Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Oxide and Metal Halide Perovskites: Temperature-Dependent Dynamic Nature of Crystal Structure and Symmetry Relations

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Abstract: In recent years, the synthesis of all-inorganic halide perovskite $Cs(Pb, Sn)X_3$ (X = Cl, Br, and I) quantum dots (QDs) and the study of their physical properties have been of great interest due to their high potential as photoactive materials in optoelectronic technologies. Indeed, this family of semiconductors exhibits an ultralow thermal conductivity and a larger Seebeck coefficient with high carrier mobility. Furthermore, perovskite lead zirconate PbZrO₃ is of great attention due to the ferroelectric state transition and exhibits high charge storage for future large-energy storage capacitors. An interesting fact about halide perovskite systems is that they exhibit structural phase transitions as a function of temperature (orthorhombic - tetragonal – cubic), which notably affect their optical, thermal, and electrical properties. Furthermore, similar dynamical order-disorder structural transitions have been proposed to occur for both of the halide perovskites,

 $Cs(Pb/Sn)X_3$ and the lead zirconate PbZrO₃ system. However, such structural phase transitions and their crystalline structure are widely debated in the literature. In this project, we will focus on studying the microscopic structural properties of these two families of Pb-based perovskites, namely for the PbZrO₃ and Cs(Pb, Sn)X₃ materials via perturbed angular correlation (PAC) spectroscopy technique. Here, hyperfine interactions between probe nuclei at specific sites in the crystalline structure of the compound and their local environment provide information at the sub-nano (atomic) scale on charge distributions in the probe neighborhood through measurements of the electric field gradient. To analyze the time scale of the possible dynamical hyperfine interactions, a suitable model will be implemented on the *PACme* software, that allows the fitting of experimental data considering stochastic hyperfine interactions. In this perspective, the evolution of the experimental perturbation functions will be analyzed in terms of the increase in the rates of reorientation of the EFG tensor at the probe site, as according to the proposed dynamic order-disorder structural transition model, the tilt and rotation modes of the octahedra units can rapidly fluctuate between distinct orientations.

1 State of the Art

The intense scientific research for alternative sources of renewable energy is due to the increasing energy demand at the global level and the scarcity of natural resources such as natural gas and fossil fuels [1]. The features of the materials to obtain optimal solar energy-conversion devices consist of environment stability, a convenient band gap energy, a high absorption coefficient, and large charge carrier mobility. In this context, a new class of perovskite-based materials has emerged as promising for the design of optoelectronic and thermoelectric devices [2,3]. In particular, all-inorganic halide perovskite Cs(Pb, Sn)X₃ nanocrystals have become successful photoluminescence materials due to their high luminescence quantum yields at room temperature [4,5,6], higher absorption coefficient, narrow emission full width at half maximum (< 42nm), and tunability of their optical band gap by modifying composition or size in the entire visible spectral region of 410-700 nm [7,8]. These colloidal CsPbX₃ nanocrystals exhibit a quantum size confinement effect where the energy gap increases as the QDs size decreases.

The metal halide perovskite structure is defined by a general formula ABX_3 in which A (Cs) and B (Pb, Sn) are cations of different sizes, and X (Cl, Br, I) is an anion. The crystal structure consists of shared BX_6 octahedra at the corners and the A ion site in the center [9,10]. The CsPbI₃ nanocrystals crystallize in an orthorhombic phase which is stable at room temperature. A phase transition around T = 300 °C to the cubic perovskite phase can be found [11]. On the other hand, for the $CsPbBr_3$, three different structural phases have been reported, depending on the synthesis route and the dimension of their crystals. Two structural phase transitions can be found at 88 °C and 130 °C, from the orthorhombic phase to a tetragonal perovskite (P4/mbm) and to the cubic perovskite (Pm-3m) phase, respectively [12]. At room temperature, it presents an orthorhombic (Pnma) crystal structure. However, experimental investigations on room temperature CsPbBr₃ structural phase initially indexed the crystalline structure with monoclinic phase [13], in accordance with the work reported by Møller [14]. But recent studies of x-ray total scattering colloidal QDs have clearly shown the orthorhombic structure CsPbBr₃ (Pnma) crystal phase. This can be related to the concentration impurities and nature of local defects, and quantum confinement conditions in CsPbX₃ perovskite NCs. In addition, an unusual structural phase transition that appears between 57 $^{\circ}C$ and 62 $^{\circ}C$ has been observed, which is stable and reversible. The phase transition sequence with temperature increase would be: orthorhombic (Pnma) – orthorhombic (Cmcm) – tetragonal (P4/mbm)- cubic (Pm3m) [15,16]. The formation of domains of different crystal phases and their coexistence can affect optical properties such as photoluminescence quantum yield. It is suggested that the excitonic recombination lifetime in $CsPbX_3$ perovskite NCs strongly depends on the structural phase transition [17,18]. Presently, there is contradicting or insufficient knowledge regarding the crystalline structures, doping-induced, and defectinduced influences on the optical, thermal, and electrical properties of a single-phase perovskite system below these transition temperatures [19].

