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BRIEF COMMUNICATION

Does Lanthanide Substitution Reduce Titanium from Ti^{4+} to Ti^{3+} in the Perovskite $CaTiO_3$ Fired at 1550°C in Air?

Comment on "Charge Compensation in Gd-Doped $CaTiO_3$"

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This note is related to the above-mentioned paper (1) and uses for its conclusions the data, interpretation, and results reported therein. The original paper deals with Gd-doped $CaTiO_3$ perovskite in which the charge compensation was interpreted to be a reduction of titanium from Ti^{4+} to Ti^{3+} for samples fired at 1550°C in air. This paper stated that the charge compensation "takes place via the formation of one formula unit of Ti^{3+} per formula unit of Gd."

The following methods and data were used in Ref. 1 to prove the existence of Ti^{3+} in $Ca_{1-x}Gd_xTiO_3$ fired in air for 1 week at 1550°C: atomic ratios were obtained from quantitative analysis using SEM and TEM techniques, X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge spectroscopy (XANES), unit cell parameters from X-ray powder diffraction (XRD), cathodoluminescence, and density measurements by helium gas pycnometry.

It is important to note that although XANES, cathodoluminescence, and density measurements showed clearly negative results for the presence of Ti^{3+}, the authors of Ref. 1 interpreted them as inconclusive. In addition, electron paramagnetic resonance (EPR) spectroscopy, which could give direct information about the presence of Ti^{3+}, was not employed.

Let us look more closely at the reported data for the unit cell parameters determined by XRD, the measured Ti 2*p* XPS spectra, and the quantitative analysis by SEM.

The unit cell parameters of orthorhombic Gd-substituted perovskite were determined by XRD. The results were interpreted in terms of changes in volume of the unit cells: $223.8\,Å^3$ for pure $CaTiO_3$, $224.2\,Å^3$ for the sample with 7.5% Gd, and $224.7\,Å^3$ for the sample with 15% Gd. The difference in volume changes between samples with maximum Gd loadings and pure $CaTiO_3$, $224.7 - 223.8 = 0.9\,Å^3$ or 0.4% ($\sim$13 times less than the volume of one oxygen ion), was interpreted as "a small but significant increase in unit cell volume." The radius of Gd^{3+} is less than that of Ca^{2+} (by $\sim 0.07\,Å$) and the radius of Ti^{3+} is larger than that of Ti^{4+} (by $\sim 0.07\,Å$). Consequently, for equal and simultaneous replacements of Ti^{4+} with Ti^{3+} (15%) and Ca^{2+} with Gd^{3+} (15%) unit cell (especially volume) changes will not give values that can be used for detecting the presence of Ti^{3+}. If there is still some variation, it should be analyzed in terms of unit cell geometry, not unit cell volume. However, more useful information can be extracted from analysis of peak intensity (structure factors) than cell volume. Therefore, there is no necessity to analyze it further, and we cannot see any evidence from the data confirming the presence of Ti^{3+}.

A close examination of the Ti 2*p* XPS spectra and their interpretations shows several symptomatic features that are worth noting. Both spectra are quite noisy in the Ti $2p_{1/2}$ peak regions and in all background regions. Consequently, the spectra have a poor peak/background ratio. The constrained psesudo-Voigt (50% Gaussian and 50% Lorentzian) peak shape function was used for fitting the $CaTiO_3$-pure sample spectrum, which was then superimposed over the Gd-substituted sample spectra. This assumption is not valid, because these spectra belong to two different samples, and simple overlaps will always give unpredictable residuals, even on various samples of pure $CaTiO_3$. Moreover, there is no Ti^{3+} peak in the as-sintered $Ca_{0.85}Gd_{0.15}TiO_3$ sample. Again, the poor fit of the XPS spectra (with no fit at all near the peak "tails"), which do not show any indication of Ti^{3+}, was interpreted in the opposite manner. The profile fitting in this case must be done with a variable linear mixing parameter $\eta = \eta L + (1 - \eta)G$ of the pseudo-Voigt function, as it was chosen. These peaks could be easily fit with just a simple Lorentzian or with a more complicated split-Pearson VII if that is required.

The last, but major, method of detecting the presence of Ti^{3+} reported in Ref. 1 was microanalysis. The accuracy of EDS microanalysis is well known: it can be varied depending

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on the method of sampling and accuracy of alignment. However, the authors of Ref. 1 state that there is "… variation in composition of individual grains from the mean … by up to 20%." It is not clear whether the variation is due to the perovskite composition or the accuracy of analysis, and this result was not investigated in Ref. 1. In any case, the microanalysis cannot be taken as final proof for the existence of Ti^{3+}, especially since this was not supported by other methods.

The authors of Ref. 1 also do not provide a justification for why Ti^{4+} should be reduced to Ti^{3+} in air in the absence of any reducing atmosphere or agent. The crystallization temperature and atmospheric conditions described are unlikely to reduce Ti^{4+} to Ti^{3+}; they favor the immediate oxidation of unstable Ti^{3+} to stable Ti^{4+}. The initial reagents do not include any Ti^{3+}, and the origin of Ti^{3+} in final products is highly questionable.

This short analysis of Ref. 1 shows that there is no evidence supporting the existence of a reduced oxidation state for titanium in $CaTiO_3$ fired at 1550°C in air for 1 week. There are no theoretical or experimental results in Ref. 1 that could verify this. The results either directly contradict the conclusions or are not sufficient to make a definite conclusion.

To the best of our knowledge, compounds with formulae $Ca_{0.85}Gd_{0.15}TiO_3$ (1) and $Ca_{0.925}Gd_{0.075}TiO_3$ (2) do not exist, as they are not charge compensated and oppose the basic laws of chemistry. The *A*-site vacancy model for ionic or mostly ionic ABO_3 is most probably correct. *A*-site-deficient perovskites are well known, and the *A*-site is totally vacant in the structure of ReO_3. For the charge compensation mechanism in this case an accurate structure is necessary, determined from neutron diffraction data (negative scattering length for Ti) with refinement of atomic occupancies. Direct detection methods for Ti^{3+} (if any) can also be used.

REFERENCES

1. E. R. Vance, R. A. Day, Z. Zhang, B. D. Begg, C. J. Ball, and M. G. Blackford, *J. Solid State Chem.* **124,** 77 (1996).
2. E. M. Larson, P. G. Eller, J. D. Purson, C. F. Pace, M. P. Eastmen, R. B. Greegor, and F. W. Lytle, *J. Solid State Chem.* **73,** 480 (1988).