Ab initio Based Interionic Interactions in Calcium Aluminotitanate Oxide Melts: Structure and Diffusion

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Abstract

Calcium aluminotitanate ($\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$) ternary oxides are of fundamental interest in Materials as well as Earth and environmental science, and a key system for several industrial applications. As their properties at the atomic scale are scarcely known, interionic interactions for the melts are built from a bottom up strategy consisting in fitting first only Al_2O_3 , CaO and TiO_2 single oxide compounds separately with a unified description of the oxygen charge and O-O interaction term. For this purpose, a mean-square difference minimization of the partial pair-correlation functions with respect to the *ab initio* reference was performed. The potentials for the ternary oxide are finally built straightforwardly by adding purely Coulomb terms for dissimilar cation-cation interactions without further fit. This general and unified approach is transferable and successfully describes the structural and diffusion properties of the three single oxides as well as the ternary melts simultaneously. A possible underlying structural mechanism at the origin of the diffusion evolution with TiO_2 content is proposed based on the formation of Ti induced triply bonded oxygen.

I. INTRODUCTION

The Calcium-Aluminotitanate ($\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$) ternary oxides are one of the key systems in Earth, environmental and Materials sciences as well as for several industrial applications. On the fundamental side, interest for geochemists and planetologists is the introduction of TiO_2 component in the ubiquitous binary calcium aluminates and the understanding of resulting influence on the glass transition temperature as well as on atomic transport properties. This would be of great importance for improving our understanding of magmatic flow and the behavior of early planets. On the industrial side, the knowledge of these fundamental properties are of utmost importance for glass manufacturers, refractory cements^{1,2} as well steel producers. For instance, in the continuous casting of aluminium or titanium containing steels, the use of silica should be avoided³. A substitute of SiO_2 might be TiO_2 due to its acidic nature as an important component to control the melting point and appropriate viscosity.

The high melting temperature of the $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ (CAT) system, above 1600 K for most compositions⁴, represent an impediment for systematic experimental investigations of the melts. Thus, the precise knowledge of the melting points, diffusion, viscosity, and structure of the melt remains scarce in contrast to the parent $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (CAS)^{5,6}. In the solid state, CAT is subject to phase decomposition at high temperature and low mechanical strength, features that have not been well established to date⁷. In this context, molecular dynamics (MD) simulations, either using *ab initio* MD (AIMD), based on the density functional theory (DFT)¹⁰, classical MD with empirical potentials^{8,9}, or a combination of the two^{11,12} represent a powerful way of systematic investigations to complement measurements. Interactions in classical MD for oxide melts and glasses are more often taken in the Born-Mayer (BM) or Born-Mayer-Huggins (BMH) form¹³, which are generally suitable for oxides¹⁴. For the purpose of a better understanding and controlling atomic transport properties and melting temperatures, atomic level simulations represent the dedicated approach. It allows the investigation of local tetrahedral network properties, known as being influential on the behavior of the viscosity and diffusion of interest here^{6,19-28}.

To our best knowledge, no specific interionic potentials were developed for the CAT system to date. One possibility would be to extract parameters of the BMH form from the work by Sator and Guillot²⁹ who proposed potentials for the nine component system

$\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$ (KNCMFATS). The latter is essentially based on a fit of the parameters to reproduce the density for a representative set of natural silicate melts with various compositions, with the constraints of using the same O effective charge and reaching the charge neutrality of the considered systems. While appealing, this approach may not guarantee a good transferability to specific CAT compositions. Another strategy would be a bottom up approach taking the parameter sets existing in the literature for single oxides to build the ternary system from them. Potentials were proposed in the literature for each of the three single components, namely CaO ^{11,15}, Al_2O_3 ³⁰⁻³⁸ and TiO_2 ,³⁹⁻⁴⁵, being often taken as a limiting case of multi-components systems^{14,18,46}. But obviously, none of them with the BMH form, possess the needed common characteristics such as the same oxygen effective charge that would be necessary to build the ternary from them readily.

This contribution aims at setting up an *ab initio* approach based on Born-Mayer-Huggins specific empirical potentials for the purpose of describing the structure as well as the dynamics for the CAT ternary melts. The strategy put forward is based on the above mentioned bottom up approach founded on a careful and accurate fitting of the single oxide components independently, and satisfying simultaneous constraints of a common effective oxygen charge and oxygen-oxygen interaction for all the single components. It is shown that it yields a good description of main characteristics of the ternary melt structure and diffusion. In a first stage, *ab initio* molecular dynamics simulations were performed (i) for CaO , Al_2O_3 and TiO_2 above their melting temperatures for fitting purpose, and (ii) for the CAT melts as an assessment of the obtained potentials. In a second stage, the technique proposed very recently by Carré *et al.*⁴⁷ was used to adjust the potentials parameters by matching the partial pair-correlation functions from classical MD with the AIMD ones, using a least square minimization. The method is extended here by making an additional trade off on the O effective charge and O-O interaction to reproduce at best self-diffusion coefficient and specific volumes for the three single oxides. Finally, the empirical potentials is assessed and discussed on their ability to predict local structural properties, thermodynamic quantities such as the melting temperature as well as self-diffusion coefficients of the three single oxides with existing experimental and *ab initio* data. The assessment is also done for two CAT compositions, namely $(\text{CaO})_{0.43}-(\text{Al}_2\text{O}_3)_{0.35}-(\text{TiO}_2)_{0.22}$ and $(\text{CaO})_{0.24}-(\text{Al}_2\text{O}_3)_{0.2}-(\text{TiO}_2)_{0.56}$ with low and higher TiO_2 content, being respectively interesting for steel industry and glass

