Color Control of Pr$^{3+}$ Luminescence by Electron-Hole Recombination Energy Transfer in CaTiO$_3$ and CaZrO$_3$

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Abstract

Controlling luminescence in phosphors able to produce several emissions from different stable excited states determines their use in optical devices. We investigate the color control mechanism that quenches the greenish-blue emission in favor of the red one in the archetype phosphor CaTiO$_3$:Pr$^{3+}$. State-of-the-art ab initio calculations indicate that direct host-to-dopant energy transfer (released by electron-hole recombination following the interband excitation and structural reorganization) selectively populates the $^1D_2$ red luminescent state of Pr$^{3+}$ and bypasses the $^3P_0$ greenish-blue emitter. Local defects can modulate the electron-hole recombination energy and so increase the red emission efficiency, as experimentally observed. The selection of red emission does not happen in CaZrO$_3$:Pr$^{3+}$ because the electron-hole recombination energy is much higher. The calculations could not support the widely accepted color control mechanism based on metal-to-metal charge transfer states. The conclusion sets new points of view for the color control of lanthanide activated inorganic phosphors.

Graphical TOC Entry
Being able to control the non-radiative decay between the $^3P_0$ and $^1D_2$ levels of Pr$^{3+}$ in oxide materials and the corresponding relative intensities of their greenish-blue ($^3P_0 \rightarrow ^3H_4$) and red ($^1D_2 \rightarrow ^3H_4$) emissions is an important goal in the field of inorganic phosphors since two decades ago.\textsuperscript{1,2} For instance, the search for Pr$^{3+}$-doped oxide phosphors useful as scintillators for fast decay X-ray computed tomography seeks chemical manipulations that could make the faster $^3P_0 \rightarrow ^3H_4$ emission (in the $\mu$s scale) dominant over the slower $^1D_2 \rightarrow ^3H_4$ emission (in the ms scale).\textsuperscript{3} The same is true, e.g., for long lasting greenish-blue luminescent materials.\textsuperscript{4} On the contrary, the search for Pr$^{3+}$-doped oxide red phosphors useful for solid-state white illumination devices, for lasers, and for other applications seeks chemistry that could make the $^1D_2 \rightarrow ^3H_4$ emission dominant.\textsuperscript{2,5}

![Figure 1: CaTiO$_3$ unit cell (left up), (PrO$_{12}$)$_{21}$-cluster with neighboring Ti atoms (right up), (PrO$_{12}$Ti$_5$O$_{24}$)$_{37}$-cluster (left bottom), and (TiO$_6$Ca$_6$Ti$_6$)$_{32}$-cluster (right bottom). Ca atoms are shown in gold, Ti in red, O in green, and Pr in violet.](image)

It is important, then, to identify the mechanism of the $^3P_0 \rightarrow ^1D_2$ non-radiative decay in order to be able to design Pr$^{3+}$-doped oxide materials with selective greenish-blue or red emissions. Historically, several interpretations were given for this decay mechanism: A multiphonon relaxation model and a model of cross-relaxation within pairs of Pr$^{3+}$ ions were considered at some point and later ruled out in CaTiO$_3$:Pr$^{3+}$ on the basis of experimental observations.\textsuperscript{1,6} Proposals of intersystem crossing through low-lying levels of the $4f^5d$ configuration\textsuperscript{1,7} were considered to be unlikely\textsuperscript{6} and shown to be in a large disagreement with \textit{ab initio} calculations on Lu$_2$O$_3$:Pr$^{3+}$.\textsuperscript{8} A fourth model, the Pr-to-metal charge transfer state model\textsuperscript{6,9} (also known as the virtual recharge model\textsuperscript{10}) found a broad acceptance up to these days. According to it, the $^3P_0 \rightarrow ^1D_2$ non-radiative decay takes place through an electron transfer from the $^3P_0$ state of Pr$^{3+}$ to a cation of the host, which leads to an intermediate metal-to-metal charge transfer state (MMCT), followed by an electron back-transfer from the host cation to the remaining Pr$^{4+}$ ion that leads to a Pr$^{3+}$ in the $^1D_2$ state. The intermediate state was initially labelled Intervalance Charge Transfer state (IVCT) but this name is conventionally reserved for the MMCT when the two metals differ only in the oxidation state.\textsuperscript{11}