Furthermore, distinct research groups have devoted time to discussing also the nature of the aristotype $Pm\overline{3}m$ cubic symmetry for these oxide and halide perovskite systems. Particularly on how the $Pm\overline{3}m$ cubic structure can be perceived as an averaged structure, a result of the system undergoing static and/or dynamical order-disorder structural tran-

sitions [20-25]. Theoretical studies, related to the halide perovskites, $Cs(Pb/Sn)X_3$, X =Cl, Br, I, have proposed the transition to the cubic symmetry can occur via dynamical order-disorder structural transition, where at high temperatures, the thermal excitations induce the $PbO_6(/SnO_6)$ octahedra to hop between equivalent rotation/tilt angles in a time-frequency in the range of a few microseconds to a few picoseconds, depending on the temperature and on the perovskite system [24, 25]. The same structural dynamic disorder phenomenon was also theoretically proposed to occur for the Lead Zirconate $PbZrO_3$ perovskite, which is known to follow a transition from the orthorhombic *Pbam* to cubic $Pm\overline{3}m$ symmetry, while increasing the system temperature near 400-500 K [20]. Experimental evidence has already been obtained on lead halide structures, such as on the $CsPbI_3$ and the hybrid organic-inorganic perovskite MAPbI₃, where it was shown that their cubic structure relies in fact on a network of nanosized symmetry broken domains [21, 22]. However, the X-ray total scattering techniques that have been used to confirm this, are not sensitive to the time scale of the rate of the structural hoppings, whereas PAC spectroscopy can be a useful technique to characterize the time scale of these dynamic structural fluctuations as a function of temperature [26,27].

In this regard, one method for investigating the implications of doping and defect induced in perovskites, and even to study electronic or structural dynamic phenomena, is to employ a local nuclear perturbed angular correlation (PAC) spectroscopy technique, which allows for the determination of the hyperfine interaction effects between electromagnetic fields and nuclear moment at the crystalline structure sites where the radioactive probe nucleus is located. Following the reports on the PbZrO₃ and Cs(Pb, Sn)X₃, X = Cl, Br, I compounds, we propose to perform PAC studies involving ion-beam implantation of isotopes on the systems that should display the dynamic nature of the aristotype cubic symmetry with hopping rates within the time scale of PAC probing isotopes.

2 Objectives

The general objective of this research project is the study of the temperature-dependent structural phase transitions, the symmetry relations, and symmetry-breaking distortions to the well-known cubic and orthorhombic phases observed in both perovskite families: Metal Halide Perovskite Cs(Pb, Sn)X₃ and Perovskite Lead Zirconate. In order to describe a model of the dynamical and local order-disorder structural transitions as a function of temperature in these systems, we will use the PAC technique to investigate the local symmetries through measurements of the electric-field gradients using a relatively small amount of a radioactive probe ion (111m Cd and 204m Pb isotopes). Additionally, the characterization of the composition, morphological and structural properties of Cs(Pb, Sn)X₃ and PbZrO₃ materials will be performed by scanning/transmission electron microscopy, X-ray diffraction, and Raman spectroscopy, scanning near-field optical microscopy, and the optoelectronic properties by UV-Vis absorption spectroscopy and photoluminescence spectroscopy. Finally, temperature-dependent molecular dynamics simulations and density functional theory calculations will allows reveal the impact of reversal phase transition, ionic exchange, defects, and dopants into the electronic structure and exciton dynamics for distinct perovskites oxide and halide systems and enable the control of nonequilibrium phase characteristics.