forming ability⁴⁸. In that case, the partial pair-correlation functions and the self-diffusion coefficients are tested against the present AIMD results. Furthermore, the influence of the evolution of the TiO₂ content as well as the substitution of TiO₂ by SiO₂ on the self-diffusion coefficients is analyzed by comparing CAS and CAT systems with the same corresponding compositions. The role of triply bonded as well as five-fold coordinated Al and Ti in the evolution of the diffusion is discussed.

II. THEORETICAL BACKGROUND AND METHODOLOGY

A. Ab initio molecular dynamics simulations

The *ab initio* simulations were performed within the density functional theory^{49,50} (DFT) using the Vienna *ab initio* simulation package^{51,52} (VASP). The projected augmented-wave method with a cut-off energy set to 600 eV (beyond the recommended value for all the systems) was used to describe the electron-ion interactions^{53,54}. Exchange-correlation effects were taken into account within the GGA functional⁵⁵. For the solid phases at $T > 0$ K, the Γ -centered grid of k -points in the irreducible part of the Brillouin zone was set to $2 \times 2 \times 2$ following the Monkhorst-Pack scheme⁵⁶, while for the melts, only the Γ -point was used.

The dynamics was performed in the canonical ensemble, namely, constant number of atoms, volume, and temperature (NVT) by means of a Nosé thermostat^{8,9}. Newton's equations of motion were integrated using the Verlet algorithm in the velocity form with a time step of 1 fs. For the liquid state, cubic simulation supercells subject to periodic boundary conditions containing the number of atoms indicated in Table I were used. For the solid state, the geometry of the supercell follows that of the primitive lattice of lime for Ca, rutile and anatase for TiO₂, and corundum for Al₂O₃. For all the systems, the size of the supercell were adjusted to get a pressure close to zero, and were less than 0.4 GPa in all the cases, which is lower than the amplitude of pressure fluctuations during the simulations. The typical duration of the runs is 40 ps for all the oxide crystals and melts, the first half being devoted to adjust the volume of the simulation supercell to get at best the zero pressure and subsequent equilibration, and the second half was carried out to produce the physical properties.

Energy and volume relaxations at 0 K using a conjugate gradient minimization were

first performed to assess the ability of the DFT calculations to reproduce the specific volume in the stable crystalline phases, namely the corundum triclinic α -phase for Al_2O_3 , the lime B1 structure for CaO , and in the anatase and rutile tetragonal phases for TiO_2 . The results of these calculations, carried out with k -points grids set respectively to $6 \times 2 \times 2$, $2 \times 2 \times 2$, and $8 \times 8 \times 8$, are gathered in Table I and compared to existing experimental data^{62–66,69,70}. The values, which are consistent with other DFT calculations^{58–61}, slightly overestimate the experimental volumes by 3.2% for CaO , 1.9% for Al_2O_3 respectively, and 4.4% and 3.2% for anatase and rutile structures of TiO_2 . Going to higher temperatures with AIMD simulations, a similar departure is observed with the measurements in the crystalline states for all three single oxides. For TiO_2 , a volume contraction of 9% is observed between anatase and rutile consistently with observations (8%)⁶⁸. Upon melting, the specific volume of Al_2O_3 is close to the two most recent experimental data^{70,71}, while for TiO_2 a departure of 6.6% is seen⁶⁹. For the latter case, it should be mentioned however that the only existing data is an extrapolation on the CaSiO_2 - TiO_2 join by Dingwell⁶⁹, and given by Alderman *et al.* for $T = 2250$ K. As will be seen in the next Section, the excellent agreement of the total structure factor with x-ray diffraction measurements of Alderman *et al.*⁴⁵ yields us hypothesize that the experimental volume is probably overestimated. For CaO , to our best knowledge no experimental data were found in the literature for the specific volume.

A departure around 3% is commonly observed for the GGA and improvement can be made using the recently developed Strongly Conditioned and Appropriately Normed (SCAN) many-body exchange correlation functional⁷², as was shown for CaO ¹¹. Nevertheless, given the good agreement with the measurement in the liquid state we chose to stay with the GGA calculations as a reference for the fitting of potentials. The comparison of GGA with SCAN for pure Al_2O_3 and TiO_2 will be considered elsewhere⁷³.

Then, for the fitting purpose with the method of Carré *et al.*⁴⁷, we determined the partial pair-correlation functions:

$$g_{ij}(r) = \frac{N}{V} \frac{n_{ij}(r)}{4\pi r_{ij}^2 \Delta r}, \quad (1)$$

where $n_{ij}(r)$ represents the mean number of particles j in a spherical shell of radius r and thickness Δr centered on particle i , with $i, j \in \{\text{Ca}, \text{Al}, \text{Ti}, \text{O}\}$. The position of the maximum of $g_{ij}(r)$ is representative of the $i - j$ bond length while the first minimum R_C gives access to the arrangement and distribution of atoms within the first spherical shell.