The strongest support to the MMCT model was provided by experimental studies on CaTiO$_3$:Pr$^{3+}$ and CaZrO$_3$:Pr$^{3+}$ by Boutinaud and co-workers,\textsuperscript{12} which showed that the greenish-blue $^3P_0 \rightarrow ^3H_4$ emission is dominant in CaZrO$_3$:Pr$^{3+}$ whereas the red $^1D_2 \rightarrow ^3H_4$ emission is the only one exhibited by CaTiO$_3$:Pr$^{3+}$. It was natural to accept as an explanation that the energy of the Pr$^{3+}$-to-Zr$^{4+}$ MMCT state was way above $^3P_0$ in CaZrO$_3$:Pr$^{3+}$, whereas the (lower) Pr$^{3+}$-to-Ti$^{4+}$ MMCT state was between $^3P_0$ and $^1D_2$ in CaTiO$_3$:Pr$^{3+}$ (cf. Fig. 4 in Ref. 12), so quenching all the greenish-blue emission in the latter material. A series of experimental studies, although not ruling out other possibilities, supported this interpretation.\textsuperscript{5,6,9,13,14} However, a direct proof of the MMCT nature of the intermediate state in CaTiO$_3$:Pr$^{3+}$ was never found.

In an attempt to support the MMCT hypothesis, we performed \textit{ab initio} wave function based multi-reference multi-configurational relativistic embedded-cluster calculations on CaTiO$_3$:Pr$^{3+}$ and CaZrO$_3$:Pr$^{3+}$. We calculated the $4f^2$ and $4f^5d$ states of Pr$^{3+}$ in CaTiO$_3$:Pr$^{3+}$ and CaZrO$_3$:Pr$^{3+}$, the Pr$^{3+}$-to-Ti$^{4+}$ MMCT states of CaTiO$_3$:Pr$^{3+}$, and the O$^{2-}$-to-Ti$^{4+}$ and O$^{2-}$-to-Zr$^{4+}$ ligand-to-metal
charge transfer (LMCT) states of CaTiO$_3$ and CaZrO$_3$. As we will see, these ab initio calculations do not support the MMCT or virtual recharge model. Instead, they indicate that the intermediate state responsible for the non-radiative decay from $^3P_0$ to $^1D_2$ in CaTiO$_3$:Pr$^{3+}$ is an O$^2$- to-Ti$^{4+}$ LMCT state of the host.

Figure 2: Potential energy curves of Pr$^{3+}$ and Pr$^{4+}$ in the Ca-site of CaTiO$_3$ along the PrO$_{12}$ breathing mode. The states of the (PrO$_{12}$)$^{21-}$ cluster with dominant $4f^2$ configuration are shown in full lines with colors: black for main free-ion character $^3H_{4,5,6}$, orange for $^3F_{2,3,4}$, cyan for $^1G_4$, red for $^1D_2$, green for mixtures of $^3P_{0,1,2}$ and $^1I_6$, and bright green for $^1S_0$. The states of main configurational characters $4f5d(e_g)$ and $4f5d(t_{2g})$ are shown in blue and maroon respectively. Pr$^{4+}$ states are shown in dashed magenta lines. Green and red emissions from the lowest level of the $^3P_{0,1,2}$ and $^1I_6$ manifold (usually referred to as $^3P_0$ emission) and the lowest $^1D_2$ level ($^1D_2$ emission), respectively, are indicated.

We performed wave function multi-reference multi-configurational relativistic embedded-cluster ab initio calculations on several clusters extracted from the materials CaTiO$_3$:Pr$^{3+}$ and CaZrO$_3$:Pr$^{3+}$ with the MOLCAS suite of programs. The CaTiO$_3$ unit cell and the clusters used are shown in Fig. 1. We summarize the methods and results here and present further details in the Supporting Information. The reliability of the methods and conditions of choice is supported by the accumulated experience on the ab initio calculation of excited states of a number of lanthanide containing materials.

We show the calculated $4f^2$ and $4f5d$ energy levels of a Pr$^{3+}$ in the Ca-site of CaTiO$_3$ with long-range compensation as a function of the Pr–O distance, $d_{Pr−O}$, in Fig. 2. Detailed spectroscopic constants, assignments, and analysis of the electronic structure of the states are presented in Tables S2 and S3 of the Supporting Information, which also contain the equivalent results for Pr$^{3+}$ in the Ti site for completeness.