3 Expecting Results

All-inorganic halide perovskite and lead perovskite oxide systems are attractive not only from a fundamental point of view but also for technological applications. Among the different synthesis methods in colloidal solution of QDs, the most widely used is hot-injection method at high-temperature and inert atmosphere [28]. After the synthesis of the QDs, the solution will be also dried to obtain a powder. For the pellet synthesis of the lead perovskite oxide system, a solid-state reaction route will be used instead. As mentioned, we will focus on the hyperfine interactions at probe nuclei that are substituted into a site in the crystal structure of these materials. Here, we will perform PAC spectroscopy measurements in $PbZrO_3$ and $Cs(Pb, Sn)X_3$ (X=Cl, Br, I) systems at temperatures up to 100 K—700 K by ion-beam implantation of ^{204m}Pb and/or ^{111m}Cd isotopes and in the presence of dynamic hyperfine interactions we will analyze the respective results using a stochastic hyperfine field model implemented in the PACme software [27]. For the PbZrO₃ system, dynamic hyperfine interactions were observed at high temperatures; however the nature of the dynamic interactions was not clarified at that time [29]. Here, we propose to study the structural transition the system follows from the *Pbam* to the Pm3m s.g. symmetry in a temperature range from 200 K to 600 K by implantation of 204m Pb and/or 111m Cd ions. In the CsPbI₃ compound, for the thermal range from 298 K to 500 K an increase of octahedra distortions related fluctuation rate was theoretically predicted from 3.08 kHz to 9.62 MHz, which is within the time-scale of the probing states of the 204m Pb and 111m Cd isotopes. While for the CsSnI₃ system, in the same thermal range, the octahedra distortions-related fluctuation rate was predicted to increase from 404 MHz to 9.92 GHz [25]. We hope to obtain extensive information about the mechanisms at the microscopic scale that rises to the origin of all numerous properties in these systems. For this purpose, we aim to overcome the issues concerning crystal-structural principles that remain within these complex materials, such as the local distribution effect of defects/impurities, symmetries relations of the local crystal field, and the correlation between phase transformations and symmetry distortions with the macroscopic properties. Also, to understand the effect in the $Cs(Pb, Sn)X_3$ NCs stability and the assembly in new configurations by combining with other semiconductors (heterostructures systems) to improve their functionalization in a variety of applications.

Summary of requested shifts: We estimate the total amount of ISOLDE beam time needed to implement the proposal as 8 shifts distributed according to the Table below.

Required isotope	Im- planted beam	Probe element	Type of exp.	Approx. Intensity $[at/\mu C]$	Target/Ion source	Required atoms per sample	# of shifts
$^{111m}_{(48m)}Cd$	¹¹¹ Cd	¹¹¹ Cd	$\gamma - \gamma$ PAC	1×10^8	Sn target; VD 5 ion source	2×10^{10}	4
$^{204m}{\rm Pb}$ (67m)	204 Pb	$^{204}\mathrm{Pb}$	$\begin{array}{c} \gamma - \gamma \\ \text{PAC} \end{array}$	5×10^7	UC2	2×10^{10}	4
Total $\#$ of requested shifts							

Table 1: Beam time request for PAC studies

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DESCRIPTION OF THE PROPOSED EXPERIMENT

Please describe here below the main parts of your experimental set-up:

Part of the experiment	Design and manufacturing				
SSP-GLM chamber, SSP-GHM	\boxtimes To be used without any modification				
Chamber	\Box To be modified				
Part 1: Existing equipment on the	\Box Standard equipment supplied by a manufacturer				
solid state labs in building 508-r-002,	\Box CERN/collaboration responsible for the design				
r-004 and r-008	and/or manufacturing				
[Part 2 of experiment/ equipment]	\Box Standard equipment supplied by a manufacturer				
	\Box CERN/collaboration responsible for the design				
	and/or manufacturing				
[insert lines if needed]					

HAZARDS GENERATED BY THE EXPERIMENT Additional hazard from <u>flexible or transported</u> equipment to the CERN site:

Domain	Hazards/Hazardous Activities		Description	
	Pressure		[pressure] [bar], [vol-	
			ume][l]	
Mechanical Safety	Vacuum		10^{-6} mbar at SSP	
			chamber 10 during col-	
			lections and 10^{-5} mbar	
			at part 1	
	Machine tools			
	Mechanical energy (moving parts)			
	Hot/Cold surfaces			
Cryogenic Safety	Cryogenic fluid		[fluid] [m3]	
Floctrical Safety	Electrical equipment and installations		[voltage] [V], [current]	
Electrical Salety			[A]	
	High Voltage equipment		[voltage] [V]	
	CMR (carcinogens, mutagens and toxic		[fluid] [quantity]	
	to reproduction)		[[muid], [quantity]	
	Toxic/Irritant		[fluid], [quantity]	
Chemical Safety	Corrosive		[fluid], [quantity]	
	Oxidizing		[fluid], [quantity]	
	Flammable/Potentially explosive atmospheres		[fluid], [quantity]	
	Dangerous for the environment		[fluid], [quantity]	
Non ionizing	Laser		[laser], [class]	
radiation Safety	UV light			
Tadiation Salety	Magnetic field		[magnetic field] [T]	
	Excessive noise			
Workplace	Working outside normal working hours			
workplace	Working at height (climbing platforms, \Box etc.)			
	Outdoor activities			
	Ignition sources			
Fire Safety	Combustible Materials			
	Hot Work (e.g. welding, grinding)			
Other hazarda				
Other nazards				