	T (K)	V_S ($\text{\AA}^3$)	N	N_{Ca}	N_{Al}	N_{Ti}	N_{O}	P_{res} (GPa)
Solid								
Al_2O_3	$0^{(C)}$	8.749 (8.4776 ^(b))	30		12		18	0
	$300^{(C)}$	8.798 (8.4952 ^(b))	240		96		144	-0.074
CaO	$0^{(B)}$	14.120 (13.8499 ^(c))	16	8			8	0
	$300^{(B)}$	14.333 (13.9158 ^(b))	216	108			108	0.06
TiO_2	$0^{(A)}$	11.773 (12.3165 ^(d))	6			2	4	0
	$300^{(A)}$	12.098 (12.3513 ^(d))	384			128	256	0.045
	$0^{(R)}$	10.704 (10.3576 ^(d))	12			4	8	0
	$2000^{(R)}$	11.222 (10.9172 ^(e))	270			90	180	
Liquid								
Al_2O_3	2400	11.413 (11.5875 ^(g))	300		120		180	0.370
CaO	3200	18.855 (—)	256	128			128	0.280
TiO_2	2250	12.640 (13.793 ^(f))	300			100	200	0.003
CAT-L	1900	13.148 (—)	300	40	64	20	176	-0.165
CAT-H	1900	13.138 (—)	300	23	38	53	186	0.05

(a) Ref.⁶², (b) Ref.⁶³, (c) Ref.⁶⁴, (d) Ref.⁶⁵, (e) Ref.⁶⁶, (f) Ref.⁶⁹, (g) Ref.⁷⁰

TABLE I: Data of the AIMD simulations for all systems listed, T , V_S , , and P_{res} correspond respectively to the temperature (0 K, means relaxation, see text), per atom volume. The total number of atoms N is divided in N_{Ca} Ca, N_{Al} Al, N_{Ti} Ti, and N_{O} O atoms. Superscript are (A): anatase; (B): lime; (C):corundum; (R): rutile. The values in brackets are experimental data with corresponding references. The experimental value for rutile at 2000 K is extrapolated linearly from the data of Sugiyama *et al.*⁶⁶.

Concerning the dynamics, self-diffusion coefficients D_i each species were determined from the linear behavior at long times of the mean-square displacement

$$R_i^2(t) = \frac{1}{N} \sum_{l=1}^{N_i} \left\langle [\mathbf{r}_l(t + t_0) - \mathbf{r}_l(t_0)]^2 \right\rangle_{t_0}, \quad (2)$$

where $\mathbf{r}_l(t)$ denotes the position of atom l at time t and N_i is the number of particles of specie i . As for the short-time dynamics, the velocity auto-correlation function (VACF) was

also used, namely

$$\Psi(t) = \frac{1}{N} \left\langle \sum_{i=1}^N [\mathbf{v}_i(t + t_0) \cdot \mathbf{v}_i(t_0)]^2 \right\rangle_{t_0}, \quad (3)$$

where $\mathbf{v}_i(t)$ denotes the velocity of atom i at time t . The angular brackets correspond to an averaging over time origins t_0 . For AIMD runs which are generally rather short, $R_{[ij]}(t)$ is considered only qualitatively to check whether the system is still liquid while an accurate determination of self-diffusion coefficients is carried out by integrating $\Psi(t)$ over time.

B. Potential fitting procedure and classical molecular dynamic simulations

Aiming firstly to build a set of empirical potentials to describe each of the three single-component oxide systems, an empirical potential in the form of the Born-Mayer-Huggins potential¹³ is chosen

$$u(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}}\right) - \left(\frac{C_{ij}}{r_{ij}}\right)^6 - \left(\frac{D_{ij}}{r_{ij}}\right)^8, \quad (4)$$

with $i, j \in \{\text{Ca, Al, Ti, O}\}$ and r_{ij} being the interatomic distance between two ions of species i and j . A potential for the ternary system will be ultimately built up and assessed by using the potentials that better described each individual single-oxide system.

The here considered form of a classical potential contains a Coulomb term, a Born repulsion as well as the dipolar expansion, for which only the van der Waals term was taken into account here. Given our previous experience on the calcium aluminosilicate (CAS) ternary^{16–18} and the aluminosilicate (AS) binary³⁸ systems, for which D/r^8 had a negligible influence. For each $i - j$ pair interaction, there are three free parameters, namely A_{ij} , ρ_{ij} and σ_{ij} to be adjusted. q_i and q_j are global parameters representing the effective charge for each atom type. Their values are constrained by charge neutrality but often depart from the nominal one^{14,46} to take into account, in an approximate way, charge transfer.

Therefore, each single component oxide possesses 10 parameters, the oxygen charge and 3 parameters for each pair. It follows that for the ternary system, a set of 31 parameters have to be adjusted. The systematic search for an optimal set of parameters in such a large parameter space becomes tedious and computationally prohibitive. Machine Learning approach could be appealing, as it was done for the solid phases of TiO_2 ⁷⁴ using the Belher-Parrinello high dimensional neural-networks⁷⁵, which results in non-linear regression force and energy matching and leading to completely numerical interactions.