These results have been obtained in two-step spin-orbit coupling SA-CASSCF/MS-CASPT2/RASSI-SO DKH calculations on
The red emitter is $7E_g$, with a very clear $^1D_2$ character. The greenish-blue emission originates in $5A_g$, with 60% $^1I$ and 40% $^3P$ characters. It is interesting that the emitting label commonly named as $^3P_0$ has a larger $^1I_0$ character, according to these calculations. The respective calculated emissions are 19170 cm$^{-1}$ and 24360 cm$^{-1}$, the experimental ones being 16600 cm$^{-1}$ and 20209 cm$^{-1}$. Two thirds of the deviations are known to have a free-ion origin.\footnote{Regarding the $^3P_0-^1D_2$ non-radiative decay, this energy diagram confirms that the intermediate state cannot have a 4f5d character, because those states lie at much higher energy than 4f$^2$ $^3P_0$. $^4f5d_e$ and 4f$^5$d$_{2g}$ levels have a very similar equilibrium Pr–O distance between themselves and with the 4f$^2$ states, contrary to what happens in CaF$_2$:Pr$^{3+}$,\textsuperscript{32} where the distances follow the pattern $d_{Pr–F}(4f5d_e) < d_{Pr–F}(4f^2) < d_{Pr–F}(4f5d_{2g})$. This is attributed to the very large Pr–O distance and weak ligand field experienced by Pr$^{3+}$ at the Ca site of CaTiO$_3$.

Now, let us discuss the Pr$^{3+}$-to-Ti$^{4+}$ MMCT states of CaTiO$_3$:Pr$^{3+}$, which are the ones invoked in the MMCT or virtual recharge model for the $^3P_0-^1D_2$ non-radiative decay. The configuration coordinate energy diagram showing them is presented in Fig. 3. It was calculated at the diabatic level\textsuperscript{33,34} using the just shown SA-CASSCF/MS-CASPT2/RASSI-SO results on the (PrO$_{12}$)$_{21}^-$ and (PrO$_{12}$)$_{20}^-$ clusters, and SA-CASSCF/MS-CASPT2 results on the (TiO$_6$)$_{8}^-$ and (TiO$_6$)$_{9}^-$ clusters, all of them embedded in CaTiO$_3$, with adiabatic corrections calculated in SA-CASSCF/MS-CASPT2 calculations on the (PrO$_{12}$Ti$_8$O$_{24}$)$_{37}^-$ cluster at the Pr$^{3+}$-to-Ti$^{4+}$ equilibrium structure (cf. Supporting Information for further details).

Before discussing further the MMCT energy diagram in Fig. 3, let us comment that the configuration coordinate used for it is indicated in Fig. 4 (and represented in Fig. S8 of the Supporting Information). In this figure, potential energy surfaces of several states are represented with isolines vs. the Pr–O and Ti–O distances: One of the Pr$^{3+}$ 4f$^2$ states is shown in black isolines and the configuration coordinate used in Fig. 2 (breathing mode of PrO$_{12}$) is represented with a black line. One of the Pr$^{3+}$-to-Ti$^{4+}$ MMCT states is shown in brown isolines.

Figure 4: Isoline representation of the potential energy surfaces of three local states of the material CaTiO$_3$:Pr$^{3+}$ vs. the Pr–O and Ti–O distances. One state of Pr$^{3+}$ in CaTiO$_3$ is shown in black, one Pr$^{3+}$-to-Ti$^{4+}$ MMCT state in brown, and one O$^{2–}$-to-Ti$^{4+}$ LMCT state in magenta. Configuration coordinates appropriate for one-dimension energy diagrams are indicated with lines: for ligand-field Pr$^{3+}$ states in black, for MMCT states of the pair Pr$^{3+}$/Ti$^{4+}$ in brown, and for O-to-Ti LMCT states in magenta.
Figure 5: Configuration coordinate energy diagrams combining the Pr$^{3+}$ states with the O$^{2-}$-to-Ti$^{4+}$ LMCT states of CaTiO$_3$:Pr$^{3+}$ (left) and the O$^{2-}$-to-Zr$^{4+}$ LMCT states of CaZrO$_3$:Pr$^{3+}$ (right).

and the brown line is the configuration coordinate used in Fig. 3. It corresponds to simultaneous contractions of the Pr–O bonds and expansions of the Ti–O bonds that accompany the electron transfer from Pr$^{3+}$ to Ti$^{4+}$.

