below 730 nm, 8%), corresponding to the regions where the maximum intensity of each component appeared. These decompositions represent different types of electronic transitions and are linked to a specific structural arrangement. Such electronic transitions are due to the existence of electronic levels in the band gap of a material, which are possible due to structural disorder.$^{11}$
Figure 2(a) shows the Ti K-edge XANES spectra of CT samples as a function of the heat treatment temperature. The physical origin of the preedge feature A is the transition of the metallic 1s electron to an unfilled d state. This forbidden electronic transition dipole is normally allowed by the mixture of p states from surrounding oxygen atoms into the unfilled d states of titanium atoms. The A peak area was attributed to the TiO$_5$ concentration and, therefore, to PL emission. Fully structurally ordered CT does not show PL emission, since all Ti atoms are coordinated to six oxygen atoms in a completely regular octahedron. Hence, this sample contained 100% of TiO$_6$ and therefore served as a reference in the XANES experiments. In this work, the preedge A feature was fitted using a Gaussian function to determine its area and to relate this area to the TiO$_5$ concentration.

As indicated in Fig. 2(b), the area of the preedge feature A peak varied as a function of the heat treatment temperature. An approximate ratio of TiO$_5$ and TiO$_6$ is 30/70 for samples heat treated in the range of 400–500 °C. The amount of TiO$_5$ decreases as the temperature increases. In particular, the amount of TiO$_5$ decreases very quickly when the powder is annealed at 550 °C due to the increasing structural order.

In this letter, we propose that PL emission is affected not only by the structural disorder in the network former but also by structural disorder in the network modifier, and that this phenomenon can be studied by means of Ca K-edge XANES experiments. Figure 3(a) shows the Ca K-edge XANES spectra of CT samples. Peak B is attributed to the preedge feature. At the edge, a feature C is also visible in the ordered sample, and a broad feature, denoted by D, can be observed after the edge. As Fig. 3(a) indicates, significant changes in these features occur in response to increasing heat treatment. The decreases in the intensity of the preedge feature B may be related to a distortion in the arrangement of the nearest neighbor oxygen atoms around the Ca ions. Moreover, the intensity of the preedge feature B is also related to the number of holes. Thus, the preedge feature B can be used to evaluate the degree of disorder around Ca ions.

The preedge feature B is commonly attributed to transitions of Ca 1s states to the Ca 3d or O 2p molecular orbital and can be related to the CaO$_{11}$ concentration, similar to the TiO$_5$ concentration related to PL emission. The B peak area can be associated with the CaO$_{11}$ concentration, and therefore to additional electronic levels in the forbidden gap state, which gives rise to PL emission. The preedge feature B was...
FIG. 3. (Color online) (a) Results of the Ca K-edge XANES spectra of CT samples annealed at 450, 500, 530, 550, and 600 °C, and (b) normalized height of the preedge feature A.

fitted using a Gaussian function to determine its area and to relate it with the CaO11 concentration [Fig. 3(b)].

The variation in the intensity of the Ca K-preedge features B as a function of the heat treatment temperature was evaluated [Fig. 3(b)], as was done with the Ti K preedge in Fig. 2(b). In fully structurally ordered CT, all the Ca atoms are coordinated to 12 oxygen atoms. Hence, this sample contains 100% of CaO12 and can be used as a reference. The intensity of the preedge feature B was found to remain practically constant in samples heat treated up to 500 °C. Increasing the temperature also caused the preedge B peak to increase, reaching a maximum value in samples heat treated at 550 °C. The preedge B peak remained practically constant at higher temperatures. Based on the XANES spectra, we propose that the local disorder in the samples whose preedge feature B is less intense is related to a change from the 11-fold (Ca–O11) to the 12-fold (Ca–O12) coordination number. There is a local order-disorder in the calcium site, which heightens the intensity of PL emission by changing the charge and, particularly, the intermediate levels.

To summarize, the results of the preedge feature Ca K-edge XANES can be related to PL emission and order-disorder in the calcium coordination. This finding indicates that the modifier lattice strongly affects the intensity of PL emission due to charge exchanges between Ca–O11 and Ca–O12 clusters and intermediate levels in the gap state. Therefore, local order-disorder depends on both modifier and former lattices.

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