In order to keep an analytical expression for the potentials and forces, a more pedestrian bottom up approach is put forward here in which interactions of the CAT ternary system in the form of the BMH model are built from its single oxides component ones. This implies immediately the following constraints: (i) Oxygen charge and O-O interactions have to be same for CaO, Al₂O₃ and TiO₂, and (ii) the charge neutrality has always to be kept. Thus q_O is the only free charge parameter. The method of Carré *et al.*⁴⁷ consists in minimizing the cost function

$$\chi_n^2 = \sum_{i < j} \int_0^{L/2} r^n (g_{ij}^{\text{REF}}(r) - g_{ij}^{\text{MODEL}}(r))^2 dr, \quad (5)$$

and therefore finding an optimal set of parameters with the smallest squared difference between partial pair-correlation functions $g_{ij}^{\text{MODEL}}(r)$ obtained by classical MD and g_{ij}^{REF} corresponding to AIMD ones that serve as a reference. In Eq. (5), L represents the size of the AIMD simulation box and n an integer. It has been shown⁴⁷ for the case of SiO₂ that this approach is more accurate than the corresponding force matching minimization. Larger values of n put more weight on larger distances of $g_{ij}(r)$. Given the fact that AIMD simulation boxes are rather small and induce possibly finite size effects in the vicinity of $L/2$, $n = 0$ was chosen here to avoid overemphasising them. Carré *et al.*⁴⁷ showed that this choice yields very similar results than $n = 1$, the latter might being slightly better for some bond-angle distribution functions. As, at first, no other feature of the system besides pair-correlation functions is evaluated when selecting a potential, the quality of the potential description might concerns only its ability to reproduce the structure of the system. As it will be seen below, the potentials are reliable on a broader range of properties.

Finding the minimum of χ_0^2 requires, for each of the three oxides, the systematic exploration of the 10-dimensional parameter space in the physical meaningful range by a grid search. Then, for each combination of the parameters, a classical MD simulation (see next section) is performed to determine the partial pair-correlation functions from which a value of χ_0^2 is calculated. Given the computational intensive character of this procedure, the fitting was performed stepwise based on physical considerations. In a first stage, we build several batches with given values of q_O ranging from -0.95 to -1.25 separated by $\Delta q_O = 0.1$ to 0.05 since it has to be the same for the three single oxides. This range corresponds to the most common values for O in many oxides^{14,29,46} and giving the most reliable results. For each batch, the grid search of the three parameters of the cation-oxygen (Ca-O, Ti-O and Al-O) is

performed first separately for CaO, Al₂O₃ and TiO₂, fixing at this stage the parameters for cation-cation potentials to reasonable published values, namely Hoang’s Ti-Ti potential⁴⁴ and Bouhadja’s potential¹⁷ for Ca-Ca, Al-Al and O-O. As a matter of fact, preliminary inspection of the sensitivity of $g_{ij}(r)$ and self-diffusion coefficients to the variation of the parameters showed that the cation-oxygen interactions are the most influential. The fitting was performed on a single temperature, namely 3200 K for CaO, 2400 K for Al₂O₃ and 2250 K for TiO₂ (see Table I). In a second stage, the O-O common potential and cation-cation specific potentials were refined essentially manually to simultaneously reproduce at best the self-diffusion coefficients as well as the solid and liquid specific volumes of the *ab initio* simulations. The atomic volume or density is found to be extremely sensitive to the O-O interaction, as was also pointed out by Alderman *et al.*⁴⁵. Stage 1 and 2 are repeated for refinement and convergence of the parameters. In a final stage, the potentials for the ternary was build by adding the dissimilar cation-cation Ca-Al, Ti-Al and Ti-Ca potential parameters, taking only the Coulomb term, a strategy that was also successfully used by Guillot and Sator²⁹. The final parameter set of Eq. (4) are given in Table II. More details on the practical setup of the method can be found in the Supplementary Information file⁷⁶.

Classical molecular dynamics simulations were performed with the LAMMPS code⁷⁹ which offers the possibility to vary potential parameters systematically for the grid search in a single input script. All simulations for the grid search were performed with the same number of atoms in the isobaric-isothermal ensemble (NPT) using a Nose-Hoover thermostat and barostat⁸ in order to reproduce precisely the thermodynamic parameters of the AIMD simulations. Periodic boundary conditions were applied in the three directions of space, and the long-range Coulomb interactions were treated within the Ewald summation method⁸. Equations of motion were solved numerically within the Verlet algorithm in the velocity form^{8,9} using a time step of 1 fs as for the AIMD. In the general case, for a given set of potential parameters, equilibration the system for 10 ps at the desired temperature is followed by a production run of 20 ps to extract the partial pair correlation. This procedure of equilibration/production is repeated for each point of the grid. The final potentials are subsequently assessed by performing MD simulations in the NVT ensemble with the same volumes and temperatures as the AIMD ones.