What we observe in Fig. 3 is that the Pr$^{3+}$-to-Ti$^{4+}$ MMCT energy levels, i.e. the energy levels of Pr$^{4+}$-Ti$^{3+}$ pairs, are too high in energy so as to play a relevant role in the $^3P_0$ non-radiative decay. This means that these calculations do not support the MMCT or virtual recharge model to explain such decay.

Having ruled out the participation of Pr$^{3+}$ 4f5d states and Pr$^{3+}$-to-Ti$^{4+}$ MMCT states in the $^3P_0$-D$_2$ non-radiative decay of CaTiO$_3$:Pr$^{3+}$, let us consider now the role that O$^{2-}$-to-Ti$^{4+}$ LMCT states of CaTiO$_3$ can play in such a decay, because it is known that energy is transferred from these states to Pr$^{3+}$ (CaTiO$_3$ interband transitions excite Pr$^{3+}$ luminescence)\(^{12}\).

An O$^{2-}$-to-Ti$^{4+}$ electron transfer in CaTiO$_3$:Pr$^{3+}$ should not have an important impact on the Pr–O distance, so that, in a first approximation, one of the corresponding LMCT states is represented in Fig. 4 with magenta isolines and the LMCT configuration coordinate is the magenta line, which passes through the minima of the Pr$^{3+}$ 4f$^2$ states. A representation of the Pr$^{3+}$ and O$^{2-}$-to-Ti$^{4+}$ LMCT states of CaTiO$_3$:Pr$^{3+}$ in a common energy diagram along the LMCT configuration coordinate is made in Fig. 5, together with the equivalent diagram for Pr$^{3+}$ and O$^{2-}$-to-Zr$^{4+}$ LMCT states of CaZrO$_3$:Pr$^{3+}$. The LMCT states have been obtained in SA-CASSCF/MS-CASPT2 calculations on the (TiO$_6$Ca$_8$Ti$_6$)$^{32+}$ and (ZrO$_6$Ca$_8$Zr$_6$)$^{32+}$ clusters embedded in CaTiO$_3$ and CaZrO$_3$, respectively. The configurational complete-active-spaces correspond to the distribution of 6 electrons in the 6 MOs of main character $t_{1g}(O_{2p})$ and $t_{2g}(Ti_{3d}$ or Zr$_{4d}$) for $g$ states, and of 12 electrons in the 9 MOs of main characters $t_{1u}(O_{2p})$, $t_{2u}(O_{2p})$, and $t_{2g}(Ti_{3d}$ or Zr$_{4d}$) for $u$ states. The results are summarized in Table 1. Further details are given in the Supporting Information.

The first important observation from Fig. 5...
and Table 1 is that the LMCT states of CaTiO$_3$ lie in the same energy range than the $^3P_0$ and $^1D_2$ states of Pr$^{3+}$, whereas the LMCT states of CaZrO$_3$ lie at much higher energy. This implies that they can be intermediates in a $^3P_0$-$^1D_2$ non-radiative decay mechanism in the first host, but irrelevant for that in the second host.

Table 1: Spectroscopic constants of the O-to-Ti and O-to-Zr LMCT states after MS-CASPT2 calculations on the (TiO$_6$Ca$_8$Ti$_6$)$^{32+}$ and (ZrO$_6$Ca$_8$Zr$_6$)$^{32+}$ clusters embedded in CaTiO$_3$ and CaZrO$_3$ respectively. Ti–O and Zr–O equilibrium distances $d_{Ti-O,e}$ and $d_{Zr-O,e}$ (Å), breathing mode harmonic vibrational frequencies $\omega_{1g}$ (cm$^{-1}$), and minimum-to-minimum transition energies $T_e$ (cm$^{-1}$). The allowed absorptions ($^1A_{1g} \rightarrow ^1T_{1u}$) are highlighted.

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Let us look at the LMCT states in more detail. The electric dipole allowed LMCT absorptions (which have $^1A_{1g} \rightarrow ^1T_{1u}$ many-electron character and $O_{2p_n1_{1u},2_{2u}} \rightarrow Ti_{3d_{2g}}(Zr_{4d_{2g}})$ main one-electron character) are shown in bold font in Table 1 for CaTiO$_3$ and CaZrO$_3$ (minimum-to-minimum transition) and with a magenta arrow in Fig. 5 (left) for CaTiO$_3$ (vertical transition). The calculated vertical allowed transition in CaTiO$_3$ is 31400 cm$^{-1}$. It should be compared with the experimental interband transition maximum, which is found to be 30000 cm$^{-1}$ by Pinel et al. (band A in Fig. 4 of Ref. 12). A DFT calculation with periodic boundary conditions reported 31500 cm$^{-1}$ for the direct band gap. The calculated minimum-to-minimum allowed transition is 29500 cm$^{-1}$. It agrees with the origin of the interband transition found in the excitation spectrum at around 28000 cm$^{-1}$. The calculated vertical and minimum-to-minimum allowed transition energies (interband absorption maximum and origin, respectively) of CaZrO$_3$ are 50600 cm$^{-1}$ and 49300 cm$^{-1}$. Kaneyoshi$^{36}$ finds a peak at 47600 cm$^{-1}$ in the excitation spectrum of CaZrO$_3$ and Rosa et al.$^{37}$ report a theoretical DFT band gap of 46000 cm$^{-1}$.

But the LMCT states involved in the electric dipole allowed absorptions are not the lowest ones. Several LMCT states that have $O_{2p_n1_{1g}} \rightarrow Ti_{3d_{2g}}$ main one-electron character and are involved in electric dipole forbidden absorptions, lie between the $^3P_0$ and $^1D_2$ states of Pr$^{3+}$ in CaTiO$_3$:Pr$^{3+}$. They can provide an efficient non-radiative decay mechanism to selectively populate $^1D_2$. In this mechanism (Fig. 5), the allowed host interband absorption $O^{2-} \rightarrow Ti^{3+}$ at around 30000 cm$^{-1}$ is followed by structural reorganization (Ti–O elongation) and electronic relaxation towards the lowest LMCT state. In this material, this state lies below $^3P_0$ and slightly above $^1D_2$, so that a host electron-hole recombination $Ti^{3+} \rightarrow O^{2-}$ takes place and its energy is non-radiatively transferred directly to the $^1D_2$ level of Pr$^{3+}$, which finally emits in red. In CaZrO$_3$:Pr$^{3+}$, however, all the $O^{2-} \rightarrow Zr^{4+}$ LMCT states are much higher than the $^3P_0$ and $^1D_2$ states of Pr$^{3+}$ and they cannot play any role in the selective population of $^1D_2$. Then, the usual non-radiative decay mechanisms in Pr$^{3+}$ materials lead to partial populations of the states $^3P_0$ and $^1D_2$, and both the greenish-blue and red emissions are shown in bold. 

...
sions occur.

At this point, it is interesting to recall that the efficiency of the red emission of CaTiO$_3$:Pr$^{3+}$ was found to be tunable with the preparation method, which can lead to different charge compensations.$^{38}$ It was also found to improve by Ba and Sr substitutions for Ca$^{39}$ and by addition of Lu$_2$O$_3$, La$_2$O$_3$, and Gd$_2$O$_3$.$^{40}$ In the same line, the photoluminescence and afterglow efficiency of CaTiO$_3$:Pr$^{3+}$ was improved by Ca excess$^{41}$ and ammonia treatment.$^{2}$ These behaviors are in agreement with the present interpretation of the reasons behind the quenching of the greenish-blue emission and enhancement of the red emission. The reason is that all these treatments are expected to produce local defects, which can modulate the electron-hole recombination energy in their proximities and, in consequence, the selective energy transfer from the host to the $^1D_2$ level of close Pr$^{3+}$ ions.