Prediction of the thermodynamic melting temperature requires the use of specific techniques such as the direct simulation of the solid-liquid interface⁸⁰ or void-nucleated melting

	q (e)	A (eV)	ρ (Å)	σ (Å)	C (eVÅ ⁶)
Ca	1.2				
Al	1.8				
Ti	2.4				
O	-1.2				
Ca-Ca		0.00382	0.0800	2.3440	6.9952
Ca-O		0.00579	0.1779	2.9940	22.1901
Al-Al		0.00290	0.0680	1.5704	14.0498
Al-O		0.00750	0.1689	2.6067	20.7448
Ti-Ti		0.00668	0.1540	2.3646	5.2488
Ti-O		0.00842	0.1921	2.8162	16.3762
O-O		0.01015	0.2140	3.2678	5.0840

TABLE II: Parameters of the BMH potentials for the CAT ternary oxide. The values of parameter D is 0 for all pair potentials. The charges are given in elementary charge units (e). The dissimilar cation-cation pair potentials Ca-Al, Ti-Al and Ti-Ca are described only by the Coulomb term.

techniques^{81,82}. As in our preceeding works^{11,83}, the method proposed by Solca *et al.*⁸⁴ was used, in which a void is created in the crystal by removing an atom as well as a certain number n of its neighbors to nucleate the melting, recalling that a single Schottky defect is known to be insufficient to induce melting at the thermodynamic melting temperature. This method was applied successfully to various systems by Agrawal *et al.*⁸². The procedure of such a void-melting simulations consist in creating single void of n atoms in a relaxed crystalline configuration at the center of the simulation box. The system is then heated up by applying a stepwise heating with an average rate $\Delta R = 3 \times 10^{12}$ K/s. The energy is monitored during the simulation and the melting is observed from a sharp increase of the enthalpy. This heating is repeated for increasing values of n from 0, which correspond to the perfect crystal situation, to the so-called critical size where the crystal destabilizes at low temperatures. The typical critical sizes found here are 30% of the atoms for all the single oxides components. All MD simulations were performed in the NPT ensemble, starting with a crystalline configuration with a large number of atoms, namely $N = 5505$ atoms in

in corundum crystal for Al_2O_3 , $N = 5832$ atom lime crystal for CaO , and $N = 5904$ atom rutile crystal for TiO_2 .

III. RESULTS

A. AIMD reference results

Having shown in Sec. II A that the *ab initio* molecular dynamics simulations reproduce the specific volume with a good accuracy, their ability in describing the experimental total structure factors of the melt is now assessed. The present simulations for Al_2O_3 and TiO_2 in the liquid state are the first AIMD simulations reported in the literature as far as we know. In Fig. 1, the total x-ray structure factors of liquid Al_2O_3 at 2400 K and liquid TiO_2 at 2250 K are shown and compared with existing experimental data^{45,71}. For both systems, a good agreement is seen on the whole curve, and especially all peak positions are well reproduced, guaranteeing that the density of the melt is well described. This tends to confirm our hypothesis that the density extrapolated by Dingwell⁶⁹ might be slightly underestimated. The pre-peak around $2.5 \text{ \AA}^{-1}$, also known as the first sharp diffraction peak is well reproduced, taking accurately into account the medium range ordering. This agreement is a good indicator of the reliability of the present AIMD simulations, and shows that finite size effects are moderate for such small system sizes. To our best knowledge, neither for liquid CaO nor for the CAT ternary oxides, measurements of structure factors have been reported in the literature. Other structural properties for the three single oxides will be presented in the next section together with the classical MD simulation using the fitted potential of the present work.

As for the dynamics, the self-diffusion coefficients of each species have been determined from the integration of the corresponding velocity auto-correlation function (Eq. 3) as well as the long time slope of the mean-square displacement (Eq. 2), both giving consistent results. For Al_2O_3 , $D_{\text{Al}} = 0.19 \pm 0.05 \text{ \AA}^2/\text{ps}$ and $D_{\text{O}} = 0.18 \pm 0.05 \text{ \AA}^2/\text{ps}$ are obtained and seen to be consistent with experimental data from tracer diffusion measurements⁸⁵ suggesting a slightly larger diffusion coefficient $D = 0.265 \text{ \AA}^2/\text{ps}$ at 2475 K. For the other oxides, we are not aware of any measurements of the diffusion. Our AIMD results for CaO and TiO_2 melts are respectively $D_{\text{Ca}} = 1.32 \pm 0.1 \text{ \AA}^2/\text{ps}$, $D_{\text{O}} = 1.64 \pm 0.1$ and $D_{\text{Ti}} = 0.39 \pm 0.05 \text{ \AA}^2/\text{ps}$,

FIG. 1: Total structure factor from X-ray diffraction (a) for pure Al_2O_3 at $T = 2400$ K and (b) pure TiO_2 at $T = 2250$ K. The open circles are respectively the experimental data of Skinner *et al.*⁷¹, and Alderman *et al.*⁴⁵. The simulation curves have been obtained with the Debye formula and a subsequent 5 point adjacent averaging smoothing.

$D_{\text{O}} = 0.29 \pm 0.05$. The Al_2O_3 and TiO_2 oxides which will play the role of network former for multi-component oxide melts²⁸ diffuse much less than CaO , known as a network modifier.