In order to illustrate this, we calculated the LMCT states of CaTiO$_3$ with a Ca vacancy next to Ti. Such vacancies have been reported to produce a shoulder in the diffuse reflectance spectra of CaTiO$_3$:Pr$^{3+}$ at slightly lower energy than the valence-to-conduction absorption band edge and to play an important role in the enhancement of its red emission by addition of rare earth oxides.$^{40}$ We got a 2400 cm$^{-1}$ lowering of the LMCT states. Although this result was obtained in MS-CASPT2 calculations on a symmetrized Ca vacancy with the (TiO$_6$Ti$_6$)$_{16+}$ cluster embedded in CaTiO$_3$ without additional geometry relaxations and it is not expected to be taken quantitatively, it clearly indicates that local defects can influence the energies of the lowest LMCT states sufficiently so as to be able to modulate the relative $^3P_0$ and $^1D_2$ populations.

Let us further discuss some other experimental observations. Pinel et al.$^{12}$ reported that a sample of CaTiO$_3$:Pr$^{3+}$ prepared by solid state reaction at 1200°C under air for 430 h instead of the regular 6 h became yellowish-brown, with an intense very broad absorption band ranging from 650 nm (15400 cm$^{-1}$) to less than 400 nm (more than 25000 cm$^{-1}$) not followed by lumi-

nescence. These features were attributed to the presence of Pr$^{4+}$, which was confirmed by an EPR study,$^6$ so that the sample is in fact a mixed-valence material CaTiO$_3$:Pr$^{3+}$,Pr$^{4+}$. We have computed an ab initio intervalence charge transfer (IVCT) configuration coordinate energy diagram at the diabatic level$^{42,43}$ for a mixed-valence Pr$^{3+}$/Pr$^{4+}$ pair in CaTiO$_3$. It is presented in Fig. S5 of the Supporting Information. The diagram predicts the lowest Pr$^{3+}$-to-

Pr$^{4+}$ IVCT absorptions to have peaks extending from 12000 cm$^{-1}$ to 24000 cm$^{-1}$, the full width at half maximum (FWHM) of each of them being typically of around 5000 cm$^{-1}$, and being followed by no emission. All this suggests that the yellowish-brown color of this sample and its corresponding very broad absorption band are due to Pr$^{3+}$-to-Pr$^{4+}$ IVCT absorption.

In the photoluminescence excitation (PLE) spectrum of the $^1D_2$ emission of CaTiO$_3$:Pr$^{3+}$, Zhang et al.$^{40}$ report a broad band at 330 nm (30300 cm$^{-1}$) and another one at 370 nm (27000 cm$^{-1}$). The same bands are shown in the continuous wave excitation spectrum of the $^1D_2$ emission by Pinel et al.$^{12}$ (The first band is attributed by the former authors to Pr$^{3+}$ 4f5d states and by the latter authors to the lowest interband transition, or O$^{2-}$-to-Ti$^{4+}$ LMCT. All these authors attribute the second band to Pr$^{3+}$-to-Ti$^{4+}$ LMCT states.) Besides, the two bands appear also in the diffuse reflectance spectra of CaTiO$_3$:Pr$^{3+}$. According to the present results both bands can be attributed to O$^{2-}$-to-

Ti$^{4+}$ LMCT, the upper one corresponding to the pure host and the lower one to Ca$^{2+}$ vacancies or other local defects. The coincidence between reflectance and PLE spectra is the result of the host-to-Pr($^1D_2$) energy transfer mechanism proposed here.

In summary, all the results discussed in this Letter indicate that the current model that attributes the $^3P_0$-$^1D_2$ non-radiative decay of Pr$^{3+}$ in some oxides to intersystem crossing through Pr-to-Ti charge transfer states is not sustained by ab initio calculations. Instead, the present ab initio calculations indicate that the mechanism responsible for a selective population of the $^1D_2$ level in CaTiO$_3$:Pr$^{3+}$, which leads to the quenching the greenish-blue emission from the $^3P_0$ level and the sole presence of the $^1D_2$ red emission, is a direct electron-hole
recombination energy transfer from the host to the $^1D_2$ level of the Pr$^{3+}$ dopant.

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Supporting Information Available

The following files are available free of charge.

- SI.pdf: Further details of the calculations, detailed spectroscopic constants and analyses of the wave functions, and additional configuration coordinate diagrams.

References


(31) Detailed embedding AIMP data libraries in electronic format are available from the authors upon request or directly at the
address http://www.uam.es/quimica/-aimp/Data/AIMPLibs.html. See also Ref. 15.