B. Assessment of the classical potentials

The quality of the BMH potentials obtained here is first tested against AIMD results for the single oxides that were used for the fitting procedure described in Sec. II B, based on the method of Carré *et al.*⁴⁷. For this purpose, we have performed the classical MD simulations in the NVT ensemble with the same volume and number of atoms, checking then for the residual pressures.

The comparison of the partial pair-correlation functions for Al_2O_3 at $T = 2400$ K, CaO at $T = 3200$ K, and TiO_2 at $T = 2250$ K are shown in Figs 2(a), (b) and (c) respectively. An overall very good agreement with AIMD is seen for the three oxides. The best one is for Al_2O_3 showing an excellent match for all three partials. All the cation-oxygen partials (M-O) are well described, as they were the main focus of the fitting procedure, but the most striking feature is the successful unified description of the O-O interactions in the very details. The latter mainly control the thermodynamics, since the density are very sensitive to them, and so do the subsequent thermodynamic parameters like the melting temperature.

FIG. 2: Partial pair-correlation functions for (a) Al_2O_3 at $T = 2400$ K, (b) for CaO at $T = 3200$ K, and (c) for TiO_2 at $T = 2250$ K. Lines and symbols correspond to classical MD and AIMD, respectively.

Fixing the density to the *ab initio* one leads to a residual pressure of 0.03 GPa for Al_2O_3 , 1 GPa for CaO , and 1.25 GPa for TiO_2 indicating that the density is well reproduced in each case. A comparison with other well-known potentials for the three oxide melts can be found in the Supplementary Information file⁷⁶, and shows that the potentials of the present work generally yield to improvements in describing the structure and diffusion.

As can be seen in Table III, the melting temperatures obtained from the void-melting technique^{11,83} are close to the experimental values^{11,86,87} for Al_2O_3 and CaO , while it is slightly overestimated for TiO_2 , which is consistent in the latter case with a more marked structure with respect to *ab initio* results as seen in Fig. 2(c). Good predictions of the self-diffusion coefficients is also obtained for Al_2O_3 and CaO , and a slight but noticeable underestimation for TiO_2 is seen with respect to AIMD values. This is consistent with the

fact that the partials for TiO_2 are more marked and $T = 2250$ K and the residual pressure is significant.

Table III gathers also the M-O structural parameters as they are more representative and influential on the microscopic network structure. The M-O bond lengths, determined from the position of the maximum of the corresponding M-O partials, are always close to the AIMD values for the liquid, and also in good agreement with the experimental values for Al_2O_3 ⁷¹ and TiO_2 ⁴⁵, obtained through a reverse Monte-Carlo (RMC) Empirical potential structure refinement (EPSR) techniques, respectively. The values for the underlying solid phases, are still reasonably well reproduced for corundum Al_2O_3 at $T = 300$ K, rutile TiO_2 at $T = 2000$ K, and to a lesser extend for lime CaO . This is striking since the solid phases were not included explicitly in the fitting procedure so that the potentials show a reasonable transferability to the underlying solid phases. The underestimation is around 1.5%, 4%, and 7% respectively for Al_2O_3 , TiO_2 , and CaO . For the latter case, this was also pointed out recently¹¹ using interactions extracted readily from the CAS BMH potentials¹⁷. The values of $n_{\text{M-O}}$ and $n_{\text{O-M}}$, corresponding respectively to the mean coordination of oxygen around cation and the one of cation around oxygen in the melts are also tabulated in III. They are again in good agreement with those obtained from AIMD and consistent with the experimental ones for alumina and titania.

The potentials are now tested for the ternary CAT melts, recalling that the dissimilar cation-cation interactions are simply included in the form of the Coulomb terms without additional parameters and fitting. Therefore this might be considered somehow as predictive. The MD simulations of the melts were performed with the same densities and the temperature of $T = 1900$ K with which the AIMD ones were carried out. In doing so, the residual pressures were -0.25 GPa and -0.35 GPa respectively for the low (CAT-L) and higher (CAT-H) TiO_2 content, indicating that the densities are well described with respect to AIMD. The obtained partial pair-correlation functions are displayed in Figs. 3 and 4 and compared to the AIMD simulations as well as classical DM performed with the potentials of Guillot and Sator, readily extracted from their parametrization of the nine component KNCMFATS oxide. Interestingly, the BMH potentials of the present work reproduce accurately all the M-O partials as well as the O-O partials for both compositions. The remaining partials are reasonably well described and are in phase with the AIMD results. Finally the less well described partials are the Ca-Ca and Ti-Ti, however it is well known that rare-earth

		T_M (K)	D_M	D_O	r_{M-O} (Å)	$r_{M-O}^{Sol.}$ (Å)	n_{O-M}	n_{M-O}
Al ₂ O ₃	CMD	2310	0.20	0.20	1.780	1.884	4.66	3.11
	AIMD		0.19	0.18	1.811	1.844	4.67	3.11
	Exp.	2328			1.800	1.850	4.40	2.93
CaO	CMD	3250	1.52	1.71	2.195	2.239	5.62	5.62
	AIMD		1.32	1.64	2.190	2.393	5.55	5.55
	Exp.	3222						
TiO ₂	CMD	2230	0.15	0.10	1.89	1.937	5.597	2.799
	AIMD		0.39	0.29	1.86	1.958	5.629	2.815
	Exp.	2147			1.88	1.962	5.000	

TABLE III: Melting temperature T_M , self-diffusion coefficients D_M for cations and D_O for oxygen as well as structural data for all single oxide melts. r_{M-O} , $r_{M-O}^{Sol.}$, n_{M-O} , and n_{O-M} correspond respectively to cation-oxygen bond distance, its value for the underlying crystalline state, the mean coordination of oxygen around cation, and the mean coordination of cation around oxygen. For the two latter quantities a cut-off radius corresponding to the first minimum of the M-O partial pair-correlation function has been used, namely 2.60 Å, 3.60 Å, and 2.80 Å, respectively for Al₂O₃, CaO, and TiO₂.

and early transition metals with empty or nearly empty d -bands are difficult to model in general⁵⁹, and probably are difficult to capture in their fine details with potentials as simple as the BMH ones. Further improvements would probably require to consider fitting the additional D/r^8 dispersion term in the BMH form given by Eq. (4), but at the expense of increasing the search space and thus the computational effort.

The diffusion coefficients are also important for the description of the dynamics in oxide melts⁸⁹, and they are known to be very sensitive to details of the potentials⁹¹. Table IV gathers the self-diffusion coefficients for each species of the melts as well as the weighted average value. A very good agreement can be seen with AIMD values is obtained as well as their the evolution with composition which is a strong indication of the accuracy of the potentials built in the present work. It can also be seen that the average diffusion coefficient is similar than the oxygen one, which confirms the general rule stating that the O diffusion is representative for that of the whole system. Even if the potential developed

FIG. 3: Partial pair-correlation functions for CAT-L with low TiO_2 content at $T = 1900$ K. Full lines and symbols correspond respectively to classical MD and AIMD of the present work. The dashed lines are classical MD simulations with the potentials of Guillot and Sator²⁹.

here represents a clear improvement in the description of the structure and dynamics with respect to the potentials of Guillot and Sator²⁹, we would like to point out their high quality and transferability to the CAT oxides, for which they were not primarily designed. It is finally worth mentioning that both potentials lead to a good representation of the structure and dynamics of these ternary oxides. They have however a very different parametrization, and more particularly in the oxygen charge, which are -1.2 and -0.945 respectively. This poses the general unsolved question of the uniqueness of the potentials for a given functional form like the BMH.

FIG. 4: Partial pair-correlation functions for CAT-H with higher TiO_2 content at $T = 1900$ K. Full lines and symbols correspond respectively to classical MD and AIMD of the present work. The dashed lines are classical MD simulations with the potentials of Guillot and Sator²⁹.

IV. DISCUSSION

In corundum alumina, the aluminium coordination environment is octahedral or tetrahedral, with respectively 6-fold and 4-fold oxygen atoms around Al. In the melt, early experiments by x-ray and neutron diffraction as well as Nuclear Magnetic Resonance (NMR), probing directly the local Al environment, concur to an average coordination numbers ranging from 4.5 to 5.6 and the values found here are typically in this range. Such coordination numbers might be compatible with the existence of AlO_x local units with $x = 4, 5$, and 6 with specific proportions and not only with $x = 4$ and 6 the structural units of the underlying crystal. While for Aluminate and aluminosilicate melts, the existence AlO_5 units, namely $x = 5$, were experimentally observed (see Refs.³⁸ and²⁸ and References therein), it

		CAT-L			CAT-H			
	Guillot	Present	AIMD	CAS	Guillot	Present	AIMD	CAS
Ca	0.22	0.10	0.09	0.008	0.11	0.05	0.04	—
Al	0.11	0.05	0.05	0.003	0.09	0.02	0.03	—
O	0.14	0.07	0.09	0.003	0.10	0.03	0.04	—
Ti	0.08	0.04	0.04	0.001	0.06	0.02	0.02	—
Total	0.14	0.07	0.08	0.0035	0.09	0.03	0.03	—

TABLE IV: Self diffusion coefficients of each species in CAT-L and CAT-H melts at $T = 1900$ K as well as the weighted average (Total.). The results of classical MD using the potentials of the present work (Present) is compared to AIMD results, classical MD with the potentials of Guillot and Sator²⁹ (Guillot) as well as the calcium aluminosilicate oxide (CAS) with the same composition and substituting Ti atoms by Si atoms and using the BMH potentials with parameters of Bouhadja et al.¹⁷. The error bars are typically of the order of 0.005.

is still not firmly established experimentally that they exist and in what proportion in pure alumina melt. Simulations with previous empirical potentials have shown the existence of 5-fold coordinated Al atoms but with a significant variability of their proportions⁴⁵.

As can be seen in Fig. 5(a), AIMD as well as classical MD simulations performed here indicate indeed the presence of 5-fold coordinated Al atoms, which are slightly in the majority with a fraction of around 45-50% together with 40-42% of 4-fold coordinated Al. 3-fold and 6-fold coordinated Al fractions are always very small. Moreover, the coordination number around oxygen is essentially 3-fold coordinated, indicating the formation of triclusters (O-3Al) which might induce edge sharing AlO_x structural units. In the recent experimental study of Skinner et al.⁷¹, using x-ray diffraction experiments combined with RMC, it was concluded that of 4-fold coordinated Al atoms with a proportion of 57% while the fraction of 5-fold is around 35%. Nevertheless, the average coordination around Al of the AIMD is 4.67 which is in good agreement with the RMC results of 4.4. Their experiments also show the presence of a majority of 3-fold coordinated O atoms with an average of 2.93 (3.11 for the AIMD). The close concordance of the structure factor with their measurement as see Fig. 1 as well as with the density, the present AIMD simulations represent the most reliable assessment of the significant presence of AlO_5 units.

FIG. 5: Distributions of coordination number from AIMD simulations for (a) Al_2O_3 at $T = 2400$ K and (b) for TiO_2 at $T = 2250$ K.

Finally, Fig. 5(b) shows also the presence of 5-fold coordinated Ti atoms exist even if the Ti coordination environment is octahedral for the underlying ideal rutile phase. It should be noted that, in the melt, the fraction of 6-fold coordination is still large while 4-fold one is small. The oxygen coordination is essentially 2- and 3-fold coordinated. The 2-fold coordinated O atoms is a characteristic feature of the strong tetrahedral network structure of SiO_2 for which almost all Si atoms are 2-fold coordinated oxygen even embedded in the binary³⁸ and ternary²⁸ systems, indicating that titania possesses a weaker network structure. The average coordination of Ti in AIMD simulations is 5.63 which is in reasonable agreement with the experiments of Aldermann *et al.*⁴⁵. Again, as for alumina, given the good agreement found for the total structure factor with measurements as shown in Fig. 1, the present simulations might attest the presence of the 5-fold Ti coordinated atoms for TiO_2 also.

Understanding the diffusion and consequently the viscosity and glass transition temperature in calcium aluminate-based oxides by introduction of TiO_2 is of utmost importance on the fundamental side and for many industrial applications. For instance, in table IV, increasing the amount of TiO_2 in CAT-L to get CAT-H leads to a decrease of the diffusivity by more than a factor of 2. This feature might be understood at the microscopic level by comparing oxygen coordination environments in 5(a) and (b). Increasing the amount of TiO_2 at the expense of Al_2O_3 decreases the amount of triply bonded oxygen known to weaken the network structure, and therefore decrease the diffusion. Another effect of this mechanism can be highlighted when a substitution of SiO_2 by TiO_2 is made in CAS oxides,

as a way of controlling the viscous flow. In table IV, are reported the self-diffusion coefficients of the CAS oxides with the same compositions as the CAT oxides considered here, in which Ti atoms are simply substituted by Si atoms. The MD simulations were carried out in the same conditions as for the CAT melts and by using the potentials of Bouhadja *et al.*¹⁷ which have proven to be realistic^{77,78}. As can be seen, the diffusion slows down at least by an order of magnitude in the case of CAT-L and even leads to a glassy state for CAT-H demonstrating the high sensitivity to the $\text{SiO}_2/\text{TiO}_2$ proportions in oxide melts. In this case, the presence of TiO_2 in CAS melts might induce more triply bonded oxygen, namely O-3Ti, O-2TiAl and O-Ti2Al as well as TiO_5 structural units. These structural features, hardly seen in the case of SiO_2 , might favor here the diffusion and therefore decrease the viscosity^{18,38}.

V. CONCLUSION

In the present contribution, Born-Mayer Huggins interionic potentials for calcium aluminotitanate melts were built on the basis of *ab initio* molecular dynamics structural data for the Al_2O_3 , CaO and TiO_2 single oxide compounds. This was performed by means of the method propounded by Carré *et al.*⁴⁷ consisting in a mean-square difference minimization of the partial pair-correlation functions with respect to the *ab initio* reference results. The bottom up strategy put forward here consists in fitting first the single compounds separately but with a unified description of the oxygen charge and O-O interaction term. The potentials for the ternary system are finally built straightforwardly by adding purely Coulomb terms for dissimilar cation-cation interactions without further fit.

This approach has proven to be successful in describing the structural and diffusion properties of the three single oxides as well as the ternary melts simultaneously, which can be seen as a interesting sign of transferability to the complete range of compositions, as it was shown for two CAT compounds with low and higher TiO_2 content.

Finally, the analysis of the two CAT compounds as well as their comparison with calcium aluminosilicate melts with the same compositions allowed us to propose a possible underlying structural mechanism at the origin of the diffusion evolution with TiO_2 content. TiO_2 might play a role of increasing the number of triply bonded oxygen (triclusters) with respect to SiO_2 or decreasing it with respect to Al_2O_3 inducing respectively a lowering or enhancement

of the diffusion. This is consistent with previous works showing the importance of triclusters as well as their AlO_5 and TiO_5 counterparts in the behavior of the diffusion and viscosity. A more systematic study of the CAT and CATS systems would be interesting to investigate further such a mechanism and their impact on the other properties like the glass forming ability or the fragility⁸⁹. The present work shows that this is possible with the obtained BMH potentials, which could be, furthermore, easily extended to CATS systems with the method proposed here. This line of research will be considered in future works.

Data statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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